Thus, while the bond order of He_2 is zero, that of He_2^+ is 1/2. Hence, He_2^+ exists while He_2 does not.

Problem 3. Of the species O_2, O_2^+ O_2^-, O_2^{2-}, which would have the maximum bond strength ?

Answer : Higher bond orders are associated with shorter bond lengths and higher bond strengths. We will first calculate the bond orders for the various species from their electronic configurations :

$$O_2 :- KK \; \sigma(2s)^2 \; \overset{*}{\sigma}(2s^2) \; \sigma(2p_z)^2 \; \pi(2p_x)^2 \; \pi(2p_y)^2 \; \overset{*}{\pi}(2p_x)^1 \; \overset{*}{\pi}(2p_y)^1$$

∴   **Bond order** $= 1/2 \,(8 - 4) = 2$

         O_2^+ : One electron is removed from $\overset{*}{\pi}(2p_y)$ ABMO.

∵   **Bond order** $= 1/2 \,(8 - 3) = 2\frac{1}{2}$

         O_2^- : One electron is added to $\overset{*}{\pi}(2p_x)$ ABMO.

∴   **Bond order** $= 1/2 \,(8 - 5) = 1\frac{1}{2}$

         O_2^{2-} : Two electrons are added to the outermost ABMO.

∴   **Bond order** $= 1/2 \,(8 - 6) = 1$

Since O_2^+ has the highest bond order, it has the shortest bond length and hence the maximum bond strength.

Electronic Configurations of Heteronuclear Diatomic Molecules

The cases of heteronuclear diatomic molecules, in which the two atoms constituting a molecule are different, may now be considered. The principles involved in the distribution of electrons are the same as discussed before.

However, the molecular orbital diagrams will not be symmetrical as in the case of homonuclear diatomic molecules. Due to the difference in the electronegativities of the atoms, the electrons in a bonding molecular orbital spend more time near the more electronegative atom. On the other hand, electrons in an antibonding molecular orbital are closer to the less electronegative atom.

While discussing the molecular orbital energy level diagrams of heteronuclear diatomic molecules, it should be kept in mind that all the atomic orbitals of same symmetry will contribute in the formation of an equal number of molecular orbitals. Any molecular orbital thus formed will have greatest contribution from that combining atomic orbital which is nearest to it in energy and least contribution from that combining atomic orbital which is farthest to it in energy.

Let us discuss the electronic configurations and molecular orbital diagrams for some common heteronuclear diatomic molecules.

Carbon Monoxide Molecule, CO. The electronic configurations of C and O atoms are $1s^2 \, 2s^2 p^2$ and $1s^2 \, 2s^2 p^4$, respectively. There are 4 electrons in the outer shell of carbon and 6 electrons in the outer shell of oxygen. Thus, a total of 10 outer electrons are to be accommodated in the molecular orbitals of CO molecule. Because of higher electronegativity of oxygen, its atomic orbitals would be of lower energy than the corresponding atomic orbitals of carbon. Due to this energy difference, the bonding and antibonding molecular orbitals receive different contributions from atomic orbitals of carbon and oxygen. The bonding molecular orbitals receive more contribution from atomic orbitals of lower energy, i.e., the atomic orbitals of oxygen and would be closer to it in energy than the antibonding molecular orbitals which would be closer to the atomic orbitals of carbon in energy, as shown in Fig. 31. The bonding molecular orbitals would have more characteristics of atomic orbitals of oxygen and antibonding molecular orbitals would have more characteristics of atomic orbitals of carbon.

The $2s$ and $2p_z$ atomic orbitals of C atom mix to produce two atomic orbitals of mixed sp_z character. The higher energy mixed sp_z orbital of C atom is closer in energy to its pure $2p_z$ orbital and has major contribution from it whereas the lower energy mixed sp_z orbital of C is closer in energy to its pure $2s$ orbital and has major contribution from it. Similarly, $2s$ and $2p_z$ atomic orbitals of oxygen atom also mix with each other (though not to the same extent to which the orbitals of C atom mix because the energy difference between $2s$ and $2p_z$ atomic orbitals of oxygen atom is higher than that between the similar atomic orbitals of C atom) to form two atomic orbitals of mixed sp_z character. The higher energy mixed sp_z orbital of O is very close in energy to its pure $2p_z$ orbital and has contribution mostly from $2p_z$ orbital whereas the lower energy mixed sp_z orbital, being very close in energy to pure $2s$ orbital of oxygen atom, has contribution mostly from $2s$ orbital of oxygen atom.
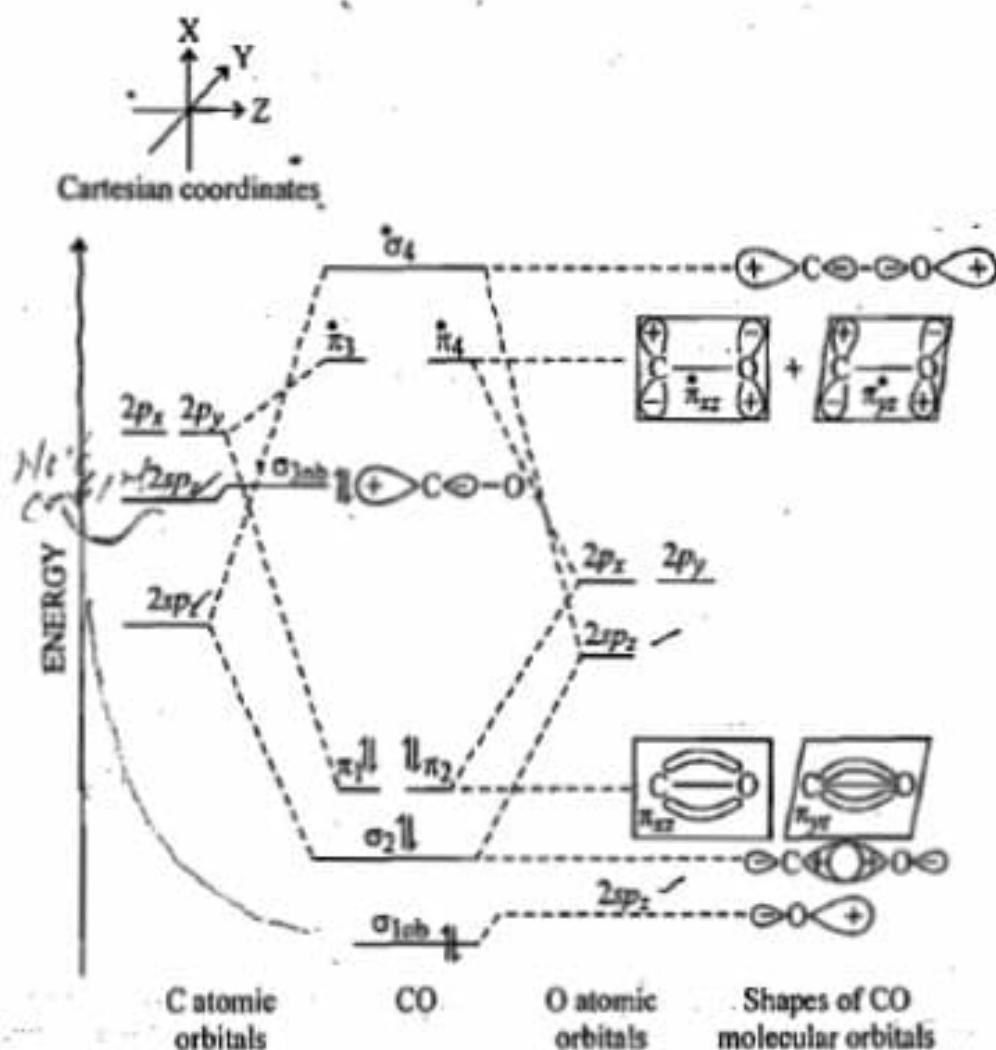
Fig. 31. Molecular orbital energy level diagram (with shapes of molecular orbitals) of CO molecule. Positions of pure $2s$ and $2p_z$ orbitals of C and O are not shown.

Since the orbital energies are lower for more electronegative O atom compared to the energies of similar orbitals of C atom, the lower energy mixed sp_z orbital of C atom is comparable in energy to the higher energy sp_z orbital of O atom, as shown in MOEL diagram of CO (Fig. 31). These two atomic orbitals of comparable energy and of same symmetry combine to give σ bonding and antibonding molecular orbitals. The lower energy sp_z orbital on O and the higher energy sp_z orbital on C atom are so far apart in energy that they *hardly* influence each other with the result that their energies remain almost unchanged. In other words, these orbitals remain *almost* non bonding. As already discussed above, the non bonding sp_z orbital on C (shown as σ_{3nb} in the figure) will have more characteristics of $2p_z$ orbital of C atom and the non bonding sp_z orbital on O atom (σ_{1nb} in the figure) will have more characteristics of $2s$ orbital of O atom. The degenerate set of $2p_x$, $2p_y$ orbitals of C and the similar degenerate set of $2p_x$, $2p_y$ orbitals of oxygen are of π symmetry to form a set of degenerate π_1, π_2 bonding molecular orbitals and another set of degenerate antibonding molecular orbitals. The electronic configuration of CO molecule is, therefore,

$$KK' \; \sigma_{1nb}^2 \; \sigma_2^2 \; \pi_1^2 \; \pi_2^2 \; \sigma_{3nb}^2$$
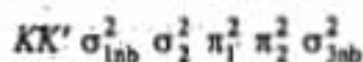
and the bond order of CO molecule is obviously 3 (due to two σ bonding and four π bonding electrons. The electrons in the non bonding orbitals do not contribute towards bonding.

Since σ_{3nb} is the highest placed occupied non bonding orbital localised on C atom, its electron pair can easily be donated for forming dative (or coordinate) bond.

Nitric Oxide Molecule, NO. The electronic configurations of N and O atoms are $1s^2 2s^2 p^3$ and $1s^2 2s^2 p^4$, respectively. There are 5 electrons in the outer shell of nitrogen and 6 electrons in the outer

shell of oxygen. Thus, a total of 11 outer electrons are to be accommodated in the molecular orbitals of NO molecule.

The spectroscopic data reveal that the order of energy levels in NO molecule is similar to the order of energy levels in O_2 and F_2 molecules meaning that due to considerable energy difference between $2s$ and $2p_z$ atomic orbitals, the mixing of orbitals on each atom is insignificant.

The electronic configuration of NO molecule is, thus,

$$\text{NO} : KK \; \sigma(2s)^2 \; \overset{.}{\sigma}(2s)^2 \; \sigma(2p_z)^2 \; \pi(2p_x)^2 \; \pi(2p_y)^2 \; \overset{.}{\pi}(2p_z)^1 \quad \text{or} \quad KK' \; \sigma_1^2 \; \overset{.}{\sigma}_2^2 \; \sigma_3^2 \; \pi_1^2 \; \pi_2^2 \; \overset{.}{\pi}_3^1$$

The **bond order** in this case is $1/2(8-3) = 2\frac{1}{2}$. This represents one σ bond and two π bonds less the antibonding effect of one unpaired electron in the $\overset{.}{\pi}_3$ molecular orbital. The presence of this antibonding electron makes the NO molecule less stable than the N_2 molecule. This is confirmed by the fact that the bond dissociation energy of nitric oxide, viz., 667·8 kJ mol^{-1}, is less than that of nitrogen which is 945·6 kJ mol^{-1}. Since NO contains an unpaired electron, it is *paramagnetic*.

As in the case of CO molecule, the bonding molecular orbitals would have greater characteristics of atomic orbitals of oxygen and the antibonding molecular orbitals would have greater characteristics of atomic orbitals of nitrogen.

Hydrogen Flouride Molecule, HF. The valence shell atomic orbitals of the same symmetry are $1s$ atomic orbital of H and $2s$ and $2p_z$ atomic orbitals of F (the z-axis is assumed to be the internuclear axis). The two $2s$ and $2p_z$ of F, being of the same symmetry, can mix with each other. However, the extent of mixing of $2s$ and $2p_z$ orbitals will be *small* because the energy gap between these two orbitals is *high*. (For effective mixing of orbitals of same symmetry, the energy gap between them should be low).

The higher energy mixed orbital of F has predominantly p_z character with very little s character and will lie only a *little lower* in energy than the pure p_z orbital. Similarly, the lower energy mixed orbital has predominantly $2s$ character with only a little $2p_z$ character and lies *slightly higher* in energy than the pure $2s$ orbital. The $1s$ orbital of hydrogen atom is more comparable in energy to the higher energy mixed sp_z orbital (which is practically $2p_z$ orbital) of F. The two combine to give σ_1 bonding and $\overset{.}{\sigma}_3$ antibonding molecular orbitals. The lower energy mixed sp_z orbital of F *cannot effectively combine* with $1s$ orbital of H atom due to large energy difference between this mixed orbital and $1s$ orbital of H atom and, therefore, remain *almost* non bonding (σ_{2nb}) orbital. The molecular orbital energy level diagram of HF is shown in Fig. 32.
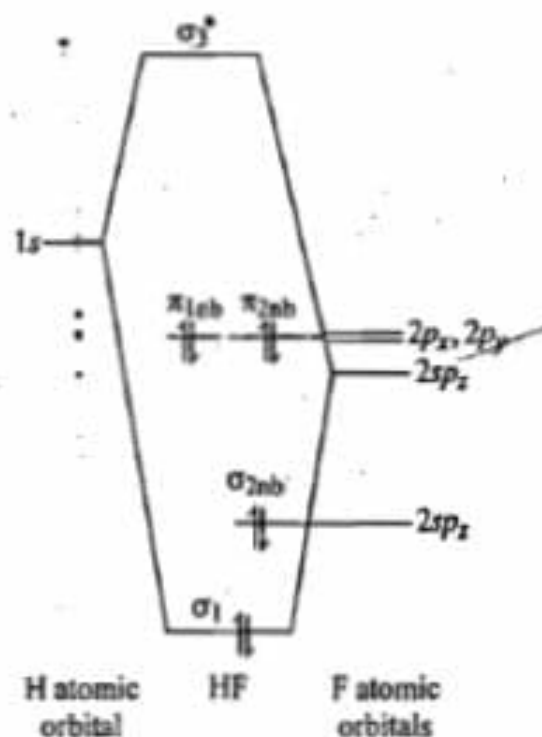
Fig. 32. Molecular orbital energy level diagram of HF molecule. The positions of pure $2p_y$ and $2s$ orbitals of F atom are not shown.

The $2p_x$ and $2p_y$ orbitals of F are suitable for forming only π bonding and antibonding molecular orbitals. Since there are no orbitals of the same symmetry as that of H atom, these remain non bonding and are designated in the figure as π_{1nb} and π_{2nb}. It is clear from the above discussion that σ_1 will have more contribution from $2p_z$ atomic orbital of F and less contribution from $1s$ atomic orbital of F atom whereas $\overset{.}{\sigma}_3$ will have more contribution from $1s$ orbital of H atom and less contribution from $2p_z$ orbital of H atom. The electronic configuration of HF molecule is thus,

$$K \; \sigma_1^2 \; \sigma_{2nb}^2 \; \pi_{1nb}^2 \; \pi_{2nb}^2$$

and the **bond order** is obviously 1 since only two electrons occupy the bonding molecular orbital σ_1 (the rest of the valence electrons are in non bonding orbitals).

As can be visualised, all the occupied orbitals are either pure F orbitals or have predominantly F orbital characteristics. Therefore, most of the electronic charge will be localised on F atom. This fact is corroborated by a considerably high dipole moment (1·9 D) observed for HF molecule.

Hydrogen Chloride Molecule, HCl. The treatment in this case is exactly similar to the one discussed for HF molecule except for the fact that the valence shell atomic orbitals of the same symmetry that are considered for the formation of molecular orbitals, are $1s$ atomic orbital of H atom and $3s$ and $3p_z$ orbitals of Cl atom. The electronic configuration of HCl molecule is :

$$KL \ \sigma_1^2 \ \sigma_{2ab}^2 \ \pi_{1nb}^2 \ \pi_{2nb}^2$$
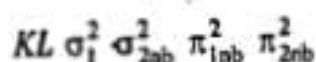
and the bond order is 1 due to two electrons in bonding molecular orbital. In the case of HCl molecule also, all the occupied orbitals are either pure Cl orbitals or have predominantly Cl orbital character. Therefore, most of the electronic charge gets accumulated on Cl atom of HCl making it considerably polar.

Term Symbols for Diatomic Molecules

Term symbols are used to designate electronic energy levels which arise out of an electronic configuration because of electrostatic repulsions amongst the electrons of a molecule. These terms are very helpful in understanding electronic spectra of molecules.

The term symbols employed for diatomic molecules are written in the following manner :

1. The symbols Σ, π and Δ are used to represent values 0, 1 and 2, respectively for $|M_L|$ or Σm_l of electrons in the diatomic molecules where m_l is the component of orbital angular momentum of a single electron along the nuclear axis and $|M_L|$ is the absolute value of similar overall component for all the electrons in the diatomic molecule. The m_l is 0, ± 1 and ± 2 for an electron in σ, π and δ molecular orbitals, respectively.

2. Since all homonuclear diatomic molecules have a centre of symmetry in the middle of their nuclear axis, the overall symmetry to inversion is indicated by u or g and is written as a right subscript of Σ, π, Δ.

3. The electron spin multiplicity is indicated by $2S + 1$ as the left superscript of Σ, π and Δ (S is the total spin of electrons in the system).

4. The term symbol is written as $^{2S+1}|M_L|_{g \text{ or } u}$.

For example, consider a H_2 molecule whose ground state electronic configuration is $\sigma^2(1s)$.

In this case, S (i.e., $s_1 + s_2$) is 0 and $|M_L|$, i.e., $(m_{l_1} + m_{l_2})$ is also 0. The σ_{1s} molecular orbital is symmetric with respect to the centre of inversion located in the middle of the nuclear axis, Therefore, the term symbol for σ_{1s}^2 should be $g \times g = g$ type. Hence, the term symbol $^{2S+1}M_{L_{g \text{ or } u}}$ for H_2 molecule in its ground state, is $^1\Sigma_g$.

Consider now hydrogen ion, H_2^+. Its ground state electronic configuration is σ_{1s}^1 so that $S = \frac{1}{2}$ and $2S + 1 = 2$. Since $|M_L| = 0$, hence the term symbol for its ground state, is $^2\Sigma_g$.

Let us now work out the term symbols for O_2 molecule. The ground state electronic configuration of O_2 is $\sigma_1^2 \ \sigma_2^2 \ \sigma_3^2 \ \pi_1^2 \ \pi_2^2 \ \pi_3^2 \ \pi_4^1$. The electrons in the filled sigma molecular orbitals and the completely filled degenerate set of pi orbitals contribute nothing to the overall component of angular momentum M_L along the nuclear axis. Since both the π molecular orbitals are symmetric with respect to the centre of symmetry of the oxygen molecule, the term symbol will be $g \times g = g$ type.

Let us first consider the case when both the unpaired electrons in π molecular orbitals have opposite spins. The m_l for each electron in π molecular orbital will be $+1$ or -1 so that $|M_L| = 0$ or 2 and $2S + 1 = 1$ (because S is $\frac{1}{2} - \frac{1}{2} = 0$). The term symbols which arise from this situation are $^1\Sigma_g$ and $^1\Delta_g$.

Now consider the case when the spins of both the electrons are in the same direction so that $S = \frac{1}{2} + \frac{1}{2} = 1$ and the spin multiplicity is 3. Since spins of both the electrons in π orbitals are in the same

direction, their m_l values *have* to be different (Paulis' exclusion principle). That is, m_l for one electron is +1 and for the other electron it is –1 (The + and – signs indicate whether the component of angular momentum m_l is parallel or antiparallel to the nuclear axis). Therefore, $|M_L|$ can only be 0 so that the term is $^3\Sigma_g$.

Out of $^3\Sigma_g$, $^1\Sigma_g$ and $^1\Delta_g$, the first term, *i.e.*, $^3\Sigma_g$, having maximum multiplicity will evidently represent the ground state term of the molecule.

The student is advised to work out the terms for Li_2, Be_2, N_2, F_2, F_2^+ molecules himself.

The term symbols for heteronuclear diatomic molecules are derived in a similar manner. Since a heteronuclear diatomic molecule has no centre of symmetry, we do not write the subscript g or u in the term symbols of such molecules.

The Σ terms are sometimes further codified by writting + or – as a right superscript depending upon whether the system is symmetric or asymmetric with respect to a plane of symmetry passing through the nuclear axis.

Molecular Orbitals of Polyatomic Species

H_3^+ Ion. The three $1s$ orbitals of H_A, H_B and H_C atoms can overlap with one another to produce an equal number of molecular orbitals. The H_3^+ ion thus formed can either have a linear geometry or a triangular planar geometry leading to two different sets of sigma overlaps. But, in both cases the linear combinations of three $1s$ atomic orbitals can be represented by the same three ψ_{MOs} in the following manner :

Various Combinations of AOs of H_A, H_B and H_C	Diagramatic Representation for	
	Linear Geometry	Triangular Geometry
$\sigma_1 = \psi_{1MO}$ $= \dfrac{1}{\sqrt{3}}\left[(\psi_{1s(A)} + \psi_{1s(B)} + \psi_{1s(C)})\right]$		
$\sigma_2 = \psi_{2MO}$ $= \dfrac{1}{\sqrt{2}}\left[(\psi_{1s(A)} - \psi_{1s(C)})\right]$		
$\sigma_3 = \psi_{3MO}$ $= \dfrac{1}{\sqrt{6}}\left[(\psi_{1s(A)} - 2\psi_{1s(B)} + \psi_{1s(C)})\right]$		

It is to be noted that each of the σ_1, σ_2, and σ_3 is a normalised function and that each ψ_{1s} is completely utilised while writting σ_1, σ_2 and σ_3. The sum of the squares of the coefficients of each of ψ_{1s} in σ_1, σ_2 and σ_3 is 1.

For H_3^+ ion having linear geometry, σ_1, which has positive overlaps between the three $1s$ orbitals, is obviously a bonding molecular orbital. The molecular orbital σ_2 in a linear geometry cannot have any

overlap and is, therefore, nonbonding while σ_3, having a negative overlap in this geometry is obviously antibonding. The two electrons of H_3^+ will occupy the bonding molecular orbital σ_1 if its geometry is linear.

For H_3^+ ion having triangular geometry, σ_1 is bonding molecular orbital having positive overlaps as is obvious from the figure but σ_2, in which H_A and H_C orbitals form a negative overlap, is antibonding and is thus of higher energy than σ_2 of linear geometry. The molecular orbital σ_3 of triangular geometry is bonding between H_A and H_C involving positive overlaps but is antibonding between H_A and H_B as also between H_B and H_C involving negative overlaps. Therefore, σ_3 of triangular geometry, though antibonding, is of lower energy than σ_3 of linear geometry (why ?). Further it can be shown with the application of group theory that σ_2 and σ_3 of triangular geometry are of equal energy. It can be easily visualised that the triangular planar geometry can be obtained from linear geometry by bending $\angle ABC$ from $180°$ to $60°$. The energies of $\sigma_1, \sigma_2, \sigma_3$ as a function of $\angle ABC$ can be *calculated*. If a correlation diagram is drawn in the case of H_3^+, it would clearly indicate that a triangular geometry of H_3^+ is more

Fig. 33. Plot of calculated energies of molecular orbitals as a function of bond angle.

stable than the linear geometry. This is because σ_1 bonding molecular orbital which contains both the bonding electrons is of lower energy in the triangular geometry of H_3^+ because of greater overlaps amongst H_A, H_B and H_c than in its linear geometry, as shown in Fig. 33.

Walsh Diagrams. Normally, we explain the experimentally observed geometries of molecules by certain devised theories and concepts such as VSEPR theory, hybridisation, etc. But Walsh actually calculated the energies of molecular orbitals of a reference geometry and, its several distortions for simple triatomic molecules. He correctly predicted the actual geometries of a number of simple triatomic molecules like H_3^+, H_2O, BeH_2, etc., by plotting a graph between the calculated energies of molecular orbitals of the reference geometry and those of the distorted geometries of a molecule *vs* the distortion parameter, *i.e.*, bond angle. The position of minimum energy of the filled molecular orbitals in the graph indicates the most stable geometry of the molecule. Such graphs are known as **Walsh diagrams**. Fig.33 discussed above, in one such diagram.

Beryllium Hydride Molecule, BeH₂. The BeH_2 molecule in gaseous state is linear. It has $D_{\infty h}$ symmetry and contains σ bonds only. From symmetry considerations, the atomic orbitals of Be capable of forming σ bonds in BeH_2 molecule are $2s$ and $2p_z$ orbitals. The p_x and p_y orbitals of Be are not suited for forming σ bonds. The orbitals of the two H atoms which are capable of forming σ bonds are $1s$ atomic orbitals. The two linear combinations of $1s$ atomic orbitals of H which are capable of forming σ bonds with $2s$ and $2p_z$ orbitals of Be are $(\psi_{1s(H_A)} + \psi_{1s(H_B)})$ and $(\psi_{1s(H_A)} - \psi_{1s(H_B)})$. The bonding and antibonding linear combinations of these orbitals are shown below. The bonding combinations have a net positive overlap of orbitals whereas antibonding combinations have a net negative overlap.

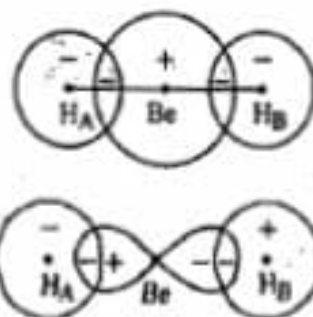$$\sigma_1 \text{ (bonding)} = a\psi_{2s}(Be) + b[(\psi_{1s}(H_A) + (\psi_{1s}(H_B)]$$
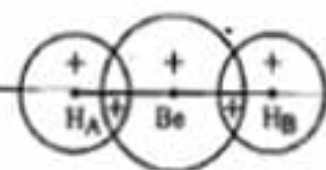
$$\sigma_2 \text{ (bonding)} = c\psi_{2p_z}(Be) + d[\psi_{1s}(H_A) - (\psi_{1s}(H_B)]$$
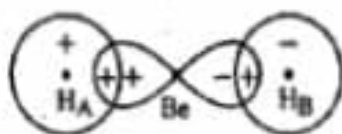
$$\sigma_3 \text{ (antibonding)} = b\psi_{2s}(\text{Be}) - a[\psi_{1s}(\text{H}_A) + (\psi_{1s}(\text{H}_B)]$$

$$\sigma_4 \text{ (antibonding)} = {}^d\psi_{2p_z}(\text{Be}) - c[(\psi_{1s}(\text{H}_A) - (\psi_{1s}(\text{H}_B)]$$

The molecular orbital energy level diagram of BeH_2 is shown in Fig. 34.

The four valence electrons occupy σ_1 and σ_2 bonding molecular orbitals.

The above simple molecular orbital treatment does not explain the equivalence of the two Be → H bonds which is experimentally established. For explaining this, the concept of hybridisation has to be introduced which is discussed in detail in the next chapter.

Although we began the discussion on BeH_2 by considering the actually observed linear geometry of the molecule, it will be shown with the help of Walsh diagram for AH_2 type of molecules (A belongs to the second period) that any nonlinear or bent geometry of the molecule AH_2 which has only 4 valence electrons to be accommodated in its molecular orbitals, will be of higher energy compared to the energy of linear geometry.
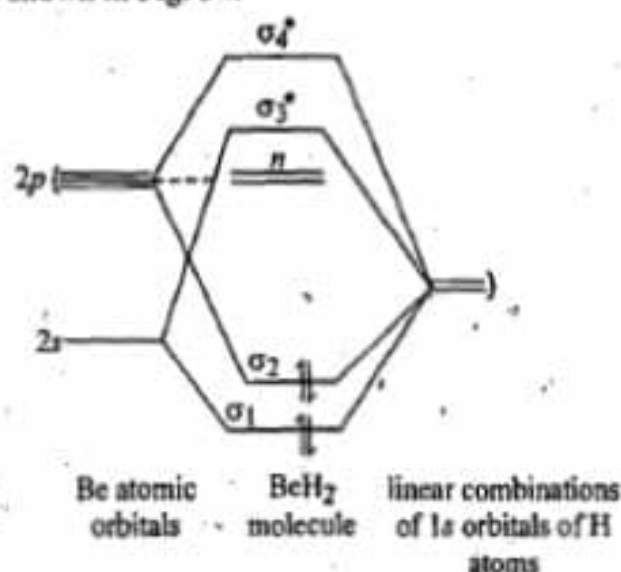
Fig. 34. Molecular orbital energy level diagram of BeH_2 molecule.

Walsh Diagrams for AH_2 Molecules

Consider a molecule AH_2 where the element A belongs to the second period of the periodic table. The molecule AH_2 can either have an angular geometry with c_{2v} symmetry or a linear geometry with $D_{\infty h}$ symmetry. The only orbital available with H atom for bonding is $1s$ orbital and the symmetry-adapted linear combinations of the two $1s$ orbitals of hydrogen atoms which are capable of forming bonds with orbitals of atom A in both the angular and the linear geometry are $\psi_{1s(H_A)} + \psi_{1s(H_B)}$ and $\psi_{1s(H_A)} - \psi_{1s(H_B)}$. These combinations are of a_1 and b_2 symmetry, respectively, in the angular AH_2 molecule and of a_{1g} and a_{1u} symmetry, respectively, in the linear AH_2 molecule. In the angular AH_2 molecule, the two atomic orbitals of A of a_1 symmetry are $2s$ and $2p_z$ orbitals and the one with b_2 symmetry is the p_y orbital. In the linear AH_2 molecule, the atomic orbital of A which is of a_{1g} symmetry is $2s$ and the atomic orbital of A which is of a_{1u} symmetry is $2p_y$. Consider the axes Y and Z which pass through A and lie in the plane of paper as shown :
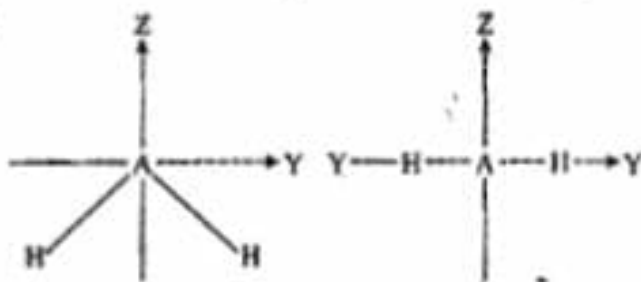
We shall first consider bonding in angular AH_2. The combination $(\psi_{1s(H_A)} + \psi_{1s(H_B)})$, which is of a_1 symmetry, combines with two mixed $2sp_z$ orbitals of A also of a_1 symmetry, to give three molecular orbitals $1a_1$, $2a_1$ and $3a_1$. The bonding $1a_1$ molecular orbital utilises the mixed sp_z orbital of A having predominant $2p_z$ character and the bonding $2a_1$ molecular orbital utilises the mixed sp_z orbital of A having predominant $2s$ character in the angular AH_2 molecule with $\angle HAH$ of $90°$. As the bond angle increases, the participation of $2p_z$ orbital in the mixed sp_z orbital in $1a_1$ decreases and that of $2s$ orbital increases with the result that in the linear geometry of AH_2, it is only the $2s$ orbital (of a_{1g} symmetry) which combines with the combination $\psi_{1s(H_A)} + \psi_{1s(H_B)}$ (also of a_{1g} symmetry) to give the bonding molecular orbital $1a_{1g}$. Since the $2p_z$ orbital of A is of higher energy than the $2s$ orbital, the lesser and lesser participating of $2p_z$ in molecular orbital $1a_1$, will cause a greater and greater decrease in the energy of the molecular orbital in going from the angular AH_2 molecule ($\angle HAH$ of $90°$) to the linear AH_2 molecule ($\angle HAH$ of $180°$).

Similarly, in the $2a_1$ molecular orbital in the angular AH_2 molecule, the contribution of $2s$ orbital goes on decreasing with increase in $\angle HAH$ with the result that in the linear AH_2 molecule with $\angle HAH = 180°$, there is zero contribution of $2s$ orbital. The contribution of the $2p_z$ orbital, on the other hand, goes on increasing with increase in $\angle HAH$ from 90° to 180°. However, $2p_z$ orbital in linear molecule is non-bonding because in the linear molecule ψ_{2p_z} and the combination $(\psi_{1s(H_A)} + \psi_{1s(H_B)})$ are of different symmetry. (The decrease in the contribution of $2s$ orbital of A with increase in $\angle HAH$ in $2a_1$ molecular orbital is understandably due to the increasing contribution of this orbital to the lowest energy bonding molecular orbital $1a_1$). In the angular AH_2 molecule, the $2a_1$ molecular orbital is of lower energy than in the linear AH_2 molecule because as can be seen from the Walsh diagram (Fig. 35), this molecular orbital has a positive overlap with the $1s$ orbitals of hydrogen whereas it has no overlap in the case of linear AH_2 molecule. The $3a_1$ molecular orbital is antibonding and this has not been shown in the figure.

The symmetry-adapted combination $(\psi_{1s(H_A)} - \psi_{1s(H_B)})$ of b_2 symmetry combines with p_y orbital of the same symmetry in the angular AH_2 molecule to give bonding and antibonding molecular orbitals of the same symmetry. Only the b_2 bonding orbital is shown in the Walsh diagram. It can be easily visualised that if we go on increasing $\angle HOH$ in the angular AH_2 molecule, the overlap between $(\psi_{1s(H_A)} - \psi_{1s(H_B)})$ and p_y orbital in the bonding b_2 molecular orbital will go on increasing and hence the energy of this molecular orbital will go on decreasing with the result that the b_2 molecular orbital has lowest energy in the linear AH_2 molecule ($\angle HOH$ of 180°).

The p_x orbital of A in both the angular and the linear AH_2 molecules is non-bonding. In fact, in the linear geometry of AH_2 molecule, both the p_x and p_y orbitals are degenerate, non-bonding and are of e_{1u} symmetry.
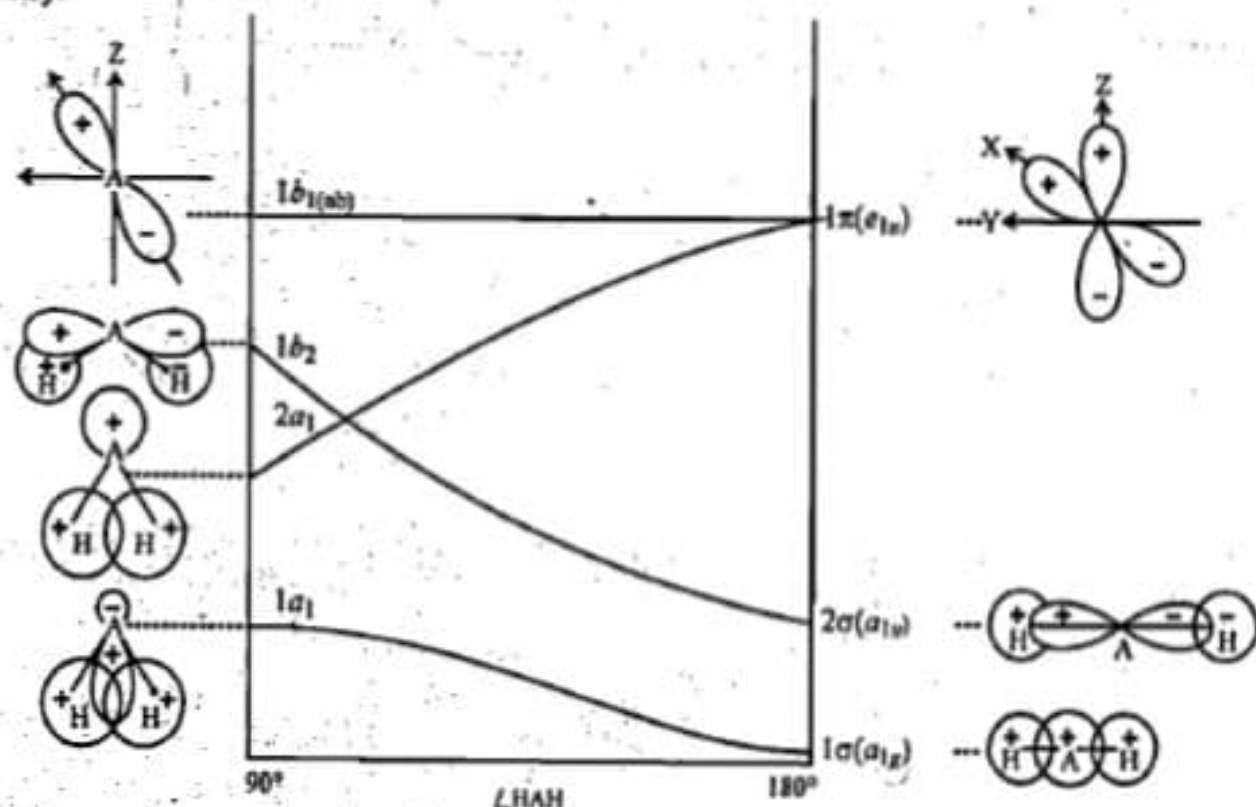
Fig. 35. Walsh diagram showing correlation between molecular orbital energy levels of angular and linear geometries of AH_2 molecule.

The various orbitals which take part in molecular orbital formation of AH_2 molecule are $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals of A and two $1s$ orbitals of hydrogen atoms. Thus, six molecular orbitals are formed out of which the four lower energy molecular orbitals are shown in Fig. 35. The four molecular orbitals can accommodate eight valence electrons which is the maximum number of electrons that are present in AH_2 molecule (A belongs to the second period).

It follows from the Walsh diagram of AH_2 molecules that a linear geometry of BeH_2 would be more favourable than the angular geometry. This is because the two filled lower energy molecular orbitals of linear geometry of BeH_2 are of lesser energy than the two lower energy molecular orbitals of angular geometry of BeH_2.

To sum up, if there are only 4 electrons to be accommdated in the molecular orbitals of the molecule AH_2 (as e.g., BeH_2), the molecule would have a lower energy linear geometry.

If however, the number of electrons to be accommodated in molecular orbitals is more than four, as, for example, in H_2O, the third molecular orbital has to be occupied which is of much lower energy in angular AH_2 molecule than in linear AH_2 molecule. The filling of the fourth non-bonding molecular orbital is of no consequence in determining the geometry of AH_2 molecule since this non-bonding molecular orbital is of the same energy in linear as well as in angular geometry of AH_2 molecule. In such a case, the molecule will have an **angular geometry**.

Carbon Dioxide Molecule, CO_2. This molecule belongs to $D_{\infty h}$ symmetry. The orbitals of carbon and oxygen atoms which can form σ bonds in the direction of bond axis (taken as Z-axis) are $2s$ and $2p_z$ orbitals. The $2s$ orbital of carbon is of a_{1g} symmetry whereas its $2p_z$ orbital is of a_{1u} symmetry. The $2s$ orbital of carbon and $2s$ orbitals of oxygen atoms are of the same symmetry. However, they differ too much in energy. Hence, the $2s$ orbitals of oxygen atoms hardly take part in σ bonding. Therefore, the $2s$ orbitals of oxygen atoms are essentially non-bonding.

The two symmetry-adapted combinations of $2p_z$ orbitals of oxygen which can form σ bonds with atomic orbitals of carbon in the Z direction are $(\psi_{2p_z(O_1)} + \psi_{2p_z(O_2)})$ of a_{1g} symmetry and $(\psi_{2p_z(O_1)} - \psi_{2p_z(O_2)})$ of a_{1u} symmetry. The +Z coordinate of each oxygen atom is taken as pointing towards the carbon atom, as shown.

The various molecular orbitals formed from the combination of atomic orbitals of C and O atoms are shown in Fig. 37 on the next page and the molecular orbital energy level diagram of CO_2 molecule is shown in Fig. 36.
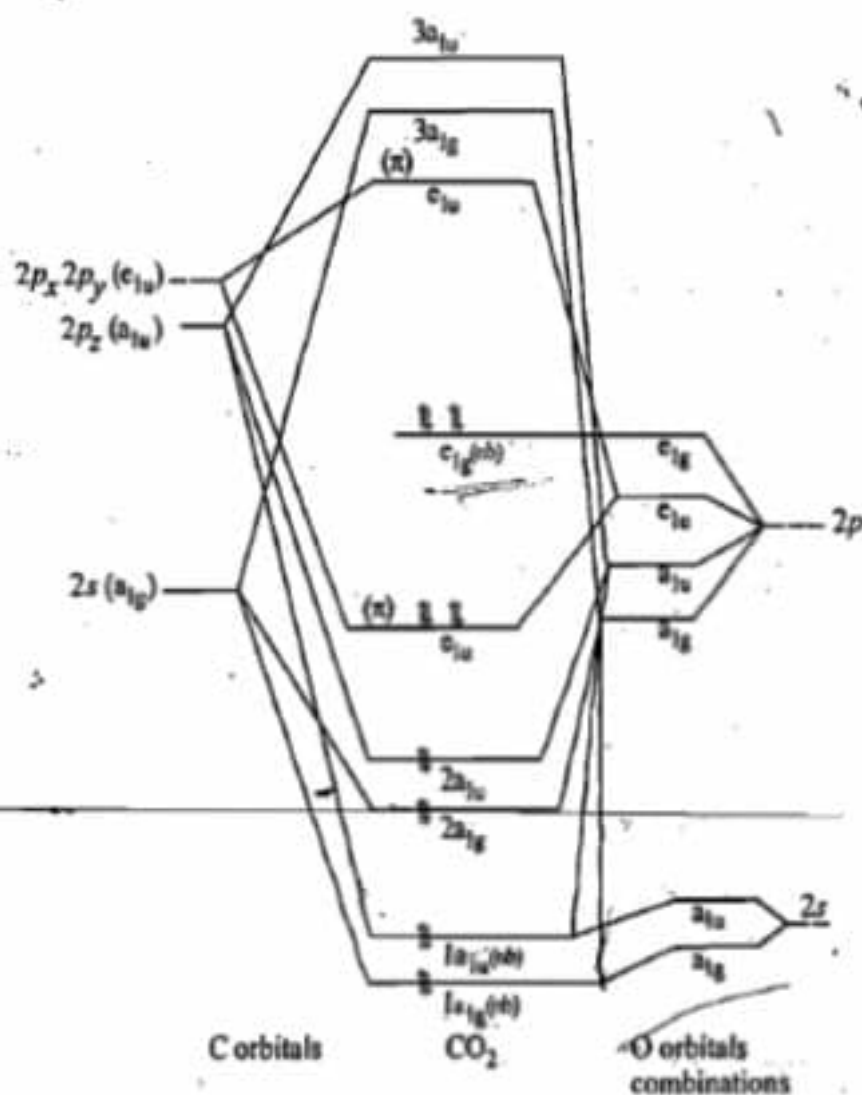
Fig. 36. Molecular orbital energy level diagram of CO_2 molecule.

Ammonia Molecule, NH₃. Each of the $2s$ and $2p_z$ orbitals of N is of the symmetry a in C_{3v} point group to which the molecule belongs. The $2p_x$ and $2p_y$ orbitals, *taken together*, are of the symmetry e. The three $1s$ orbitals of three H atoms can linearly combine with one another to give three combinations one of which is of the symmetry a and the rest of the two combinations, taken together, are of the symmetry e. The linear combination a of $1s$ atomic orbitals of H combine with $2s$, $2p_z$ orbitals of N (each one having the symmetry a) to give an *equal number* of molecular orbitals (i.e., three molecular orbitals). In the same way, the two linear combinations e of $1s$ atomic orbitals combine with p_x, p_y orbitals (also of the symmetry e) to give two sets of doubly degenerate molecular orbitals. It is possible to write the wave functions and draw the diagrams of all the seven molecular orbitals of NH₃ as was done in the above mentioned examples of H_3^+ ion and BeH₂. The molecular orbital energy level diagram of NH₃ is shown in Fig. 38.
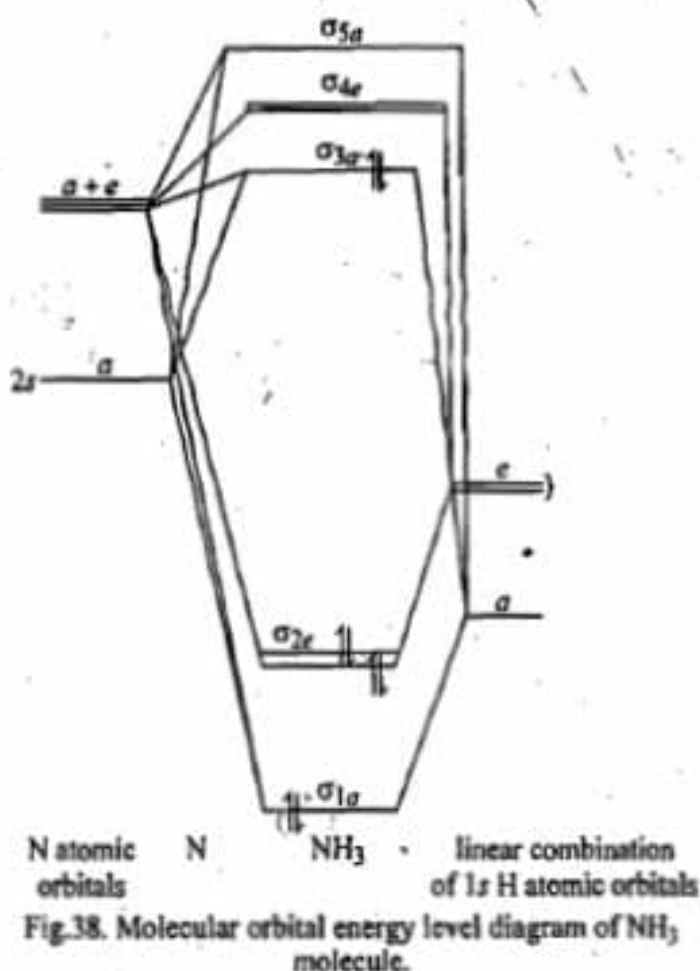
The electronic configuration of NH₃ is $\sigma_{1a}^2\,\sigma_{2e}^4\,\sigma_{3a}^2$. The two electrons in the highest occupied molecular orbital (HOMO), which is

N atomic orbitals   N   NH₃   linear combination of $1s$ H atomic orbitals

Fig.38. Molecular orbital energy level diagram of NH₃ molecule.

almost non-bonding, are practically localised on N atom. The remaining occupied molecular orbitals are of bonding type. This simple molecular orbital description of NH₃ tallies with the conventional picture of NH₃ having a lone pair of electrons on N atom and three N–H σ bonds. But it does not explain the equivalence of the three N–H bonds and the observed ∠ NHN. These are explained on the basis of the VSEPR theory and/or the concept of hybridisation as discussed in the next chapter on Hybridisation and Shapes of Molecules.

Problem 4. Of the following species, which has the shortest bond length : NO, NO⁺, NO²⁺, NO⁻?

Answer : We shall first calculate the bond orders for the given species from their electronic configurations.

$$NO:\ KK\ \sigma(2s)^2\sigma(2s)^2\sigma(2p_z)^2\pi(2p_x)^2\pi(2p_y)^2\overset{\bullet}{\pi}(2p_x)^1$$

$$\text{or}\quad KK'\sigma_1^2\sigma_2^{*2}\sigma_3^2\pi_1^2\pi_2^2\pi_3^{*1}$$

∴ Bond order $= 1/2\,(8-3) = 2\tfrac{1}{2}$

NO⁺ : One electron is removed from the antibonding $\overset{\bullet}{\pi}_3$ MO.

Bond order $= 1/2(8-2) = 3$

NO²⁺ : One electron is removed from the antibonding $\overset{\bullet}{\pi}_3$ MO and the other electron is removed from the bonding π_1 (or π_2) MO.

Bond order $= 1/2\,(7-2) = 2\tfrac{1}{2}$

NO⁻ : One electron is added to the antibonding $\overset{\bullet}{\pi}_3$ MO.

Bond order $= 1/2\,(8-4) = 2$

Evidently, the species NO⁺ has the highest bond order and thus has the shortest bond length.

Problem 5. Write the electronic configuration of CN⁻. What is its bond order ?

Answer : The order of molecular orbitals is the same as in CO. Only the extent of mixing of $2s$ and $2p_z$ orbitals of N occurs to a greater extent in CN⁻ compared to a similar mixing of the orbitals of O in

CO. The electronic configuration is similar to CO. Thus,

$$CN^- : KK' \; \sigma_{1sb}^2 \; \sigma_2^2 \; \pi_1^2 \; \pi^2 \; \sigma_{3sb}^2$$
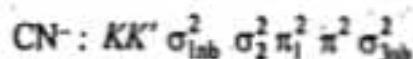
and the bond order is 3 due to the presence of six electrons in the bonding orbitals and the rest in nonbonding orbitals. The nonbonding σ_{1sb} is localised on N atom and has predominantly s character whereas σ_{3sb} is localised on C atom and has predominantly p_z character.

Comparison Between Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT)

Common Features. Valence bond and Molecular orbital theories have the following features in common :

1. 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 the order of increasing energy. If there are more than one vacant orbitals having the same energy, they would first be filled *singly*.

2. In normal covalent bond formation, the essential interaction, according to both the theories, is the sharing of the bonding electron charge density by both nuclei and concentration of electron charge density between the nuclei.

3. In bond formation, the orbitals of the bonding atoms must overlap according to both the theories.

4. The energies of the overlapping orbitals, according to both the theories, must be comparable and their symmetries should be the same.

Differences

1. While VBT *starts with individual atoms* and considers the interaction between them, MOT *starts with the nuclei* of the constituent atoms.

2. In the valence bond theory, only the half-filled orbitals of the valence shell take part in bonding and the remaining orbitals retain their identity. In molecular orbital theory, however, all the atomic orbitals, whether filled or unfilled, would overlap to form molecular orbitals, provided they have proper symmetry and comparable energy.

3. The wave function in original VBT does not give any weightage to ionic structures (the concept of ionic contribution was incorporated later on as a modification to the original theory). The MOT inherently gives equal weightage to covalent and ionic structures. For example, ψ_{BMO} for H_2 molecule is given by

$$\psi_{BMO} = (\psi_A + \psi_B)_1 (\psi_A + \psi_B)_2$$

$$= (\psi_A)_1 (\psi_B)_2 + (\psi_A)_2 (\psi_B)_1 + (\psi_A)_1 (\psi_A)_2 + (\psi_B)_1 (\psi_B)_2$$

In this equation, the first two expressions refer to covalent structures and the last two refer to ionic structures.

4. While VBT fails to account for the paramagnetic character of oxygen, MOT offers a satisfactory explanation.

5. While resonance plays an important role in VBT, this concept has no place in MOT.

6. MOT is more exact than the VBT. However, the calculations involved in MOT are much more tedious than those involved in VBT.

METALLIC BOND

Metals are characterised by high electrical and thermal conductivity, bright lustre, malleability, ductility and high tenstile strength. It has been observed that metals, generally, have low ionisation energies because the valency electrons can be taken out relatively easily.

The following three models have been proposed to account for the nature of bonding in metals :

1. *The Free Electron Model. The 'Electron Sea' Model.*

2. *The Valence Bond Model.*

3. *The Band Model : Molecular Orbital Approach.*

1. The Free Electron Model. The 'Electron Sea' Model

According to this model, a metal behaves as if *it is an assemblage of positive ions (kernels) immersed in a 'sea' of mobile electrons* (Fig. 38). *Thus, each electron belongs to a number of positive ions and each positive ion belongs to a number of electrons.*

The force of attraction which binds a metal atom kernel to a number of electrons within its sphere of influence is known as a **metallic bond.**

Explanation of Metallic Properties. All the metallic properties such as electrical and thermal conductivity, bright lustre, malleability, ductility, elasticity, etc., can be explained satisfactorily on the basis of the metallic structure described above.

METALLIC KERNEL   SEA OF ELECTRONS
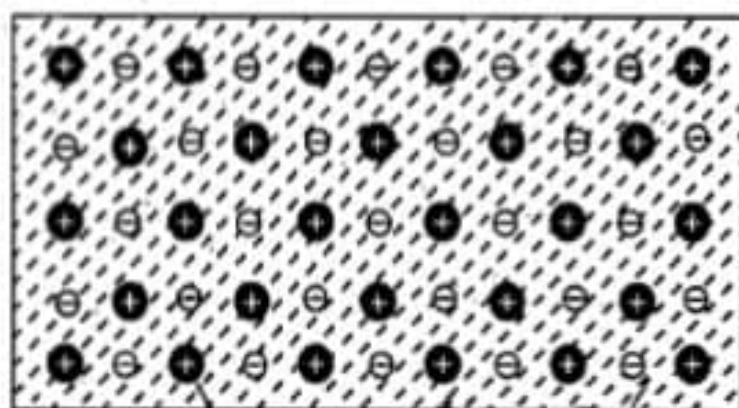
Fig. 38. The electron sea model for metals.

1. The **high electrical conductivity** of metals, for example, is due to the presence of the mobile valency electrons. They move readily in an electric field and thus conduct electricity throughout the metal from one end to the other.

2. The **high thermal conductivity** is also due to the presence of these mobile electrons. If one part of a metal is heated, the electrons in that part acquire a large amount of kinetic energy. Being free, these electrons move rapidly through the crystal and convey heat (*i.e.*, conduct heat) to other parts of the metal.

3. The **bright metallic lustre** can also be explained as due to the presence of the highly mobile electrons. As a beam of light comprising of electromagnetic waves falls on the surface of a metal, the electric field associated with light waves sets the electrons present on the surface of the metal into to and fro oscillations. Now, a moving charge always emits electromagnetic energy. Hence, oscillating electrons emit electromagnetic energy in the form of light. Thus, when light falls on a metal surface, it appears as if light is being reflected. The surface, therefore, emits the typical metallic lustre.

4. The model of free valency electrons can also explain the **softness, malleability** and **ductility** associated with metals. The metallic bond holding the positive ions (say, M^+) and the valency electrons is *non-directional*. In other words, the force of attraction between the M^+ ions and the valency electrons is uniform in all directions. Also the bonds holding the crystal lattice in metals are not rigid unlike those in covalent solids, such as ice which are rigid. The result is that M^+ ions can be easily moved from one lattice site to another. In terms of the crystal, nothing has been changed. The environment of each metal ion remains the same as before since delocalized electrons are available everywhere.

The nearest neighbours can thus be changed easily and new metal bonds can be formed readily. This explains why metals are malleable, *i.e.*, they can be flattened out into thin sheets when hammered. A crystal of ice, on the other hand, is hard. It is neither malleable nor ductile. It is brittle, *i.e.*, it breaks into small pieces when hammered. This is obviously due to the fact that atoms in water (oxygen and hydrogen) are covalently bonded to each other. Covalent bond is thus *rigid* and *highly directional.*

The ease with which the metal ions can be moved from one lattice site to another is also responsible for the fact that the metals are *ductile, i.e.*, they can be drawn into wires by very little expenditure of energy. This also explains why metals like sodium and potassium are *soft* and can easily be cut with a knife.

5. Metals have **high tensile strength,** *i.e., they can resist stretching without breaking.* This is due to

the existence of strong electrostatic attraction between the positively charged metal ions and the 'sea' of negative electrons surrounding them. Substances which have covalent bonds, do not possess high tensile strength. This is due to the absence of electrostatic forces of attraction in the crystal, there being no oppositely charged units in the lattice.
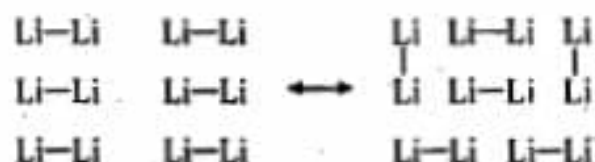
6. Metals possess **elasticity.** *Elasticity is a property by virtue of which a substance can resist a deforming force or a property by virtue of which a substance can recover its original form soon after the removal of the deforming force.* The elasticity of metals is also due to the ease with which metal ions can move from one lattice site to another.

7. The delocalized electron model can also explain the well known observation that *only a small force is needed to* **bend** *a straight copper wire sharply.* However, straightening of a bent wire is not so easy. It requires much more force to do so. Not only that ; a small kink always remains. The reason is that the formation of a sharp bend amounts to separation of some of the metal ions from their adjacent electrons and also from their nearest ion neighbours. The previous pattern of ions and electrons is disturbed and a new pattern is set up in the crystal giving rise to new planes and new edges. It is not so easy to restore the previous pattern because the new planes and edges formed during the bending do not ordinarily fit together to restore the original pattern once again.
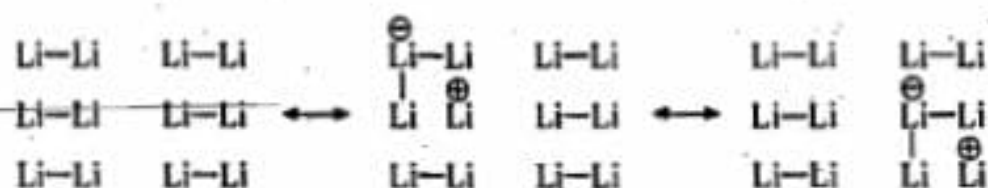
Limitations of the model. The free electron model, however, cannot explain vast variations in properties of certain metals. For example, while mercury melts at such a low temperature as $-39°C$, tungsten melts at such a high temperature as $3300°C$. While metals, in general, are good conductors of electricity, copper is more than 50 times better conductor than bismuth. Similarly, while metals like sodium and potassium are so soft that they can be cut easily with a knife, osmium is so hard that it can scratch even glass.

2. The Valence Bond Model

An examination of the crystal lattice of lithium atom reveals that each Li atom in this lattice is surrounded by eight nearest Li atoms and six next to nearest Li atoms. Because of the presence of only one valence electron, each Li atom is capable of forming only one normal covalent bond with one of its nearest Li atoms. This Li– Li covalent bond is assumed to resonate **mainly** between all the eight neighbours and **to some extent** between the six next to the nearest neighbours. In this way, each Li atom would bind all its neighbours. The resonance of the Li – Li bonds, which is similar to the resonance of the double bonds in benzene, stabilizes the metallic bond. The resonance of Li – Li bonds between a few Li atoms is shown below :

$$
\begin{array}{cccc}
\text{Li–Li} & \text{Li–Li} & & \text{Li} \quad \text{Li–Li} \quad \text{Li} \\
& & & \quad | \qquad\qquad\quad | \\
\text{Li–Li} & \text{Li–Li} & \longleftrightarrow & \text{Li} \quad \text{Li–Li} \quad \text{Li} \\
\text{Li–Li} & \text{Li–Li} & & \text{Li–Li} \quad \text{Li–Li}
\end{array}
$$

More stabilisation results from resonance of the following type :

$$
\begin{array}{ccccccc}
\text{Li–Li} & \text{Li–Li} & & \overset{\ominus}{\text{Li}}\text{–Li} & \text{Li–Li} & & \text{Li–Li} & \text{Li–Li} \\
& & & | \quad \overset{\oplus}{} & & & & \overset{\ominus}{} \\
\text{Li–Li} & \text{Li–Li} & \longleftrightarrow & \text{Li} \quad \text{Li} & \text{Li–Li} & \longleftrightarrow & \text{Li–Li} & \text{Li–Li} \\
& & & & & & & | \quad \overset{\oplus}{} \\
\text{Li–Li} & \text{Li–Li} & & \text{Li–Li} & \text{Li–Li} & & \text{Li–Li} & \text{Li} \quad \text{Li}
\end{array}
$$

Although the valence bond model does meet some success in explaining some of the characteristics of metals, yet it is only qualitative in nature. The cause of metallic bonding is best explained on the basis of the Band Model involving the concept of molecular orbitals.

As already discussed in this chapter, atomic orbitals overlap to produce molecular orbitals. For example, 1s atomic orbital of one H atom overlaps with the 1s atomic orbital of the other H atom to form two molecular orbitals of H_2 molecule. The energy of one of the resulting molecular orbitals is higher and of the other is lower than the energy of either of the combining atomic orbitals. The energies of the two molecular orbitals are represented in the form of two energy levels whose magnitudes vary with the internuclear distance between the two atoms, as shown in Fig. 39.

The energy separation between the two molecular orbital energy levels at equilibrium internuclear distance r_0 is presented by AB.

In general, if there are n atomic orbitals, one on each atom, in a metallic crystal, they may overlap to give n molecular orbitals corresponding to n energy levels. It is essential, however, that the atomic orbitals have the same symmetry and are associated with the same or similar amount of energy. Thus, the larger the number of atomic orbitals satisfying the above conditions, the larger would

Fig. 39. Variation of the two molecular orbital energy levels with internuclear distance in the case of H_2 molecule. r_0 is the equilibrium internuclear distance.

be the number of molecular orbitals each of which can be represented by a separate energy level. The energy separation between any two adjacent energy levels would go on decreasing with increase in the number of overlapping orbitals. Consequently, if we have an exceedingly large number of overlapping orbitals, the energy separation between any two adjacent energy levels would be exceedingly small so that we get an almost *continuous energy band*, as shown in Fig. 40.
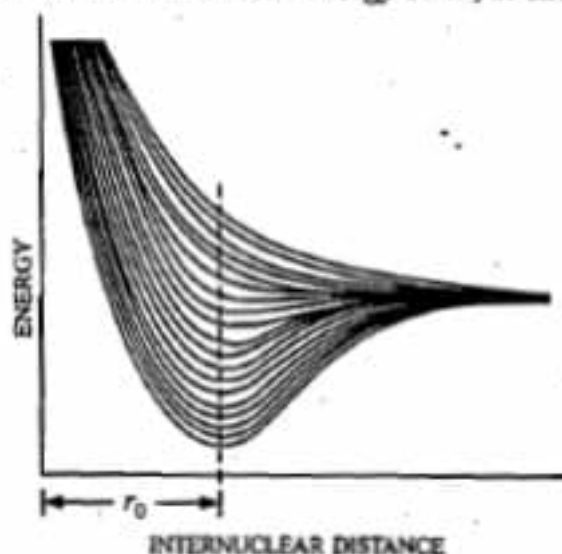
Fig. 40. An almost continuous energy band of energy levels of molecular orbitals obtained by overlapping of an exceedingly large number of atomic orbitals.
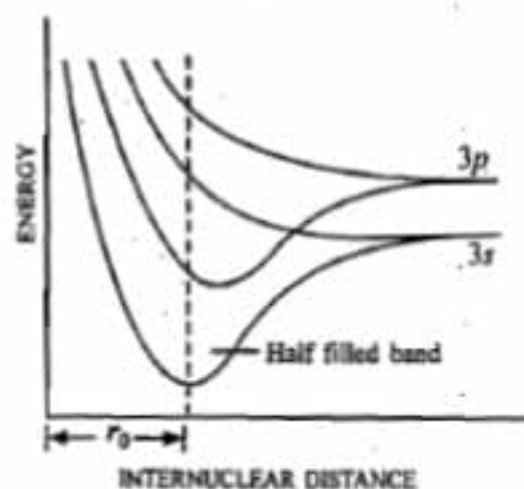
Fig. 41. The valence band of sodium metal. The dotted line indicates equilibrium internuclear distance.

A similar situation exists in case of metals. A metal lattice has an extremely large number of atoms. The atomic orbitals on these atoms with same symmetry and same energy overlap resulting in an almost continuous energy band of extremely large number of energy levels of molecular orbitals. Each energy level in this band is capable of holding two electrons. The overlaping of 3s and 3p orbitals (valence orbitals) in the crystal lattice of **sodium metal** is shown in Fig. 41.

The overlapping of inner orbitals of same symmetry and same energy produces molecular orbitals which are completely occupied by inner electrons. Also, there is considerable energy gap between the valence orbital energy bands and the inner orbital energy bands so that the electrons from the completely filled inner orbital energy band cannot be excited to the valence orbital energy bands. The fully, filled inner orbital energy bands are not shown in the figure. Since the molecular orbitals are common to all

bands of atoms in the lattice, the electrons in the energy levels of these energy bands are common and belong to the whole lattice. In other words, they are completely delocalised.

Since sodium atom has only a single electron in the $3s$ orbital, therefore, in the case of sodium metal, only half of the $3s$ energy level band is occupied by electrons and even on slightest excitation, these electrons can move to the higher energy levels in this band. The mobility of these electrons makes the sodium metal a good conductor of electricity. A similar situation occurs in all the other alkali metals in which the valence energy level band is always half-filled.

The situation in the case of alkaline earth metals is, however, different. In these cases, the outermost valence orbital is fully filled with two electrons so that no vacant energy level of the energy band is available for the electrons to jump to. However, at the equilibrium internuclear distance, the $3s$ energy band and the $3p$ energy band overlap so that some of the vacant energy levels of $3p$ band and the filled energy levels of $3s$ band fall in the same energy range. Consequently, the $3s$ electrons can be easily excited to the $3p$ energy levels in this range. The resulting mobility of electrons makes the alkaline earth metals also good conductors of electricity.

In an **insulator**, there is a large energy gap between the lowest vacant energy band and the highest fully filled energy band even at the equilibrium internuclear distance (Fig. 41). As a result, the electrons cannot be easily excited from the fully filled energy band to the vacant energy band. This makes the material non-conducting.
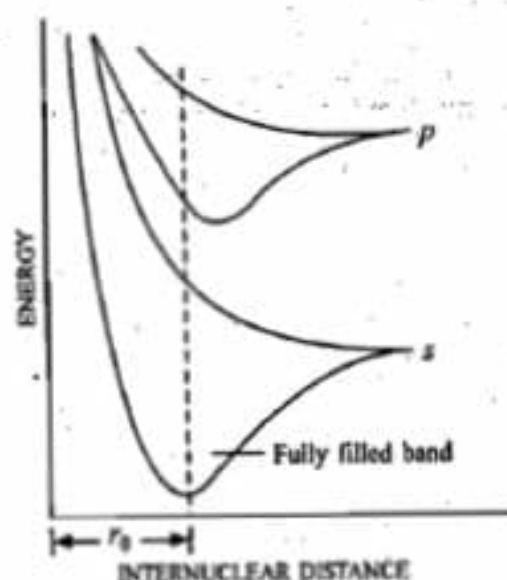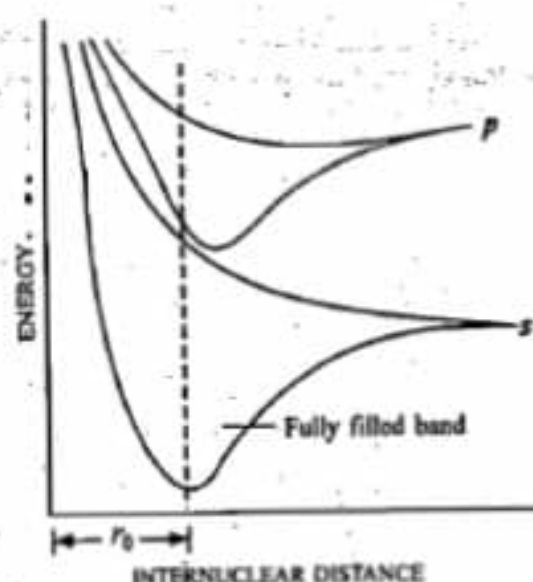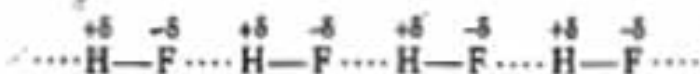
Fig. 42. The valence bands of an insulator.   Fig. 43. The valence bands of a semi- conductor.

In a semi-conductor, there is a lesser energy gap between the two energy bands (Fig. 43). Although the electrons are not very easily excited from the filled to the vacant energy bands yet these can be excited if an appropriate amount of energy is made available.

HYDROGEN BOND

In compounds of hydrogen with *strongly electronegative* elements, such as fluorine, oxygen and nitrogen, the electron pair shared between the two atoms lies far away from the hydrogen atom. As a result, the hydrogen atom becomes *electropositive* with respect to the other atom. This phenomenon of charge separation in the case of hydrogen fluoride is represented as $\overset{+\delta}{H} - \overset{-\delta}{F}$. Such a molecule is said to be polar, as already discussed. The molecule behaves as a **dipole** because one end carries a positive charge and the other end a negative charge. The electrostatic force of attraction between such molecules should be very strong. This is because the *positive end of one molecule* attracts and is attracted by the *negative end of the other molecule*. Thus, *two or more molecules may associate together to form large clusters of*

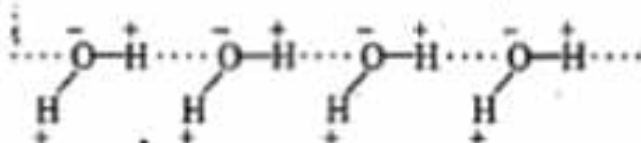*molecules.* This is illustrated below for the association of several molecules of hydrogen fluoride :

$$\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots$$

The cluster of HF molecules may be described as $(HF)_n$.

The attractive force which binds hydrogen atom of one molecule with electronegative atom (such as fluorine) of another molecule, generally of the same substance, is known as **hydrogen bond.**

In this case, while the length of the covalent bond between F and H atoms is found to 1·00 Å, the length of the hydrogen bond between F and H atoms of neighbouring molecules has been found to be 1·55 Å.

Water molecule, because of its bent structure, is also a dipole, oxygen end carrying a negative charge and hydrogen end carrying a positive charge, as shown. Hydrogen bonding takes place in this case as well, as shown below :

The cluster of water molecules may be described as $(H_2O)_n$.

Alcohols and carboxylic acids also form associated molecules for the same reason, as illustrated below.

Alcohols   Carboxylic acid
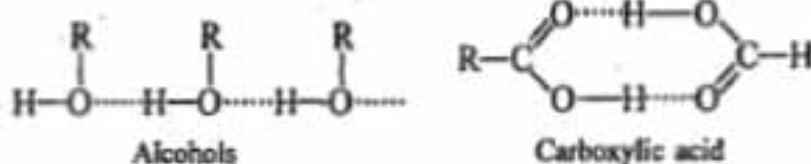
It is seen that in water and alcohols, the hydrogen bonding (or the association of molecules) may extend to several molecules as indicated above but in carboxylic acids, the hydrogen bonding is limited to the association of two molecules only.
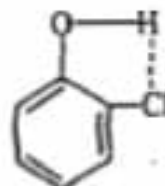
The nature of hydrogen bond. The hydrogen bond *is a class in itself.* It arises from electrostatic forces between the positive end (pole) of one molecule and the negative end (pole) of *another* molecule of the same or some other polar substance. For instance, extensive hydrogen bonding occurs between molecules of water, molecules of ethanol as also between molecules of water and molecules of ethanol. The strength of hydrogen bond has been found to vary between 10 – 40 kJ per mole (*i.e.*, per $6·022\times10^{23}$ bonds) while that of a covalent bond has been found to be of the order of 400 kJ per mole. Thus, a hydrogen bond is very much weaker than a covalent bond.

Intramolecular Hydrogen Bonding. In addition to *intermolecular* hydrogen bonding resulting from electrostatic forces of attraction between the positive and negative ends of *different molecules* of the same substance, cases of **intramolecular hydrogen bonding** are also known. *These involve the electrostatic forces of attraction between hydrogen and an electronegative element both present in the* **same molecule.**

Interesting examples are provided by *o*-nitrophenol and *o*-chlorophenol :
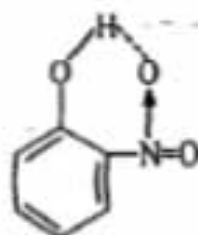

o-Nitrophenol showing intamolecular   *o*-Chlorophenol showing intramolecular
hydrogen bonding   hydrogen bonding

Para nitrophenol and para chlorophenol, on account of larger distances between the two groups, do not show any intramolecular hydrogen bonding. On the other hand, they show the usual *intermolecular hydrogen bonding*, as illustrated below :
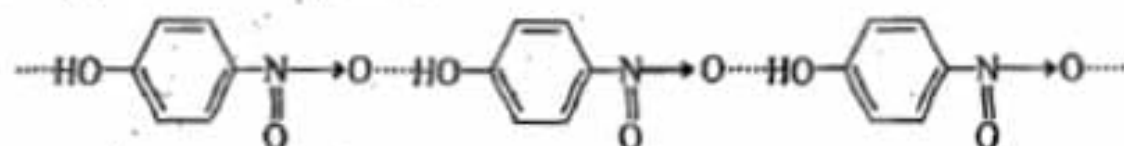
Intermolecular hydrogen bonding in *p*-nitrophenol
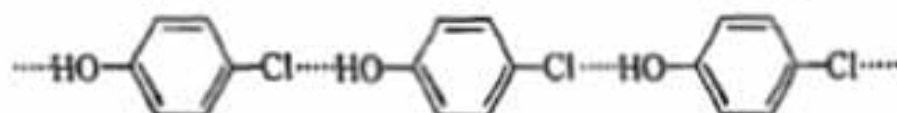
Intermolecular hydrogen bonding in *p*-chlorophenol

As a result of intermolecular hydrogen bonding, the para derivatives undergoes association as shown above, resulting in an increase in molar mass and hence an increase in boiling point. In ortho derivative, on account of *intramolecular hydrogen bonding*, no such association is possible. Consequently, the ortho derivatives are more volatile than the para derivatives.

Consequences of Hydrogen Bonding. 1. Boiling Points of Binary Hydrogen Compounds. Let us consider boiling points of binary compounds of hydrogen with various elements of Groups 15, 16 and 17, given in Table 10.

TABLE 10

Boiling Points of Binary Hydrogen Compounds with Elements of Groups 15, 16 and 17

Group 15			Group 16			Group17		
Formula	Molar mass	B.P. (°C)	Formula	Molar mass	B.P. (°C)	Formula	Molar mass	B.P. (°C)
SbH_3	125	−17·0	H_2Te	130	−1·8	HI	127·9	−3·5
AsH_3	78	−55·1	H_2Se	81	−42·0	HBr	80·9	−67·1
PH_3	34	−84·6	H_2S	33	−59·6	HCl	36·5	−85·0
NH_3	17	−33·0	H_2O	18	+100	HF	20·0	+19·4

It is seen that although the boiling point in each group *decreases with decrease in molar mass*, there is a sudden *reversal* in the case of ammonia, water and hydrogen fluoride in Groups 15, 16 and 17, respectively. The unusually high boiling point of each compound, evidently, is a consequence of strong intermolecular forces due to hydrogen bonding.

Thus, while H_2S, in which there is no hydrogen bonding, is a *gas*, H_2O, in which there is considerable hydrogen bonding, is a *high boiling liquid*.

Some Unique Properties of Water. Water has some unique properties. Two of these are :

1. *Density in the solid state (ice) is less than that in the liquid state.* This is somewhat unusual because in most substances density in the solid state is more than that in the liquid state.

2. *Water contracts when heated between 0°C and 4°C.* This is again unusual because most substances expand when heated in all temperature ranges.

Both these peculiar features which are due to hydrogen bonding, are discussed below :

1. In ice, the hydrogen bonding between H_2O molecules is more extensive than in liquid water. A substance in solid state has a definite structure and the molecules are more rigidly fixed relative to one

another than in liquid state. In ice, the H_2O molecules are *tetrahedrally oriented with respect to one another.* This has been shown in Fig. 44.

At the same time, each oxygen atom is surrounded tetrahedrally by four hydrogen atoms, two of these are bonded covalently and the other two by hydrogen bonds (Fig. 44).

The hydrogen bonds are *weaker* and, therefore, *longer* than the covalent bonds. This arrangement gives rise to an *open cage-like structure,* as shown in the figure. There are evidently a number of 'holes' or open spaces in this structure. These 'holes' are formed because the hydrogen bonds holding the H_2O molecules in ice *are directed at certain definite angles.* In liquid water such hydrogen bonds are fewer in number. Therefore, as ice melts, a large number of hydrogen bonds are broken. The molecules, therefore, move into the 'holes' or open spaces and come closer to one another than they were in the solid state. *This results in a sharp increase in the density.* The density of liquid water is, therefore, higher than that of ice.
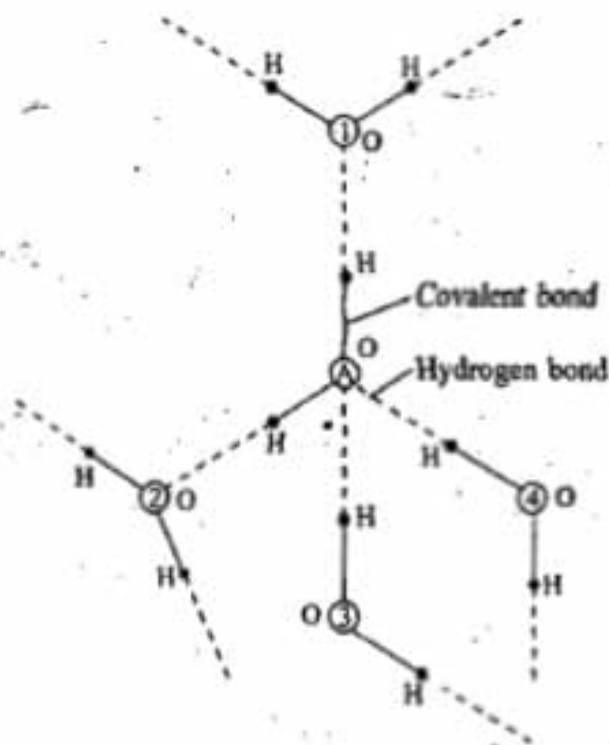

Fig. 44. The tetrahedral open cage-like crystal structure of ice. The central oxygen atom A is surrounded tetrahedrally by the oxygen atoms marked 1, 2, 3 and 4.

2. As liquid water is heated from 0° to 4°C, hydrogen bonds continue to be broken and the molecules come closer and closer together. This leads to *contraction.* However, there is also some expansion of water due to rise in temperature as in other liquids. It appears that upto 4°C, the former effect predominates and hence there is net *contraction in volume.* Above 4°C, however, the normal expansion effect, due to rise in temperature, predominates and hence *the volume increases as the temperature rises.*

Importance of Hydrogen Bonding in Sustaining Life. It can be easily realised that without hydrogen bonding, water would have existed as a gas like hydrogen sulphide. In that case, no life would have been possible on this globe.

Hydrogen bonding also exists in all living organisms whether of animal or of vegetable kingdom. Thus, it exists in various tissues, organs, blood, skin and bones in animal life. It plays an important role in determining structure of proteins which are so essential for life.

Hydrogen bonding plays an important role in making wood fibres more rigid and thus makes it an article of great utility to meet requirements of housing, furniture, etc. The cotton, silk or synthetic fibres owe their rigidity and tensile strength to hydrogen bonding. Thus, hydrogen bonding is of vital importance for our clothing as well. Most of our food materials also consist of hydrogen bonded molecules. Sugars and carbohydrates, for example, have many OH groups. The oxygen of one such group in one molecule is bonded with OH group of another molecule through hydrogen bonding. The stickiness of glue (a protein) or honey (which consists mainly of water and sugar) is also due to hydrogen bonding between the OH or other such groups of different molecules with one another. Hydrogen bonding is thus a phenomenon of great importance in everyday life.

INTERMOLECULAR FORCES

It is now fully established that forces of attraction exist between polar as well as non-polar molecules. These are known as **intermolecular forces** or **cohesive forces** or **van der Waals forces.** These forces originate from two types of interactions, viz., 1. *Dipole-Dipole Interaction* and 2. *Induced dipole–Induced dipole Interaction.*

1. Dipole–Dipole Interaction. In the case of *polar molecules* which have permanent dipoles, the van der Waals' forces are mainly due to electrical interaction between the dipoles known as **dipole–dipole interaction**. For instance, gases such as ammonia, sulphur dioixde, hydrogen fluoride, hydrogen chloride, etc., have permanent dipoles as a result of which there is appreciable dipole–dipole interaction between the molecules of these gases. The magnitude of this type of interaction depends upon the dipole moments of the molecules concerned. The greater the dipole moments, the greater is the dipole–dipole interaction. Because of the attractive interaction, these gases can be easily liquified.

The average interaction energy of the two molecules with permanent dipole moments μ_1 and μ_2 is given by the expression :

$$\text{Interaction energy, } \phi\,(r) = -2 \left(\frac{\mu_1 \mu_2}{4\pi\varepsilon_0}\right)^2 \left(\frac{1}{r^6}\right)\left(\frac{1}{3kT}\right) \qquad ...(37)$$

where r is the distance between the molecules, k is the Boltzmann constant and $4\pi\varepsilon_0$ is the permittivity factor for the medium.
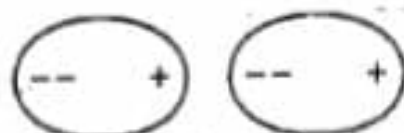
2. Induced dipole-Induced dipole Interaction. London Forces or **Dispersive Forces.** It is now well known that van der Waals forces exist even in non-polar diatomic molecules such as O_2 and N_2 and also in non-polar monoatomic molecules such as He, Ne, Ar, etc. This attraction is evident from the condensation of these gases into liquids at sufficiently high pressures and low temepratures. The existence of van der Waals forces in these molecules could not be understood for several years.

In 1930, F. London provided a satisfactory explanation for the existence of forces of attraction between non-polar molecules according to which electrons of a non-polar molecule keep on oscillating with respect to the nuclei of the atoms. As a result of this, at a given instant, positive charge may be concentrated in one region and negative charge in another region of the same molecule. Thus, a non-polar molecule may become momentarily self-polarised. This polarised molecule may induce a dipole moment in a neighbouring molecule, as shown in Fig. 45.

| (a) | (b) |
| shows average charge distribution in a non-polar molecule. | shows induced dipole–induced dipole interaction. |

Fig. 45. Origin of cohesive forces in non-polar molecules.

The electrostatic forces of attraction between induced dipoles and the original dipoles (due to oscillation of electrons) are known as **London forces**. These forces are also called **dispersive forces** because the well known phenomenon of dispersion of light is also connected with these dipoles. For a pair of adjacent molecules, London forces vary inversely as the *sixth power* of the distance between them, i.e., $F \propto 1/r^6$.

The approximate interaction energy in this case is given by

$$\phi\,(r) = -\left(\frac{3E_1 E_2}{2(E_1 + E_2)}\right)\left(\frac{\alpha_1 \alpha_2}{(4\pi\varepsilon_0)^2 r^6}\right) \qquad ...(38)$$

where E_1 and E_2 are the ionization energies of the two molecules. Other parameters have the same significance as mentioned above.

The van der Waals' attraction in *non-polar molecules* is thus *exclusively* due to London forces. In the case of polar molecules showing permanent dipoles, however, other electrostatic forces due to dipole – dipole interaction also contribute towards the van der Waals attraction, as already discussed.

QUESTIONS

1. (a) What is an ionic bond ?

   (b) Discuss carefully the formation of an ionic bond in terms of decrease of energy. Derive from it the conditions for the formation of ionic bonds.

   (c) Explain giving suitable examples why ions with three positive or three negative charges are rare ?

2. (a) Discuss the formation of a covalent bond on the basis of the orbital overlap concept. What is meant by a sigma bond ?

   (b) Differentiate between a sigma bond and a pi bond. Explain why a sigma bond is stronger than a pi bond ?

   (c) Explain the term covalency. How would you account for variable covalency of an element ? What is the maximum covalency which an element can exhibit ?

   (d) Construct a plot of potential energy versus internuclear distance between two hydrogen atoms.

3. (a) What do you understand by polar and non-polar molecules ? Is it possible for the non-polar molecules to have polar bonds ? Justify you answer with examples.

   (b) Explain why CO_2 and CCl_4 molecules are non-polar while $CHCl_3$ molecule is polar ?

   (c) What is meant by dipole moment ? Can its magnitude give an idea about the structure of a molecule ? Explain giving examples.

   (d) Which is more polar, H_2S or H_2O and why ?

4. (a) What is the difference between coordinate bond and covalent bond ?

   (b) Under what circumstances can a fully filled orbital participate in bond formation? Discuss with an example.

   (c) PCl_5 exists while NCl_5 does not. Explain.

5. What is Valence Bond theory ? Explain.

   In the potential energy diagram for H_2 molecule, the combined wave function ψ for two hydrogen atoms $\psi = \psi_A$ (1)ψ_A (2) (where ψ_A (1) and ψ_B (2) represent wave functions for two hydrogen atoms H_A and H_B associated with electrons 1 and 2, respectively), results in decrease in energy of the system by 24 kJ mol^{-1}. But the experimental value is 458 kJ mol^{-1}. What improvements in the wave functions of the system are made to account for this difference?

6. (a) What is resonance ? Discuss by taking example of CO_3^{2-} ion.

   (b) What do you understand by the term resonance energy ? What are the essential rules for writing resonating structures?

7. (a) What is Molecular Orbital theory ?

   (b) Give the electron charge density diagrams for bonding and antibonding molecular orbitals.

   (c) Predict the bond order in C_2 molecule with the help of MO diagram.

8. (a) What do you understand by the terms bonding and antibonding molecular orbitals ? Why are they so called ? Illustrate your answer by taking into consideration the structure of hydrogen ion H_2^+.

   (b) Is B_2 molecule paramagnetic or diamagnetic ? Discuss.

9. Explain how the atomic orbitals combine to form bonding and antibonding molecular orbitals. What are the limitations to such combinations ? Explain why in a homonuclear molecule, an s orbital of one atom cannot combine with a p_z or a p_y orbital of another atom of the same element.

10. (a) Draw molecular orbital diagram for HF molecule.

11. Explain on the basis of MO theory as to why

    (a) Oxygen molecule is paramagnetic while nitrogen molecule is diamagnetic.

    (b) Hydrogen forms diatomic molecule while helium remains monoatomic.

    (c) The bond order in O_2^- is less than that in O_2 which, in turn, is less than that in O_2^+.

12. (a) The internuclear distances in some O—O bonds are as follows :

O_2^+	O_2	O_2^-	O_2^{2-}
1·12 Å	1·21 Å	1·30 Å	1·49 Å

   (i) Account for the gradation of the internuclear distances in the above series.

   (ii) Which of these species are paramagnetic ?

   (b) Is it correct to say that bond energy in a diatomic molecule always increases when an electron is lost ?

   (c) "While in the case of F_2 molecule, all the orbitals are molecular, in case of HF molecule there is only one orbital which is molecular." Comment on this statement.

(*ii*) Which of these species are paramagnetic ?

(b) Is it correct to say that bond energy in a diatomic molecule always increases when an electron is lost ?

(c) "While in the case of F_2 molecule, all the orbitals are molecular, in case of HF molecule there is only one orbital which is molecular." Comment on this statement.

13. (a) Discuss with the help of the MO theory the formaiton of N_2, O_2 and F_2 molecules. How does the theory explain the difference in the reactivity of N_2, O_2 and F_2 ?

(b) Discuss carefully the electronic configurations of NO, CO, HF and HCl molecules.

14. Draw the MO diagrams for the following species :

Be_2, HHe (hypothetical), O_2^-, CO, BN

Explain the magnetic character of these species.

15. Write the electronic configuration of NO molecule.

(a) What is the bond order ?   (b) Will the bond length be shorter or larger than in NO^+ ?

(c) How many unpaired electrons will be present ?   (d) What will be the bond order in NO^+ ?

16. With the help of molecular orbital diagrams explain why

(a) the bond order in N_2^+ ion is less than that in N_2 molecule whereas the bond order in O_2^+ is greater than that in O_2 molecule.

(b) the bond energy of NO^+ is higher than that of NO.   (c)   the bond length of CO^+ is larger than that of CO.

17. (a) Write the electronic configuration of a diatomic molecule having bond order three.

(b) Compare briefly valence bond and molecular orbital theories.

18. What is meant by metallic bond ? Illustrate the nature of metallic bond on the basis of (i) Electron sea model.
(ii) Valence bond model and (iii) The band model (MO approach).

19. Discuss in details the band model of metallic bond. What type of energy bands are obtained in, (i) sodium metal
(ii) an insulator (iii) semi-conductor

20. What is meant by hydrogen bonding ? Discuss the nature and consequences of hydrogen bonding. Discuss the importance of hydrogen bonding in sustaining life. Why do H_2O and HF have abnormally high boiling points ?

21. (a) What are intermolecular forces ? How do these forces originate ?

(b) What are London forces ? What is their origin ?

22. Explain why in the valence bond treatment of H_2, $\psi_{+\ complete}$ is called a singlet state while $\psi_{-\ complete}$ is called a triplet state.

23. What are term symbols ? What is the advantage of using three term symbols ? Wrtie down the term symbols for the following :

H_2^+ molecular ion, O_2 molecule, F_2 molecule, N_2 molecule F_2^+ molecular ion, Be_2, Li_2

24. What are Walsh diagrams ? To what use these diagrams are put ? Explain with the help of a Walsh diagram that[1] the BeH_2 molecule would have a linear geometry and H_2O molecule would have an angular geometry.

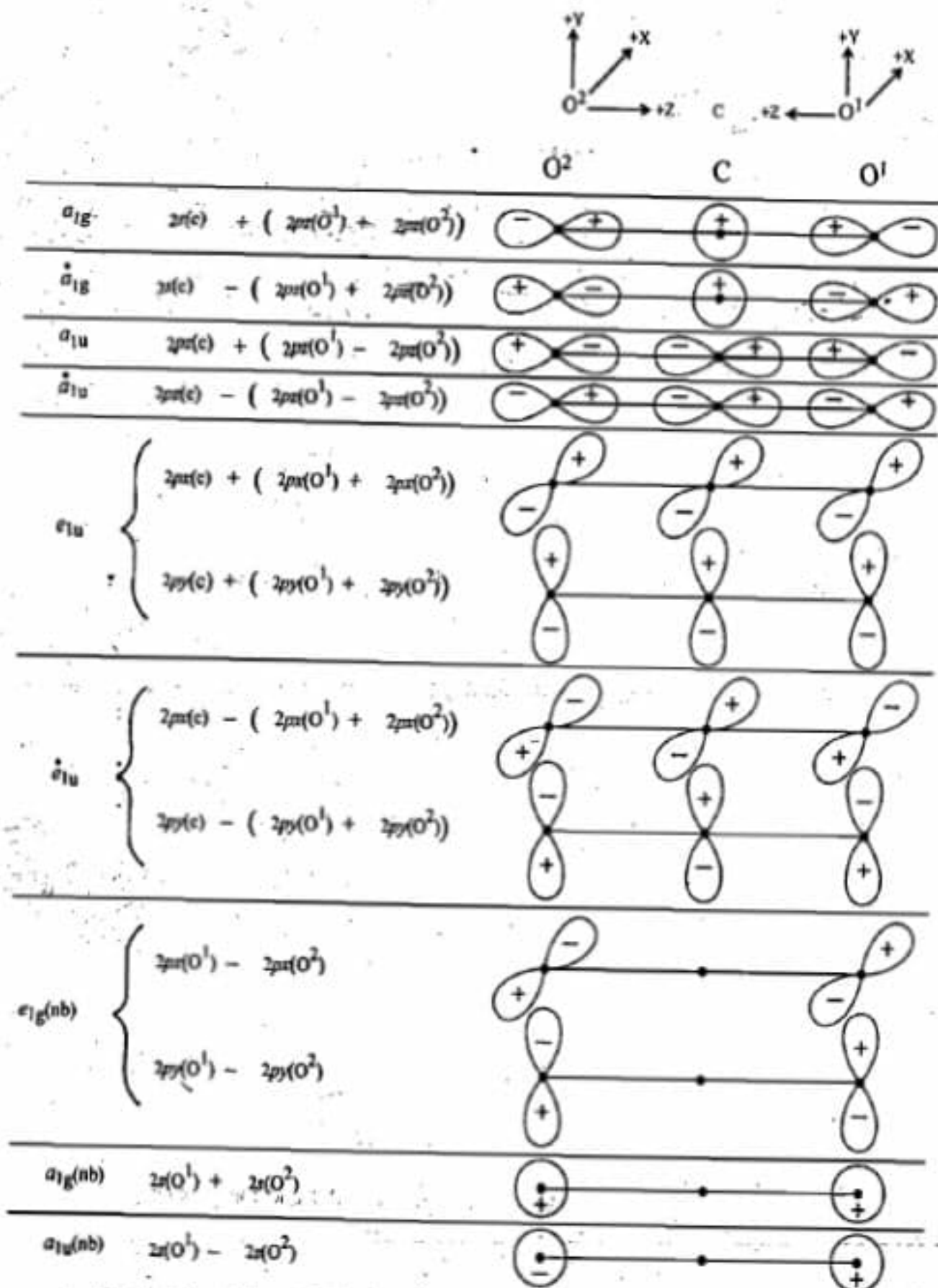25. Discuss the geometry of CO_2 molecule on the basis of Walsh diagram.

Fig. 37. The various molecular orbitals formed from the combination of atomic orbitals of C and O atom to form CO_2 molecule.

It is evident that CO_2 molecule has 16 valence electrons to be accommodated in its molecular orbitals so that its electronic configuration is written as :

$$CO_2 : 1\bar{a}_{1g}^2(nb)\ 1a_{1u}^2(nb)\ 2a_{1g}^2\ 2a_{1u}^2\ e_{1u}^4(\pi)\ e_{1g}^4(nb)$$