UNIT 4   VALENCE BOND THEORY

Structure

4.1   INTRODUCTION

In Unit 3, covalent bond formation was explained on the basis of Lewis theory. For the same purpose, two quantum mechanical approaches namely valence bond theory and molecular orbital theory are available. These two theories seek to describe the structure of molecules, their shape and their energy. Valence bond method, proposed by Heitler and London (1927), is based on the assumption that a molecule is formed by the interaction of valence electrons and that atoms in a molecule maintain their individuality so far as the inner electrons are concerned. Molecular orbital theory, developed by Hund, Mulliken and Hückel (1930) considers the entire molecule as a new unit with all the electrons moving under the influence of all the nuclei and all the other electrons. Molecular orbital theory will be discussed in Unit 5; here we concentrate on valence bond theory.

In this unit, we shall explain the main principles of valence bond approach and apply the same to describe the structural aspects of hydrogen and other simple molecules. The concepts, resonance and hybridisation, are explained as developments in the evolution of valence bond theory. In Unit 3, shapes of some molecules were derived by using VSEPR theory. It is interesting to see how same conclusions are arrived at in a different way using hybridisation concept.

Objectives

After studying this unit, you should be able to :

- explain the principles of valence bond method and apply the same to derive the structure of hydrogen molecule,

- list and illustrate the rules of resonance,

- explain the term hybridisation and list its types,

- explain the structures of methane, ethane, ethylene and acetylene using hybridisation theory, and

- apply valence bond theory to explain the structure of benzene.

4.2   THE ORIGIN OF VALENCE BOND AND MOLECULAR ORBITAL THEORIES

The two approaches, valence bond theory and molecular orbital theory, arise by the different ways of arriving at the solution of the Schrödinger equation for the molecules. The Schrödinger equation (Eq. 4.1) can be written for the molecules as in the case of atoms.

$$H\psi = E\psi \qquad \qquad \text{.... (4.1)}$$

Here H is the Hamiltonian operator for the system and E is the energy of the system.

The exact solution of Eq. 4.1 in the case of any molecule is impossible. Even for the simplest molecule hydrogen, H has the form,

$$H = \frac{h^2}{8\pi^2 m}\left[\nabla_1^2 + \nabla_2^2 \right] - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z_a}{r_{a1}} + \frac{Z_b}{r_{b1}} + \frac{Z_a}{r_{a2}} + \frac{Z_b}{r_{b2}} - \frac{Z_a Z_b}{R} - \frac{1}{r_{12}} \right)$$

where 1 and 2 denote the two electrons and a and b the two nuclei. R is the internuclear distance, r_{a1} distance between electron 1 and nucleus a etc.; r_{12} is the interelectronic distance between the electrons 1 and 2.

In the above H, the kinetic energy of nuclei has not been considered as they, being too massive relative to electrons, are assumed to be stationary. This is known as **Born Oppenheimer Approximation**. The solution of Eq. 4.1 is impossible due to the presence of $1/r_{12}$ term in the Hamiltonian H. Therefore, one has to solve Eq. 4.1 by an approximate method.

Two types of mathematical approaches are used to solve the Eq. 4.1. These approaches differ in the manner of choosing ψ. Once ψ is constructed, the average energy E of the molecule can be calculated using the equation,

$$E = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} \qquad \qquad .... (4.2)$$

Also E is calculated as a function of the internuclear distance R. In Eq. 4.2, ψ^* is the complex conjugate of the wave function, ψ.

In one of the approaches, known as Valence Bond (VB) method, approximate wave functions are constructed from those of the separate atoms. This approach is, in a sense, the quantum mechanical description of the Lewis concept of electron pair bond; hence the name—valence bond method. In the second approach, the molecular orbital (MO) method, the approximate wave functions are constructed from the molecular orbitals which in turn are constructed from the atomic orbitals of the constituent atoms. The electrons of the molecule are then assigned to these molecular orbitals on the basis of Aufbau principle. In this unit, we take up the study of valence bond approach and its application to simple molecules. We shall study the details of the molecular orbital theory in Unit 5.

4.3 PRINCIPLES OF VALENCE BOND THEORY

The main steps used in valence bond method, in arriving at the structure of a molecule, are given below :

i) Molecular wave function for the combining electrons is formed as a product of wave functions of electrons of the constituent atoms. For example, if the wave functions for $1s$ electron on each of the two hydrogen atoms are ψ_A and ψ_B, then the molecular wave function ψ is given by,

$$\psi = \psi_A \cdot \psi_B \qquad \qquad .... (4.3)$$

In other words the **constituent atoms retain their identity** when they combine to form a molecule.

ii) Various trial functions ψ are designed, depending on the assumptions regarding molecule formation. Setting up different trial functions, indicates our attempts to describe the structure of molecule in different ways, taking into account various factors such as effective nuclear charge, resonance, indistinguishability of bonding electrons etc.

iii) Each trial function is fitted into an appropriate Schrödinger equation (Eq. 4.2) and the energy values, E, are obtained as a function of interatomic distance, R.

iv) E vs R diagrams, known as energy diagrams, are drawn for each trial function (Fig. 4.1). **The curves with minima represent stabilising features for molecule formation.** The difference between the total energy of the two isolated atoms and the energy corresponding to minima of the curve, gives the bond energy, calculated according to a particular trial function. The value of R at the minima point is the equilibrium interatomic distance or bond distance.

These steps are repeated for various trial functions. That trial function, for which calculated bond energy and bond distance values, agree closely with experimental values, is taken as the correct one, and the structural features assumed in designing such a trial function, are also considered valid.

In the next section, the above procedure is applied to determine the structural features of hydrogen molecule. Before we take that up, you can try the following SAQ.

SAQ 1

What are the deciding factors in choosing a particular trial function for a molecule?

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4.4 VALENCE BOND THEORY OF HYDROGEN MOLECULE

In this section, we will apply the principles of valence bond theory, discussed in the last section, to the case of H_2 molecule.

We shall begin with two hydrogen atoms far apart so that no appreciable interaction between them occurs. Let us assume that the total energy of these two hydrogen atoms is represented by the point L in Fig. 4.1. Arbitrarily this has been placed on the zero of the scale. Although the two hydrogen atoms are identical, for the sake of convenience, we may label the electrons as 1 and 2 and the nuclei as A and B; the orbital wave functions of the two electrons 1 and 2 contained in two hydrogen atoms A and B would then be given by $\psi_A(1)$ and $\psi_B(2)$, respectively. Using Eq. 4.3, the trial molecular wave function for the hydrogen molecule (in reality a system of two separated H atoms) can be written as,

$$\psi_1 = \psi_A(1).\psi_B(2)$$

Using the above wave function in Eq. 4.2, the energy E of the system comprising two identical hydrogen atoms can be calculated as a function of the internuclear distance R. From the values of E and R, energy diagram 4.1a is drawn. The energy difference between L (total energy of the two isolated hydrogen atoms) and the minima of the curve 4.1a, gives the calculated bond energy of 24 kJ mol^{-1}. The equilibrium interatomic distance is calculated to be 90 pm. But the actual bond energy and interatomic distance for hydrogen molecule are 436 kJ mol^{-1} and 74 pm, respectively.

At the equilibrium interatomic distance r_0, a molecule has a stable existence. At interatomic distance greater than or less than r_0, it is less stable.
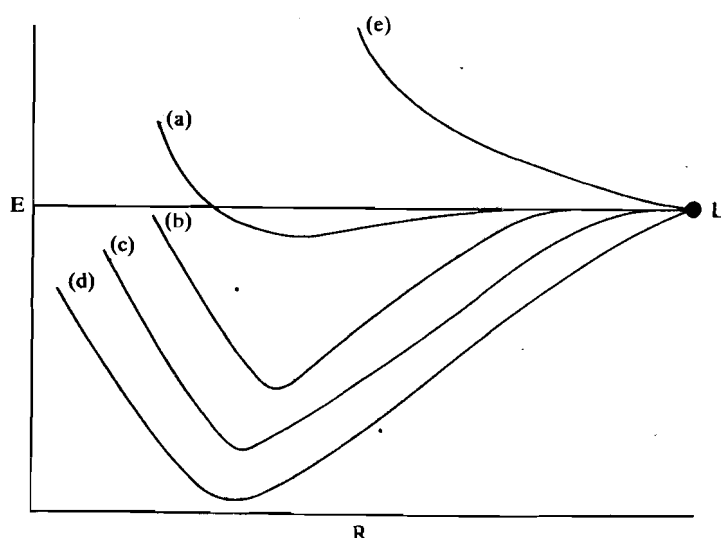

Fig. 4.1 : Theoretical energy curves (a–c, e) for hydrogen molecule compared with the experimental curve (d).

This means that the assumption used in trial function ψ_1 that electron 1 resides on hydrogen atom A and electron 2 resides on hydrogen atom B is not acceptable.

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A refined wave function, ψ_{cov}, is then designed which allows for either of the electrons to reside on either of the hydrogen atoms. Also it is assumed that the two electrons are shared equally since the atoms are identical. This trial function is called ψ_{cov} to denote covalent bonding.

$$\psi_{cov} = \psi_A(1). \ \psi_B(2) + \psi_A(2). \ \psi_B(1) \qquad \ldots (4.4)$$

This trial function ψ_{cov} is tried in Eq. (4.2) in place of ψ and energy values at different R values are obtained. The bond energy and bond distance, according to this calculation are 303 kJ mol^{-1} and 86.9 pm, respectively. The E vs R curve is shown in Fig. 4.1(b). This trial function again requires further refinement.

A wave function ψ_2, is then designed keeping in mind the following features :

i) The two electrons mutually shield one another from the nuclear charge. Hence, the effective nuclear charge value Z^* must be used, instead of $Z = 1$.

ii) Hydrogen molecule can be given covalent structure (I) and ionic structures (II and III) as shown below :

$$\text{H : H} \qquad {}^-\text{H: H}^+ \qquad {}^{'+}\text{H :H}^-$$
$$\text{I} \qquad\qquad \text{II} \qquad\quad \text{III}$$
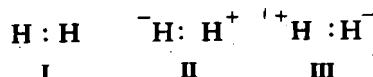
The wave function corresponding to ionic forms is given by,

$$\psi_{ion} = \psi_A(1). \ \psi_A(2) + \psi_B(1). \ \psi_B(2) \qquad \ldots (4.5)$$

The first term in the right hand side denotes a situation, when both the electrons are on hydrogen atom A, and the second term, when the two electrons are on hydrogen atom B. The structures (I – III) are called canonical or resonating structures and the actual structure is the resonance hybrid of all these three structures. You will study more about resonance in the next section. This mixing of ionic and covalent forms is called **ionic - covalent resonance.**

A combined wave function ψ_2 is formed using ψ_{cov} and ψ_{ion} as follows :

$$\psi_2 = C_1 \left(C_2 \psi_{cov} + C_3 \psi_{ion} \right) \qquad \ldots (4.6)$$

In the equation, C_1, C_2 and C_3 are constants depending on how much of the ionic wave function is mixed with the covalent wave function. When the wave function ψ_2 is used in Eq. 4.2, and energy values calculated for various values of R, curve of the type 4.1(c) is obtained. The bond energy and bond distance values, according to this calculation, are found to be 388 kJ mol^{-1} and 74.9 pm, respectively. Thus the addition of new terms to the trial function, brings the bond energy and bond distance values closer to experimental values. The resonance structures (I – III) seem to describe the structure of hydrogen molecule much better than covalent structure (I) alone. In Table 4.1, a summary of bond energy and bond distance values, obtained for trial functions mentioned above, is given.

Table 4.1 : Bond Energy and Bond Distance For Various Trial Functions of Hydrogen Molecule

Trial Function		Energy	Distance	Curve
Type	Significance	(kJ mol^{-1})	(pm)	representing trial function
ψ_1	A system of two isolated H atoms; two electrons are distinguishable	24	90	4.1a
ψ_{cov}	Covalent structure and indistinguishable electrons	303	86.9	4.1b
ψ_2	Effective nuclear charge and ionic-covalent resonance recognised	388	74.9	4.1c
Experimental curve		436	74	4.1d

A trial function, combining as much as 100 terms, has been found to yield bond energy and bond distance values almost equal to experimental values. The energy diagram corresponding to experimental values is given in Fig. 4.1(d).

Valence bond theory throws light on the fact that no bond is 100% ionic or 100% covalent. It is further inferred that the electron density distribution is symmetrical

about the axis passing through the nuclei, Fig. 4.2. Such bonds, with symmetrical electron density about internuclear axis, are called σ bonds.
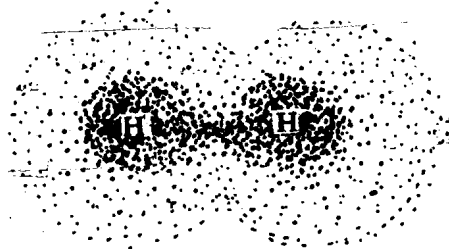

Fig. 4.2 : σ bond in hydrogen molecule.

In constructing atomic wave functions such as ψ_A (1), ψ_B (2), etc., the spins of combining electrons have been assumed to be opposite. Hence hydrogen molecule formation can also be considered as a process of spin pairing. On the other hand, if the two H atoms approach in such a way that the spins are in the same direction, then the net force of interaction is strongly repulsive. As two hydrogen atoms having same spin value approach each other, the energy of the system increases. This situation is indicated by the curve 4.1 (e). Try the following SAQ, to see if you have understood the ideas developed above.

SAQ 2

Explain the fact that for H_2 molecule, covalent structure is more important than ionic structures. (Hint : Use the bond energy values).

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4.5 RESONANCE OR ELECTRON DELOCALISATION

Sometimes the properties of a molecule or ion are not adequately represented by a single Lewis structure. In the last section, we saw how the structure of hydrogen could not be represented by one of the three structures (I), (II) and (III) alone and had to be conceived on the basis of contribution from all the three. Such structures are known as resonance structures. They differ in the arrangement of electrons, keeping the atomic arrangement the same.
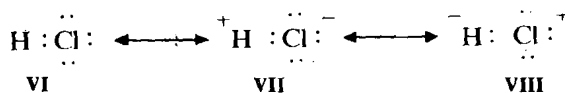
Let us take another example; say sulphur dioxide.
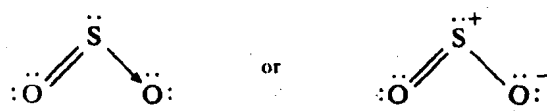
The charges represented are formal charges, which you studied in section 3.4 of Unit 3. According to the above structure, the two sulphur-oxygen bonds must be of different types, one being a single bond and the other a double bond. But in sulphur dioxide molecule, both the bonds are of same length. So in the case of this molecule also, two or more valence bond structures such as (IV) and (V), have to be used to depict the molecule. The molecule is said to be a resonance hybrid of the structures (IV) and (V), which are in turn known as **resonating or canonical structures.**
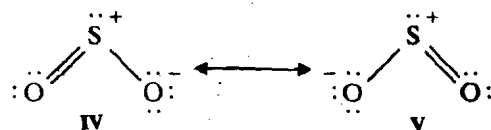
The actual structure of sulphur dioxide does not correspond to either of the resonance structures alone; but it is intermediate between these two resonance structures. There is only one type of sulphur dioxide molecule and it can have only one structure. The electrons do not flip within the molecule; i.e., for no moment of time, the molecule has any one resonance structure. The two resonance structures of sulphur dioxide are equivalent. But in some cases, like hydrogen chloride, all the resonance structures may not be equivalent.

$$H : \overset{..}{\underset{..}{Cl}} : \longleftrightarrow \overset{+}{H} : \overset{..}{\underset{..}{Cl}} :^{-} \longleftrightarrow \overset{-}{H} : \overset{..}{Cl} :^{\top}$$

VI   **VII**   **VIII**

A π bond is formed by the lateral (sideways) overlap of atomic orbitals. The electrons giving rise to a π bond are called π electrons
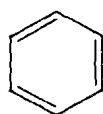
The ionic – resonance structures, having lower bond order value than covalent structures, are of less importance. Thus, ionic structures (VII) and (VIII) of hydrogen chloride having zero bond order are of less importance than covalent structure (VI) having bond order value of one. This is due to the involvement of σ electrons which is rarely significant in resonance structures. Resonance structures in majority of cases, involve variable distribution of π electrons. Hence, resonance is also known as delocalisation of π electrons.
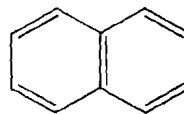
Double bond in alkenes is said to be localised since its location is fixed between two particular carbon atoms.

Localisation of π electrons means fixing π electrons between two particular atoms, as in ethylene.

$$\begin{array}{ccc} H & & H \\ \diagdown & & \diagup \\ & C = C & \\ \diagup & & \diagdown \\ H & & H \end{array}$$

Ethylene
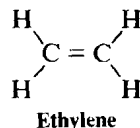
Compounds like benzene and naphthalene have a delocalised π electron structure which means π electrons are not fixed between any two particular carbon atoms.

The percentage contribution each resonating structure makes to the resonance hybrid indicates how far the characteristics of the molecule are explained by a particular structure.

Benzene   **Naphthalene**

π electron delocalised over all the carbon atoms.

Some structures may be of lower energy than others and hence make major contribution to the hybrid. The resonance forms must be evaluated to determine their importance and relative contribution to the resonance hybrid. The percentage contribution, that each resonance structure makes to the resonance hybrid, is derived by the solution of Schrödinger equation, set up for the molecule.

The heat of hydrogenation is the quantity of heat evolved or absorbed when one mole of an unsaturated compound adds on hydrogen.

The stabilisation, a molecule or ion attains, due to contributing resonance structures, is described in terms of resonance energy. A substance that has a considerable resonance energy is said to be resonance stabilised. As an illustration, let us calculate resonance energy for benzene. The resonance energy for benzene is the difference between the heat of hydrogenation calculated for a structure with three localised double bonds and the experimental value. The heat of hydrogenation for the localised structure of benzene is calculated on the assumption that the three double bonds of benzene add on hydrogen like three molecules of cyclohexene. That is, the calculated heat of hydrogenation of benzene is thrice the heat of hydrogenation of cyclohexene (363 kJ). But the experimentally determined heat of hydrogenation of benzene is 209 kJ mol^{-1}.
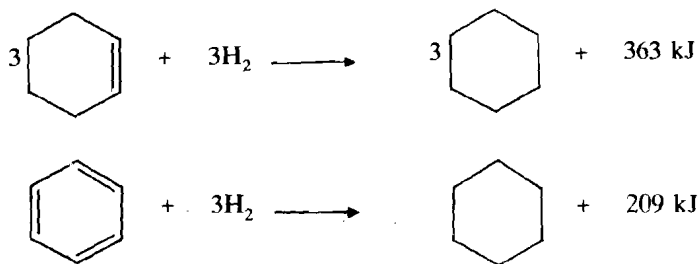

The difference between the calculated and the experimental values of heat of hydrogenation for benzene is (363 – 209 =) 154 kJ mol^{-1}. Thus, the resonance energy of benzene is 154 kJ mol^{-1}. Compared to this, the resonance energy of naphthalene is 315 kJ mol^{-1}. Hence, naphthalene has greater resonance stability than benzene.

Let us now see the rules that are useful in deciding the relative importance of resonance structures of a molecule or ion.

1) The resonance forms of a given species differ in the arrangement of electrons, and not in the arrangement of nuclei.

Thus for carbon dioxide, having the arrangement of atoms as OCO, the structure, OOC, is not a resonance structure.

2) In case resonance structures have charge separation, two atoms that are bonded together should not have formal charges with the same sign. Thus, of the three structures for FNO_2, structure (XI) is not a resonance structure, since it suffers from electrostatic repulsion from adjacent positive charges.

IX   X   XI
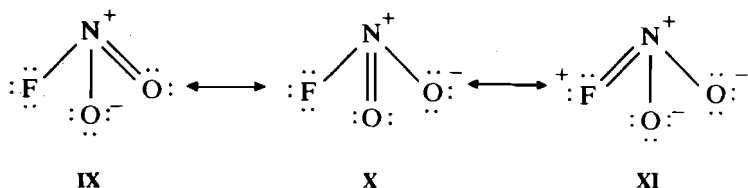
3) The structures without formal charges are more important than those with formal charges. For benzene, the resonance structures of Kekule (XII and XIII) and Dewar types (XIV–XVI) which do not have formal charges are more important than the ionic structures (XVII and XVIII).

Kekule structures   Dewar structures   Ionic structures

XII   XIII   XIV   XV   XVI   XVII   XVIII
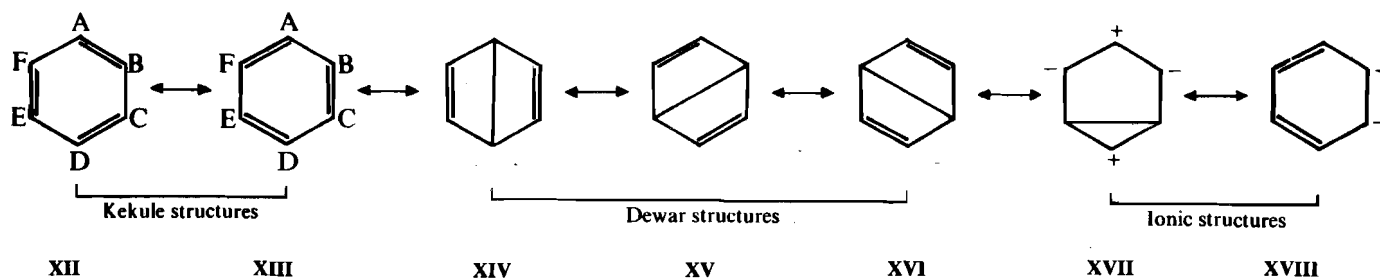
4) While giving formal charges, the more electronegative atom should carry a formal negative charge and the less electronegative atom should carry a formal positive charge. Thus, of the resonance structures of hydrogen chloride, structure (VIII) is less important since the more electronegative atom chlorine has a formal positive charge.

5) The resonance forms of a molecule or ion have usually the same number of shared electrons. Of the three structures (XIX – XXI) for cyanate ion, (XXI) is less important as a resonance structure, since it has only three shared pairs. The other two structures (XIX) and (XX) have four shared pairs each.

XIX   XX   XXI
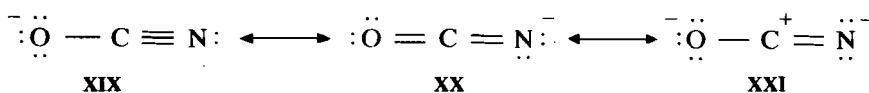
6) Resonance hybrid is said to be stabilised if two or more of its resonating structures are energetically equivalent. The two Kekule structures of benzene which are equivalent are largely responsible for its considerable resonance energy and resonance stabilisation.

7) Delocalisation of electrons in an unsaturated system is maximum when the molecule is coplanar.

Benzene, a resonance stabilised molecule, has been found to be a planar molecule with equal electron density around six carbon atoms, as per X-ray diffraction studies. On the other hand, bicyclohexadiene, **an isomer of benzene**, is not much resonance stabilised due to its nonplanarity.


Bicyclohexadiene   **Very minor**

8) The compounds of third and higher period elements can have resonance structures involving d orbitals whereas those of second period elements do not have. The compounds of phosphorus and sulphur, for example, exhibit resonance structures involving d orbitals. These two elements in their compounds can expand their outer shells to more than eight electrons. This behaviour is not expected of compounds of second period elements such as nitrogen due to nonavailability of d orbitals.
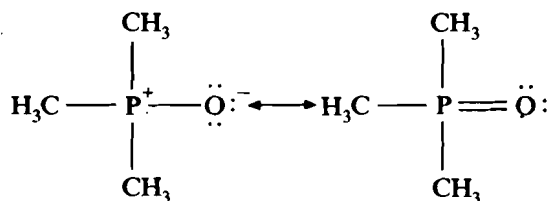
Trimethylamine oxide, for example has only a single structure while trimethylphosphine oxide has two resonance structures.

Isomers have individual existence; resonating structures do not have.

Diffraction is the bending of light rays over the edges of an object. The diffraction of x-rays is maximum in places of atomic sites. X-ray diffraction helps in the location of atomic sites.
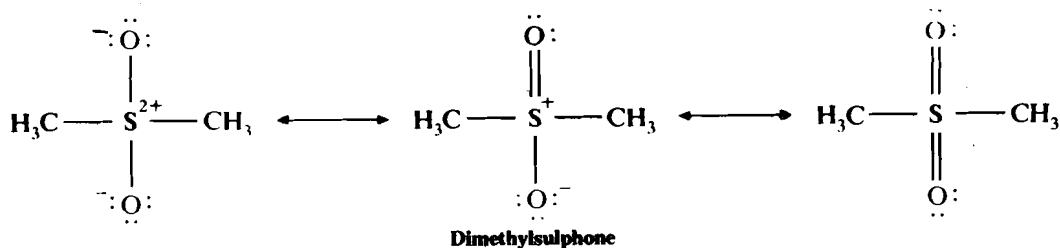
$$H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}\overset{+}{-}\overset{..}{\underset{..}{O}}:^-$$
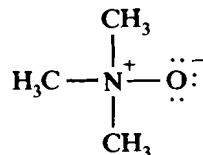
Trimethylamine oxide; resonance structures not possible.

$$H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}\overset{+}{-}\overset{..}{\underset{..}{O}}:^- \longleftrightarrow H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}} = \overset{..}{O}:$$

Trimethylphosphine oxide

Similarly, dimethylsulphone has the following resonance structures :

$$H_3C - \overset{\overset{\displaystyle ^-:\overset{..}{O}:}{|}}{\underset{\underset{\displaystyle ^-:\overset{..}{O}:}{|}}{S}}^{2+} - CH_3 \longleftrightarrow H_3C - \overset{\overset{\displaystyle \overset{..}{O}:}{\|}}{\underset{\underset{\displaystyle :O:^-}{|}}{S}}^+ - CH_3 \longleftrightarrow H_3C - \overset{\overset{\displaystyle \overset{..}{O}:}{\|}}{\underset{\underset{\displaystyle O:}{\|}}{S}} - CH_3$$

Dimethylsulphone

Using the above rules, attempt the following SAQ

. **SAQ 3**

Write the resonance structures of nitrate ion. (*Hint* : Start with Lewis structure of NO_3^- ion).

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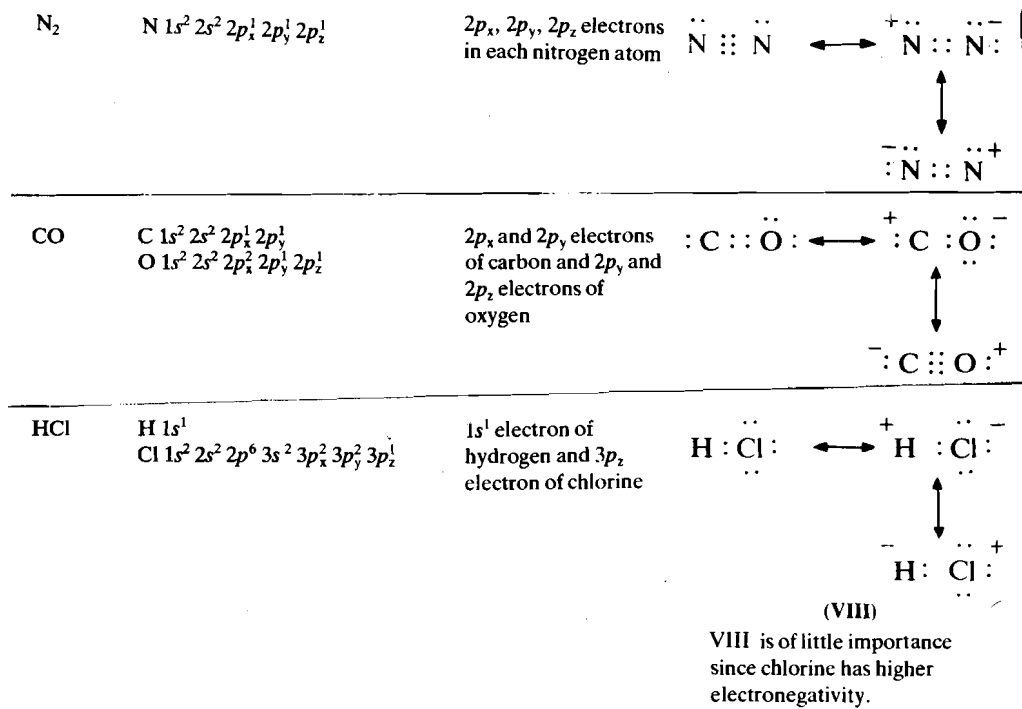
4.6 VALENCE BOND DESCRIPTION OF SOME MORE MOLECULES

Valence bond method can be applied to describe the structure of many covalent molecules. According to valence bond method, whenever we have two atoms, each with at least one unpaired electron, they may unite to form a bond in which these two electrons are paired. In order to arrive at the structure of a molecule, various trial functions are designed, as was done in the case of hydrogen molecule, till a satisfactory trial function, which can explain the properties of the molecule, such as bond energy and bond length, is obtained. The structural features corresponding to the acceptable trial function are taken into account while describing the actual molecular structure.

The resonance structures of some molecules, obtained using the above procedure, are given in Table 4.2.

Table 4.2 : Valence Bond Structures of Some Molecules

Molecule	Electron configuration of the combining atoms	Unpaired electrons	Resonance structures
Cl_2	$Cl\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$	$3p_z$ electron in each chlorine atom	$:\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}: \longleftrightarrow \ ^+:\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}:^- $ $\updownarrow$ $^-:\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}:^+$

N_2	N $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	$2p_x$, $2p_y$, $2p_z$ electrons in each nitrogen atom	N :: N ⟷ $^+$N :: N:$^-$ ↕ $^-$:N :: N$^+$
CO	C $1s^2 2s^2 2p_x^1 2p_y^1$ O $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	$2p_x$ and $2p_y$ electrons of carbon and $2p_y$ and $2p_z$ electrons of oxygen	: C :: O : ⟷ $^+$: C :O: ↕ $^-$: C :: O:$^+$
HCl	H $1s^1$ Cl $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$	$1s^1$ electron of hydrogen and $3p_z$ electron of chlorine	H : Cl: ⟷ $^+$H :Cl:$^-$ ↕ $^-$H: Cl:$^+$ (VIII) VIII is of little importance since chlorine has higher electronegativity.

Based on the above principles, we would be tempted to give the following structures for oxygen molecule :

$$:\ddot{O}::\ddot{O}: \longleftrightarrow {}^-:\ddot{O}:\ddot{O}:{}^+ \longleftrightarrow {}^+:\ddot{O}:\ddot{O}:{}^- $$
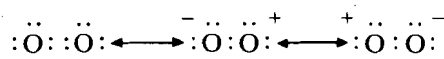
But these structures do not explain the experimentally known paramagnetic character of oxygen. Let us see if molecular orbital theory, which we are going to study in next unit, is able to explain this behaviour of oxygen.

In the next section, we shall see hybridisation of orbitals which is another aspect of valence bond theory. Using the above principles, attempt the following SAQ.

SAQ 4

Explain valence bond structures of fluorine molecule.

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4.7 HYBRIDISATION OF ORBITALS

Principles of valence bond theory used so far in describing the structure of molecules, are not sufficient to explain the structure of methane. The electron configuration of carbon in the ground state is $1s^2 2s^2 2p_x^1 2p_y^1$. The concepts of valence bond approach enunciated above predict the pairing of two unpaired electrons in $2p_x$ and $2p_y$ orbitals of carbon with $1s$ electron of each of the two hydrogen atoms to form CH_2 molecule. But CH_2 is not a stable molecule. The simplest stable hydrocarbon is methane, CH_4. How are we to explain this?

To reconcile the valence bond theory with experimental evidence, Pauling devised a model in which one of the $2s$ electrons of carbon atom is promoted to the empty $2p_z$ orbital. The $2s$ and three $2p$ orbitals of carbon atom are mixed to form four equivalent orbitals, known as **sp^3 hybrid orbitals.** The axes of sp^3 orbitals are oriented in space, toward the corners of a regular tetrahedron. That is, the angle between any two orbital axes is 109°28' [Fig. 4.3(a)]. **The process of mixing two or more orbitals of different energies to give an equal number of new hybrid orbitals of lower energy is known as hybridisation.** Anyhow, it should be remembered that hybridisation is a mathematical concept. The promotion of electrons to higher levels and mixing of orbitals are both mental construction which are useful in thinking about bond formation.
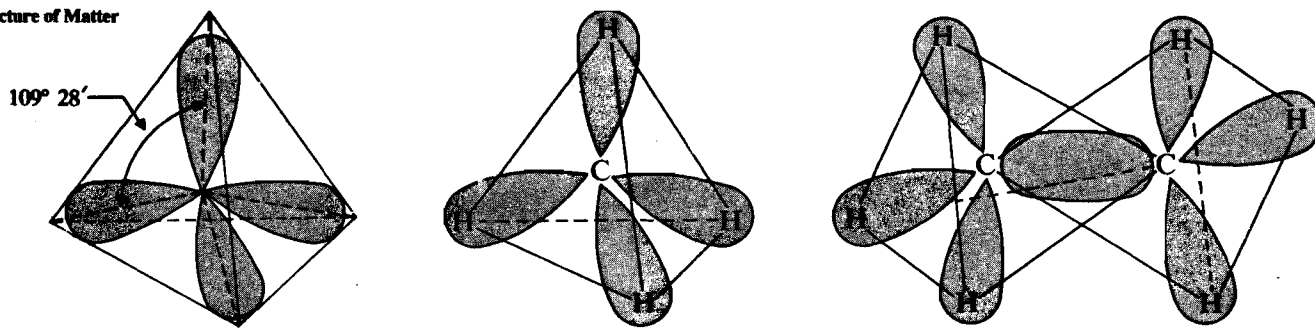
109° 28'—→

Fig. 4.3

a) Four sp^3 atomic orbitals for carbon (small back lobes of orbitals omitted).

b) Tetrahedral structure of methane.

c) Structure of ethane.

The most acceptable trial function for methane indicates that the hybrid orbital has one-fourth s character and three-fourth p character. The four unpaired electrons in the four sp^3 hybrid orbitals of carbon, combine with $1s$ electron of each of the four hydrogen atoms, to form four σ bonds. The energy liberated in the formation of four C-H bonds is more than that required for :

i) the promotion of $2s$ electron to $2p_z$ orbital.

ii) mixing s and p orbitals.

iii) keeping the four unpaired electrons free from mutual or orbital spin interactions.

Methane is tetrahedral in shape, Fig. 4.3b, with a bond angle of 109°28'. In section 3.6 of last unit, we derived the same conclusion based on VSEPR theory. In ethane, (Fig. 4.3c), and in other higher alkanes also, carbon atoms are in sp^3 hybridised state. The C-C bond length in ethane has been found to be 154 pm. The covalent radius for sp^3 hybridised carbon is 77 pm.

Let us now focus our attention on the structure of ethylene. One of the $2s$ electrons in each of the two carbon atoms is promoted to the empty $2p_z$ level as before. The $2s$, $2p_x$ and $2p_y$ orbitals are hybridised to yield three sp^2 hybrid orbitals (Fig. 4.4a). The $2p_z$ orbital is not used for hybridisation. Each sp^2 hybrid orbital has one-third s character and two-third p character.
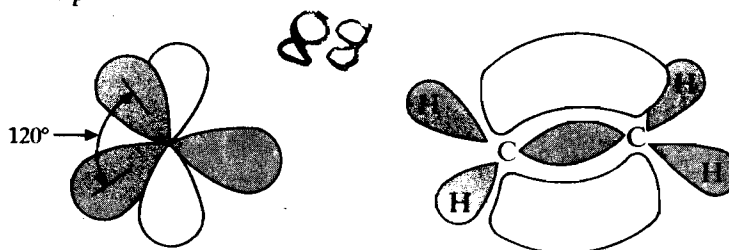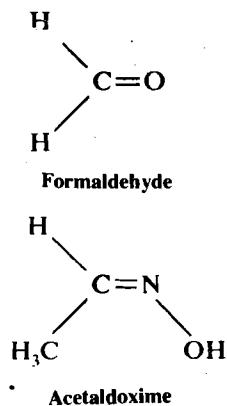

120°—→

Fig. 4.4

a) Diagram illustrating the three trigonal sp^2 hybrid orbitals of the carbon atom (shown in grey colour), which lie in the same plane and the one unhybridised p orbital which is perpendicular to the plane.

b) Structure of ethylene.

Formaldehyde

Acetaldoxime

Each of the two carbon atoms in ethylene forms three σ bonds, two σ bonds being formed with two hydrogen atoms and one σ bond with the other carbon atom. The fourth bond, a π bond, is formed by the lateral overlap of the $2p_z$ orbitals of the two carbon atoms. Ethylene, therefore, has a double bond between the two carbon atoms [Fig. 4.4(b)], one being a σ bond and the other a π bond, the latter being perpendicular to the plane of the molecule. The C=C bond length is 134 pm which is less then C—C bond length in ethane. The covalent radius for sp^2 hybridised double bonded carbon is 67 pm. The bond angle in ethylene and other sp^2 hybridised systems is approximately 120° and the molecule is said to have trigonal shape. That is, the orbitals around each carbon atom are directed towards the vertices of a triangle. On the basis of VSEPR theory also, the same conclusion can be obtained. The structural aspects around the double bonded carbon atoms in other alkenes also are similar to those in ethylene. In compounds like formaldehyde and acetaldoxime, double bonded carbon atom is in sp^2 hybridised state.

In the next section, you will see as to how sp^2 hybridisation concept is used in combination with resonance to explain the structure of benzene.

In acetylene, the carbon atoms are in sp hybridised state. Again one of 2s electrons is promoted to empty $2p_z$ level in each of the two carbon atoms. The mixing of 2s orbital and $2p_x$ orbital produces two sp hybrid orbitals with their axes arranged in a linear fashion [Fig. 4.5(a)]. Each sp hybrid orbital has 50% s character and 50% p character. The two sp hybrid orbitals of each of the carbon atoms form two σ bonds, one between each carbon and a hydrogen and another between the two carbon atoms. The two $2p_y$ and $2p_z$ orbitals of each carbon atom, which are not used in hybridisation, combine to give two π bonds, which are perpendicular to each other and also to the plane of the molecule. The two π bonds are represented as a cylindrical envelope around the two carbon atoms. Thus, in acetylene, there is a triple bond between the two carbon atoms, Fig. 4.5(b). The bond angle is 180° and the molecule is linear; VSEPR theory, also could be used to get the same conclusion. The C≡C length is 120 pm and the covalent radius for sp hybridised triple bonded carbon is 60 pm.

Wherever carbon atom is attached to four other atoms, it is sp^3 hybridised. When it is attached to three other atoms it is sp^2 hybridised and, if attached to two other atoms, it is sp hybridised.
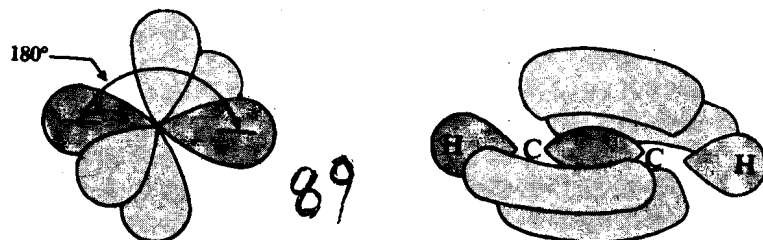

Fig. 4.5

a) Diagram of the two linear sp hybrid orbitals of the carbon atom, which lie in a straight line (shown in grey colour) and the two unhybridised p orbitals (shown in red colour).
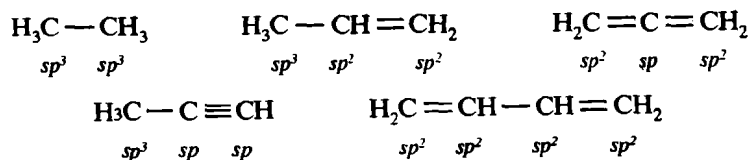
b) structure of acetylene.

You can see that among sp^3, sp^2 and sp hybridised carbon atoms, covalent radius is the highest for sp^3 and least for sp hybridised state; s character is the highest for sp and least for sp^3. Increase of s character in the hybridised carbon atom causes a decrease in its covalent radius since s electrons are more tightly held than p electrons. It is worth remembering that in section 3.4.3 of the previous unit, we have mentioned that the bond length decreases as bond order increases. From Table 4.3, you can have a comparative account of ethane, ethylene and acetylene with respect to structural features.

A substance, which releases H⁺ ion more readily than another, is said to be more acidic. Since s character is the highest for sp hybridised carbon (50%) and least for sp^3 hybridised carbon (25%), C-H bond in acetylene is the most acidic, that in ethylene is less acidic and that in ethane is the least acidic. The greater s character results in the bond electrons of C-H bond being pulled strongly towards carbon atom, thereby releasing H⁺ more easily.

Table 4.3 : Comparison of Ethane, Ethylene and Acetylene

Name of the Compound	Hybridisation type	Structure	Type of bonds for each carbon atom	Bond Angle	Carbon-carbon bond	
					Bond type	Bond length/pm
Ethane	sp^3	H—C—C—H (with H's)	4 σ bonds	109°28'	Single bond	154
Ethylene	sp^2	C=C (with H's)	3 σ bonds & 1 π bond	120°	Double bond	134
Acetylene	sp	H—C≡C—H	2 σ bonds & 2 π bonds	180°	Triple bond	120

Carbon-carbon bond lengths given in Table 4.3 correspond to single, double and triple bonds formed by sp^3, sp^2 and sp carbon atoms, respectively. But single bond can occur between any two similarly or dissimilarly hybridised carbon atoms. Similarly double bonds of the type $sp^2 - sp^2$, $sp^2 - sp$ and $sp - sp$ are possible. Some examples are given below :

$$H_3C - CH_3 \qquad H_3C - CH = CH_2 \qquad H_2C = C = CH_2$$
$$sp^3 \quad sp^3 \qquad\qquad sp^3 \quad sp^2 \quad sp^2 \qquad\qquad sp^2 \quad sp \quad sp^2$$

$$H_3C - C \equiv CH \qquad H_2C = CH - CH = CH_2$$
$$sp^3 \quad sp \quad sp \qquad\qquad sp^2 \quad sp^2 \quad sp^2 \quad sp^2$$

Carbon-carbon bond lengths depend both on bond type and hybridisation state of linked carbon atoms, as given in Table 4.4.

Table 4.4 : Hybridisation States, Bond Types and Bond Lengths

Bond type	(Bond length)/pm	Bond type	(Bond length)/pm	Bond type	(Bond length)/pm
C - C		C = C		C - H	
$sp^3 - sp^3$	154	$sp^2 - sp^2$	134	$C_{sp^3} - H$	111
$sp^3 - sp^2$	150	$sp^2 - sp$	131	$C_{sp2} - H$	110
$sp^3 - sp$	146	$sp - sp$	128	$C_{sp} - H$	108
$sp^2 - sp^2$	148				
$sp^2 - sp$	143	C ≡ C			
$sp - sp$	138	$sp - sp$	120		

Hybridisation is not limited to s and p orbitals only but may, in general, involve the mixing of other types of orbitals also, provided energy difference is not much. Hybrid orbitals involving d orbitals occur quite commonly among the heavier elements and are particularly important in complexes of the transition elements. Although hybrid orbitals are generally equivalent, in some cases nonequivalent hybrid orbitals also occur. Thus, in dsp^3 hybridisation, whether it is trigonal bipyramid or square pyramid, two types of bonds, axial (a) and equatorial (e) are seen. Under VSEPR theory of the previous unit, you studied that two types of bonds, axial and equatorial are present in a molecule having a total of five electron pairs around the central atom. In Table 4.5, hybridisations involving d orbitals are given.

Table 4.5 : Hybridisations Involving d Orbitals

Type	Orbitals used	Geometry	Hybrid orbitals equivalent (E) or nonequivalent (N)	Example
d^2sp^3 or sp^3d^2	$s, p_x, p_y, p_z,$ $d_{z^2}, d_{x^2-y^2}$	Octahedral	E	$SF_6, [Fe(CN)_6]^{4-}$
dsp^3 or sp^3d	$s, p_x, p_y, p_z,$ d_{z^2}	Trigonal bipyramid	N	PF_5, PCl_5
dsp^3 or sp^3d	$s, p_x, p_y, p_z,$ $d_{x^2-y^2}$	Square pyramid	N	IF_5
dsp^2	$s, p_x, p_y,$ $d_{x^2-y^2}$	Square planar	E	$[Cu(NH_3)_4]^{2+}$
sd^3	$s, d_{xy}, d_{yz}, d_{zx}$	Tetrahedral	E	CrO_4^{2-} and MnO_4^- (both sd^3 and sp^3 possible)

The structure of many of the coordination complexes and of molecules like phosphorus pentachloride and sulphur hexafluoride can be explained using hybridisation theory. Earlier you studied in Unit 3, based on VSEPR theory, that sulphur hexafluoride is octahedral in shape. We can arrive at this conclusion using the concept of hybridisation also. For sulphur, the ground state configuration is $1s^2 2s^2 2p^6$ $3s^2 3p_x^2 3p_y^1 3p_z^1$. The $3s$ and $3p_x$ electrons are unpaired, excited to $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals and the six orbitals, namely, $3s, 3p_x, 3p_y, 3p_z, 3d_{x^2-y^2}$ and $3d_{z^2}$ are hybridised to obtain six orbitals of sp^3d^2 type. Each of these six orbitals has an unpaired electron. Pairing of these six unpaired electrons with the $2p_z$ electron in each of the six fluorine atoms gives rise to sulphur hexafluoride molecule. This is diagrammatically illustrated below :
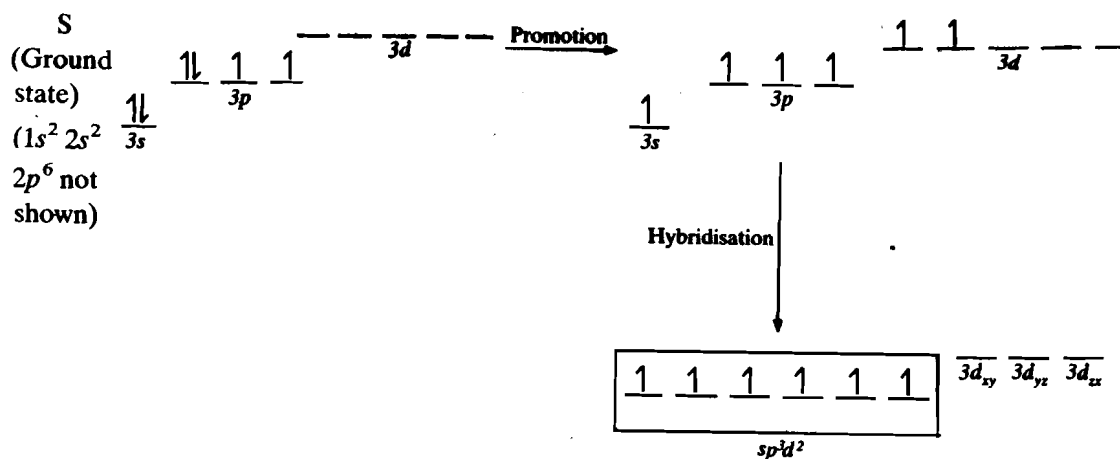
S
(Ground
state)
$(1s^2\,2s^2$

$2p^6$ not
shown)

Fig. 4.6 : sp^3d^2 hybridisation in sulphur atom; six unpaired electrons available for pairing with $2p_x$ electrons of six fluorine atoms.
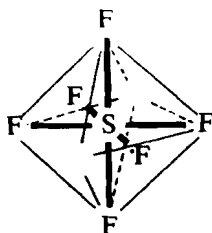

Fig. 4.7 : Structure of sulphur hexafluoride.

The orbitals of sp^3d^2 type have lobes directed to the vertices of an octahedron. In other words, sulphur hexafluoride is octahedral, Fig. 4.7.

Using the above ideas, why don't you try the following SAQ?

SAQ 5

Explain the type of hybridisation in phosphorus pentachloride.

....

....

....

4.8 VALENCE BOND DESCRIPTION OF BENZENE

The valence bond picture of benzene can be explained using the two concepts, hybridisation and resonance. Each of the six carbon atoms in benzene is in sp^2 hybridised state, forming three bonds, two to adjacent carbon atoms and one to a hydrogen atom. Because sp^2 orbitals are planar, all the six carbon and six hydrogen atoms are in the same plane and the bond angles are 120°. Each carbon atom has still an unpaired electron in the $2p_z$ orbital. The next question is to see how these six $2p_z$ electrons pair up. The valence bond description of pairing of $2p_z$ electrons can be understood first by considering Kekule structures and then Dewar and ionic structures.

Even among the two Kekule structures, the overall wave function is formed for only the first Kekule structure (XII), to start with. If the carbon atoms are labeled A, B, C, ...F and the electrons, 1, 2, ...6, then wave function for one π bond is Ψ_A (1)· Ψ_B (2) + Ψ_A (2)· Ψ_B (1) because formally it is like an isolated hydrogen molecule. For second π bond, the wave function is Ψ_C (3) Ψ_D (4) + Ψ_C (4)· Ψ_D (3) and for the third, it is Ψ_E (5)· Ψ_F (6) + Ψ_E (6)·Ψ_F (5). The overall wave function for the first Kekule structure is

$$\psi_{VB}^{K1} = \{\psi_A\,(1).\ \psi_B\,(2) + \psi_A\,(2)\cdot\psi_B\,(1)\}.\ \{\psi_C(3).\ \psi_D\,(4) + \psi_C\,(4).\ \psi_D\,(3)\}.$$

$$\{\psi_E\,(5).\ \psi_F\,(6) + \psi_E\,(6)\ \psi_F\,(5)\} \qquad \qquad ....(4.7)$$

The overall wave function is obtained as the product of the independent wave functions as per the principle explained in section 4.3. The expression in Eq. 4.7 may

look complicated but it can be analysed in the same way as for the hydrogen molecule. As it stands, Eq. 4.7 does not permit any π electron density between carbon atoms B and C, D and E, and F and A. This structure implies that two sets of bond lengths, 148 pm and 134 pm, must exist, one for sp^2 hybridised single bonded carbon atoms and other for double bonded ones. Experimentally determined carbon-carbon bond lengths are all equal, viz., 139.7 pm. Hence, the above trial function needs to be improved.

As a next step, another wave function ψ_{VB}^{K2} is formed, for the second Kekule structure, where the π bond formation is assumed between carbon atoms B and C, D and E and F and A (XIII). Mixing these two wave functions for Kekule structures, wave function ψ_K is written as,

$$\psi_K = \psi_{VB}^{K1} + \psi_{VB}^{K2} \qquad \qquad ....(4.8)$$

From energy considerations, it can be shown that even ψ_K needs to be improved.

Further refinements are possible, if we take into account the following features :

i) Bonding may occur between non-neighbouring atoms and a better description is obtained by considering Dewar structures (XIV – XVI). However, Dewar structures imply the presence of diagonal C−C bonds having bond distance value of 280 pm. This is larger than even the C−C bond length in alkanes. These diagonal bonds are weak rendering small contribution of Dewar forms to the resonance hybrid.

ii) As in the case of hydrogen molecule, we should allow ionic – covalent mixing, taking into account structures of the kind (XVII) and (XVIII). Actually there are many such ionic structures. Anyhow, ionic structures (XVII) and (XVIII), are less important than covalent structures, (XII – XVI), as per rule (3) stated in section 4.5.

Resonance hybrid of benzene is said to have around 80% contribution from Kekule structures and 20% contribution from Dewar structures. This means properties of benzene are better explained by Kekule structures than by Dewar structures.

Although inclusion of more terms in the trial function gives a better description of the structure of benzene, the treatment becomes much more complicated. In spite of all the mathematical complexity, valence bond theory leads to the following facts regarding benzene structure :

i) All carbon-carbon bond lengths are equal to 139.7 pm which is in between single and double bond lengths. This means double bonds are not localised between any two carbon atoms, i.e., benzene has a delocalised π electron structure.

ii) The actual structure of benzene is a resonance hybrid of the structures of the type (XII – XVIII).

iii) The resonance stabilisation energy, has been found to be 154 kJ mol

iv) It predicts a planar hexagonal structure with a bond angle of 120°.

From the above discussion we can infer that the π electrons are not localised between particular pairs of carbon atoms. The six π electrons are delocalised over all the carbon atoms. Summing up all the above structural features, a delocalised π electron structure of benzene can be written as :
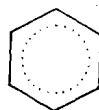
Inner circle denotes symmetrical distribution of π electron density over all the six carbon atoms.

Using the above ideas, try to answer the following SAQ.

SAQ 6

Between ethylene and benzene, suggest two structural aspects of similarity and dissimilarity.

....

....

....
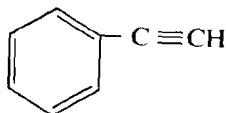
4.9 SUMMARY

In this unit, we have described the development of valence bond theory and its applications to simple molecules. The concepts of resonance and hybridisation have also been explained. Using the principles of valence bond theory, the structures of methane, ethylene, acetylene and benzene are discussed. In the next unit, you will study the structure of molecules like hydrogen, oxygen and carbon monoxide in the light of molecular orbital theory.

4.10 TERMINAL QUESTIONS

1) What are the essential steps involved in arriving at the structure of a molecule using valence bond theory?

2) Identify the type of hybridisation for each of the carbon atoms.

i) $H_3C - CH = CH_2$

ii) $C \equiv CH$

iii) $H_3C - \overset{\overset{O}{\|}}{C} - OH$

3) Explain the shape of CCl_4 molecule on the basis of VSEPR and hybridisation theories.

4) For the following statements, mark T for correct statements and F for false ones.

a) Electrons in a hydrogen molecule are distinguishable ☐

b) More terms in the trial function lead to a more acceptable bond energy value ☐

c) Homonuclear molecules like N_2, O_2 etc. do not have ionic terms in their valence bond structures ☐

d) Carbon atom, in carbonate ion, is in sp^2 hybridised state ☐

e) Covalent radius of carbon increases with increase of s character in different hybridisation states ☐

5) Explain the structure of mercuric chloride on the basis of hybridisation theory.

6) Differentiate the following isomers on the basis of theoretical carbon-carbon bond lengths :

$H_3C - CH_2 - CH = CH_2$ $H_3C - CH = CH - CH_3$
         1 - Butene   2 - Butene

7) Carbon dioxide is linear as per VSEPR theory. Explain the type of hybridisation in the carbon atom of this molecule, in keeping with its linear structure.

4.11 ANSWERS

Self Assessment Questions

1) That trial function, for which bond energy and bond length values are closest to experimental values, is accepted as the correct one.

2) By assuming a covalent structure with indistinguishable electrons, the bond energy calculations is improved from a value of 24 kJ mol^{-1} to 303 kJ mol^{-1}. But this value is improved to only 388 kJ mol^{-1} by taking into account the screening effect of the electron and the possibility of ionic and covalent structures. Hence, covalent structure has greater importance than other factors.

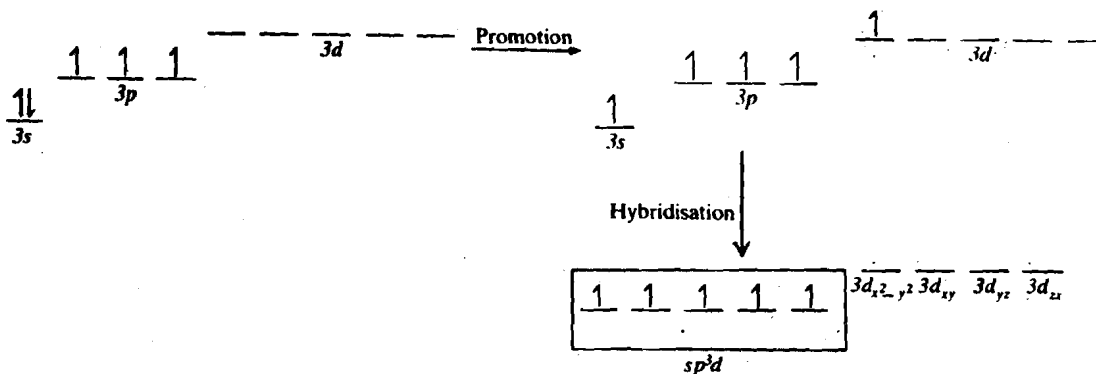3) Lewis structure for nitrate ion is
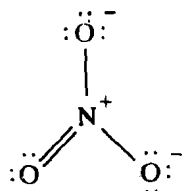
The resonance structures are :
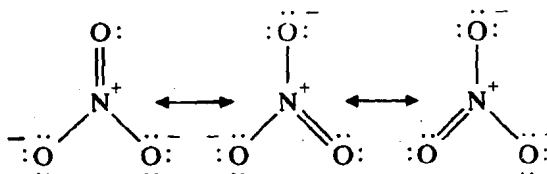
4) The $2p_z$ electrons in the two fluorine atoms get paired to give fluorine molecule. The following resonance structures are possible :
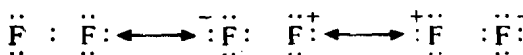
5)

P
(Ground state)
($1s^2 2s^2 2p^6$
not shown)

The five unpaired electrons in the sp^3d hybrid orbitals pair up with five unpaired electrons, one from each of the five chlorine atoms.

6) **Similarities :**

i) Both have sp^2 hybridised carbon atoms.

ii) Both have bond angle of 120°.

Dissimilarities :

i) Carbon-carbon bond lengths are different in the two molecules.

ii) Ethylene has localised π electrons while benzene has a delocalised π electron structure.

Terminal Questions

1) Molecular wave functions are formed and E vs R curves are drawn. The wave function giving E and R values, agreeing closely with experimental bond energy and bond distance, is taken as the acceptable wave function. The structural features assumed in arriving at the wave function are assumed to be correct.

2) i) $H_3C - CH = CH_2$
    $sp^3 \quad sp^2 \quad sp^2$
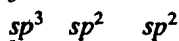
ii) — C $\equiv$ CH ; all the carbon atoms of benzene ring are sp^2 hybridised.
   $sp \quad sp$

iii) $\underset{sp^3 \quad sp^2}{H_3C-\overset{\overset{\textstyle O}{\|}}{C}-OH}$
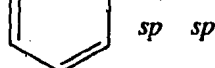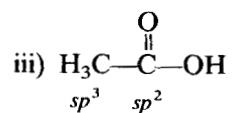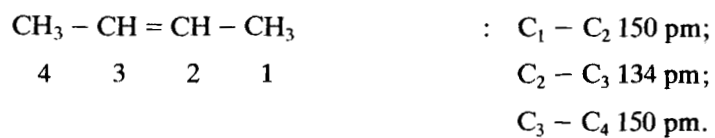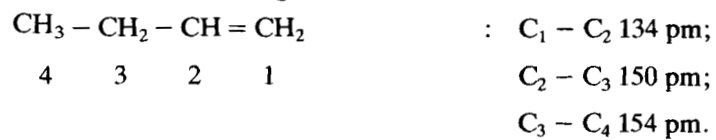
3) Tetrahedral on the basis of both the concepts.

4) (a) F   (b) T   (c) F   (d) T   (e) F.

5) sp hybridisation; its structure is linear.

6) The bond lengths are given in Table 4.4.

$$CH_3 - CH_2 - CH = CH_2 \qquad : \quad C_1 - C_2 \; 134 \text{ pm};$$
$$ 4 \quad\;\; 3 \quad\;\; 2 \quad\;\; 1 \qquad\qquad C_2 - C_3 \; 150 \text{ pm};$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad C_3 - C_4 \; 154 \text{ pm}.$$

$$CH_3 - CH = CH - CH_3 \qquad : \quad C_1 - C_2 \; 150 \text{ pm};$$
$$ 4 \quad\;\; 3 \quad\;\; 2 \quad\;\; 1 \qquad\qquad C_2 - C_3 \; 134 \text{ pm};$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad C_3 - C_4 \; 150 \text{ pm}.$$

7) Carbon atom is sp hybridised.

UNIT 5 MOLECULAR ORBITAL THEORY

Structure

5.1 INTRODUCTION

You have learnt in Units 1 and 2 the basic concepts of atomic structure and you know that the electrons occupy different orbitals namely s, p, d, and f, depending upon their energy. These orbitals are filled up in accordance with various rules like Pauli's exclusion principle, *aufbau* principle and Hund's rule. Let us now extend these ideas to molecules and try to understand the molecular structure on the basis of formation of molecular orbitals. When we talk about molecules, we know that molecules are made of atoms and in a molecule, the constituent atoms are held together by forces of attraction. In ionic compounds, these forces of attraction are electrostatic in nature. In case of covalent molecules, the atoms share the electron pairs. In the last unit, the formation of covalent linkage has been explained on the basis of valence bond theory. You will now study an alternative approach for the formation of molecules which is called Molecular Orbital Theory. Here you will learn how electrons are assigned into various molecular orbitals in homonuclear and heteronuclear diatomic molecules.

Objectives

After studying this unit, you should be able to :

- state the principles of molecular orbital theory and linear combination of atomic orbitals,
- define bonding, antibonding and nonbonding orbitals,
- illustrate the various combinations of s and p orbitals with diagrams,
- write the various molecular orbitals in a homonuclear diatomic molecule according to the increasing order of energy and draw their energy level diagram,
- state the molecular orbital configuration for simple homonuclear diatomic molecules, and
- predict the electron configuration for simple heteronuclear diatomic molecules.

5.2 MOLECULAR ORBITAL THEORY

A molecule is defined as a stable combination of two or more atoms. By stable combination, we mean that when two atoms form a molecule, the energy of the new entity is less than the sum of the energies of the isolated atoms. In case the atoms constituting a molecule are identical, they form the homonuclear molecules and examples are molecules of various elements, like H_2, N_2 and O_2. In other cases,. when the atoms constituting a molecule are of different elements, they form heteronuclear molecules; examples being the molecules of compounds, like HCl and H_2O. Molecules of varying complexities exist in nature including the simple ones like CO_2, SO_2, CH_4, NH_3 and the complex polyatomic molecules like proteins and carbohydrates. Whatever be the nature of molecules, they are built up from the atoms according to certain basic laws. In the last unit you have already read about the valence bond approach. Let us now study the molecular orbital theory which also deals with the formation of the molecules from the atoms from a different angle.