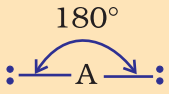
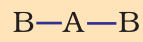
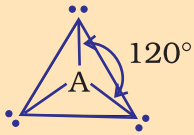
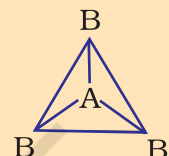
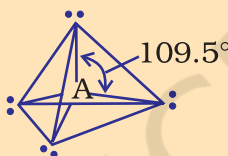
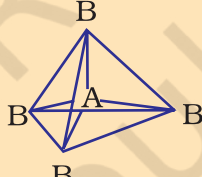
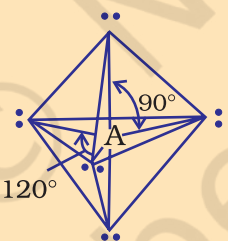
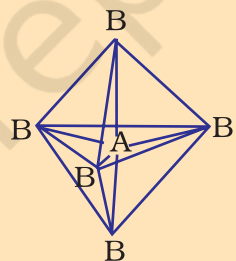
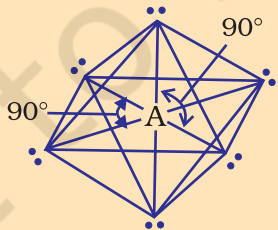
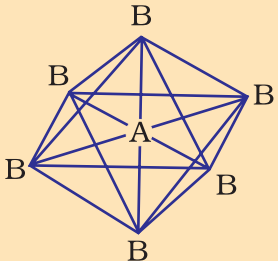
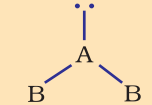
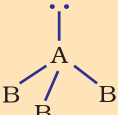
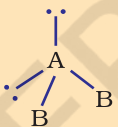
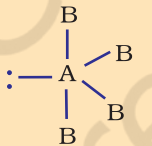
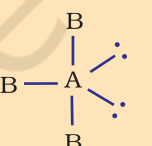
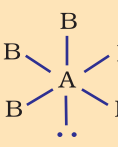
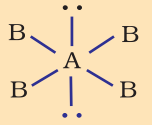


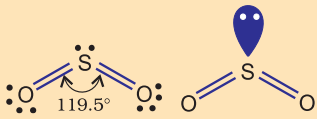
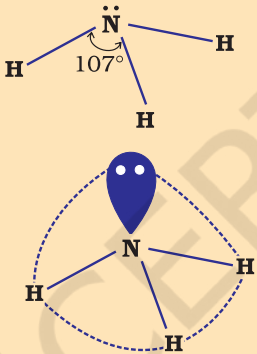
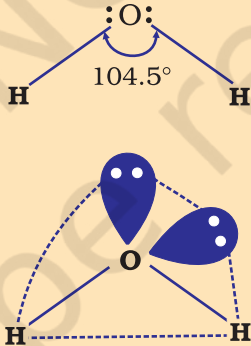
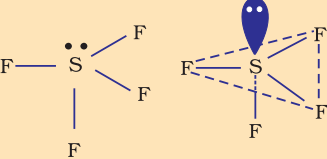
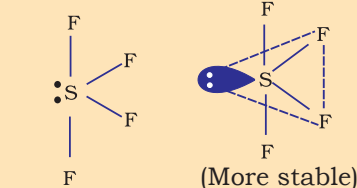
**Table 4.6 Geometry of Molecules in which the Central Atom has No Lone Pair of Electrons**

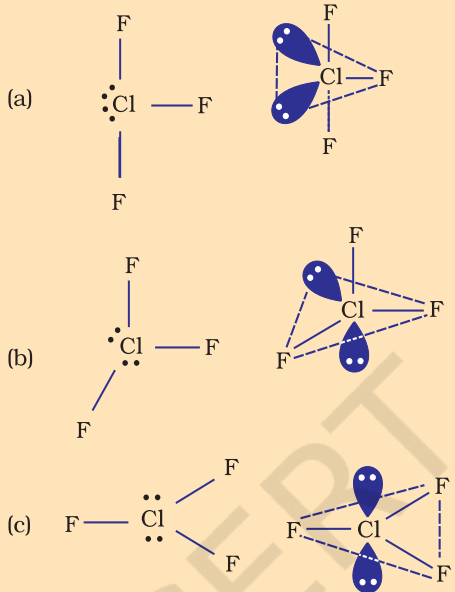
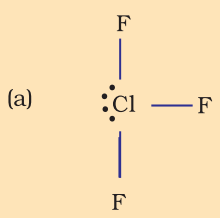
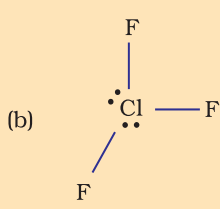
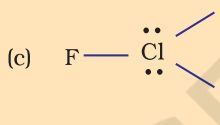
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 <p>Linear</p>	 <p>Linear</p>	BeCl <sub>2</sub> , HgCl <sub>2</sub>
3	 <p>Trigonal planar</p>	 <p>Trigonal planar</p>	BF <sub>3</sub>
4	 <p>Tetrahedral</p>	 <p>Tetrahedral</p>	CH <sub>4</sub> , NH <sub>4</sub> <sup>+</sup>
5	 <p>Trigonal bipyramidal</p>	 <p>Trigonal bipyramidal</p>	PCl <sub>5</sub>
6	 <p>Octahedral</p>	 <p>Octahedral</p>	SF <sub>6</sub>

**Table 4.7 Shape (geometry) of Some Simple Molecules/Ions with Central Ions having One or More Lone Pairs of Electrons(E).**

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
$AB_2E$	2	1	 Trigonal planer	Bent	$SO_2$
$AB_3E$	3	1	 Tetrahedral	Trigonal pyramidal	$NH_3$
$AB_3E_2$	2	2	 Tetrahedral	Bent	$H_2O$
$AB_4E$	4	1	 Trigonal bi-pyramidal	See saw	$SF_4$
$AB_3E_2$	3	2	 Trigonal bi-pyramidal	T-shape	$ClF_3$
$AB_5E$	5	1	 Octahedral	Square pyramid	$BrF_5$
$AB_4E_2$	4	2	 Octahedral	Square planer	$XeF_4$

**Table 4.8 Shapes of Molecules containing Bond Pair and Lone Pair**

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
$AB_2E$	4	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to $119.5^\circ$ from $120^\circ$ .
$AB_3E$	3	1		Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to $107^\circ$ from $109.5^\circ$ .
$AB_2E_2$	2	2		Bent	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to $104.5^\circ$ from $109.5^\circ$ .
$AB_4E$	4	1	<div style="display: flex; justify-content: space-around;"> <div> <p>(a)</p>  </div> <div> <p>(b)</p>  </div> </div>	See-saw	In (a) the lp is present at axial position so there are three lp—bp repulsions at $90^\circ$ . In (b) the lp is in an equatorial position, and there are two lp—bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw.

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
$\text{AB}_3\text{E}_2$	3	2	 <p>(a) </p> <p>(b) </p> <p>(c) </p>	T-shape	In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped).

#### 4.5 VALENCE BOND THEORY

As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like  $\text{H}_2$  ( $435.8 \text{ kJ mol}^{-1}$ ,  $74 \text{ pm}$ ) and  $\text{F}_2$  ( $155 \text{ kJ mol}^{-1}$ ,  $144 \text{ pm}$ ), although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules.

Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

**Valence bond theory** was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion

of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements (Units 2), the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. A rigorous treatment of the VB theory in terms of these aspects is beyond the scope of this book. Therefore, for the sake of convenience, valence bond theory has been discussed in terms of qualitative and non-mathematical treatment only. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules.

Consider two hydrogen atoms A and B approaching each other having nuclei  $N_A$  and  $N_B$  and electrons present in them are represented by  $e_A$  and  $e_B$ . When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between:

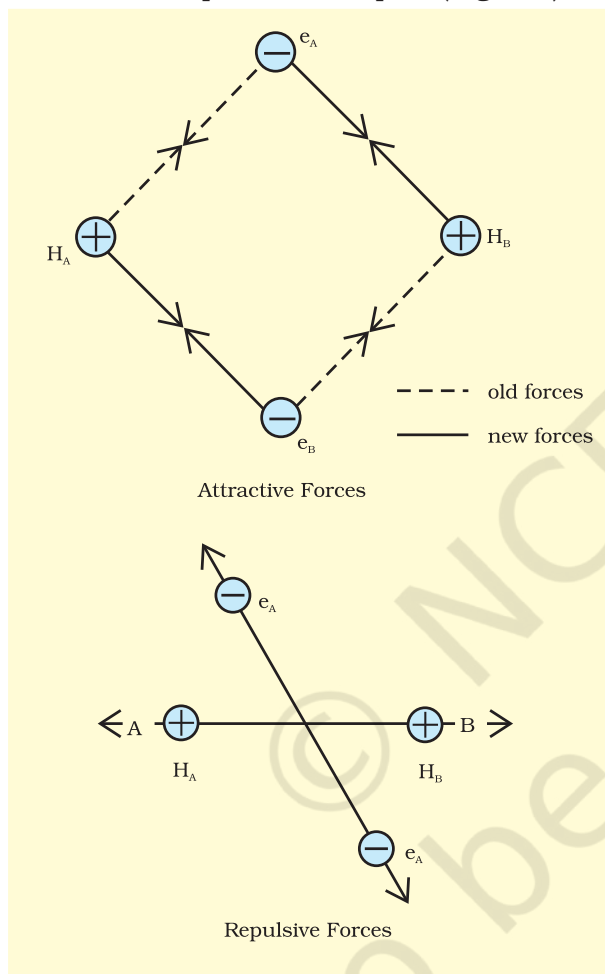
- nucleus of one atom and its own electron that is  $N_A - e_A$  and  $N_B - e_B$ .

- (ii) nucleus of one atom and electron of other atom i.e.,  $N_A - e_B$ ,  $N_B - e_A$ .

Similarly repulsive forces arise between

- (i) electrons of two atoms like  $e_A - e_B$ ,  
 (ii) nuclei of two atoms  $N_A - N_B$ .

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig. 4.7).

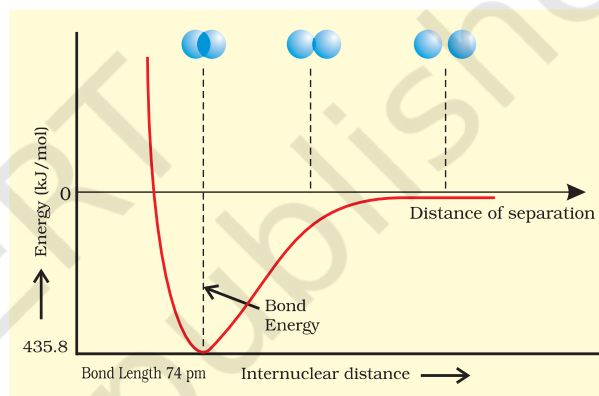
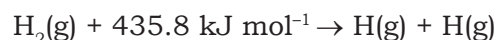


**Fig. 4.7** Forces of attraction and repulsion during the formation of  $H_2$  molecule

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded

together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as **bond enthalpy**, which is corresponding to minimum in the curve depicted in Fig. 4.8. Conversely, 435.8 kJ of energy is required to dissociate one mole of  $H_2$  molecule.



**Fig. 4.8** The potential energy curve for the formation of  $H_2$  molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of  $H_2$ .

#### 4.5.1 Orbital Overlap Concept

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

### 4.5.2 Directional Properties of Bonds

As we have already seen, the covalent bond is formed by overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of 1s-orbitals of two H atoms.

In case of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , the geometry of the molecules is also important in addition to the bond formation. For example why is it so that  $\text{CH}_4$  molecule has tetrahedral shape and HCH bond angles are  $109.5^\circ$ ? Why is the shape of  $\text{NH}_3$  molecule pyramidal?

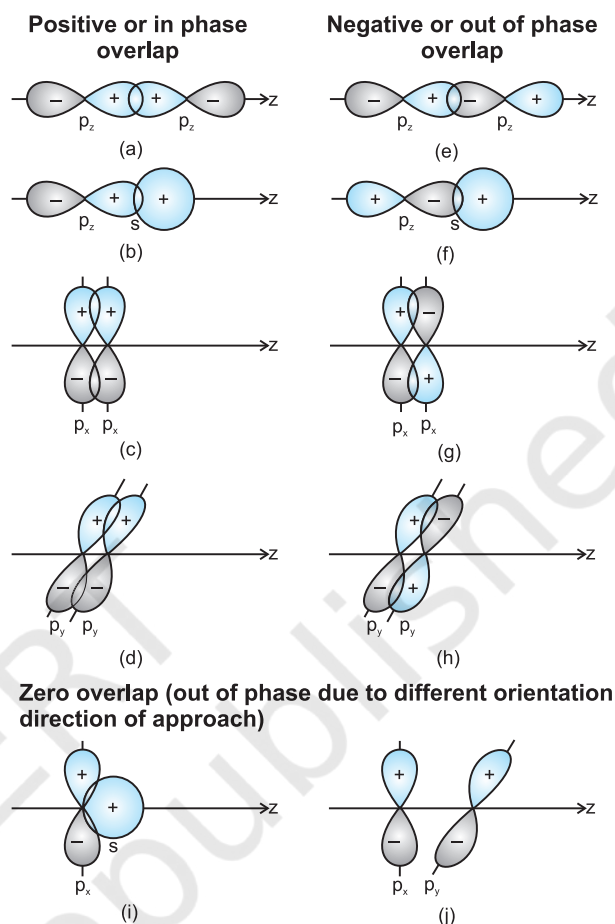
The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , etc. in terms of overlap and hybridisation of atomic orbitals.

### 4.5.3 Overlapping of Atomic Orbitals

When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space (Fig. 4.9). Positive and negative sign on boundary surface diagrams in the Fig. 4.9 show the sign (phase) of orbital wave function and are not related to charge. Orbitals forming bond should have same sign (phase) and orientation in space. This is called positive overlap. Various overlaps of s and p orbitals are depicted in Fig. 4.9.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. We know that the shapes of  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to use VB theory to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

Let us first consider the  $\text{CH}_4$  (methane) molecule. The electronic configuration of carbon in its ground state is  $[\text{He}]2s^2 2p^2$  which in the excited state becomes  $[\text{He}] 2s^1 2p_x^1 2p_y^1 2p_z^1$ . The energy required for this excitation is compensated by the release of energy due to overlap between the orbitals of carbon and the



**Fig. 4.9** Positive, negative and zero overlaps of s and p atomic orbitals

hydrogen. The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1s orbitals of the four H atoms which are also singly occupied. This will result in the formation of four C-H bonds. It will, however, be observed that while the three p orbitals of carbon are at  $90^\circ$  to one another, the HCH angle for these will also be  $90^\circ$ . That is three C-H bonds will be oriented at  $90^\circ$  to one another. The 2s orbital of carbon and the 1s orbital of H are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond cannot be ascertained. This description does not fit in with the tetrahedral HCH angles of  $109.5^\circ$ . Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in  $\text{CH}_4$ . Using similar procedure and arguments, it can be seen that in the case of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules, the HNH



and HOH angles should be  $90^\circ$ . This is in disagreement with the actual bond angles of  $107^\circ$  and  $104.5^\circ$  in the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules respectively.

#### 4.5.4 Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping:

(i) Sigma( $\sigma$ ) bond, and (ii) pi( $\pi$ ) bond

(i) **Sigma( $\sigma$ ) bond** : This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

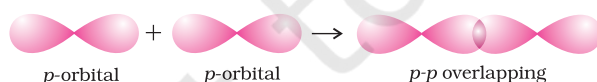
- **s-s overlapping** : In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :



- **s-p overlapping**: This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.

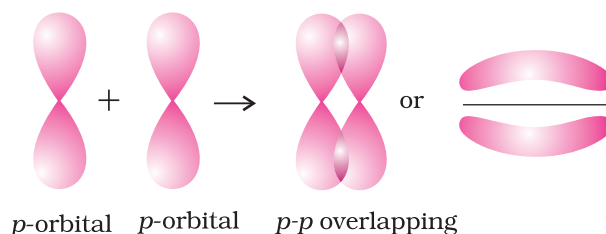


- **p-p overlapping** : This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



(ii) **pi( $\pi$ ) bond** : In the formation of  $\pi$  bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds

above and below the plane of the participating atoms.



#### 4.5.5 Strength of Sigma and pi Bonds

Basically the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that in the formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed in addition to a sigma bond.

#### 4.6 HYBRIDISATION

In order to explain the characteristic geometrical shapes of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  etc., Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals**. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new  $sp^3$  hybrid orbitals.

**Salient features of hybridisation:** The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.

- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

#### Important conditions for hybridisation

- The orbitals present in the valence shell of the atom are hybridised.
- The orbitals undergoing hybridisation should have almost equal energy.
- Promotion of electron is not essential condition prior to hybridisation.
- It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

#### 4.6.1 Types of Hybridisation

There are various types of hybridisation involving  $s$ ,  $p$  and  $d$  orbitals. The different types of hybridisation are as under:

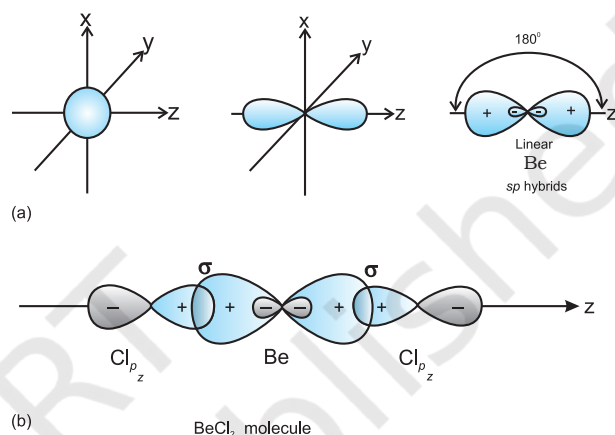
**(I)  $sp$  hybridisation:** This type of hybridisation involves the mixing of one  $s$  and one  $p$  orbital resulting in the formation of two equivalent  $sp$  hybrid orbitals. The suitable orbitals for  $sp$  hybridisation are  $s$  and  $p_z$ , if the hybrid orbitals are to lie along the  $z$ -axis. Each  $sp$  hybrid orbital has 50%  $s$ -character and 50%  $p$ -character. Such a molecule in which the central atom is  $sp$ -hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation.

The two  $sp$  hybrids point in the opposite direction along the  $z$ -axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

#### Example of molecule having $sp$ hybridisation

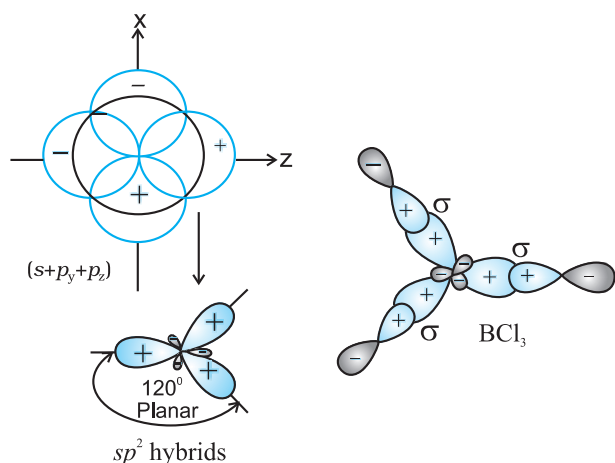
**$\text{BeCl}_2$ :** The ground state electronic configuration of Be is  $1s^2 2s^2$ . In the excited state one of the  $2s$ -electrons is promoted to

vacant  $2p$  orbital to account for its bivalency. One  $2s$  and one  $2p$ -orbital gets hybridised to form two  $sp$  hybridised orbitals. These two  $sp$  hybrid orbitals are oriented in opposite direction forming an angle of  $180^\circ$ . Each of the  $sp$  hybridised orbital overlaps with the  $2p$ -orbital of chlorine axially and form two Be-Cl sigma bonds. This is shown in Fig. 4.10.



**Fig.4.10** (a) Formation of  $sp$  hybrids from  $s$  and  $p$  orbitals; (b) Formation of the linear  $\text{BeCl}_2$  molecule

**(II)  $sp^2$  hybridisation :** In this hybridisation there is involvement of one  $s$  and two  $p$ -orbitals in order to form three equivalent  $sp^2$  hybridised orbitals. For example, in  $\text{BCl}_3$  molecule, the ground state electronic configuration of central boron atom is  $1s^2 2s^2 2p^1$ . In the excited state, one of the  $2s$  electrons is promoted to vacant  $2p$  orbital as

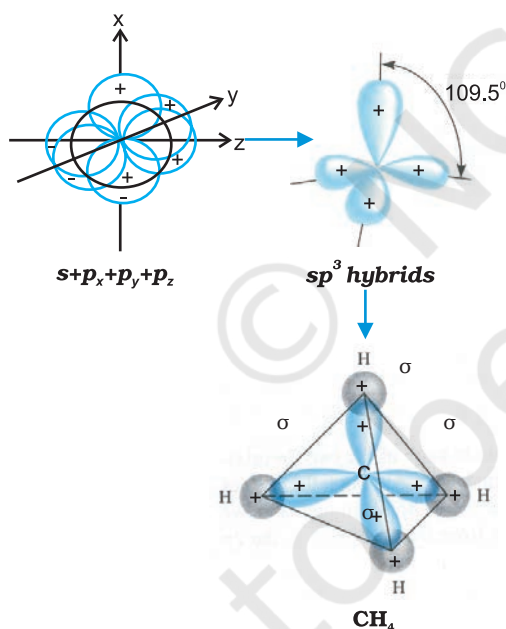


**Fig.4.11** Formation of  $sp^2$  hybrids and the  $\text{BCl}_3$  molecule



a result boron has three unpaired electrons. These three orbitals (one  $2s$  and two  $2p$ ) hybridise to form three  $sp^2$  hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with  $2p$  orbitals of chlorine to form three B-Cl bonds. Therefore, in  $\text{BCl}_3$  (Fig. 4.11), the geometry is trigonal planar with ClBCl bond angle of  $120^\circ$ .

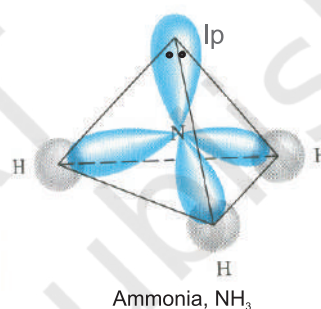
**(III)  $sp^3$  hybridisation:** This type of hybridisation can be explained by taking the example of  $\text{CH}_4$  molecule in which there is mixing of one  $s$ -orbital and three  $p$ -orbitals of the valence shell to form four  $sp^3$  hybrid orbital of equivalent energies and shape. There is 25%  $s$ -character and 75%  $p$ -character in each  $sp^3$  hybrid orbital. The four  $sp^3$  hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between  $sp^3$  hybrid orbital is  $109.5^\circ$  as shown in Fig. 4.12.



**Fig.4.12** Formation of  $sp^3$  hybrids by the combination of  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  atomic orbitals of carbon and the formation of  $\text{CH}_4$  molecule

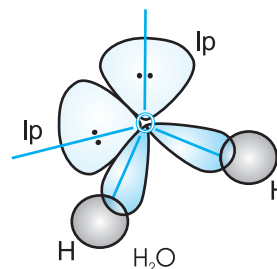
The structure of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules can also be explained with the help of  $sp^3$  hybridisation. In  $\text{NH}_3$ , the valence shell (outer) electronic configuration of nitrogen in the

ground state is  $2s^2 2p_x^1 2p_y^1 2p_z^1$  having three unpaired electrons in the  $sp^3$  hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with  $1s$  orbitals of hydrogen atoms to form three N-H sigma bonds. We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to  $107^\circ$  from  $109.5^\circ$ . The geometry of such a molecule will be pyramidal as shown in Fig. 4.13.



**Fig.4.13** Formation of  $\text{NH}_3$  molecule

In case of  $\text{H}_2\text{O}$  molecule, the four oxygen orbitals (one  $2s$  and three  $2p$ ) undergo  $sp^3$  hybridisation forming four  $sp^3$  hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four  $sp^3$  hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to  $104.5^\circ$  from  $109.5^\circ$  (Fig. 4.14) and the molecule thus acquires a V-shape or angular geometry.



**Fig.4.14** Formation of  $\text{H}_2\text{O}$  molecule

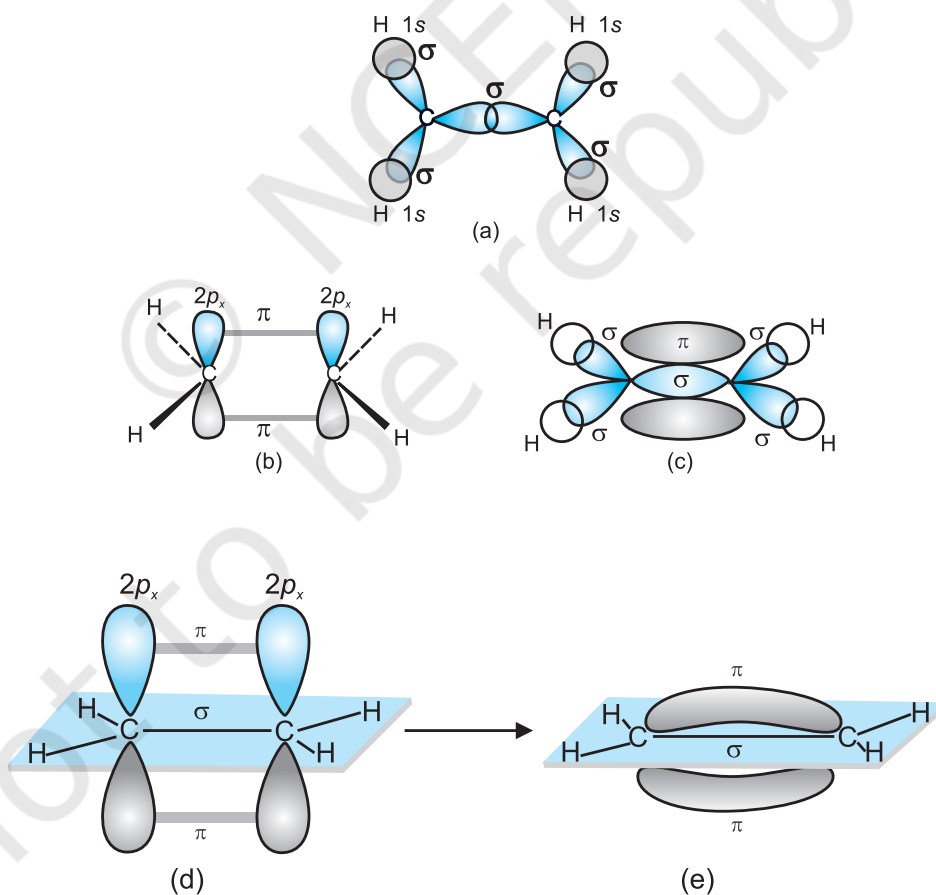
### 4.6.2 Other Examples of $sp^3$ , $sp^2$ and $sp$ Hybridisation

**$sp^3$  Hybridisation in  $C_2H_6$  molecule:** In ethane molecule both the carbon atoms assume  $sp^3$  hybrid state. One of the four  $sp^3$  hybrid orbitals of carbon atom overlaps axially with similar orbitals of other atom to form  $sp^3-sp^3$  sigma bond while the other three hybrid orbitals of each carbon atom are used in forming  $sp^3-s$  sigma bonds with hydrogen atoms as discussed in section 4.6.1(iii). Therefore in ethane C-C bond length is 154 pm and each C-H bond length is 109 pm.

**$sp^2$  Hybridisation in  $C_2H_4$ :** In the formation of ethene molecule, one of the  $sp^2$  hybrid orbitals of carbon atom overlaps axially with  $sp^2$  hybridised orbital of another carbon atom to form C-C sigma bond. While the other two  $sp^2$  hybrid orbitals of each carbon atom are

used for making  $sp^2-s$  sigma bond with two hydrogen atoms. The unhybridised orbital ( $2p_x$  or  $2p_y$ ) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form weak  $\pi$  bond, which consists of two equal electron clouds distributed above and below the plane of carbon and hydrogen atoms.

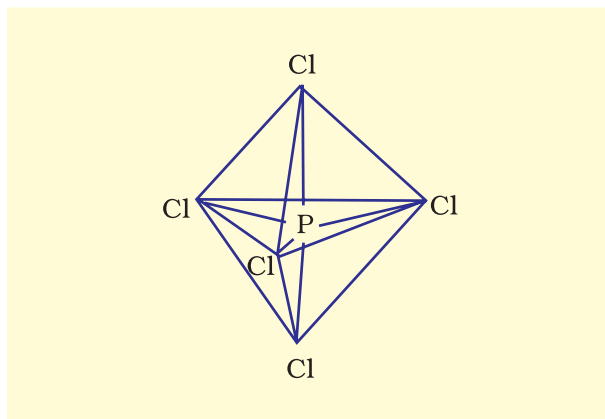
Thus, in ethene molecule, the carbon-carbon bond consists of one  $sp^2-sp^2$  sigma bond and one pi ( $\pi$ ) bond between  $p$  orbitals which are not used in the hybridisation and are perpendicular to the plane of molecule; the bond length 134 pm. The C-H bond is  $sp^2-s$  sigma with bond length 108 pm. The H-C-H bond angle is  $117.6^\circ$  while the H-C-C angle is  $121^\circ$ . The formation of sigma and pi bonds in ethene is shown in Fig. 4.15.



**Fig. 4.15** Formation of sigma and pi bonds in ethene



Now the five orbitals (*i.e.*, one *s*, three *p* and one *d* orbitals) are available for hybridisation to yield a set of five  $sp^3d$  hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as depicted in the Fig. 4.17.

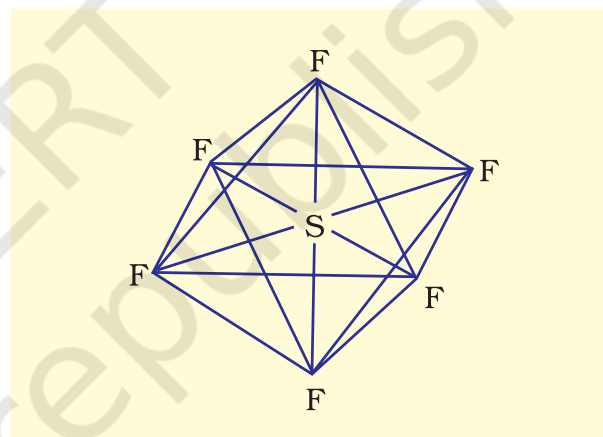
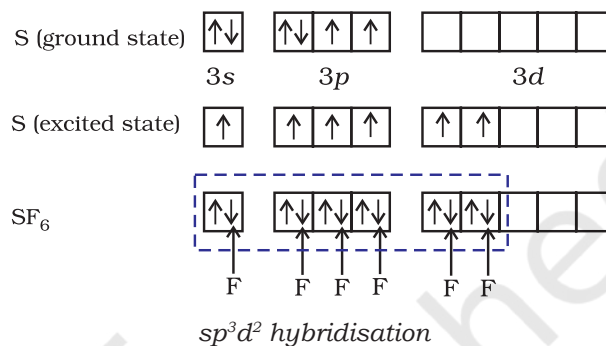


**Fig. 4.17** Trigonal bipyramidal geometry of  $\text{PCl}_5$  molecule

It should be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent. In  $\text{PCl}_5$  the five  $sp^3d$  orbitals of phosphorus overlap with the singly occupied *p* orbitals of chlorine atoms to form five P–Cl sigma bonds. Three P–Cl bond lie in one plane and make an angle of  $120^\circ$  with each other; these bonds are termed as equatorial bonds. The remaining two P–Cl bonds—one lying above and the other lying below the equatorial plane, make an angle of  $90^\circ$  with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes  $\text{PCl}_5$  molecule more reactive.

**(ii) Formation of  $\text{SF}_6$  ( $sp^3d^2$  hybridisation):** In  $\text{SF}_6$  the central sulphur atom has the ground state outer electronic configuration  $3s^23p^4$ . In the excited state the available six orbitals *i.e.*, one *s*, three *p* and two *d* are singly occupied by electrons. These orbitals hybridise to form six new  $sp^3d^2$  hybrid orbitals, which are projected towards the six corners of a regular octahedron in  $\text{SF}_6$ . These

six  $sp^3d^2$  hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds. Thus  $\text{SF}_6$  molecule has a regular octahedral geometry as shown in Fig. 4.18.



**Fig. 4.18** Octahedral geometry of  $\text{SF}_6$  molecule

## 4.7 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 :

- The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus,



an atomic orbital is monocentric while a molecular orbital is polycentric.

- (iv) 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**.
- (v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- (vi) 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.
- (vii) 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.

#### 4.7.1 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 :

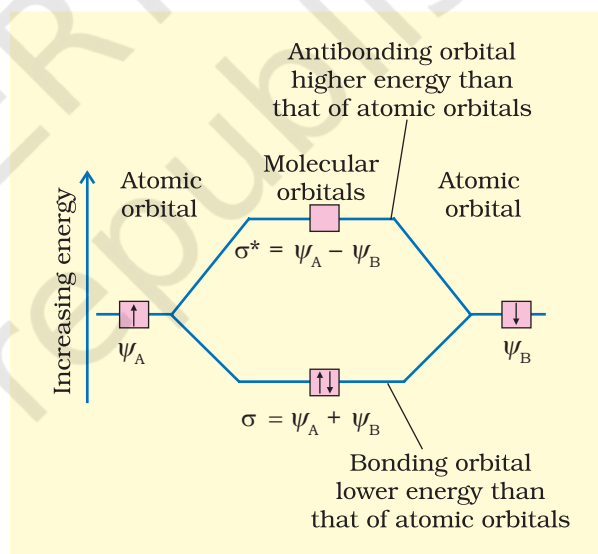
$$\psi_{MO} = \psi_A \pm \psi_B$$

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. 4.19.



**Fig.4.19** 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.

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. Infact, 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.

#### 4.7.2 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.

**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.

#### 4.7.3 Types of Molecular Orbitals

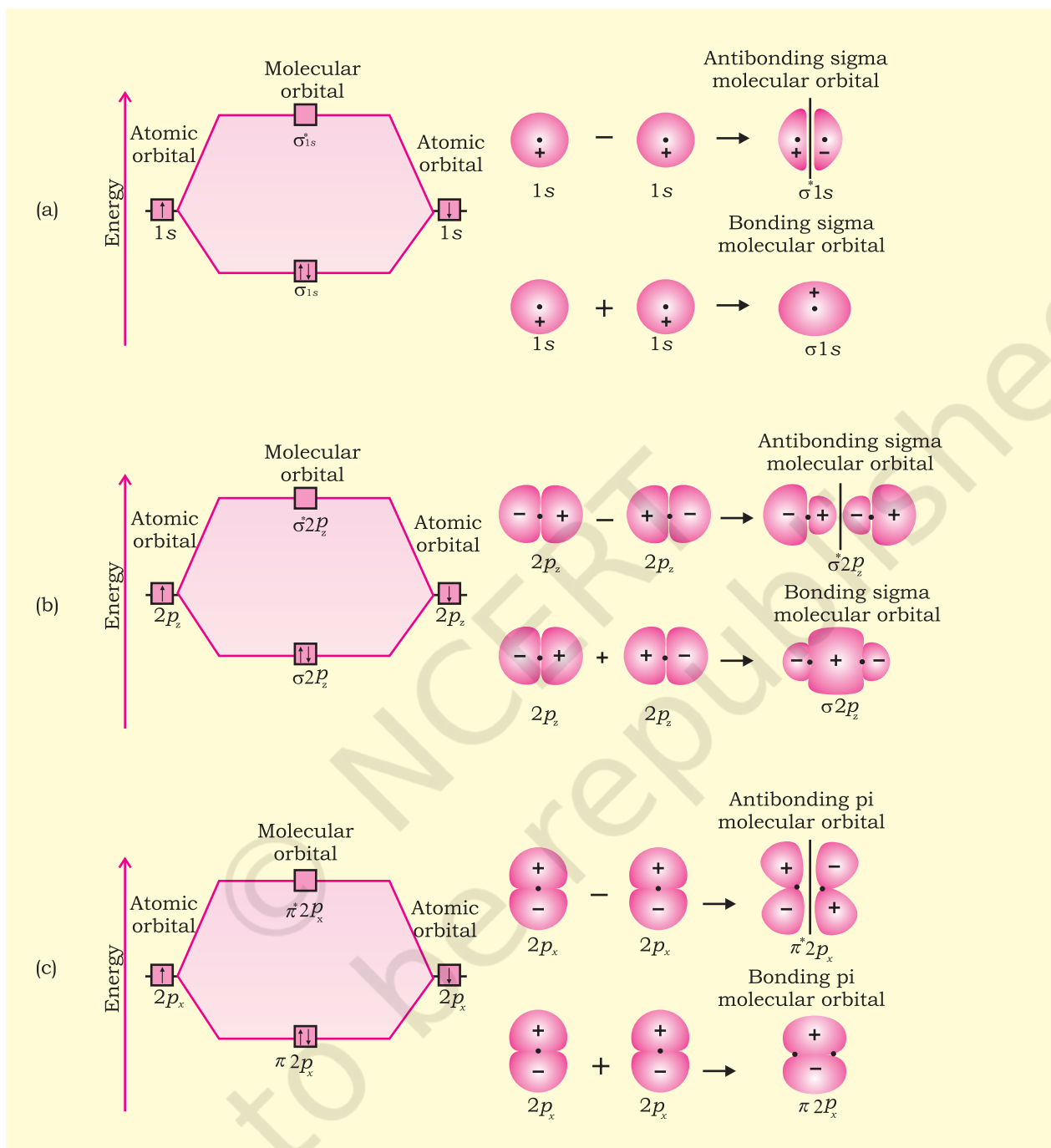
Molecular orbitals of diatomic molecules are designated as  $\sigma$  (sigma),  $\pi$  (pi),  $\delta$  (delta), etc.

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. 4.20(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. 4.20(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.

#### 4.7.4 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



**Fig. 4.20** Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) 2p<sub>z</sub> atomic orbitals and (c) 2p<sub>x</sub> atomic orbitals.

on two atoms) give rise to the following eight molecular orbitals:

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

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

However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules  $Li_2$ ,  $Be_2$ ,  $B_2$ ,  $C_2$ ,  $N_2$ . For instance, it has been observed experimentally that for molecules such as  $B_2$ ,  $C_2$ ,  $N_2$ , 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.**

#### 4.7.5 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

- the molecule is stable if  $N_b$  is greater than  $N_a$ , and
- 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.

#### 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.

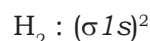
#### Magnetic nature

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.,  $O_2$  molecule.

### 4.8 BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES

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

**1. Hydrogen molecule ( $H_2$ ):** 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



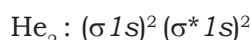
The bond order of  $H_2$  molecule can be calculated as given below:

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

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  $438 \text{ kJ mol}^{-1}$  and bond length equal to 74 pm. Since no

unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

**2. Helium molecule ( $\text{He}_2$ ):** The electronic configuration of helium atom is  $1s^2$ . Each helium atom contains 2 electrons, therefore, in  $\text{He}_2$  molecule there would be 4 electrons. These electrons will be accommodated in  $\sigma 1s$  and  $\sigma^* 1s$  molecular orbitals leading to electronic configuration:

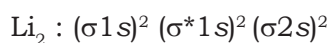


$$\text{Bond order of } \text{He}_2 \text{ is } \frac{1}{2}(2 - 2) = 0$$

$\text{He}_2$  molecule is therefore unstable and does not exist.

Similarly, it can be shown that  $\text{Be}_2$  molecule  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$  also does not exist.

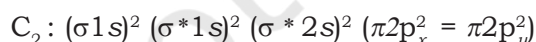
**3. Lithium molecule ( $\text{Li}_2$ ):** The electronic configuration of lithium is  $1s^2, 2s^1$ . There are six electrons in  $\text{Li}_2$ . The electronic configuration of  $\text{Li}_2$  molecule, therefore, is



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

From the electronic configuration of  $\text{Li}_2$  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  $\text{Li}_2$  molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic  $\text{Li}_2$  molecules are known to exist in the vapour phase.

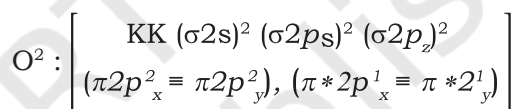
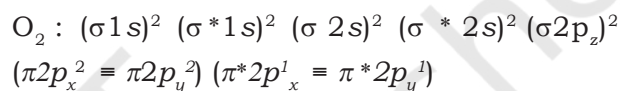
**4. Carbon molecule ( $\text{C}_2$ ):** The electronic configuration of carbon is  $1s^2 2s^2 2p^2$ . There are twelve electrons in  $\text{C}_2$ . The electronic configuration of  $\text{C}_2$  molecule, therefore, is



The bond order of  $\text{C}_2$  is  $\frac{1}{2}(8 - 4) = 2$  and  $\text{C}_2$  should be diamagnetic. Diamagnetic  $\text{C}_2$  molecules have indeed been detected in

vapour phase. It is important to note that double bond in  $\text{C}_2$  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  $\text{N}_2$  molecule can be discussed.

**5. Oxygen molecule ( $\text{O}_2$ ):** The electronic configuration of oxygen atom is  $1s^2 2s^2 2p^4$ . Each oxygen atom has 8 electrons, hence, in  $\text{O}_2$  molecule there are 16 electrons. The electronic configuration of  $\text{O}_2$  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. 4.21 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.

[ ]



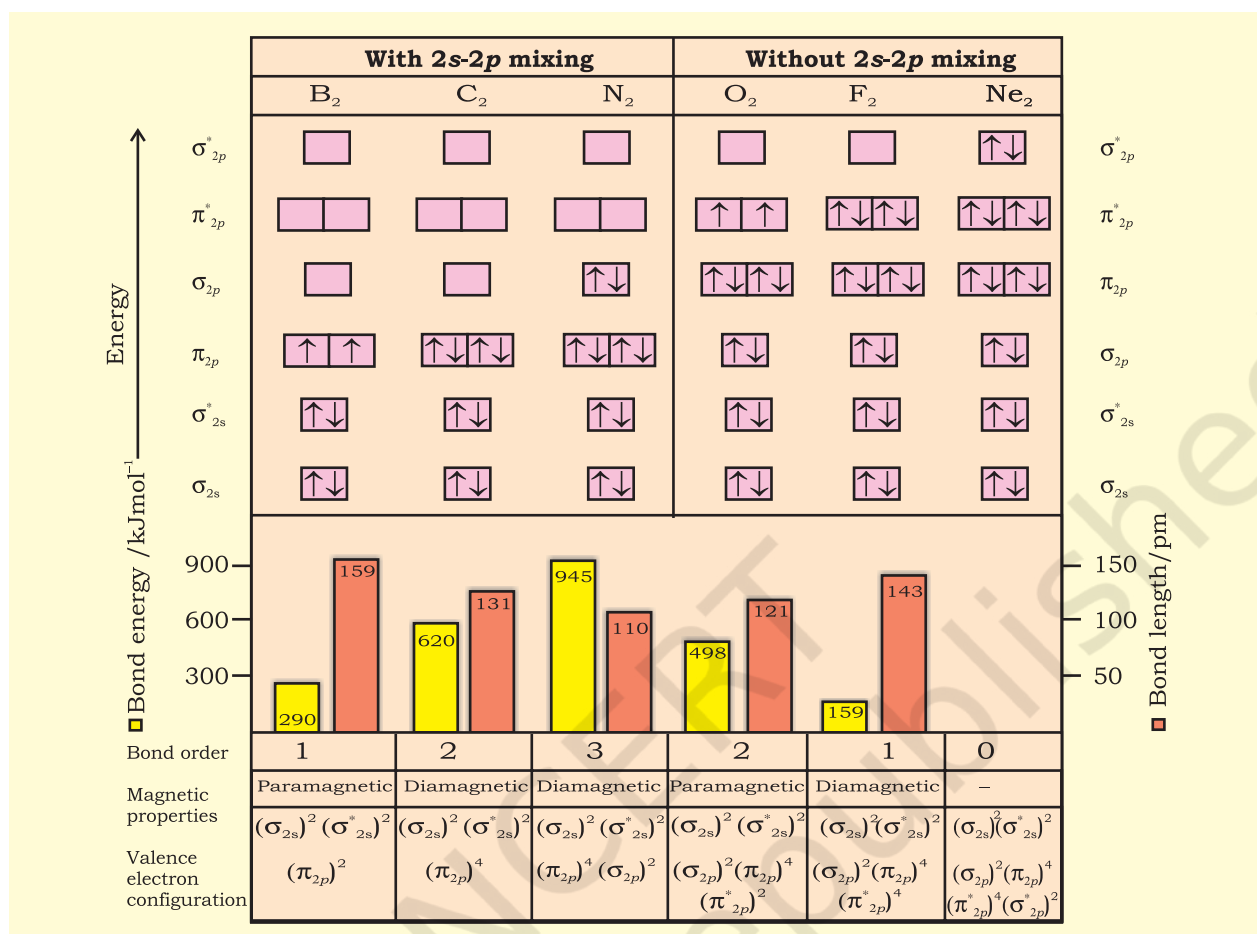
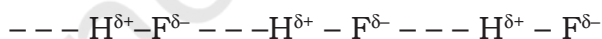


Fig. 4.21 MO occupancy and molecular properties for B<sub>2</sub> through Ne<sub>2</sub>.

## 4.9 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.

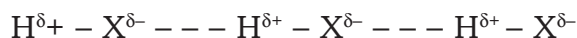
Hydrogen bond is represented by a dotted line (— — —) while a solid line represents the covalent bond. **Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.**

### 4.9.1 Cause of Formation of Hydrogen Bond

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' attain 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.

#### 4.9.2 Types of H-Bonds

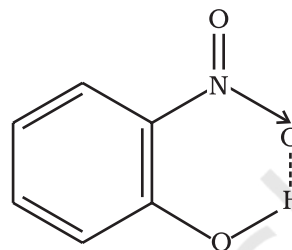
There are two types of H-bonds

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

**(1) Intermolecular hydrogen bond :** It is formed between two different molecules of the same or different compounds. For example,

H-bond in case of  $\text{HF}$  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.



**Fig. 4.22** Intramolecular hydrogen bonding in *o*-nitrophenol molecule

### SUMMARY

Kössel's first insight into the mechanism of formation of electropositive and electronegative ions related the process to the attainment of noble gas configurations by the respective ions. Electrostatic attraction between ions is the cause for their stability. This gives the concept of **electrovalency**.

The first description of **covalent bonding** was provided by Lewis in terms of the sharing of electron pairs between atoms and he related the process to the attainment of noble gas configurations by reacting atoms as a result of sharing of electrons. The Lewis dot symbols show the number of valence electrons of the atoms of a given element and Lewis dot structures show pictorial representations of bonding in molecules.

An ionic compound is pictured as a three-dimensional aggregation of positive and negative ions in an ordered arrangement called the crystal lattice. In a crystalline solid there is a charge balance between the positive and negative ions. The crystal lattice is stabilized by the **enthalpy of lattice formation**.

While a single covalent bond is formed by sharing of an electron pair between two atoms, multiple bonds result from the sharing of two or three electron pairs. Some bonded atoms have additional pairs of electrons not involved in bonding. These are called lone-pairs of electrons. A Lewis dot structure shows the arrangement of bonded pairs and lone pairs around each atom in a molecule. **Important parameters, associated with chemical bonds, like: bond length, bond angle, bond enthalpy, bond order and bond polarity have significant effect on the properties of compounds.**

A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions (representations) based on the same skeletal structure are written and these taken together represent the molecule or ion. This is a very important and extremely useful concept called **resonance**. The contributing structures or *canonical forms* taken together constitute the resonance hybrid which represents the molecule or ion.

The **VSEPR model** used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other and, therefore, tend to remain as far apart as possible. According to this model, *molecular geometry is determined by repulsions between lone pairs and lone pairs; lone pairs and bonding pairs and bonding pairs and bonding pairs*. The order of these repulsions being :  $lp-lp > lp-bp > bp-bp$

The **valence bond (VB) approach** to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically the VB theory discusses bond formation in terms of overlap of orbitals. For example the formation of the  $H_2$  molecule from two hydrogen atoms involves the overlap of the  $1s$  orbitals of the two H atoms which are singly occupied. It is seen that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium inter-nuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilization of the molecule. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. It is however seen that the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account.

For explaining the characteristic shapes of polyatomic molecules Pauling introduced the concept of **hybridisation of atomic orbitals**.  $sp$ ,  $sp^2$ ,  $sp^3$  hybridizations of atomic orbitals of Be, B, C, N and O are used to explain the formation and geometrical shapes of molecules like  $BeCl_2$ ,  $BCl_3$ ,  $CH_4$ ,  $NH_3$  and  $H_2O$ . They also explain the formation of multiple bonds in molecules like  $C_2H_2$  and  $C_2H_4$ .

The **molecular orbital (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 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.

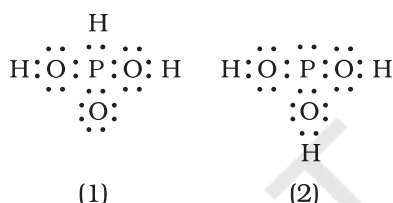
The electronic configuration of the molecules is written by filling electrons in the molecular orbitals in the order of increasing energy levels. As in the case of atoms, the Pauli exclusion principle and Hund's rule are applicable for the filling of molecular orbitals. Molecules are said to be stable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

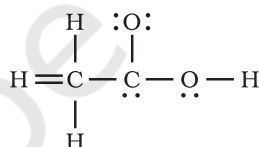
### EXERCISES

- 4.1 Explain the formation of a chemical bond.
- 4.2 Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.
- 4.3 Write Lewis symbols for the following atoms and ions:  
S and  $S^{2-}$ ; Al and  $Al^{3+}$ ; H and  $H^-$
- 4.4 Draw the Lewis structures for the following molecules and ions :  
 $H_2S$ ,  $SiCl_4$ ,  $BeF_2$ ,  $CO_3^{2-}$ ,  $HCOOH$
- 4.5 Define octet rule. Write its significance and limitations.

- 4.6 Write the favourable factors for the formation of ionic bond.
- 4.7 Discuss the shape of the following molecules using the VSEPR model:  
 $\text{BeCl}_2$ ,  $\text{BCl}_3$ ,  $\text{SiCl}_4$ ,  $\text{AsF}_5$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$
- 4.8 Although geometries of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.
- 4.9 How do you express the bond strength in terms of bond order ?
- 4.10 Define the bond length.
- 4.11 Explain the important aspects of resonance with reference to the  $\text{CO}_3^{2-}$  ion.
- 4.12  $\text{H}_3\text{PO}_3$  can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing  $\text{H}_3\text{PO}_3$  ? If not, give reasons for the same.



- 4.13 Write the resonance structures for  $\text{SO}_3$ ,  $\text{NO}_2$  and  $\text{NO}_3^-$ .
- 4.14 Use Lewis symbols to show electron transfer between the following atoms to form cations and anions : (a) K and S (b) Ca and O (c) Al and N.
- 4.15 Although both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are triatomic molecules, the shape of  $\text{H}_2\text{O}$  molecule is bent while that of  $\text{CO}_2$  is linear. Explain this on the basis of dipole moment.
- 4.16 Write the significance/applications of dipole moment.
- 4.17 Define electronegativity. How does it differ from electron gain enthalpy ?
- 4.18 Explain with the help of suitable example polar covalent bond.
- 4.19 Arrange the bonds in order of increasing ionic character in the molecules:  $\text{LiF}$ ,  $\text{K}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{SO}_2$  and  $\text{ClF}_3$ .
- 4.20 The skeletal structure of  $\text{CH}_3\text{COOH}$  as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.



- 4.21 Apart from tetrahedral geometry, another possible geometry for  $\text{CH}_4$  is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why  $\text{CH}_4$  is not square planar ?
- 4.22 Explain why  $\text{BeH}_2$  molecule has a zero dipole moment although the Be-H bonds are polar.
- 4.23 Which out of  $\text{NH}_3$  and  $\text{NF}_3$  has higher dipole moment and why ?
- 4.24 What is meant by hybridisation of atomic orbitals? Describe the shapes of  $sp$ ,  $sp^2$ ,  $sp^3$  hybrid orbitals.
- 4.25 Describe the change in hybridisation (if any) of the Al atom in the following reaction.  
 $\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^-$

- 4.26 Is there any change in the hybridisation of B and N atoms as a result of the following reaction?  
 $\text{BF}_3 + \text{NH}_3 \rightarrow \text{F}_3\text{B.NH}_3$
- 4.27 Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  molecules.
- 4.28 What is the total number of sigma and pi bonds in the following molecules?  
(a)  $\text{C}_2\text{H}_2$  (b)  $\text{C}_2\text{H}_4$
- 4.29 Considering x-axis as the internuclear axis which out of the following will not form a sigma bond and why? (a) 1s and 1s (b) 1s and  $2p_x$ ; (c)  $2p_y$  and  $2p_y$  (d) 1s and 2s.
- 4.30 Which hybrid orbitals are used by carbon atoms in the following molecules?  
 $\text{CH}_3\text{-CH}_3$ ; (b)  $\text{CH}_3\text{-CH=CH}_2$ ; (c)  $\text{CH}_3\text{-CH}_2\text{-OH}$ ; (d)  $\text{CH}_3\text{-CHO}$  (e)  $\text{CH}_3\text{COOH}$
- 4.31 What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving one example of each type.
- 4.32 Distinguish between a sigma and a pi bond.
- 4.33 Explain the formation of  $\text{H}_2$  molecule on the basis of valence bond theory.
- 4.34 Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.
- 4.35 Use molecular orbital theory to explain why the  $\text{Be}_2$  molecule does not exist.
- 4.36 Compare the relative stability of the following species and indicate their magnetic properties;  
 $\text{O}_2, \text{O}_2^+, \text{O}_2^-$  (superoxide),  $\text{O}_2^{2-}$  (peroxide)
- 4.37 Write the significance of a plus and a minus sign shown in representing the orbitals.
- 4.38 Describe the hybridisation in case of  $\text{PCl}_5$ . Why are the axial bonds longer as compared to equatorial bonds?
- 4.39 Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?
- 4.40 What is meant by the term bond order? Calculate the bond order of :  $\text{N}_2, \text{O}_2, \text{O}_2^+$  and  $\text{O}_2^-$ .



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## UNIT 5

# THERMODYNAMICS

## Objectives

After studying this Unit, you will be able to

- explain the terms : system and surroundings;
- discriminate between close, open and isolated systems;
- explain internal energy, work and heat;
- state first law of thermodynamics and express it mathematically;
- calculate energy changes as work and heat contributions in chemical systems;
- explain state functions:  $U$ ,  $H$ .
- correlate  $\Delta U$  and  $\Delta H$ ;
- measure experimentally  $\Delta U$  and  $\Delta H$ ;
- define standard states for  $\Delta H$ ;
- calculate enthalpy changes for various types of reactions;
- state and apply Hess's law of constant heat summation;
- differentiate between extensive and intensive properties;
- define spontaneous and non-spontaneous processes;
- explain entropy as a thermodynamic state function and apply it for spontaneity;
- explain Gibbs energy change ( $\Delta G$ ); and
- establish relationship between  $\Delta G$  and spontaneity,  $\Delta G$  and equilibrium constant.

*It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.*

**Albert Einstein**

Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air. The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell. Thus, various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state. In this unit, we would like to answer some of the important questions through thermodynamics, like:

*How do we determine the energy changes involved in a chemical reaction/process? Will it occur or not?*

*What drives a chemical reaction/process?*

*To what extent do the chemical reactions proceed?*



## 5.1 THERMODYNAMIC TERMS

We are interested in chemical reactions and the energy changes accompanying them. For this we need to know certain thermodynamic terms. These are discussed below.

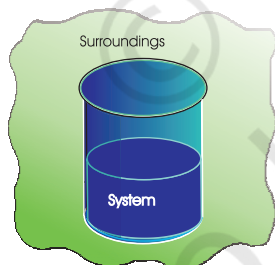
### 5.1.1 The System and the Surroundings

A **system** in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the **surroundings**. The surroundings include everything other than the system. System and the surroundings together constitute the universe.

The universe = The system + The surroundings

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings (Fig. 5.1).



**Fig. 5.1** System and the surroundings

Note that the system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. It is necessary to think of the system as separated from the surroundings by some sort of wall which may be real or imaginary. The wall that separates

the system from the surroundings is called **boundary**. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.

### 5.1.2 Types of the System

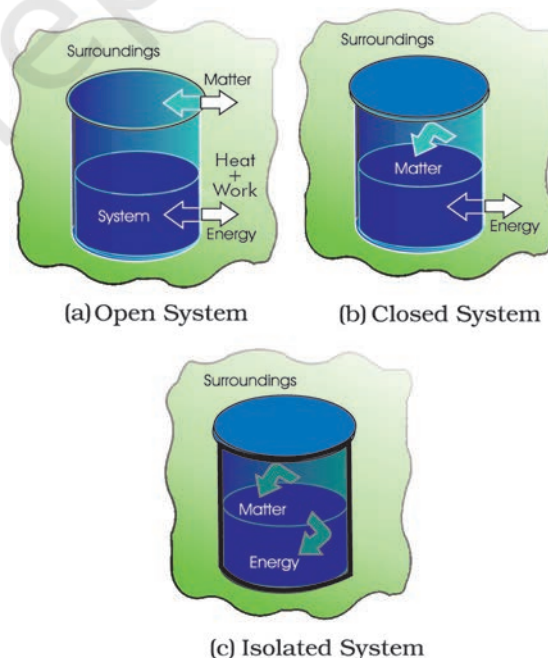
We, further classify the systems according to the movements of matter and energy in or out of the system.

#### 1. Open System

In an open system, there is exchange of energy and matter between system and surroundings [Fig. 5.2 (a)]. The presence of reactants in an open beaker is an example of an open system\*. Here the boundary is an imaginary surface enclosing the beaker and reactants.

#### 2. Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings [Fig. 5.2 (b)]. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.



**Fig. 5.2** Open, closed and isolated systems.

\* We could have chosen only the reactants as system then walls of the beakers will act as boundary.

### 3. Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings [Fig. 5.2 (c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

#### 5.1.3 The State of the System

The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure ( $p$ ), volume ( $V$ ), and temperature ( $T$ ) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because, we deal with average measurable properties of the system. We specify the state of the system by **state functions** or **state variables**.

The **state** of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure ( $p$ ), volume ( $V$ ), temperature ( $T$ ), amount ( $n$ ) etc. Variables like  $p$ ,  $V$ ,  $T$  are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once these minimum number of macroscopic properties are fixed, others automatically have definite values.

The state of the surroundings can never be completely specified; fortunately it is not necessary to do so.

#### 5.1.4 The Internal Energy as a State Function

When we talk about our chemical system losing or gaining energy, we need to introduce

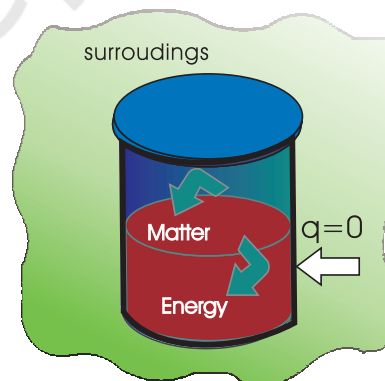
a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy,  $U$  of the system, which may change, when

- heat passes into or out of the system,
- work is done on or by the system,
- matter enters or leaves the system.

These systems are classified accordingly as you have already studied in section 5.1.2.

#### (a) Work

Let us first examine a change in internal energy by doing work. We take a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and we call this type of system as **adiabatic**. The manner in which the state of such a system may be changed will be called adiabatic process. Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. Here, the wall separating the system and the surroundings is called the adiabatic wall (Fig. 5.3).



**Fig. 5.3** An adiabatic system which does not permit the transfer of heat through its boundary.

Let us bring the change in the internal energy of the system by doing some work on it. Let us call the initial state of the system as state A and its temperature as  $T_A$ . Let the internal energy of the system in state A be called  $U_A$ . We can change the state of the system in two different ways.