By- SHAILENDRA SHUKLA SIR

Nature of Covalent Bonds-

To explain the nature of covalent bonds, following two theories have been proposed-

(1) Valence Bond Theory (VBT)

This theory was for the first time proposed by Hietler and London and then modified by Pauling and Slater. It is based upon the pairing of electrons and neutralization of their spins. The main postulates of this theory are as under-

(1) The covalent bonds are formed by overlapping of atomic orbitals, but in molecule atomic orbitals completely retain their identity. Thus, shape, size and other parameters of atomic orbitals remain unchanged in the molecule.

Thus, in molecules, the electrons are found in atomic orbitals. Hence, this theory is also called Atomic Orbital Theory (AOT).

(2) In overlapping, there occurs pairing of electrons and neutralization of their spins.

(3) The strength of a covalent bond depends upon the extent of overlapping between the atomic orbitals. The larger the extent of Overlapping, more stronger is the bond formed.

The extent of Overlapping is given by the overlap integral "S". If ψ_A and ψ_B are the wave functions of combining atomic orbitals, then, the overlap integral "S" is given by following expression-

$$S = \int \psi_A \, . \, \psi_B \, \partial r$$

Here, if-

- **(i) S > 0 (+ve), then there occurs attraction between the atoms and stable covalent bonds are formed.**
- **(ii) S < 0 (-ve), then there occurs repulsion between the atoms and covalent bonds are not formed.**
- **(iii) S = 0, then there occurs neither attraction nor repulsion between the atoms. Here also, stable covalent bonds are not formed.**

(5) The inter-nuclear distance after the formation of covalent bonds is called bond length of respective bond.

(6) The energy released during formation of a covalent bond is called bond energy of respective bond. It provides stability to the covalent bonds formed. The larger the value of bond energy, more stronger is the bond formed.

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Limitations of VBT-

This theory successfully explains the formation of molecules like H_2, Cl_2, NH_3, CH_4 etc. However, it has following limitations-

(1) It could not explain the formation of odd election molecule ions like H_2^+ molecule ion.

(2) It could not explain the magnetic behaviour of molecules. For example, according to this theory, O_2 molecule should not contain any unpaired election and therefore, it should be diamagnetic in nature. However, in practice, it is found to be paramagnetic.

(3) It does not give any idea about resonance.

Energy Profile of Covalent Bonds

The covalent bonds are formed by overlapping of atomic orbitals. Here, two half-filled atomic orbitals having elections with opposite spin, come close together, share some common space and their unpaired elections get paired up in the shared space. Thus, covalent bond gets formed.

If inter-nuclear distance (r) of combining atoms are plotted against potential energy of the system, following curves are obtained-

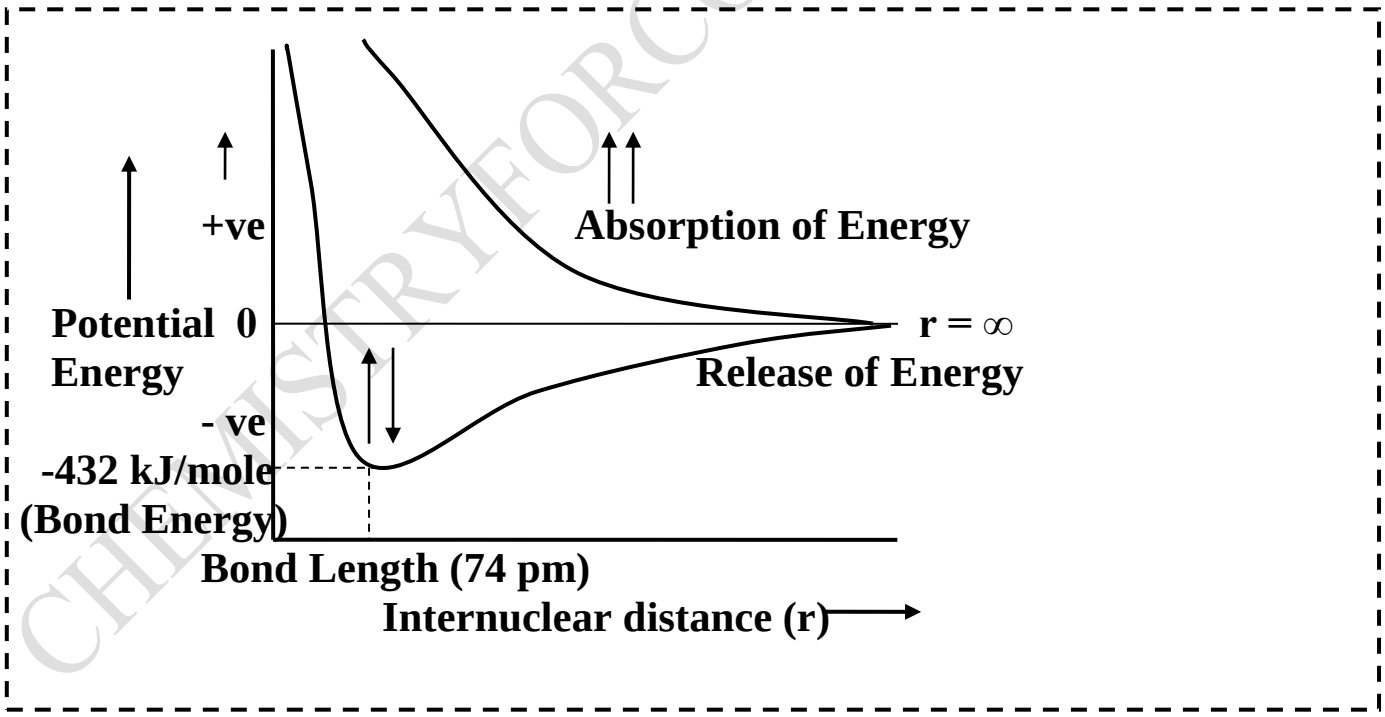


Fig.-Variation of Potential Energy with Internuclear distance (r) for H_2 molecule

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From the curves, it is clear that-

(1) When r = ∞, there occurs neither attraction nor repulsion between the atoms. Hence, potential energy of the system is zero.

(2) When orbitals contain elections with opposite spin, attraction between the atoms increases with decrease of inter-nuclear distance (r). Hence, energy is released from the system and potential energy of the system becomes negative.

(3) For a definite value of inter-nuclear distance (r), potential energy of the system takes highest negative value. This state corresponds to the state of bond formation. The energy released corresponding to this state is called bond energy and inter-nuclear distance corresponding to this state is called bond length.

(4) If inter-nuclear distance is decreased further, strong repulsion start operating between the atoms. It results in steep rise in potential energy of the system.

(5) When orbitals contain elections with same spin, repulsion between the atoms increases with decrease of inter-nuclear distance (r). Hence, energy is absorbed by the system and potential energy of the system goes on increasing continuously. Here, covalent bond is not formed.

(2) Molecular Orbital Theory (MOT)

In order to explain the nature of covalent bonds, this theory was for the first time proposed by Hund and Milliken. The main postulates of this theory are as under-

(1) The covalent bonds are formed by overlapping of atomic orbitals, but in molecule atomic orbitals completely lose their identity and form new type of orbitals called molecular orbitals.

(2) Molecular orbitals are formed by linear combination of atomic orbitals (LCAO Method). Here, nuclei of combining atoms come close together along a line and when they are at a definite distance, their atomic orbitals having nearly same energy and lying on same axis get merged together and form completely new type of orbitals called molecular orbitals.

(3) The number of molecular orbitals formed in linear combination of atomic orbitals is always equal to the number of atomic orbitals involved in combination.

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(4) One half of the total number of molecular orbitals formed in LCAO method, have energy lesser than the energy of combining atomic orbitals. In these orbitals, election density is relatively higher and therefore, they increase attractive state between the atoms and help in bond formation. Hence, these orbitals are called Bonding Molecular Orbitals (BMOs).

(5) On the other hand, the rest half of the molecular orbitals formed in LCAO method, have energy more than the energy of combining atomic orbitals. In these orbitals, election density is relatively lesser and therefore, they increase repulsive state between the atoms and oppose bond formation. Hence, these orbitals are called Anti-Bonding Molecular Orbitals (ABMOs).

(6) The shape, size and energy of the molecular orbital formed, depends upon those of atomic orbitals involved in combination.

(7) Molecular orbitals are polycentric i.e. they contain more than one nucleus. Here, electrons move under the influence of all the nuclei.

(8) In molecular orbitals elections are filled following the same rules, as in case of atomic orbitals. Thus, Pauli's exclusion principle, Hund's rule and Aufbau's principle are completely followed during filling of molecular orbitals.

Mathematical Treatment of MOT-

Let Ψ_A and Ψ_B are the wave functions of two combining orbitals, then the wave function of the molecular orbitals formed by their combination will be as under-

$$\Psi_{M.O.} = \Psi_A \pm \Psi_B$$

Here, during addition overlap, wave functions get added up and form bonding molecular orbital, while in subtraction overlap, they get subtracted up and lead to the formation of anti-bonding molecular orbital.

If Ψ_b and Ψ_a are wave functions of bonding and anti-bonding molecular orbitals respectively, then-

$$\Psi_b = \Psi_A + \Psi_B$$

$$\text{and} \quad \Psi_a = \Psi_A - \Psi_B$$

Here, the square of wave function gives the probability density (election density) in respective orbital. Hence,

$$\text{Probability density in BMO} = (\Psi_b)^2$$

$$= (\Psi_A + \Psi_B)^2$$

$$= (\Psi_A^2 + \Psi_B^2) + 2\,\Psi_A\Psi_B$$

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Similarly, Probability density in ABMO $= (\Psi_a)^2$

$= (\Psi_A - \Psi_B)^2$

$= (\Psi_A^2 + \Psi_B^2) - 2\Psi_A\Psi_B$

It is clear that, the probability density in BMO is greater by a factor of $2\Psi_A\Psi_B$, while that in ABMO is lesser by a factor of $2\Psi_A\Psi_B$ than the sum of the probability densities of combining atomic orbitals.

Linear Combination of Atomic Orbitals

According to Molecular Orbital Theory (MOT), the molecular orbitals are formed by linear combination of atomic orbitals (LCAO Method). Here, nuclei of combining atoms come close together along a line and when they are at a definite distance, their atomic orbitals having nearly same energy and lying on same axis get merged together and form completely new type of orbitals called molecular orbitals.

The linear combination of atomic orbitals for a homo-nuclear di-atomic molecule of type A_2 can be explained under following heads-

(1) Combination of 1s orbitals- 1s- orbitals of both the constituent atoms combine together by addition and subtraction overlap to form σ(1s) and σ*(1s) molecular orbitals respectively.

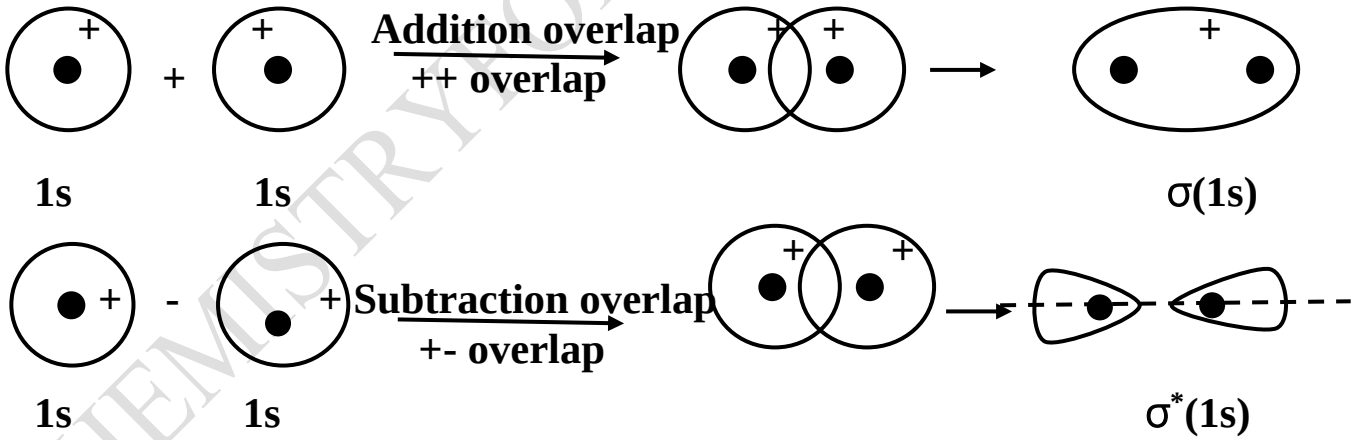


Fig.- Formation of σ(1s) and σ*(1s) molecular orbitals

Here, the molecular orbitals formed are symmetrical about inter-nuclear axis. Hence, they are termed as sigma molecular orbitals.

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(2) Combination of 2s orbitals- Similar to1s- orbitals, 2s- orbitals of both the constituent atoms also combine together by addition and subtraction overlap to form σ(2s) and σ*(2s) molecular orbitals respectively

(3) Combination of $2p_z$ orbitals- As per international conventions, z-axis is considered to be inter-nuclear axis. Hence, $2p_z$ orbitals of both the constituent atoms combine together in head-wise manner by addition and subtraction overlap to form σ ($2p_z$) and σ *($2p_z$) molecular orbitals respectively.

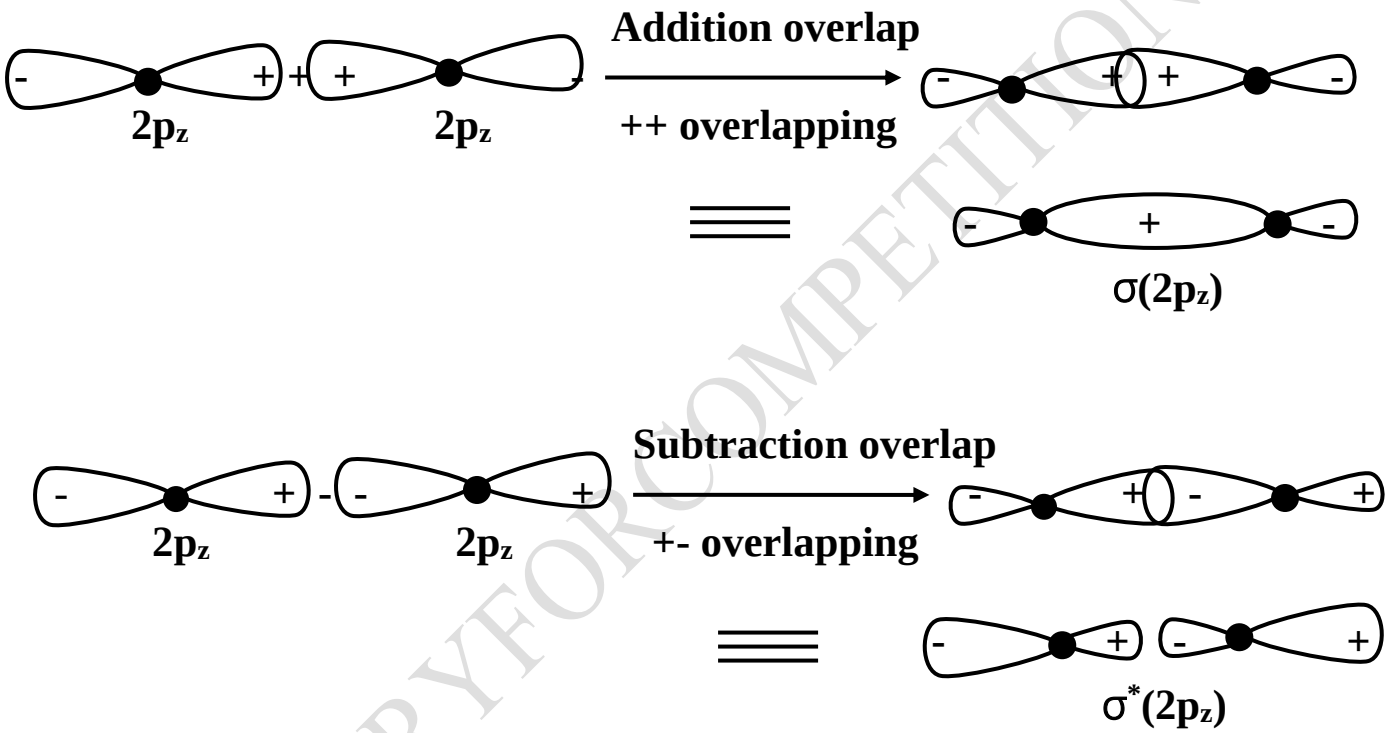


Fig.- Formation of σ($2p_z$) and σ*($2p_z$) molecular orbitals

Here also, the moleculer orbitals formed are symmetrical about inter-nuclear axis. Hence, they are termed as sigma moleculer orbitals.

(4) Combination of $2p_x$ orbitals- $2p_x$ orbitals are perpendicular to $2p_z$ orbitals. Hence, these orbitals of both the constituent atoms combine together in side wise manner by addition and subtraction overlap to form $\pi(2p_x)$ and $\pi^*(2p_x)$ molecular orbitals respectively.

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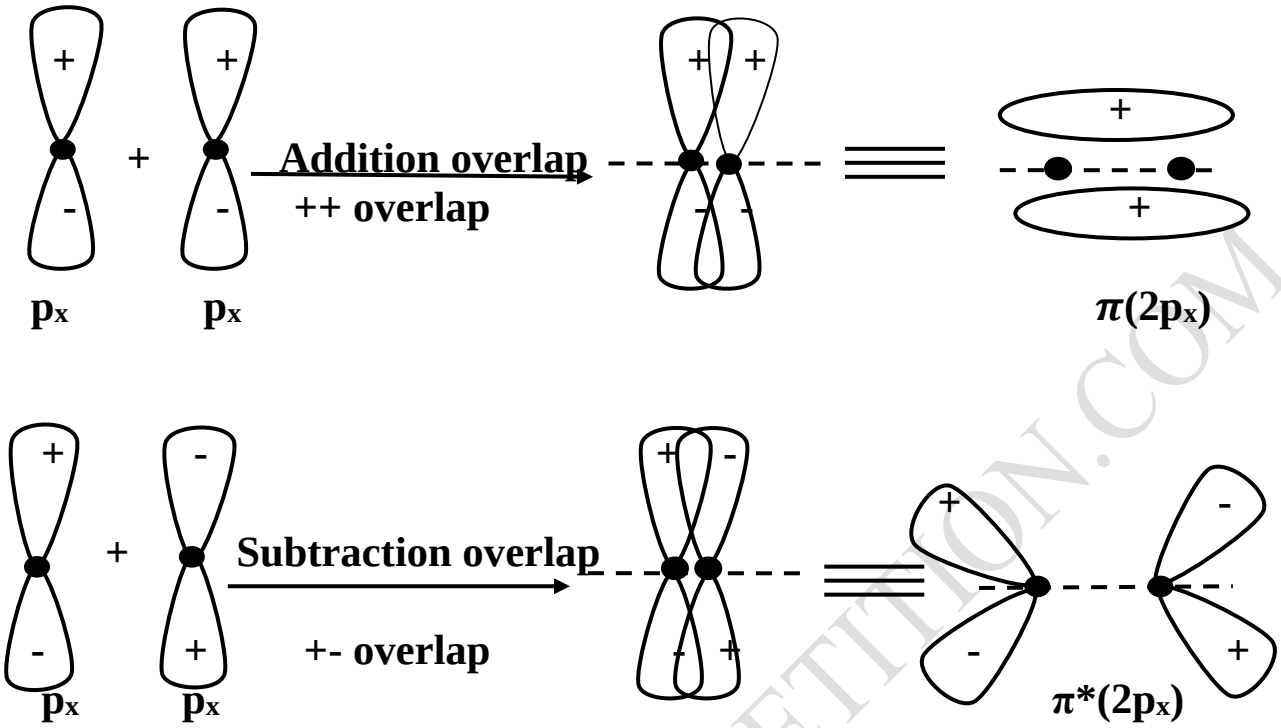


Fig.- Formation of $\pi(2p_x)$ and $\pi^*(2p_x)$ molecular orbitals

Here, the molecular orbitals formed are not symmetrical about inter-nuclear axis. Hence, they are called as pi molecular orbitals.

(5) Combination of $2p_y$ orbitals- Similar to $2p_x$ orbitals, $2p_y$ orbitals of both the constituent atoms combine together in side wise manner by addition and subtraction overlap to form $\pi(2p_y)$ and $\pi^*(2p_y)$ molecular orbitals respectively.

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Difference Between BMO and ABMO-

BMO	ABMO
(1) It is formed by addition overlap (++overlap) of atomic orbitals, where wave functions of combining atomic orbitals get added up. For example, if Ψ_A and Ψ_B are wave functions of combining atomic orbitals, then the wave function of BMO (Ψ_b) formed by their combination will be as under- $\Psi_b = \Psi_A + \Psi_B$	**(1) It is formed by subtraction overlap (+-overlap) of atomic orbitals, where wave functions of combining atomic orbitals get subtracted up. For example, if Ψ_A and Ψ_B are wave functions of combining atomic orbitals, then the wave function of ABMO (Ψ_a) formed by their combination will be as under-** $\Psi_a = \Psi_A - \Psi_B$
(2) In these orbitals, election density is higher than the sum of the election densities of combining atomic orbitals. If Ψ_A and Ψ_B are wave functions of combining atomic orbitals, then- Election density in BMO=$(\Psi_A + \Psi_B)^2$ $= (\Psi_A^2 + \Psi_B^2) + 2\,\Psi_A\Psi_B$	**(2) In these orbitals, election density is lesser than the sum of the election densities of combining atomic orbitals. If Ψ_A and Ψ_B are wave functions of combining atomic orbitals, then-** Election density in ABMO= $(\Psi_A-\Psi_B)^2$ $= (\Psi_A^2 + \Psi_B^2) - 2\,\Psi_A\Psi_B$
(3) These orbitals have energy lesser than the energy of combining atomic orbitals.	**(3) These orbitals have energy greater than the energy of combining atomic orbitals.**
(4) These orbitals increase attractive state between the atoms and help in bond formation.	**(4) These orbitals increase repulsive state between the atoms and oppose bond formation.**

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Molecular Orbital Energy Level Diagrams-

The diagram which represents the relative energy of different molecular orbitals of a molecule is called Molecular Orbital Energy Level Diagrams (MO Diagram).

Infact, the energy of a molecular orbital depends upon following two factors-

1. **Energy of combining atomic orbitals**
2. **Extent of overlapping between the atomic orbitals**

If energy of combining atomic orbitals is more, then the energy of molecular orbitals formed by their combination is more. For example, the energy of σ (2s) orbital is more than the energy of σ (1s) orbital.

Similarly, if the extent of overlapping between the atomic orbitals is more, there is more lowering in energy of BMO and consequently, more elevation in energy of corresponding ABMO. For example, the energy of σ ($2p_z$) molecular orbital is lesser than the energy of π ($2p_x$) and π ($2p_y$) molecular orbital. On the other hand, the energy of σ* ($2p_z$) molecular orbital is more than the energy of π* ($2p_x$) and π* ($2p_y$) molecular orbital.

On experimental basis, following two types of molecular orbital energy level diagrams (MO Diagrams) have been found for diatomic molecules of second period-

(i) For Li_2 to N_2 molecules-

σ (1s) < σ* (1s) < σ (2s) < σ* (2s) < π ($2p_x$) = π ($2p_y$) < σ ($2p_z$) < π* ($2p_x$) = π* ($2p_y$) < σ* ($2p_z$)

(ii) For O_2, F_2 and Ne_2 molecules-

σ (1s) < σ* (1s) < σ (2s) < σ* (2s) < σ ($2p_z$) < π ($2p_x$) = π ($2p_y$) < π* ($2p_x$) = π* ($2p_y$) < σ* ($2p_z$)

Here, for Li_2 to N_2 molecules, the energy of σ ($2p_z$) molecular orbital is exceptionally higher than the energy of π ($2p_x$) and π ($2p_y$) molecular orbitals. In fact, in lighter elements of second period (Li to N), the energy difference of 2s and $2p_z$ orbitals is very small and they lye on same axis. Hence, there occurs mixing of energy between these orbitals. It is the reason, why the energy of σ ($2p_z$) molecular orbital becomes exceptionly higher than π ($2p_x$) and π ($2p_y$) molecular orbitals.

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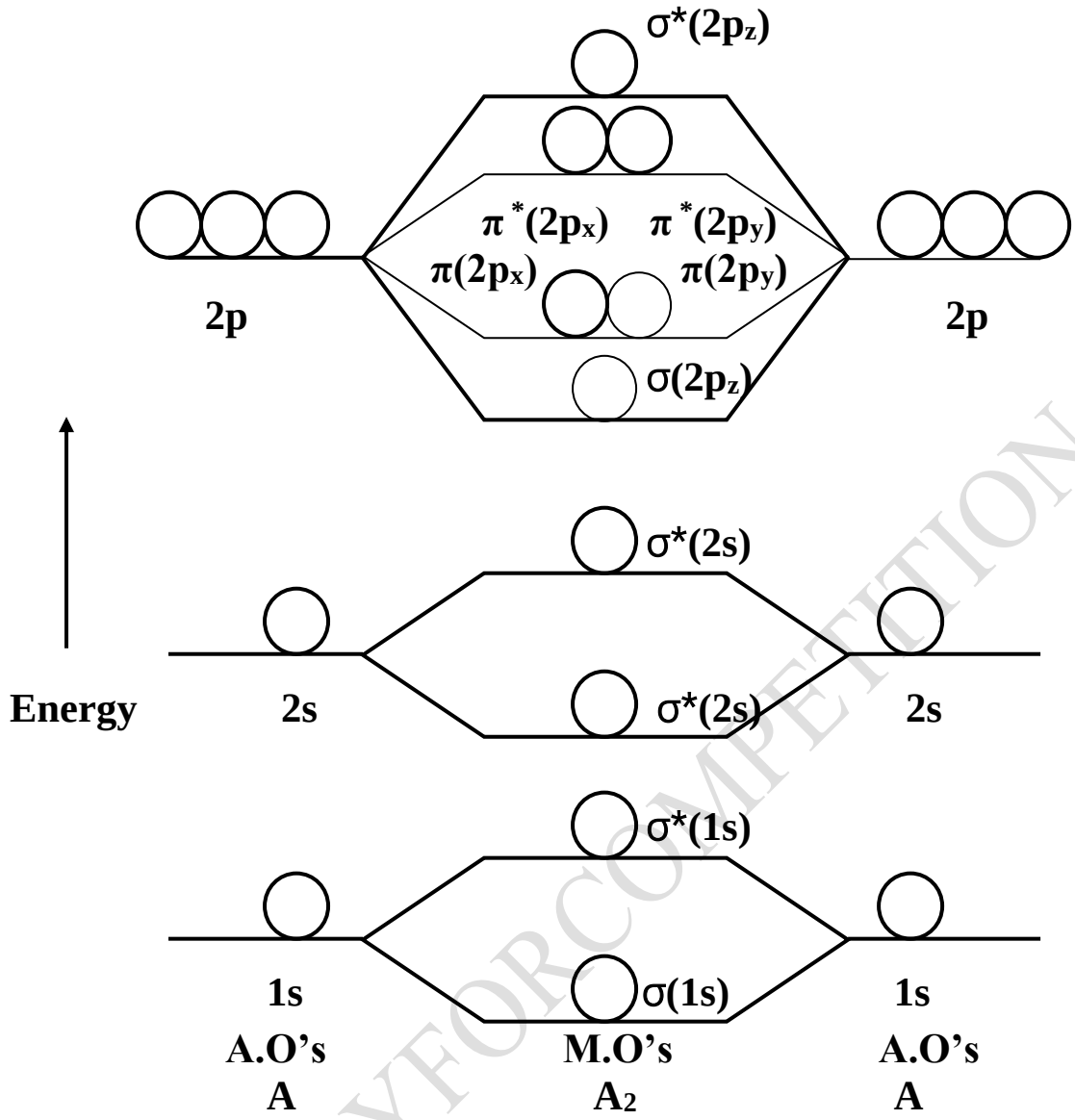


Fig.- M.O. Diagram for O_2, F_2 and Ne_2 molecules

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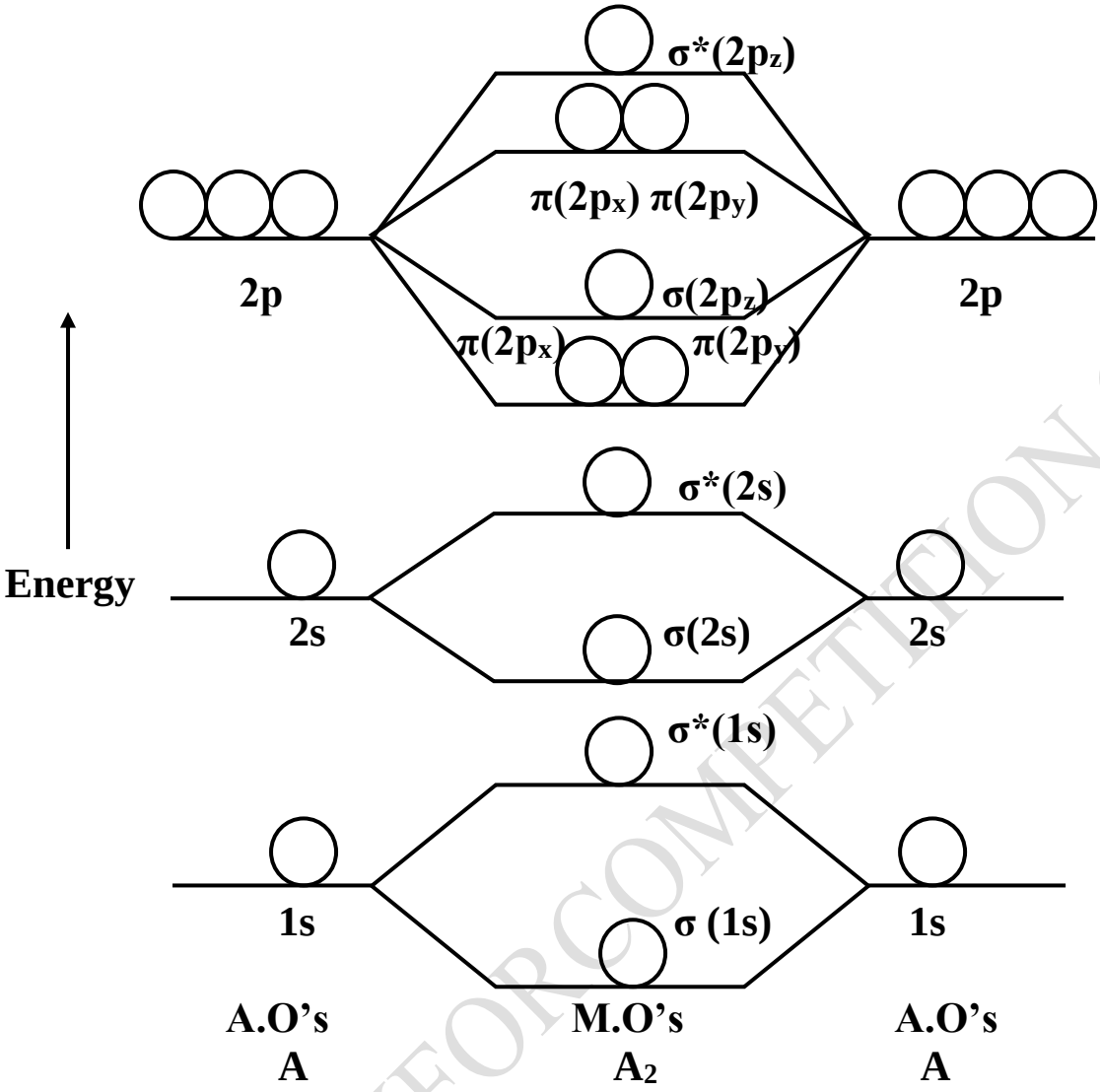


Fig.- M.O. Diagram for Li_2 to N_2 molecules

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APPLICATIONS-

(1) Formation of H_2 Molecule- **H_2 molecule is made up of two hydrogen atoms each having following electronic configuration-**

$$H\ (1) = 1s^1$$

Thus, H_2 molecule contains in all 2 elections and its molecular orbital energy level diagram can be represented as under-

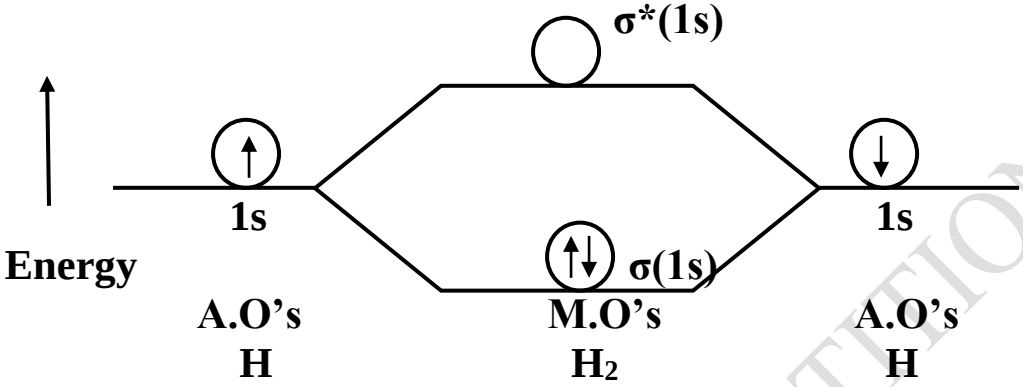


Fig.- M.O. Diagram of H_2 molecule

Thus, the electronic configuration of H_2 molecule will be as under-

H_2 molecule - $\sigma(1s)^2, \sigma^*(1s)^0$

Hence, $$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{2-0}{2}$$

$$= 1$$

Since, bond order is positive, the molecule will form and will be stable. Being, bond order 1, there will present single bond between two hydrogen atoms in H_2 molecule.

From M.O. Diagram, it is clear that, H_2 molecule does not contain any unpaired electron. Hence, it is not attracted in magnetic field and is diamagnetic in nature. Its magnetic moment is zero.

$$\mu = \sqrt{n(n+2)}\ B.M.$$

Where, n= number of unpaired electrons

$$\therefore \quad \mu = \sqrt{0(0+2)}\ B.M.$$

$$= 0 \text{ B.M.}$$

(2) Formation of H_2^+ Molecule ion- **H_2^+ molecule ion is obtained by removal of one electron from H_2 molecule.**

$$H_2 \longrightarrow H_2^+ + e^-$$

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Thus, H_2^+ ion contains only 1 election. It can be considered to be made up of one H-atom and one H^+ ion having following electronic configurations-

H (1) = $1s^1$

H^+ ion = $1s^0$

Thus, molecular orbital energy level diagram of H_2^+ ion can be represented as under-

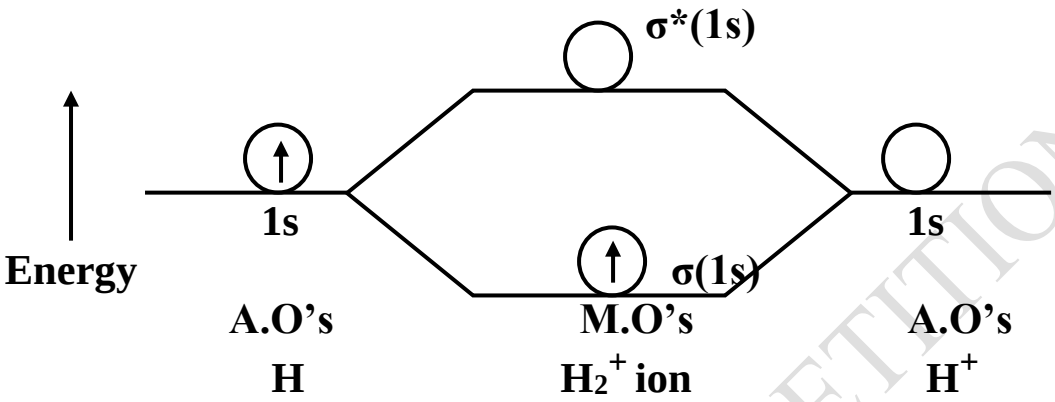


Fig.- M.O. Diagram of H_2^+ ion

Thus, the electronic configuration of H_2^+ ion will be as under-

H_2^+ ion - $\sigma(1s)^1, \sigma^*(1s)^0$

Hence, $$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{1-0}{2}$$

$$= \frac{1}{2}$$

Since, bond order is positive, H_2^+ ion will form and will be stable.

From M.O. Diagram, it is clear that, H_2^+ ion contains an unpaired electron. Hence, it is attracted in magnetic field and is paramagnetic in nature. Here, magnetic moment,

$$\mu = \sqrt{n(n+2)}\ B.M.$$

Where, n= number of unpaired electrons

$$\therefore \quad \mu = \sqrt{1(1+2)}\ B.M.$$

$$\mu = \sqrt{3}\ B.M.$$

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(3) Formation of hypothetical He_2 Molecule- **He_2 molecule is made up of two He atoms each having following electronic configuration-**

He (2) = $1s^2$

Thus, He_2 molecule contains in all 4 elections and its molecular orbital energy level diagram can be represented as under-

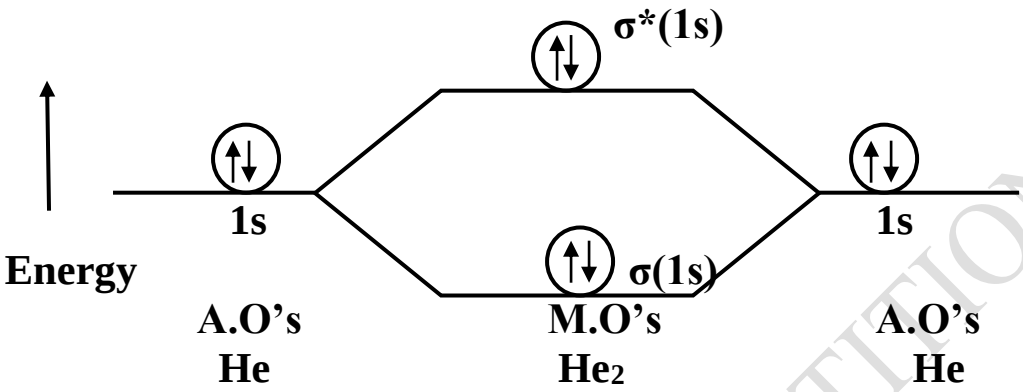


Fig.- M.O. Diagram of He_2 molecule

Thus, the electronic configuration of He_2 molecule will be as under-

He_2 molecule - $\sigma(1s)^2, \sigma^*(1s)^2$

Hence, $$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{2-2}{2}$$

$$= 0$$

Since, bond order is zero, He_2 molecule will be unstable and will not formed.

From M.O. Diagram, it is clear that, hypothetical He_2 molecule does not contain any unpaired electron. Hence, it will not attracted in magnetic field and is diamagnetic in nature. Its magnetic moment is zero.

$$\mu = \sqrt{n(n+2)}\ B.M.$$

Where, n= number of unpaired electrons

$$\therefore \quad \mu = \sqrt{0(0+2)}\ B.M.$$

$$= 0 \text{ B.M.}$$

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(4) Formation of He_2^+ Molecule ion- He_2^+ molecule ion is considered to be obtained by removal of one electron from hypothetical He_2 molecule.

$$He_2 \longrightarrow He_2^+ + e^-$$

Thus, He_2^+ ion contains in all 3 elections. It can be considered to be made up of one He-atom and one He^+ ion having following electronic configurations-

He (2) = $1s^2$

He^+ ion = $1s^1$

Thus, molecular orbital energy level diagram of He_2^+ ion can be represented as under-

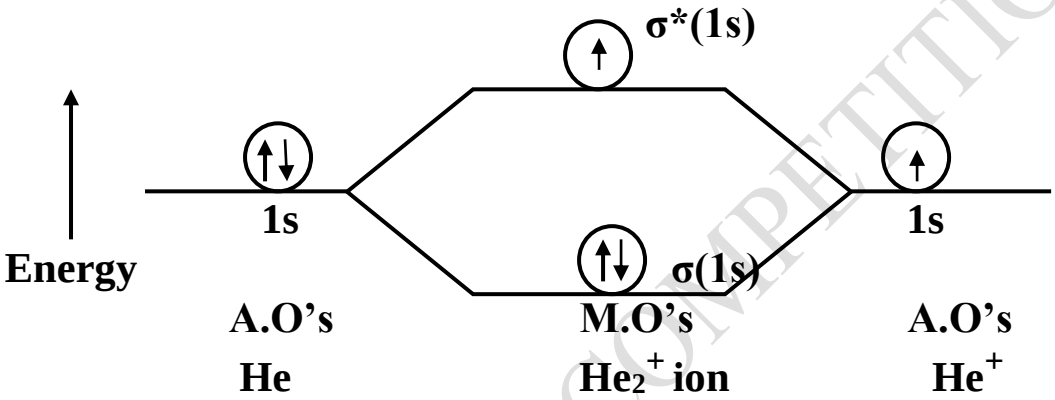


Fig.- M.O. Diagram of He_2^+ ion

Thus, the electronic configuration of He_2^+ ion will be as under-

He_2^+ ion - $\sigma(1s)^2, \sigma^*(1s)^1$

Hence, $$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-1}{2} = \frac{1}{2}$$

Since, bond order is positive, He_2^+ ion will form and will be stable.

From M.O. Diagram, it is clear that, He_2^+ ion contains an unpaired electron. Hence, it is attracted in magnetic field and is paramagnetic in nature. Here, magnetic moment,

$$\mu = \sqrt{n(n+2)}\ B.M.$$

Where, n= number of unpaired electrons

$$\therefore \quad \mu = \sqrt{1(1+2)}\ B.M.$$

$$\mu = \sqrt{3}\ B.M.$$

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(5) Formation of N_2 Molecule- **N_2 molecule is made up of two nitrogen atoms each having following electronic configuration-**

$$N\ (7) = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$$

Thus, N_2 molecule contains in all 14 elections and its molecular orbital energy level diagram can be represented as under-

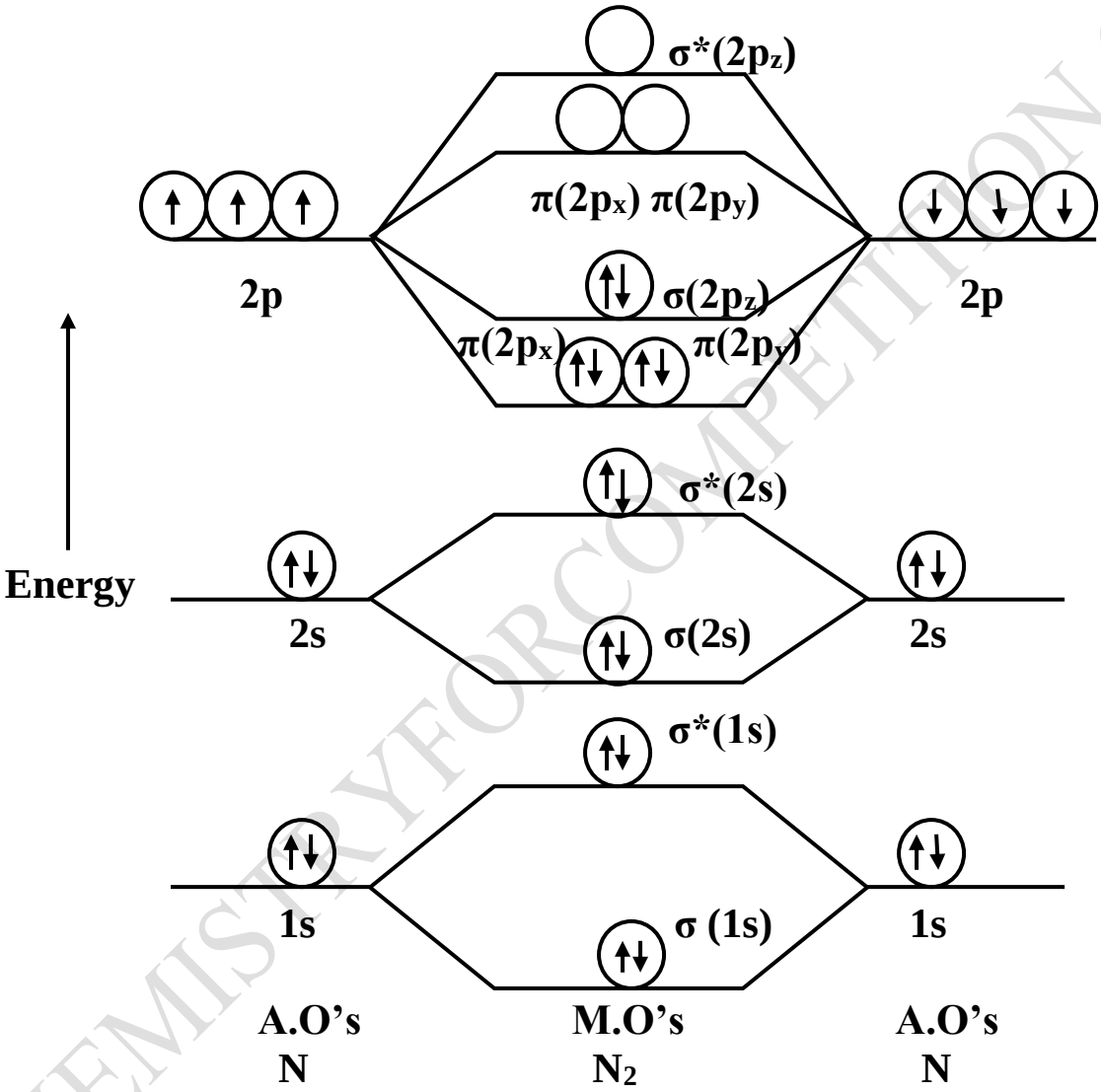


Fig.- M.O. Diagram of N_2 molecule

Thus, the electronic configuration of N_2 molecule will be as under-

N_2 molecule - $\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \pi(2p_x)^2, \pi(2p_y)^2, \sigma(2p_z)^2$

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Hence,

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

Since, bond order is positive, the molecule will form and will be stable. Being, bond order 3, there will present triple bond between two nitrogen atoms in N_2 molecule.

From M.O. Diagram, it is clear that, N_2 molecule does not contain any unpaired electron. Hence, it is not attracted in magnetic field and is diamagnetic in nature. Its magnetic moment is zero.

$$\mu = \sqrt{n(n+2)}\ B.M.$$

Where, n= number of unpaired electrons

$$\therefore \quad \mu = \sqrt{0(0+2)}\ B.M.$$
$$= 0 \text{ B.M.}$$

(6) Formation of N_2^+ Ion- N_2^+ is obtained by removal of one electron from N_2 molecule.

$$N_2 \longrightarrow N_2^+ + e^-$$

Thus, N_2^+ ion contains only 13 election. It can be considered to be made up of one N-atom and one N^+ ion having following electronic configurations-

N (7) = $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

N^+ ion = $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$

Thus, molecular orbital energy level diagram of N_2^+ ion can be represented as under-

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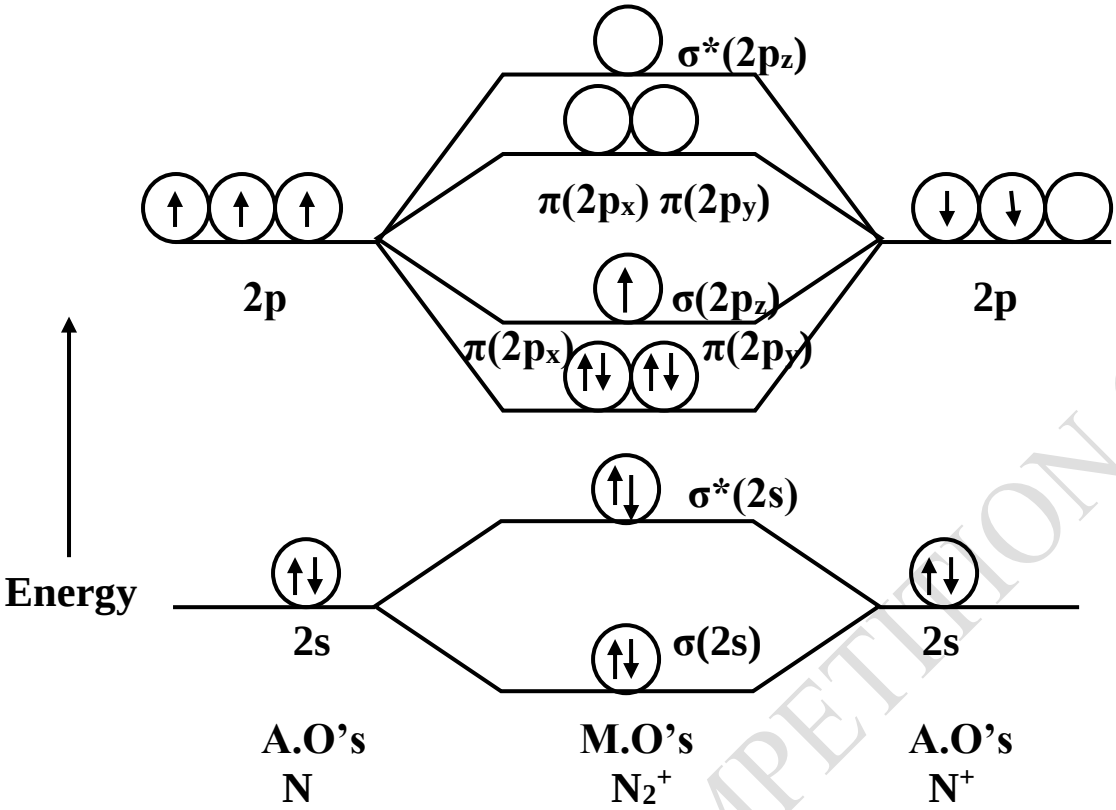


Fig.- M.O. Diagram of N_2^+ ion

Thus, the electronic configuration of N_2^+ ion will be as under-

N_2^+ ion - $\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \pi(2p_x)^2, \pi(2p_y)^2, \sigma(2p_z)^1$

Hence, $$\text{Bond order} = \frac{N_b - N_a}{2}$$
$$= \frac{9-4}{2}$$
$$= 2.5$$

Since, bond order is positive, N_2^+ ion will form and will be stable.

From M.O. Diagram, it is clear that, N_2^+ ion contains an unpaired electron. Hence, it is attracted in magnetic field and is paramagnetic in nature. Its magnetic moment is zero.

$$\mu = \sqrt{n(n+2)}\ B.M.$$

Where, n= number of unpaired electrons

$$\therefore \quad \mu = \sqrt{1(1+2)}\ B.M.$$
$$= \sqrt{3}\ B.M.$$

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(7) Formation of O_2 Molecule- **O_2 molecule is made up of two oxygen atoms each having following electronic configuration-**

$$O\ (8) = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$$

Thus, O_2 molecule contains in all 16 elections and its molecular orbital energy level diagram can be represented as under-

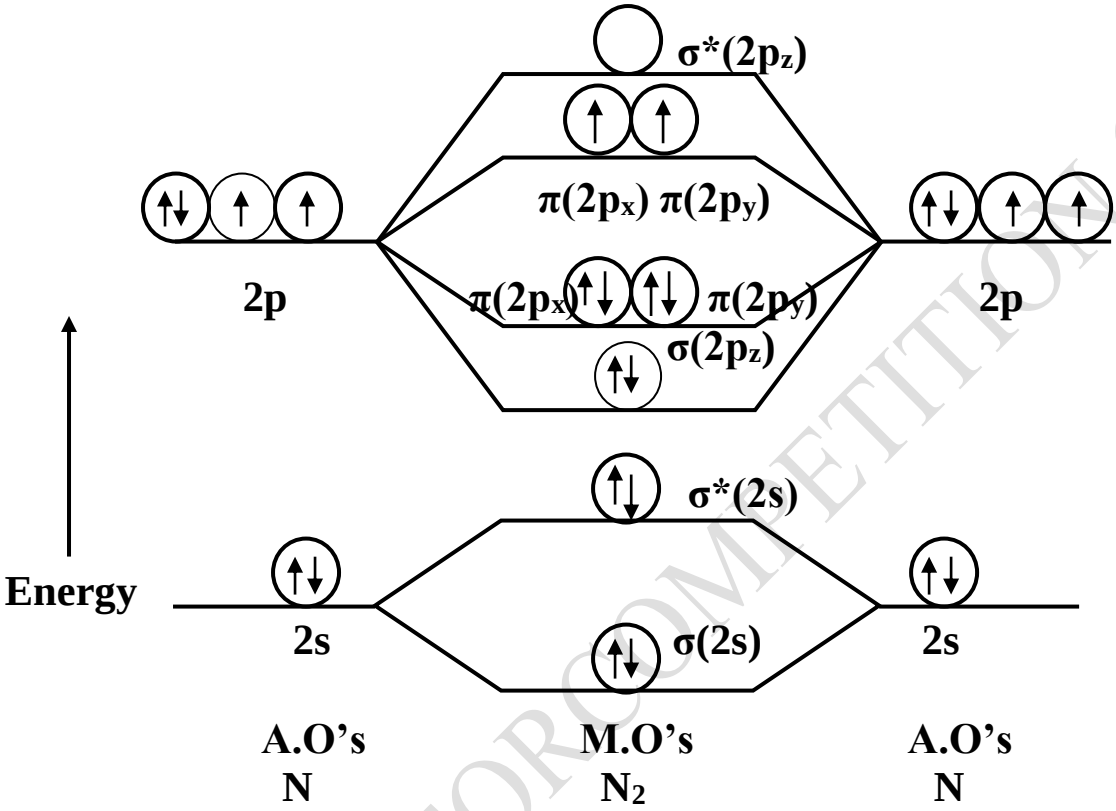


Fig.- M.O. Diagram of O_2 molecule

Thus, the electronic configuration of O_2 molecule will be as under-

O_2 molecule - KK $\sigma(2s)^2, \sigma^*(2s)^2, \pi(2p_x)^2, \pi(2p_y)^2, \sigma(2p_z)^2$

Hence, $$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{8-4}{2}$$

$$= 2$$

Since, bond order is positive, the molecule will form and will be stable. Being, bond order 2, there will present double bond between two oxygen atoms in O_2 molecule.

From M.O. Diagram, it is clear that, O_2 molecule contains two unpaired electrons. Hence, it is attracted in magnetic field and is paramagnetic in nature.

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(8) Formation of O_2^+ Ion- **O_2^+ ion is obtained by removal of one electron from O_2 molecule.**

$$O_2 \longrightarrow O_2^+ + e^-$$

Thus, O_2^+ ion contains only 15 elections. It can be considered to be made up of one O-atom and one O^+ ion having following electronic configurations-

$$O\ (8) = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$$
$$O^+ \text{ ion} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$$

Thus, molecular orbital energy level diagram of O_2^+ ion can be represented as under-

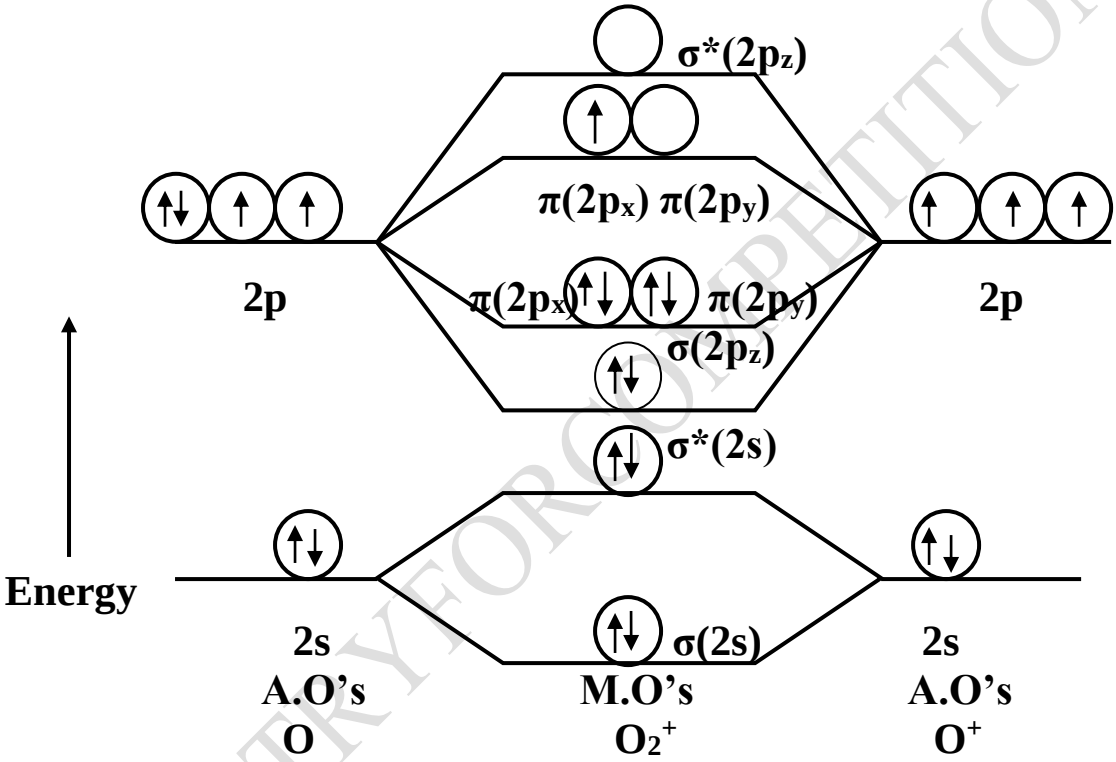


Fig.- M.O. Diagram of O_2^+ ion

Thus, the electronic configuration of O_2^+ ion will be as under-

$$O_2^+ \text{ ion} - KK\ \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_z)^2, \pi(2p_x)^2, \pi(2p_y)^2, \pi^*(2p_x)^1$$

Hence,

$$\text{Bond order} = \frac{N_b - N_a}{2}$$
$$= \frac{8-3}{2}$$
$$= 2.5$$

Since, bond order is positive, O_2^+ ion will form and will be stable.

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From M.O. Diagram, it is clear that, O_2^+ ion contains an unpaired electron. Hence, it is attracted in magnetic field and is paramagnetic in nature. Here, magnetic moment-

$$\mu = \sqrt{n(n+2)}\ B.M.$$

Where, n= number of unpaired electrons

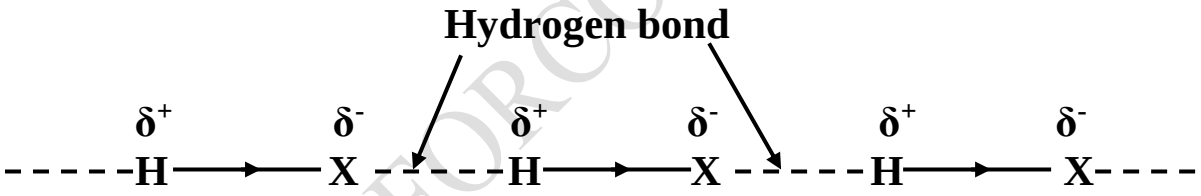
$$\therefore \quad \mu = \sqrt{1(1+2)}\ B.M.$$

$$= \sqrt{3}\ B.M.$$

Hydrogen Bonding

When hydrogen atom is covalently bonded with highly electronegative atoms, such as F, O or N, then shared election pair gets shifted towards more electronegative bonded atom. Thus, electronegative atom acquire partial negative charge while hydrogen atom acquire partial positive change. This positively charged hydrogen attracts electronegative atom of same or different molecule and forms a weak bond called hydrogen bond and this phenomenon is called hydrogen bonding.

Hydrogen bond is represented by dotted lines (---------).For example,



Here, X = F, O or N

In hydrogen bonding, hydrogen atom acts like bridge between two highly electronegative atoms, hence, it is also called hydrogen bridging. Here, hydrogen atom doesn't lie just middle of the two highly electronegative atoms, but it is close to the atom to which it is bonded with covalent bond and is farther from the atom to which it is bonded with hydrogen bond.

Conditions of hydrogen bonding-

Following are two important conditions of hydrogen bonding-

(1) Hydrogen atom should be covalently bonded with highly electronegative atoms such as F, O or N.

(2) The atomic size of the electronegative atom should be smaller.

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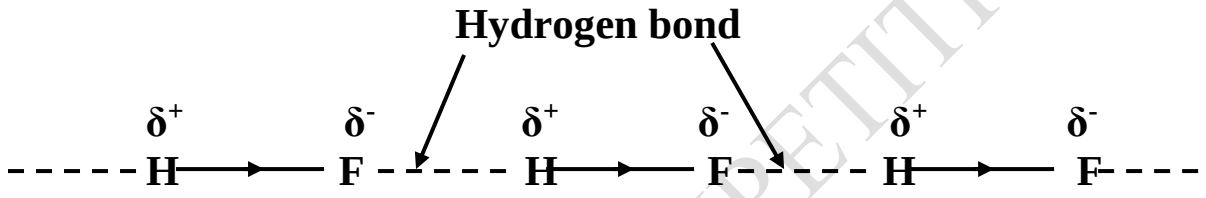
The larger the electronegativity of electronegative atom, more stronger is the hydrogen bond formed. Similarly, if atomic size of the electronegative atom is smaller, the hydrogen bond formed is stronger.

Types of hydrogen bonding

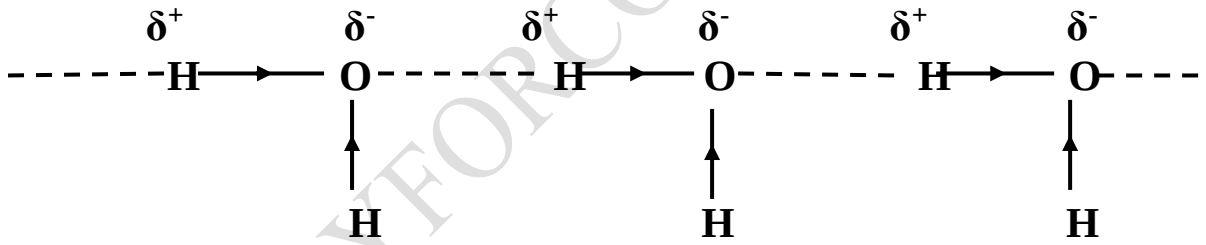
Hydrogen bonding may be of following two types-

(1) Inter-molecular Hydrogen bonding- If hydrogen bond is formed between hydrogen atom of one molecule and electronegative atom of another molecule of same or different substance, then it is called inter-molecular hydrogen bond and this phenomenon is called inter-molecular hydrogen bonding. For example,

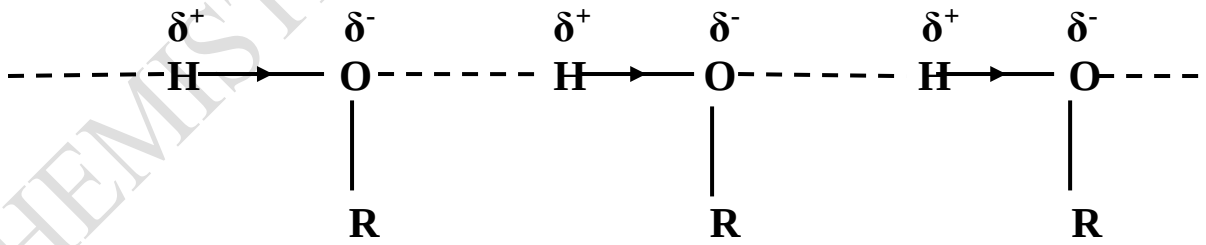
(1) Hydrogen bonding in HF-



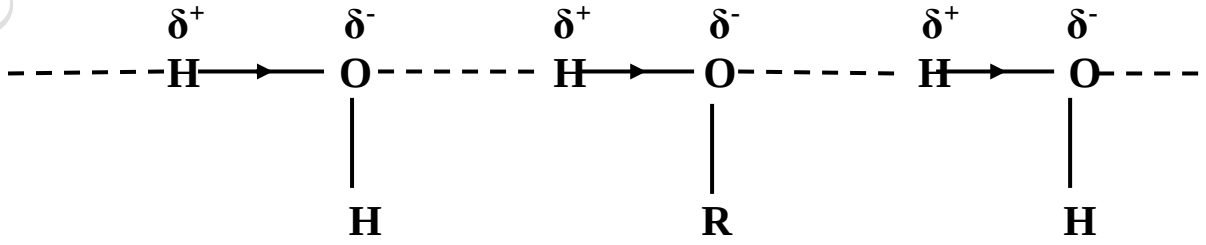
(2) Hydrogen bonding in water-



(3) Hydrogen bonding in alcohols-



(4) Hydrogen bonding in water and alcohols-

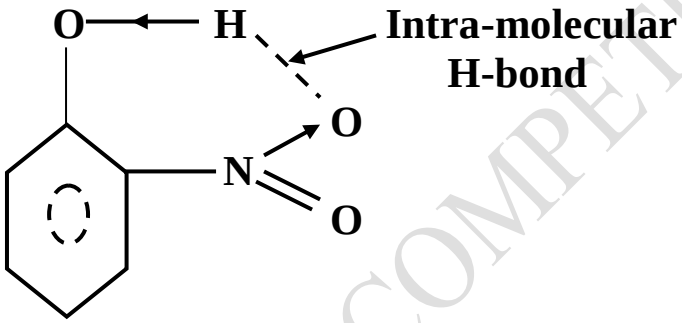


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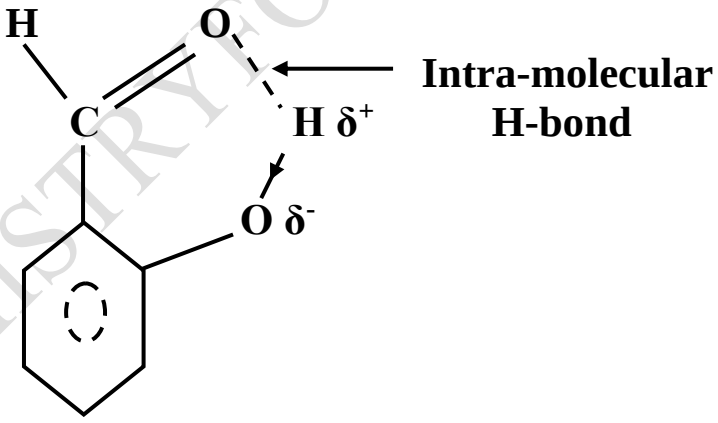
Intermolecular hydrogen bonding causes association of molecules and therefore, it affects the physical properties of the substances to the large extent. However, it has negligible effect on the chemical properties of the substances.

(1) Intra-molecular Hydrogen bonding- If hydrogen bond is formed within the molecule, then it is termed as intra-molecular hydrogen bond and this phenomenon is called intra-molecular hydrogen bonding. Here, hydrogen atom of one group forms hydrogen bond with electronegative atom of another group of same molecule. For example,

(1) Hydrogen bonding in ortho nitro phenol



(2) Hydrogen bonding in ortho hydroxy benzaldehyde (Salicylaldehyde)



Intra-molecular hydrogen bonding causes cyclization of molecules called chilation and therefore, it has negligible effect on the physical properties of the substances. However, it affects the chemical properties of the substances to some extent.

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Consequences of hydrogen bonding

(1) Effect on physical state of substances-

Inter molecular hydrogen bonding causes association of molecules and therefore, affects the physical state of substances to a large extent. For example,

HF is liquid at room temperature while, HCl is gas. In fact, HF involves inter-molecular hydrogen bonding and therefore, exist as associated liquid at room temperature.

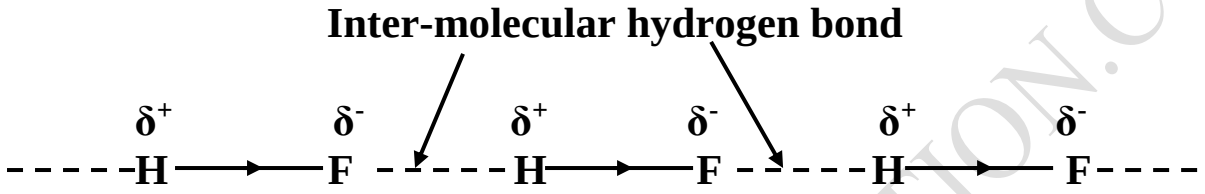


Fig.- Inter-molecular H-bonding in HF

On the other hand, due to relatively bigger atomic size and lesser electronegativity of chlorine atom, HCl does not involve inter-molecular hydrogen bonding and therefore, exist as gas at room temperature.

Similarly, H_2O is liquid at room temperature while, H_2S is gas. In fact, H_2O involves inter-molecular hydrogen bonding and therefore, exist as associated liquid at room temperature.

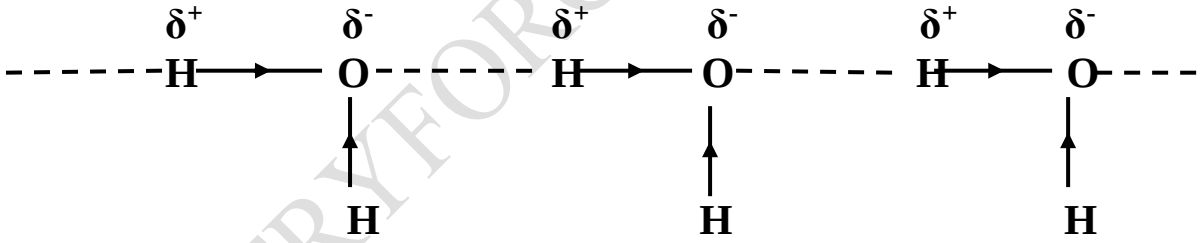


Fig.- Inter-molecular H-bonding in water

On the other hand, due to relatively bigger atomic size and lesser electronegativity of sulphur atom, H_2S does not involve inter-molecular hydrogen bonding and therefore, exist as gas at room temperature.

(2) Increase of melting and boiling points-

Due to inter-molecular hydrogen bonding, additional inter-molecular attraction operates amongst the molecules. Hence, melting and boiling points of substances gets increased. For example, boiling point of alcohols is higher than haloalkanes of comparable molecular mass.

In fact, alcohols involve inter-moleculer hydrogen bonding and therefore, have relatively higher boiling points.

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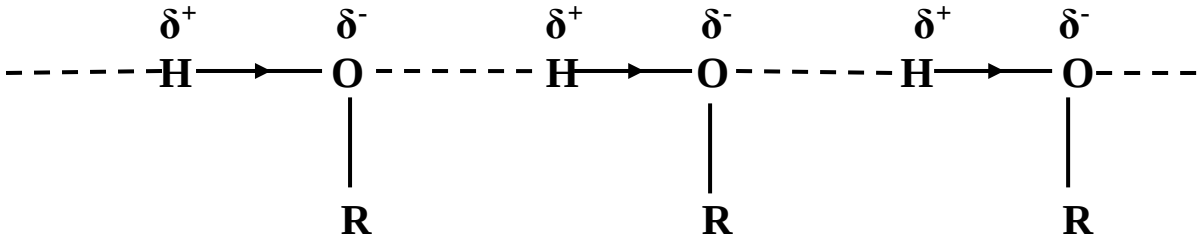


Fig.- Inter-molecular Hydrogen bonding in alcohols

On the other hand, haloalkanes do not involve inter-molecular hydrogen bonding and therefore, they have relatively lesser boiling points.

(3) Effect on water Solubility-

In general, organic substances are insoluble in water. However, those organic substances which from inter-molecular hydrogen bond with water are soluble in water. For example, alcohols from inter-molecular hydrogen bond with water and therefore, are soluble in water.

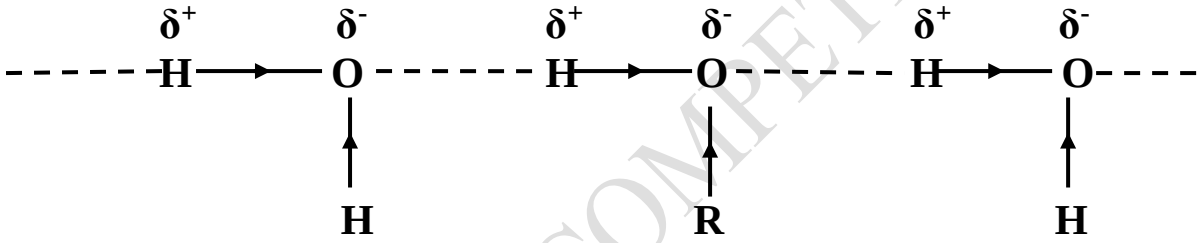


Fig.- Inter-molecular hydrogen bonding in water and alcohols

On the other hand, haloalkanes do not form inter-molecular hydrogen bond with water and therefore, are insoluble in water.

Q. Density of ice is lesser than that of water. Give the reason.

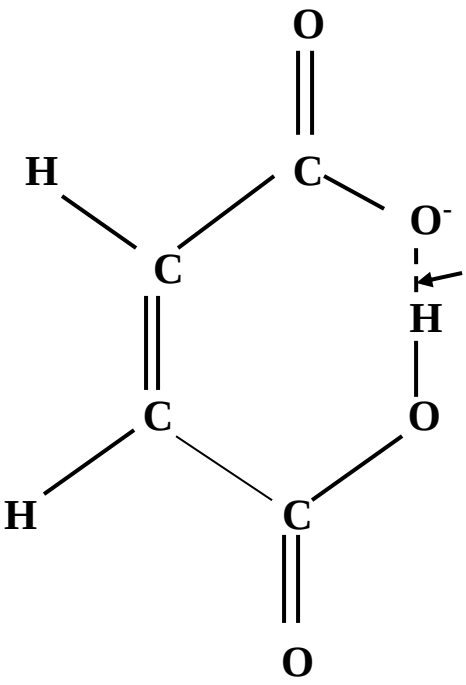
Ans. Ice Crystals have open cage like structure, where each water molecule remains tetrahedrally surrounded and hydrogen bonded with four other water molecules. Here, some space remains vacant inside the crystals. Hence, the volume of a definite amount of ice is always more than that of water. Thus, the density of ice is lesser than that of water and ice float over water.

Consequences of Intra-molecular H-bonding

(1) Effect on acidic strength of maleic and fumeric acids

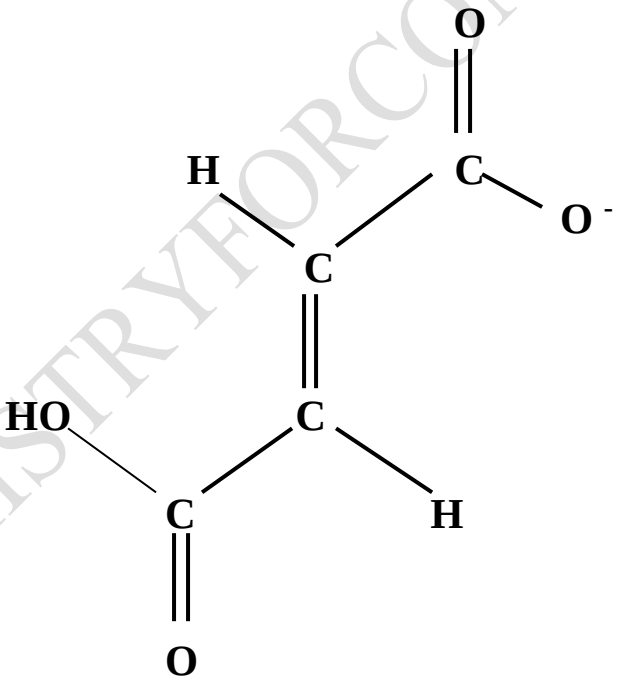
The acidic strength of maleic acid is found to be more than that of the fumeric acid. It is because, after removal of a proton, the anion formed in case of maleic acid gains stability by intra-molecular hydrogen bonding.

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Intra-molecular H-bonding in maleate ion

No such intra-molecular hydrogen bonding is possible in case of anion obtained from fumeric acid.



Fumerate ion (intra-molecular hydrogen bonding is not possible)

Hence, maleic acid has more tendency to remove proton to form maleate ion and its acidic strength is relatively high.

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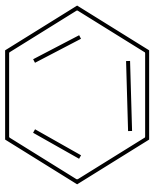
Resonance

In general, a single electronic structure is given to a molecule and it is supposed to explain all the properties of the molecule. In most of the cases, this expectation is completely fulfilled. However, there are certain molecules, for which a single electronic structure does not explain all the properties of the molecule. The electronic structure to these molecules is given by resonance. Thus, Resonance is a method to give the electronic structure to those molecules for which a single the electronic structure cannot be given.

In this method, all the possible electronic structures are written for the molecule, by changing the position of π- electron pairs and lone pairs, but keeping the position of atoms unchanged. All these structures explain almost all the properties of molecule, but not all the properties of molecule. Hence, these are not the actual structure of molecule and therefore, have no physical existence. The molecule is not found in any of these forms. Thus, these structures are hypothetical and are called resonance structures or canonical forms. The actual structure of the molecule is considered to lie any where amongst these structures and is called resonance hybrid. It has its physical existence and the molecule always exists in this form. It explains all the properties of the molecule, but it can't be represented on paper.

Resonance hybrid is not the mixture of resonance structures, but it is 100% in itself. It does not exist in one resonance form for some time and in other resonance form for another time. In fact, it always exists in its own form but it can't be represented on paper.

For example, in general, following electronic structure having single and double bonds in alternate positions are given to benzene.

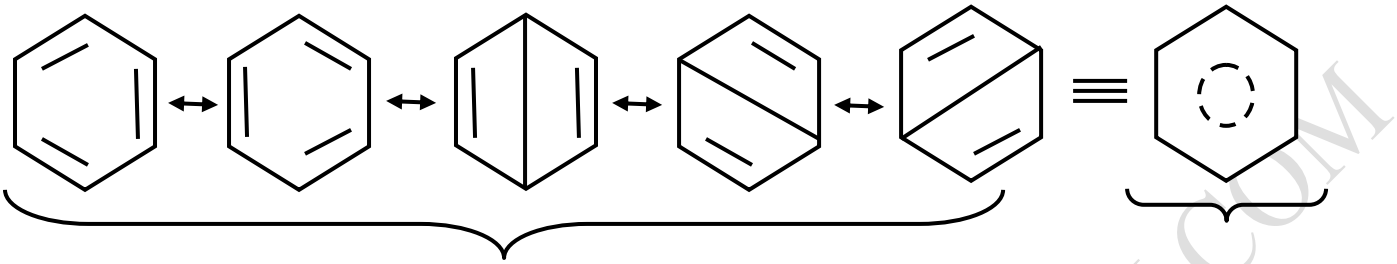


Benzene (Kekule's structure)

As per this structure, benzene molecule must contain two types of carbon-carbon bonds, one having bond length equal to 1.54 A^0 (corresponding to carbon-carbon single bonds), while the other having bond length equal to 1.34 A^0. However, in benzene, none of the carbon-carbon bond is of 1.54 A^0 or 1.34 A^0, but all the carbon-carbon bonds in benzene molecule are of same bond length of 1.39 A^0. Hence, this is not the actual

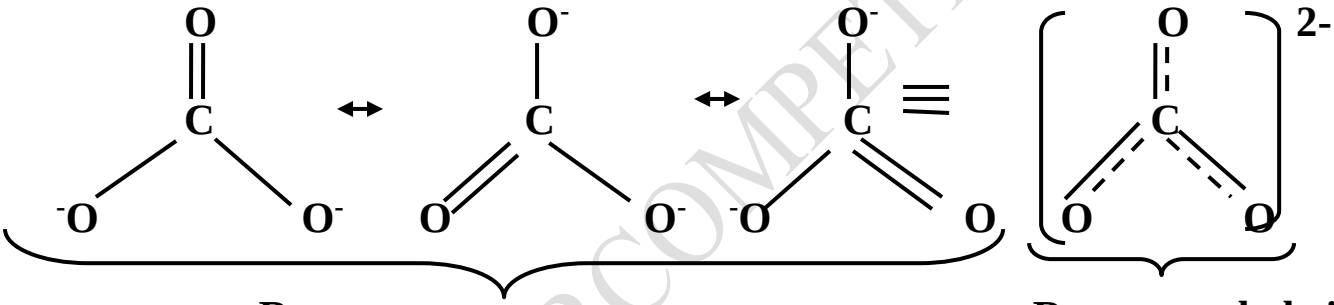
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structure of benzene. The actual structure of benzene is given by resonance and it is considered to be resonance hybrid of following five resonance structures.



Resonance structures **Resonance hybrid**

Similarly, carbonate ion (CO_3^{2-}) is considered to be resonance hybrid of following three resonance structures.



Resonance structures **Resonance hybrid**

Conditions of resonance

Following are two important conditions to show the phenomenon of resonance-

(1) The species (molecule or ion) should be planar.

(2) The species should involve conjugation i.e. it should contain single and multiple bonds in alternate conditions or lone pair in alternation of multiple bonds.

Criteria of resonance

The important criteria of resonance are as under-

(1) Shortening of bond length of single bonds and lengthening of bond length of multiple bonds.

(2) Presence of resonance energy.

(3) Increase of stability of the species.

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Resonance energy

Resonance hybrid has lesser energy than any of the resonance structures. Here, the difference of the energy of most stable resonance structure and resonance hybrid is called resonance energy of the species. Mathematically,

$$\text{Resonance energy} = \left(\begin{array}{l}\text{Energy of most}\\ \text{stable resonance}\\ \text{structure}\end{array}\right) - \left(\begin{array}{l}\text{Energy of}\\ \text{resonance}\\ \text{hybrid}\end{array}\right)$$

Resonance energy provides stability to the species. The larger the value resonance energy of a species, more is its stability.

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