

## 1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 1)
Module Name/Title	Chemical bonding and molecular structure: Part 4
Module Id	kech_10404
Pre-requisites	Knowledge about atomic structure, polarity of bonds, electronic configuration
Objectives	After going through this lesson, the learners will be able to understand the following: <ul style="list-style-type: none"><li>• Molecular Orbital theory</li><li>• Linear combination of Atomic Orbitals (LCAO)</li><li>• Bond order and its calculation</li><li>• Stability and Magnetic character of molecule</li><li>• Comparing stability of various molecules and ions</li><li>• Molecular orbital theory of homonuclear diatomic molecules</li><li>• Hydrogen bonding</li></ul>
Keywords	Molecular orbital theory, LCAO, bond order, paramagnetism and diamagnetism, hydrogen bond

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### 1. Molecular Orbital Theory

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are :

- i. The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- ii. The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- iii. While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital
- iv. it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomicorbital is monocentric while a molecular orbital is polycentric.
- v. The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as **bonding molecular orbital** while the other is called **antibonding molecular orbital**.
- vi. The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- vii. Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.
- viii. The molecular orbitals like atomic orbitals are filled in accordance with the aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.

## Formation of Molecular Orbitals Linear Combination of Atomic Orbitals (LCAO)

According to wave mechanics, the atomic orbitals can be expressed by wave functions ( $\psi$ 's) which represent the amplitude of the electron waves. These are obtained from the solution of Schrödinger wave equation. However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtain directly from the solution of Schrödinger wave equation. To overcome this problem, an approximate method known as **linear combination of atomic orbitals (LCAO)** has been adopted.

Let us apply this method to the homonuclear diatomic hydrogen molecule. Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1s orbital. The atomic orbitals of these atoms may be represented by the wave functions  $\psi_A$  and  $\psi_B$ . Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below :

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

Therefore, the two molecular orbitals  $\sigma$  and  $\sigma^*$  are formed as :

$$\sigma = \psi_A + \psi_B$$

$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital  $\sigma$  formed by the addition of atomic orbitals is called the **bonding molecular orbital** while the molecular orbital  $\sigma^*$  formed by the subtraction of atomic orbital is called **antibonding molecular orbital** as depicted in Fig. 1.

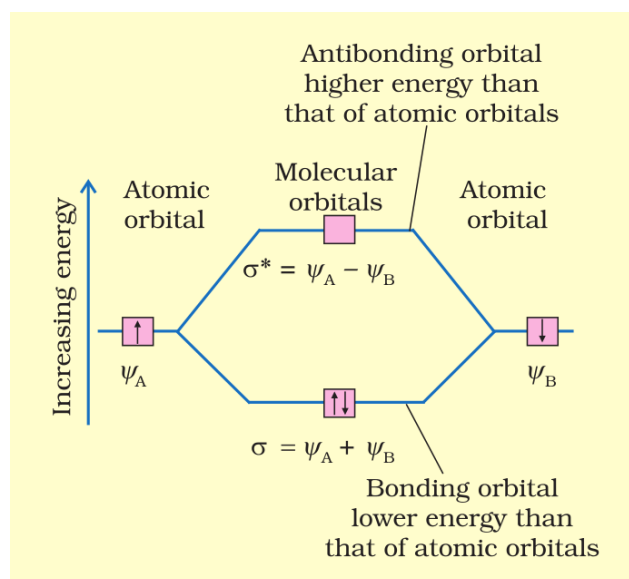


Fig.1 Formation of bonding ( $\sigma$ ) and antibonding ( $\sigma^*$ ) molecular orbitals by the linear combination of atomic orbitals  $\psi_A$  and  $\psi_B$  centered on two atoms A and B respectively.

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Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other due to constructive interference while in the formation of antibonding molecular orbital, the electron waves cancel each other due to destructive interference. As a result, the electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei. In fact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilise a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of the atomic orbitals that have combined to form it. In contrast, the electrons placed in the antibonding molecular orbital destabilise the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei, which causes a net increase in energy.

It may be noted that the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals. The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

### **The conditions for the combination of Atomic Orbitals**

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

**1. The combining atomic orbitals must have the same or nearly the same energy.** This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. This is not true if the atoms are very different.

**2. The combining atomic orbitals must have the same symmetry about the molecular axis.** By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example,  $2p_z$  orbital of one atom can combine with  $2p_z$  orbital of the other atom but not with the  $2p_x$  or  $2p_y$  orbitals because of their different symmetries.

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**3. The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

### Types of Molecular Orbitals

Molecular orbitals of diatomic molecules are designated as  $\sigma$ (sigma),  $\pi$ (pi),  $\delta$ (delta), etc.

In this nomenclature, the **sigma ( $\sigma$ ) molecular orbitals are symmetrical around the bond-axis while pi ( $\pi$ ) molecular orbitals are not symmetrical.** For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the  $\sigma$  type and are designated as  $\sigma$  1s and  $\sigma^*$  1s [Fig. 4.20(a), page 124]. **If internuclear axis is taken to be in the z-direction, it can be seen that a linear combination of  $2p_z$ - orbitals of two atoms also produces two sigma molecular orbitals designated as  $\sigma$   $2p_z$  and  $\sigma^*$   $2p_z$ .**[Fig..2(b)]

Molecular orbitals obtained from  $2p_x$  and  $2p_y$  orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals, are labelled as  $\pi$  and  $\pi^*$  [Fig. 2(c)]. A  $\pi$  bonding MO has larger electron density above and below the inter-nuclear axis. The  $\pi^*$  antibonding MO has a node between the nuclei.

### Energy Level Diagram for Molecular Orbitals

We have seen that 1s atomic orbitals on two atoms form two molecular orbitals designated as  $\sigma$  1s and  $\sigma^*$  1s. In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals:

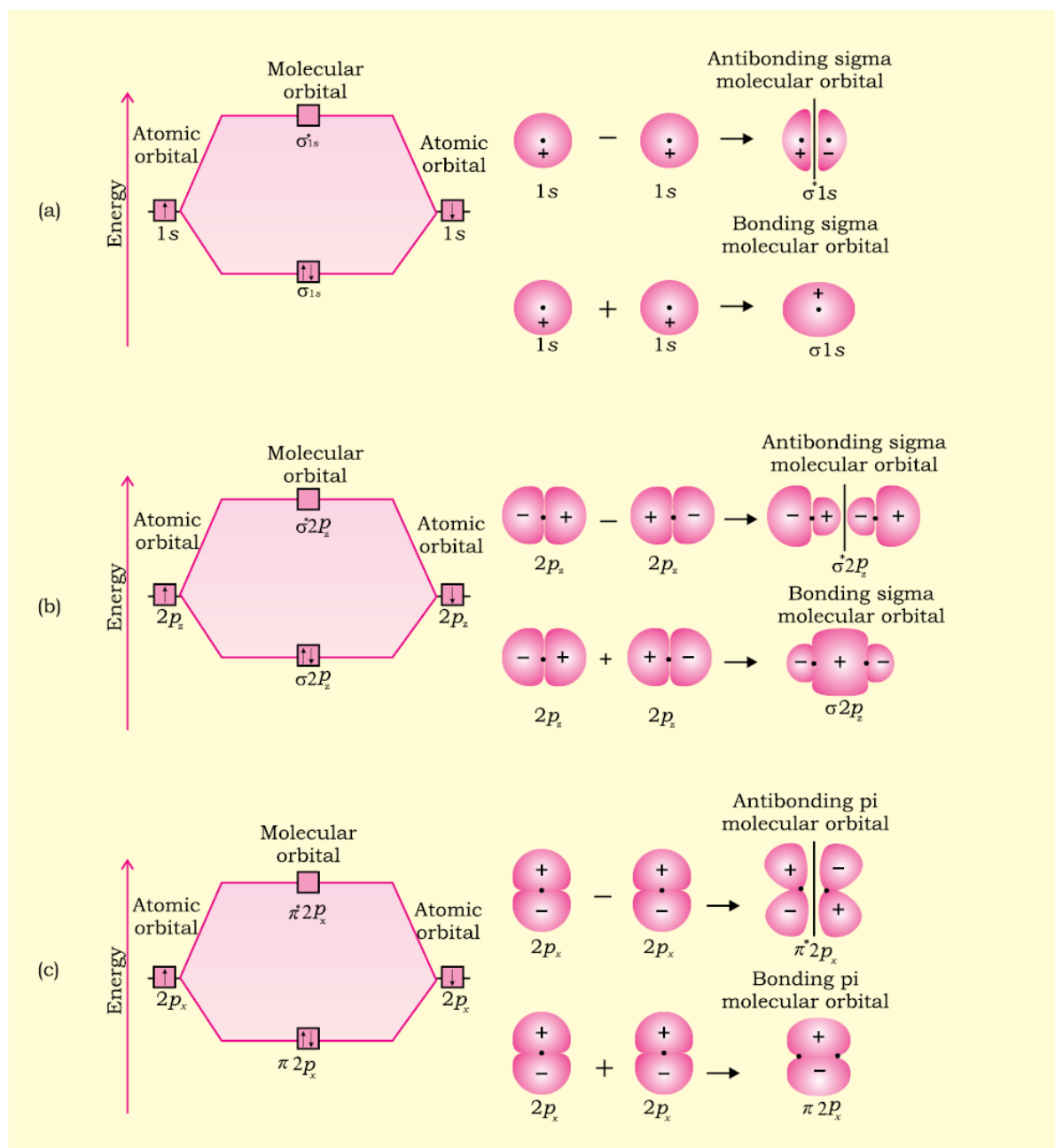


Fig. 2 Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b)  $2p_z$  atomic orbitals and (c)  $2p_x$  atomic orbitals.

Antibonding MO  $\sigma^* 2s \sigma^* 2p_z \pi^* 2p_x \pi^* 2p_y$

Bonding MOs  $\sigma 2s \sigma 2p_z \pi 2p_x \pi 2p_y$

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for  $O_2$  and  $F_2$  is given below :

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_z} < (\pi_{2p_x} = \pi_{2p_y}) < (\pi^*_{2p_x} = \pi^*_{2p_y}) < \sigma^*_{2p_z}$$

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However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$ . For instance, it has been observed experimentally that for molecules such as  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$  etc. the increasing order of energies of various molecular orbitals is

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

The important characteristic feature of this order is that the **energy of  $\sigma 2p_z$  molecular orbital is higher than that of  $\pi 2p_x$  and  $\pi 2p_y$  molecular orbitals.**

### **Electronic Configuration and Molecular Behaviour**

The distribution of electrons among various molecular orbitals is called the **electronic configuration of the molecule**. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

**Stability of Molecules:** If  $N_b$  is the number of electrons occupying bonding orbitals and  $N_a$  the number occupying the antibonding orbitals, then

- (i) the molecule is stable if  $N_b$  is greater than  $N_a$ , and
- (ii) the molecule is unstable if  $N_b$  is less than  $N_a$ .

In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable.

### **Bond order**

**Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e.,**

$$\text{Bond order (b.o.)} = \frac{1}{2} (N_b - N_a)$$

The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows: A positive bond order (i.e.,  $N_b > N_a$ ) means a stable molecule while a negative (i.e.,  $N_b < N_a$ ) or zero (i.e.,  $N_b = N_a$ ) bond order means an unstable molecule.

### **Nature of the bond**

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively as studied in the classical concept.

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### ***Bond-length***

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

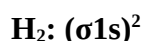
### ***Magnetic nature***

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O<sub>2</sub> molecule.

## **2. Bonding in some Homonuclear Diatomic Molecules**

In this section we shall discuss bonding in some homonuclear diatomic molecules.

**1. Hydrogen molecule (H<sub>2</sub>):** It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in  $\sigma_{1s}$  molecular orbital. So electronic configuration of hydrogen molecule is

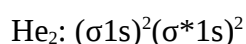


The bond order of H<sub>2</sub> molecule can be calculated as given below:

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

This means that the two hydrogen atoms are bonded together by a **single covalent bond**. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol<sup>-1</sup> and bond length equal to 74 pm. Since **no unpaired electron** is present in hydrogen molecule, therefore, it is **diamagnetic**.

**2. Helium molecule (He<sub>2</sub>):** The electronic configuration of helium atom is 1s<sup>2</sup>. Each helium atom contains 2 electrons, therefore, in He<sub>2</sub> molecule there would be 4 electrons. These electrons will be accommodated in  $\sigma_{1s}$  and  $\sigma^*_{1s}$  molecular orbitals leading to electronic configuration:



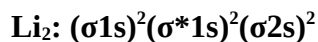
Bond order of He<sub>2</sub> is  $\frac{1}{2}(2 - 2) = 0$

**He<sub>2</sub> molecule is therefore unstable and does not exist.**



Similarly, it can be shown that **Be<sub>2</sub> molecule**  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$  also does not exist.

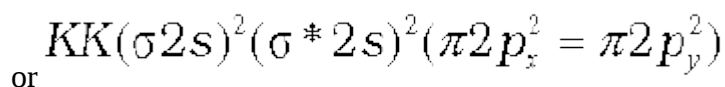
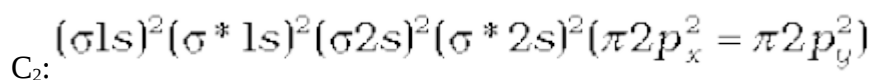
**3. Lithium molecule (Li<sub>2</sub>):** The electronic configuration of lithium is  $1s^2, 2s^1$ . There are six electrons in Li<sub>2</sub>. The electronic configuration of Li<sub>2</sub> molecule, therefore, is



The above configuration is also written as **KK** $(\sigma 2s)^2$  where **KK** represents the closed K shell structure  $(\sigma 1s)^2 (\sigma^* 1s)^2$ .

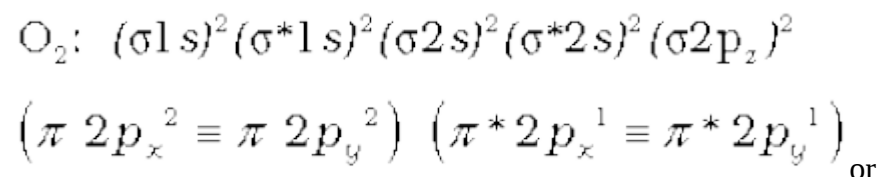
From the electronic configuration of Li<sub>2</sub> molecule it is clear that there are four electrons present in bonding molecular orbitals and two electrons present in antibonding molecular orbitals. Its **bond order, therefore, is**  $\frac{1}{2} (4 - 2) = 1$ . It means that Li<sub>2</sub> molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li<sub>2</sub> molecules are known to exist in the vapour phase.

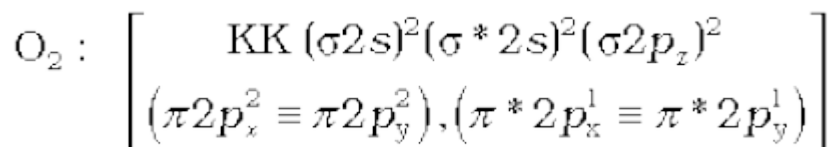
**4. Carbon molecule (C<sub>2</sub>):** The electronic configuration of carbon is  $1s^2 2s^2 2p^2$ . There are twelve electrons in C<sub>2</sub>. The electronic configuration of C<sub>2</sub> molecule, therefore, is



The bond order of C<sub>2</sub> is  $\frac{1}{2} (8 - 4) = 2$  and C<sub>2</sub> should be diamagnetic. Diamagnetic C<sub>2</sub> molecules have indeed been detected in vapour phase. It is important to note that double bond in C<sub>2</sub> consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond. In a similar fashion the bonding in N<sub>2</sub> molecule can be discussed.

**5. Oxygen molecule (O<sub>2</sub>):** The electronic configuration of oxygen atom is  $1s^2 2s^2 2p^4$ . Each oxygen atom has 8 electrons, hence, in O<sub>2</sub> molecule there are 16 electrons. The electronic configuration of O<sub>2</sub> molecule, therefore, is





From the electronic configuration of  $\text{O}_2$  molecule it is clear that ten electrons are present in bonding molecular orbitals and six electrons are present in antibonding molecular orbitals. Its bond order, therefore, is

$$\text{Bond order} = \frac{1}{2} [N_b - N_a] = \frac{1}{2} [10 - 6] = 2$$

So in oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in  $\pi^*_{2p_x}$  and  $\pi^*_{2p_y}$  molecular orbitals, therefore,  **$\text{O}_2$  molecule should be paramagnetic, a prediction that corresponds to experimental observation.** In this way, the theory successfully explains the paramagnetic nature of oxygen.

Similarly, the electronic configurations of other homonuclear diatomic molecules of the second row of the periodic table can be written. In Fig.3 are given the molecular orbital occupancy and molecular properties for  $\text{B}_2$  through  $\text{Ne}_2$ . The sequence of MOs and their electron population are shown. The bond energy, bond length, bond order, magnetic properties and valence electron configuration appear below the orbital diagrams.

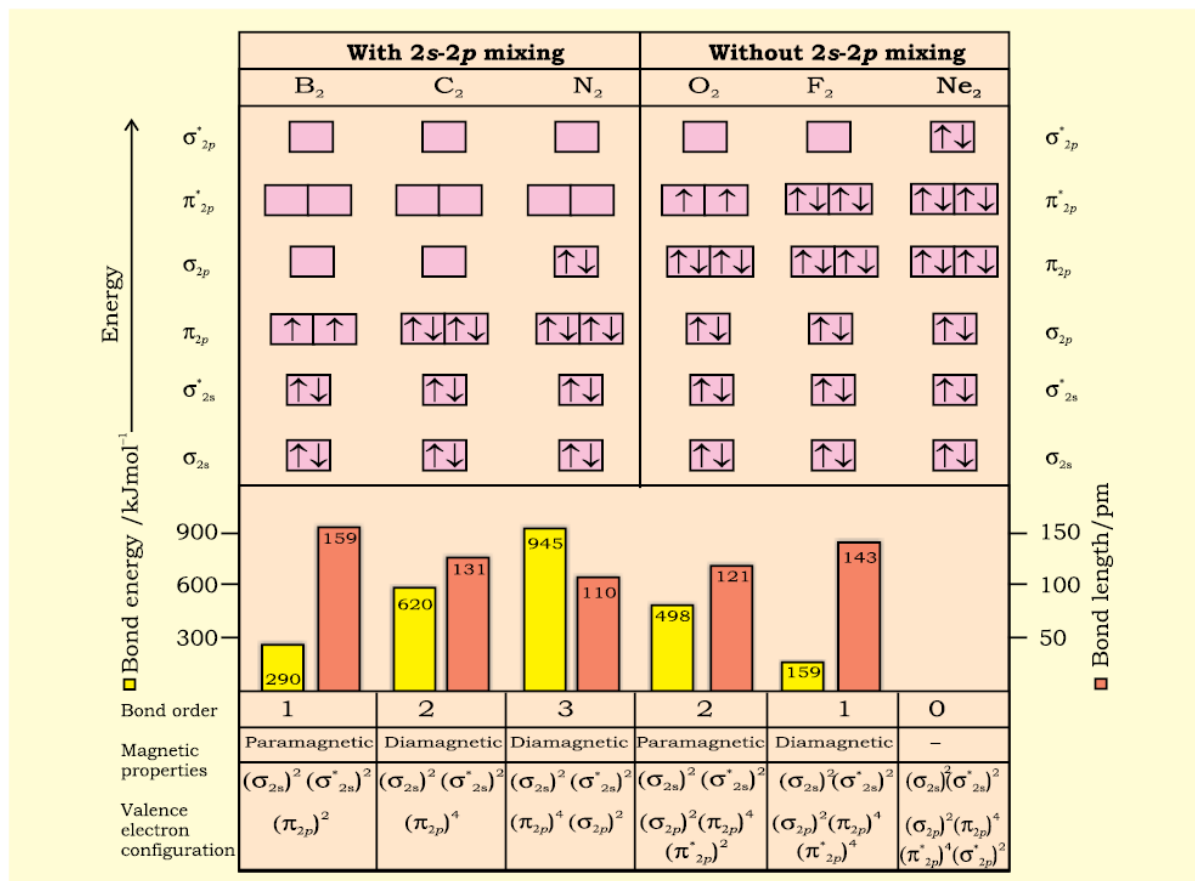
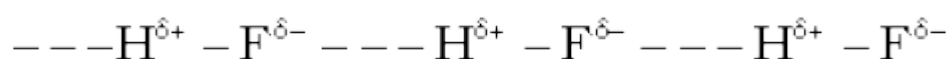


Fig. 3 MO occupancy and molecular properties for  $\text{B}_2$  through  $\text{Ne}_2$ .

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### 3. Hydrogen Bonding

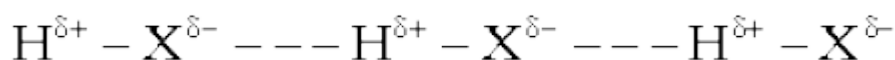
Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are attached to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond and is weaker than the covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as depicted below :



Here, hydrogen bond acts as a bridge between two atoms which holds one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line ( - - - ) while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

#### Cause of formation of Hydrogen Bonding

When hydrogen is bonded to strongly electronegative element 'X', the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge ( $\delta^+$ ) while 'X' attains fractional negative charge ( $\delta^-$ ). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as :



The magnitude of H-bonding depends on the physical state of the compound. It is maximum in the solid state and minimum in the gaseous state. Thus, the hydrogen bonds have strong influence on the structure and properties of the compounds.

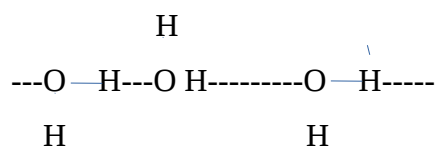
#### Types of H-Bonds

There are two types of H-bonds

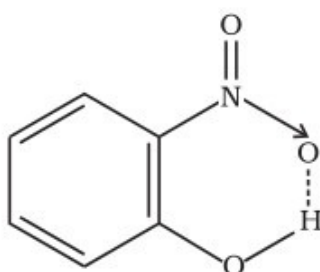
- (i) Intermolecular hydrogen bond
- (ii) Intramolecular hydrogen bond

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**(1) Intermolecular hydrogen bond :**It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules, etc.



**(2) Intramolecular hydrogen bond :**It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in *o*-nitrophenol the hydrogen is in between the two oxygen atoms.



*Intramolecular hydrogen bonding in *o*-nitrophenol molecule*

#### 4. Conditions for hydrogen bonding

The following conditions are necessary for the formation of hydrogen bonding

i) **High electronegativity of atom bonded to hydrogen.** The molecule should contain an atom of high electronegativity such as F, O or N bonded to hydrogen atom. The common examples are HF, H<sub>2</sub>O and NH<sub>3</sub>

ii) **Small size of electronegative atom.** The size of electronegative atom should be quite small. This is due to the fact that the smaller the size of electronegative atom, the greater will be its attraction for the bonded electron pair. This will cause greater polarity in the bond between H and electronegative atom which results in stronger hydrogen bond. For example NH<sub>3</sub> shows hydrogen bonding while HCl does not, although both N and Cl have the same electronegativity (3.0). Hydrogen bonds are not formed by Cl because of its bigger size than nitrogen.

**Differences between hydrogen bond and Covalent bond.** The main points differences hydrogen bond and covalent bond are:

<b>HYDROGEN BOND</b>	<b>COVALENT BOND</b>
Hydrogen bond involves dipole-dipole attractions.	Covalent bond involves sharing of electrons.
It is formed between hydrogen atom and a highly electronegative atom(F,O,N)	It is formed between any two electronegative atoms which may be of the same element or of different elements.
Strength of hydrogen bond is very small e.g bond strength of H.....F bond is 41.83kJ/ mol	Bond strength of covalent bond is sufficiently high. For example bond strength of H-H bond is 433kJ / mol.

### **Examples of hydrogen Bonded compounds.**

A few examples of compounds which exhibit hydrogen bonding are discussed below:

**1. Hydrogen fluoride.** In the solid state , hydrogen fluoride consists of long zig-zag chain of molecules associated together through hydrogen bonds. Thus, hydrogen fluoride molecule is represented as  $(HF)_n$  . In the liquid or gaseous state, the chain however, becomes linear.

**2. Water.** Hydrogen bonding exists in water molecules also. In addition to two covalent (O-H) bonds in water, oxygen atom forms two hydrogen bonds. As a result of hydrogen bonds, each oxygen is tetrahedrally surrounded by four hydrogen atoms , two by covalent bonds and two by hydrogen bonds. The associated water molecules may be expressed as  $H_2O)_n$

**3. Ammonia.** Ammonia molecules has an electronegative nitrogen atom bonded to three hydrogen atoms. Due to difference in electronegativity between nitrogen and hydrogen, each hydrogen atom acquires positive charge. Thus, in the molecule, there one negative site and three positive sites so that the molecules of ammonia associates through hydrogen bonding to form long chain.

### **Influence of Hydrogen Bonding on the Properties.**

Hydrogen bonding has important effect on many physical properties such as melting point, boiling point and solubility of the compounds. The main characteristics of compounds having hydrogen bonds are given below.

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**1. Association.** Due to intermolecular hydrogen bonding two or more molecules of a compound exists as associated molecules. For example , carboxylic acids (RCOOH) exists as dimers even in the vapour state .

**2. Higher melting and boiling points.** The compounds containing hydrogen bonds have high melting and boiling points. It is due to the fact that because of hydrogen bonding, the electrostatic force of attraction in the molecules become large. Consequently, larger energy is required to separate these molecules before they can melt or boil. The influence of hydrogen bonding on melting and boiling points can be understood comparing the melting and boiling points of the hydrides of elements of groups 14, 15, 16 and 17.

HYDRIDE	m.p (K)	b.p(K)
CH <sub>4</sub>	89.0	111.5
NH <sub>3</sub>	195.5	239.6
H <sub>2</sub> O	273.0	373.0
HF	180.7	292.4

The melting and boiling points of hydrides of elements of these group are also plotted against their molecular masses. The melting and boiling points increases as the molecular mass increases in group 14. This is mainly due to the fact that as the size of elements of groups 14 increases, the number of electrons also increases. As a result, Van der Waals forces also increase and therefore, melting and boiling points increase. However, Hydrogen of group 15, 16 and 17 do not show this trend. In these groups, the melting and boiling points also increase with increasing molecular mass with the exception of first member. But, the first member NH<sub>3</sub> (group 15), H<sub>2</sub>O (group 16) and HF (group 17) have abnormally high melting and boiling points. The relatively high melting and boiling point of the first member of each group is due to the intermolecular hydrogen bonding shown by these compounds. For example, the boiling point of HF is much more than that of HCl due to larger hydrogen bonding in the former. Similarly, we can account for the higher values of boiling points of NH<sub>3</sub> and H<sub>2</sub>O in their group.

It is interesting to note that hydrogen bond in HF is stronger than H<sub>2</sub>O. However , water boils at a higher temperature than HF. This is due to the reason that each H<sub>2</sub>O molecules is bonded to four other H<sub>2</sub>O molecules through hydrogen bonds whereas each HF molecule is bonded to two other HF molecules through hydrogen bonds.

**3. Influence on the physical state.** Hydrogen bonding also influences the physical state of the substances ( solid, liquid or gas). For example, both O and S belong to same group but

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H<sub>2</sub>O is a liquid at ordinary temperature, while H<sub>2</sub>S is a gas. This is explained on the basis of electronegativity values.

H<sub>2</sub>O molecules

Electronegativity of O = 3.5

Electronegativity of H = 2.1

H<sub>2</sub>S molecules

Electronegativity of S = 2.5

Electronegativity of H = 2.1

In water, oxygen is highly electronegative so that it forms hydrogen bonds. As a result, the molecules of H<sub>2</sub>O get associated with one another and this raises the boiling point of water. Consequently, water exists as liquid at room temperature. On the other hand, the electronegativity difference of atoms in H<sub>2</sub>S is less and hydrogen bonding in H<sub>2</sub>S is almost negligible. As a result H<sub>2</sub>S is not associated and exists as a gas at room temperature.

4. **Solubility:** Hydrogen bonding also influences the solubility of one substance in another. For ex- alcohol is highly soluble in water due to hydrogen bonding with water molecules. :

5. **Volatility:** The compounds involving hydrogen bonded between different molecules such as NH<sub>3</sub>, H<sub>2</sub>O and HF have higher boiling points. Therefore, they are less volatile as compound to the other corresponding members of their groups. The enthalpies of vaporisation follows almost the same pattern as shown by their melting points and boiling points. For ex- in group 17, the enthalpies of vaporisation decrease in the order.

HCl < HBr < HI < HF

Similarly in groups 15 and 16 the trends are

H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te < H<sub>2</sub>O

PH<sub>3</sub> < AsH<sub>3</sub> < SbH<sub>3</sub> < NH<sub>3</sub>

Q. Arrange the following in the decreasing order of their boiling points HF, HCl, HBr

Ans. HF > HBr > HCl

Q. Do o-nitrophenol and p-nitrophenol have hydrogen bonding in their molecules? Explain which of the two has higher boiling point?

Ans. Both have hydrogen bonding. o-nitrophenol has intramolecular hydrogen bonds. But due to larger distance between -NO<sub>2</sub> and -OH groups in p-nitrophenol, there is no such bonding.

## 5. Summary

The molecular bonding (MO) theory describes bonding in terms of the combination and arrangement of atomic orbitals to form molecular orbitals that are associated with the molecule as a whole. The number of molecular orbitals are always equal to the number of atomic orbitals from which they are formed. Bonding molecular orbitals increase electron density

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between the nuclei and are lower in energy than the individual atomic orbitals. Antibonding molecular orbitals have a region of zero electron density between the nuclei and have more energy than the individual atomic orbitals.

The electronic configuration of the molecules is written by filling electrons in the molecular orbitals in the order of increasing energy levels. As in the case of atoms, the Pauli exclusion principle and Hund's rule are applicable for the filling of molecular orbitals. Molecules are said to be stable if the number of electrons in bonding molecular orbitals is greater than in antibonding molecular orbitals.

**Hydrogen bond** is formed when a hydrogen atom finds itself between two highly electronegative atoms such as F, O and N. It may be intermolecular (existing between two or more molecules of the same or different substances) or intramolecular (present within the same molecule). Hydrogen bonds have a powerful effect on the structure and properties of many compounds.