



CHEMICAL BONDING

In lesson 1 you have learnt about the structure of atom while in the lesson 2 you studied about the classification of elements and the variation in atomic properties. You know that molecules are obtained by the combination of two or more than two atoms of the same or different elements. In this lesson you will study

- Why do atoms combine?
- What are the different ways in which the atoms can combine?, and
- What are the shapes of different molecules?

The answers to these questions are of fundamental importance to the study of chemistry, as you would discover while studying the later parts of this course.



Objectives

After reading this lesson you will be able to

- explain the formation of bond in terms of potential energy diagram and octet rule;
- list different types of bonds;
- define ionic bond and cite some examples;
- write Lewis structures of some simple molecules;
- list the characteristics of ionic compounds;
- define covalent bond and cite some examples;
- list the characteristics of covalent compounds;
- state valence shell electron pair repulsion (VSEPR) theory;
- predict the geometry of molecules with the help of VSEPR theory;
- explain the hybridisation of atomic orbitals involving s, p and d orbitals and illustrate with examples;



- tabulate the geometry of some molecules showing sp , sp^2 , sp^3 , dsp^2 , and dsp^3 hybridisation;
- explain the formation of σ and π bonds in CH_4 , C_2H_4 and C_2H_2 ;
- explain molecular orbital theory;
- write the molecular orbital configuration of H_2 , N_2 , O_2 and F_2 molecules;
- define bond length and bond order and relate them and
- explain hydrogen bonding with the help of examples.

5.1 What is a Chemical Bond

When two atoms of same or different elements approach each other, the energy of the combination of the atoms becomes less than the sum of the energies of the two separate atoms at a large distance. We say that the two atoms have combined or a bond is formed between the two. The bond is called a **chemical bond**. Thus *a chemical bond may be visualised as an effect that leads to the decrease in the energy*. The combination of atoms leads to the formation of a molecule that has distinct properties different from that of the constituent atoms.

A question arises, “How do atoms achieve the decrease in energy to form the bond?”. The answer lies in the electronic configuration. As you are aware, the noble gases do not react with other elements to form compounds. This is due to their stable electronic configuration with eight electrons (two in case of helium) in their outermost shells. The formation of a bond between two atoms may be visualised in terms of their acquiring stable electronic configurations. That is when two atoms (other than that of noble gases) combine they will do so in such a way that they attain an electronic configuration of the nearest noble gas.

The stable electronic configuration of the noble gases can be achieved in a number of ways; by losing, gaining or sharing of electrons. Accordingly, there are different types of chemical bonds, like,

- Ionic or electrovalent bond
- Covalent bond
- Co-ordinate covalent bond

In addition to these we have a special kind of bond called hydrogen bond. Let us discuss about different types of bonds, their formation and the properties of the compounds so formed.

5.2 Ionic or Electrovalent Bond

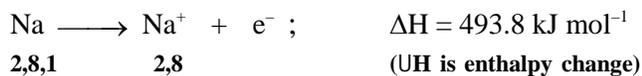
According to Kossel’s theory, in the process of formation of ionic bond the atoms acquire the noble gas electronic configuration by the gain or loss of electrons. Let us consider the formation of $NaCl$ in terms of Kossel’s Theory.

The electronic configuration of sodium atom (atomic number 11) is 2,8,1. Since it is highly electropositive, it readily loses an electron to attain the stable configuration of the nearest noble gas (neon) atom. It becomes a positively charged sodium cation (Na^+) in the process

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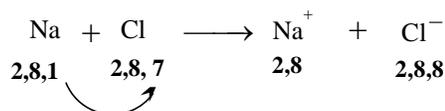
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On the other hand, a chlorine atom (electronic configuration: 2,8,7) requires one electron to acquire the stable electronic arrangement of an argon atom. It becomes a negatively charged chloride anion (Cl⁻) in the process.



According to **Kossel's** theory, there is a **transfer** of one electron from sodium atom to chlorine atom and both the atoms attain noble gas configuration.



The positively charged sodium ion and the negatively charged chloride ion are held together by electrostatic attractions. The bond so formed is called an **electrovalent** or an **ionic bond**. Thus *the ionic bond can be visualised as the electrostatic force of attraction that holds the cation and anion together*. The compounds so formed are termed as ionic or electrovalent compounds.

5.2.1 Energetics of Ionic Compound Formation

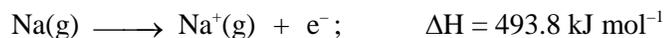
We have just described the formation of an ionic compound (NaCl) as a result of transfer of electrons as proposed by Kossel. You may raise a question here that when **more energy is required** (ionisation energy) to form a sodium ion from sodium atom, **than that released** (electron affinity) in the formation of chloride ion from chlorine atom then how do we say that the formation of NaCl is accompanied by a decrease in energy? Your question is quite justified but let us assure you that there is no anomaly. Let us look at the whole process somewhat closely to clarify your doubts.

The formation of NaCl from sodium and chlorine can be broken down into a number of steps as :

- a) **Sublimation** of solid sodium to gaseous sodium atoms.



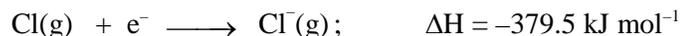
- b) **Ionization** of gaseous sodium atom to give sodium ion.



- c) **Dissociation** of gaseous chlorine molecule into chlorine atoms



- d) Conversion of gaseous chlorine atom to chloride ion (**addition of electron**)





e) Formation of NaCl from sodium and chloride ions. (**Crystal or lattice formation**).



The energy released in this step is **lattice energy**.

The net reaction would be



The overall energy change can be computed by taking the sum of all the energy changes:

$$\Delta H = (180.7 + 493.8 + 120.9 - 379.5 - 754.8) = -410.9 \text{ kJ mol}^{-1}$$

Thus we see that the net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. The approach we have just followed is based on the law of conservation of energy and is known as **Born-Haber cycle**.

Of the five different types of energies involved, two (sublimation and dissociation energies) are generally have low values than the rest. Therefore, the three energy terms i.e., ionization energy, electron affinity and lattice energy are important in determining the formation of an ionic compound. On the basis of the above discussion we can say that the formation of an ionic compound is favoured by

- i. Low ionisation energy of the metal,
- ii. High electron affinity of the other element (non-metal), and
- iii. High lattice energy

5.2.2 Characteristic Properties of Ionic Compounds

- These exist as crystalline solids in which the ions are arranged in a regular three dimensional structure. The ionic compounds are generally hard and brittle in nature.
- These compounds have high melting and boiling points due to strong electrostatic interactions between the ions.
- These are generally soluble in water and less soluble in non-polar solvents like ether, alcohol, etc.
- These conduct electricity when in molten state or in aqueous solutions.

Kossel's theory explains bonding quite well but only for a small class of solids composed of electropositive elements of Group 1 and 2 with highly electronegative elements. Secondly, this theory is incapable of explaining the formation of compounds like, SO_2 or O_2 , etc. For example in case of O_2 , there is no reason to expect that one atom of oxygen would lose two electrons while the other accepts them. The problem was solved by Lewis theory of covalent bonding.

5.3 Covalent Bond

Like Kossel, Lewis also assumed that atoms attain noble gas electronic configuration in the process of bond formation. However, the way the noble gas electronic configuration

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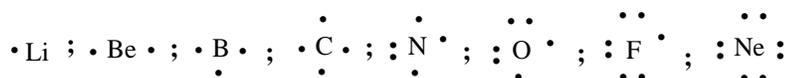
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is achieved, is different. Lewis proposed that this is achieved by “sharing of a pair of electrons” between the two atoms. Both the atoms contribute an electron each to this pair. For example, two hydrogen atoms form a molecule by sharing a pair of electrons. If electrons are indicated as dots, formation of hydrogen molecule can be shown as



This shared pair of electrons contributes towards the stability of both the atoms and is said to be responsible for ‘bonding’ between the two atoms. Such a bond is called **covalent bond** and the compounds so obtained are called covalent compounds. In the process of suggesting the process of chemical bonding Lewis provided a very convenient way of representing bonding in simple molecules. This is called **Lewis electron-dot structures** or simply **Lewis structures**.

In Lewis structure each element is represented by a **Lewis symbol**. This symbol consists of the normal chemical symbol of the element surrounded by number of dots representing the electrons in the valence shell. Since the electrons are represented by dots, these are called electron-dot structures. The Lewis symbols of some elements are as:

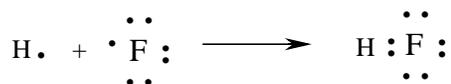


You may note here that while writing the Lewis symbols, single dots are placed first on each side of the chemical symbol then they are paired up. The Lewis structure of a molecule is written in terms of these symbols

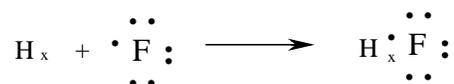
In terms of Lewis symbols the ionic bond formation in NaCl can be represented as



and the covalent bond formation in HCl is represented as

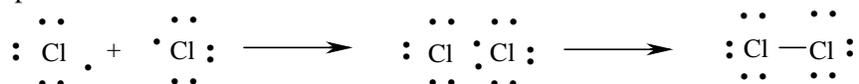


Sometimes the electrons contributed by different atoms are represented by different symbols. For example, formation of HF may also be shown as



In this case the hydrogen electron is shown as a cross while the electrons of fluorine are represented by dots. There is no difference between electrons; it is just a presentation for the sake of convenience.

In terms of Lewis structures the formation of a chlorine molecule from two chlorine atoms may be represented as





Here each chlorine atom with seven valence electrons, contributes one electron to the shared pair. In the process of bond formation both the chlorine atoms acquire the electronic configuration of argon. In the same way, the formation of oxygen molecule involves sharing of two pairs of electrons between the two oxygen atoms. In this case both the atoms contribute two electrons each and acquire eight electrons or an octet in their valence shell.

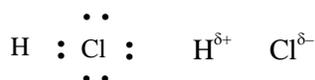


You may have noticed that in the process of bond formation, the elements of second period acquire eight electrons in their valence shell. This is called '**Octet rule**'. You may also note that in case of H_2 and Cl_2 the atoms are linked by a single line while in case of O_2 the atoms are linked by two lines. These lines represent bonds. When two atoms are bound by sharing a single pair of electron, they are said to be joined by a single bond. And when, two pairs of electrons are shared (as in case of O_2), the two atoms are said to be bound by a double bond. In nitrogen (N_2) the two atoms are joined by a triple bond as they share three pairs of electrons.

In a Lewis representation the electrons shown to be involved in the bond formation are called bonding electrons; the pair of electrons is called '*bond pair*' and the pairs of electrons not involved in the bonding process are called '*lone pairs*'. The nature of the electron pair plays an important role in determining the shapes of the molecules. This aspect is discussed later in Section 5.4.

5.3.1 Polar Covalent Bond

In a chemical bond the shared electron pair is attracted by the nuclei of both the atoms. When we write the electron dot formula for a given molecule this shared electron pair is generally shown in the middle of the two atoms indicating that the two atoms attract it equally. However, actually different kinds of atoms exert different degrees of attraction on the shared pair of electrons. A more electronegative atom has greater attraction for the shared pair of electrons in a molecule. As a consequence in most cases the sharing is not equal and the shared electron pair lies more towards the atom with a higher electronegativity. For example, in HCl , the shared pair of electron is attracted more towards more electronegative chlorine atom. As a result of this unequal sharing of the electron pair, the bond acquires polarity or partial ionic character.



In an extreme case, the difference in the electronegativity may be so high that the electron pair is practically under the influence of a single atom. In other words the polarization of the bond is complete i.e., we have a case of ionic bonding. Thus, though the Lewis theory talks about covalent bonding it can account for the formation of ionic compounds also.

5.3.2 Coordinate Covalent Bond

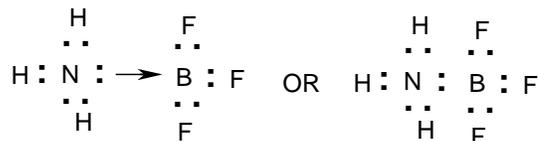
You have learnt that in the formation of a covalent bond between the atoms, each atom contributes one electron to the shared electron pair, However, in some cases both the electrons of the shared pair are contributed by only one species (atom, molecule or ion) A

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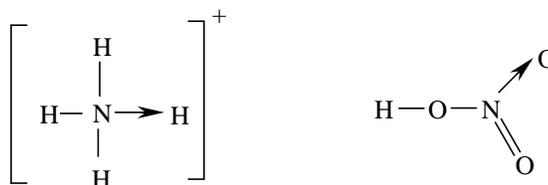


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common example is the formation of a bond between boron trifluoride (BF_3) and ammonia (NH_3). BF_3 is an electron deficient molecule and can accept a pair of electrons. The molecule of ammonia on the other hand is electron rich. It has a lone pair of electron on the nitrogen atom and that can be donated. Electron rich ammonia donates a pair of electron to electron deficient BF_3 . Such electron donor-acceptor bonds are called **coordinate covalent** or **dative bonds**.



A coordinate bond is normally represented by an arrow pointing from a donor atom to the acceptor atom. A coordinate bond is identical to a covalent bond in terms of its polarity and strength. The two are different only in the way they are formed. We cannot distinguish between covalent and coordinate covalent bond, once these are formed. HNO_3 and NH_4^+ ion are some more common examples of formation of a coordinate bond.



Intext Question 5.1

1. Define electrovalent bond.
.....
2. Show the formation of a nitrogen molecule from two nitrogen atoms in terms of Lewis theory.
.....
3. What do you understand by a polar covalent bond? Give two examples.
.....
4. What is a coordinate covalent bond ? How is it different from a covalent bond?
.....

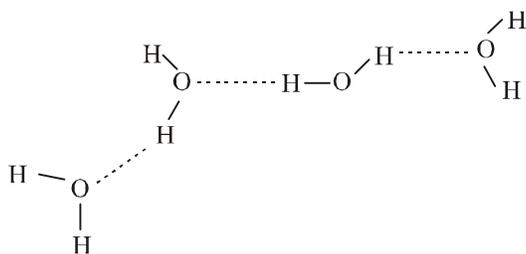
5.3.3 Characteristic properties of Covalent Compounds

- The covalent compounds have low melting and boiling points due to weak forces of interaction between the molecules.
- The covalent compounds are poor conductors of electricity as these lack ionic species.
- The covalent compounds are generally insoluble in water and dissolve in nonpolar solvents like benzene, carbon tetrachloride etc.

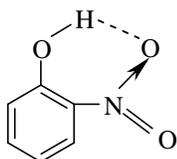


5.3.4 Hydrogen Bonding

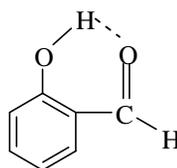
It is a special type of attraction between a hydrogen atom bonded to a strongly electronegative atom (like nitrogen, oxygen or fluorine) and the unshared pair of electrons on another electronegative atom. Hydrogen bond is a weak bond, the strength being just about $4\text{--}25\text{ kJ mol}^{-1}$. It is quite small as compared to the covalent bond, which needs a few hundreds of kJ mol^{-1} of energy to break. However, it is strong enough to be responsible for the high boiling points of H_2O and HF etc. In fact it is due to hydrogen bonding only that water exists as a liquid. The low density of ice also can be explained in terms of hydrogen bonding.



Due to the difference in the electronegativity between hydrogen and the other electronegative atom, the bond connecting them becomes polar. The hydrogen atom acquires a positive charge while the electronegative atom bears the negative charge. Hydrogen bonding results from the electrostatic interaction between the positively charged hydrogen atom and the negatively charged electronegative atom. The second electronegative atom may be a part of the same molecule or it may belong to a different molecule. Accordingly, there are two types of hydrogen bonds. If the hydrogen bond is formed between two different molecules it is called **intermolecular hydrogen bond**. When the hydrogen bond exists within the same molecule, it is called **intramolecular hydrogen bonding**. Salicyldehyde and o-nitrophenol are two common examples of the molecules showing intramolecular hydrogen bonding whereas in water, intermolecular hydrogen bonding exists.



o-nitrophenol



Salicyldehyde

Hydrogen bonding plays an important role in the structure and function of many biomolecules like proteins and nucleic acids.

5.4 Valence Shell Electron Pair Repulsion (VSEPR) Theory

In a molecule the constituent atoms have definite positions relative to one another i.e., the molecules have a definite shape. The theories of bonding that we have discussed so far do not say anything about the shape of the molecules. A simple theory called VSEPR theory

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was put forth by Sidgwick and Powell in 1940 to explain the shapes of molecules. It was later refined and extended by Nyholm and Gillespie in 1957. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be stated in terms of two postulates:

POSTULATE 1

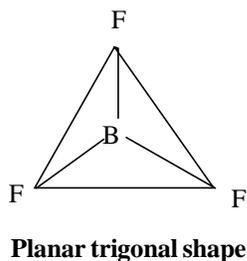
The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion. In other words, the chemical bonds in the molecule will be energetically most stable when they are as far apart from each other as possible. Let us take up some examples.

BeCl₂ is one of the simple triatomic molecules. In this molecule, the central atom, beryllium has an electronic configuration of $1s^2 2s^2$. That is it has two electrons in its valence shell. In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. According to the postulate given above, these electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of 180° which gives the molecule a linear shape.



Other molecules of this type would also have a similar shape.

BF₃ : In boron trifluoride, the central atom, boron has an electronic configuration of $1s^2 2s^2 2p^1$. That is, it has three electrons in its valence shell. In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. Thus there are a total of 6 valence electrons or three pairs of valence electrons. According to the VSEPR postulate, these electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of 120° which gives the molecule a planar trigonal shape.

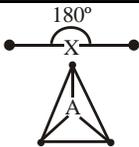
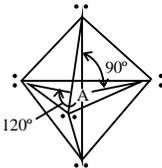


Thus different molecules would have different shapes depending on the number of valence shell electrons involved. The geometric shapes associated with various numbers of electron pairs surrounding the central atom are given in Table 5.1.



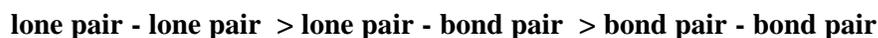
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Table 5.1: Geometric arrangements of electron pairs around central atom.

Molecule Type	Number of electron pairs	Predicted geometry	Representative structure	Examples
AX_2 AX_3	2 3	Linear Planer trigonal		$HgCl_2, BeH_2$ BF_3, BCl_3
AX_4	4	Tetrahedral		$CCl_4, CH_4, SiCl_4$
AX_5	5	Trigonal bipyramidal		PCl_5, PF_5
AX_6	6	Octahedral		SF_6, PF_6^-

POSTULATE 2

The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than that between two bond pairs The order of repulsive force between different possibilities is as under.



The shapes of the molecules given in Table 5.1. correspond to the molecules containing only bond pair electrons. The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted from the above mentioned shapes.

Let us take an example of three molecules namely, methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom. But the nature of these is different in the three cases. In methane molecule the central carbon atom has 4 valence electrons and it shares 4 electrons with four hydrogen atoms. So there are a total of 4 bond pairs and according to Table 5.1 it should have a tetrahedral shape. In case of ammonia also there are four pairs of electrons but their nature is different. Three of these are bond pairs while one is a lone pair. Similarly, in case of water again there are four pairs of electrons ; two are bond pairs while two are lone pairs. Due to the differences in the mutual repulsion between bond pair - bond pair and lone pair - bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape. The number and nature of electron pairs and the geometries of these three molecules are given in Table 5.2.



Table 5.2: Molecular geometries of molecules with 4 electron pairs with different combinations of lone pairs and bond pairs.

Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH ₄	4	0	tetrahedral		109.5
NH ₃	3	1	trigonal pyramidal		107
H ₂ O	2	2	angular or bent		104.5

We have so far learnt that a chemical bond formation between two atoms can occur by transfer (ionic bonding) or sharing (covalent bonding) of electrons. The processes of bond formation and the bonding in simple molecules can be conveniently represented in terms of electron – dot structures. Further, the VSEPR theory provides a good idea of the shapes of the molecules. But! have you noticed that we have been representing electrons as well defined dots i.e., localized particles. This is in contradiction with the probabilistic (orbital) representation of the electron that you have learnt in lesson 3. Let us learn how do we explain the process of bond formation in terms of modern theories that incorporate the wave mechanical representation of atom.



Intext Question 5.2

1. What are the basic postulates of VSEPR theory?

.....

2. Predict the shape of methane (CH₄) on the basis of VSEPR theory.

.....

5.5 Modern Theories of Chemical Bonding

The theories of chemical bonding proposed (in 1916) by Kossel and Lewis are called as classical theories of bonding. These do not take into account the wave mechanical or quantum mechanical principles. After the development of quantum mechanical description of atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding. These are Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Let us discuss these theories in brief.



5.5.1 Valence Bond Theory

Valence bond theory was proposed by Heitler and London in 1927, to describe the formation of hydrogen molecule from its atoms. Linus Pauling and others further developed it. In this approach the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The strength of the bond depends on the effectiveness or extent of the overlapping. Greater the overlapping of the orbitals, stronger is the bond formed. Let us take the example of bonding in hydrogen molecule to understand the VB approach.

Suppose that the two hydrogen atoms are at infinite distance from each other. Their electrons are in their respective $1s$ orbitals and are under the influence of the corresponding nuclei. As the two atoms approach each other their $1s$ orbitals begin to overlap which lead to decrease in energy, Fig.5.1. At a distance equal to the bond length the overlapping is maximum and the energy is minimum. The overlapping can be equated to the sharing of electrons between the atoms. The electrons occupying the shared region of orbitals are under the influence of both the nuclei.

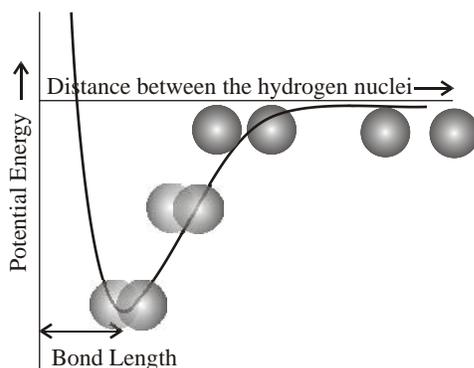
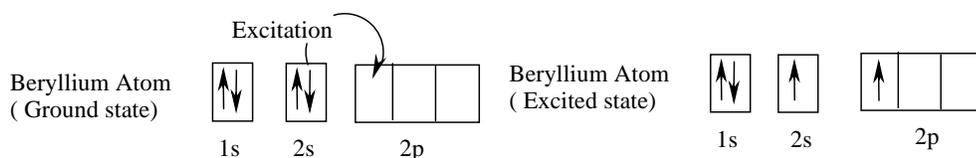


Fig. 5.1 : Formation of hydrogen molecule from overlapping of two hydrogen atoms

This simple approach can be used to explain the bonding in simple diatomic molecules like HF , F_2 etc.. However, to explain bonding in molecules containing more than two atoms some additional concepts like excitation and hybridisation need to be used.

5.5.1.1 Hybridisation

Let us take up the example of bonding in a triatomic molecule; say beryllium hydride (BeH_2) to understand the concept of hybridisation of orbitals and the need for the same. The atomic number of beryllium is 4. Its electronic configuration is $1s^2 2s^2$. In order to form bonds with two hydrogen atoms the valence electrons ($2s^2$) of beryllium atom must overlap with the $1s$ electrons of the two hydrogen atoms. Since the valence shell of beryllium atom contains both the electrons in the same orbital (i.e., $2s$) it cannot overlap with the $1s$ orbital of hydrogen atoms containing one electron. [You know that an orbital can contain a maximum of two electrons with opposite spin]. Pauling got over this problem by suggesting that in the process of bond formation an electron from the $2s$ orbital of beryllium atom gets momentarily excited to the empty $2p$ orbital as shown below.



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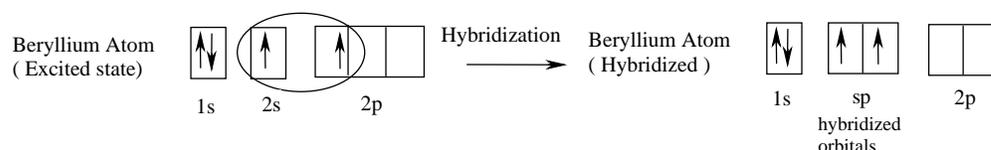


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Now the two valence electrons are in two singly occupied orbitals which can overlap with the 1s orbitals of the two hydrogen atoms and form two bonds. The problem is still not over. The two bonds formed by these overlaps would be of different nature. One of these would involve overlapping of 2s orbital of beryllium with 1s orbital of hydrogen while the other would involve overlapping of 2p orbital of beryllium with 1s orbital of hydrogen. However, experimentally the two bonds are found to be equivalent.

This problem is solved with the help of a concept called **hybridisation** of orbitals. According to this two or more than two non equivalent orbitals (having different energies and shapes) of comparable energies mix or hybridize and give rise to an equal number of equivalent (same energies and shapes) hybrid orbitals.

In case of BeCl_2 the two singly occupied orbitals (2s and 2p) hybridize to give two sp -hybrid orbitals. This is called **sp -hybridisation**. These hybrid orbitals lie along the z-direction and point in opposite directions.



These hybrid orbitals can now overlap with the 1s orbitals of hydrogen atoms to give the linear molecule of BeCl_2 as shown below, Fig. 5.2.

The concept of hybridisation as illustrated above can be used to describe the bonding and shapes of different molecules by considering hybridisation of suitable orbitals. Let us take up some more cases involving hybridisation of s and p orbitals.

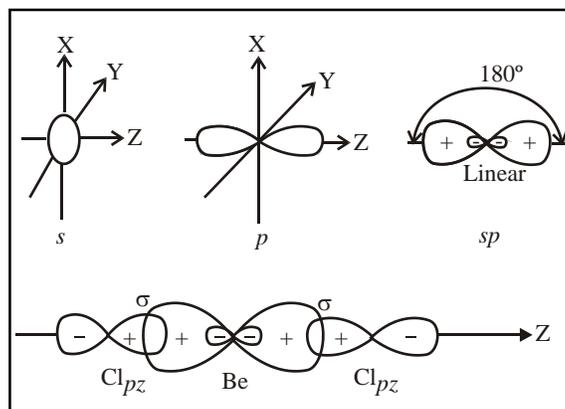
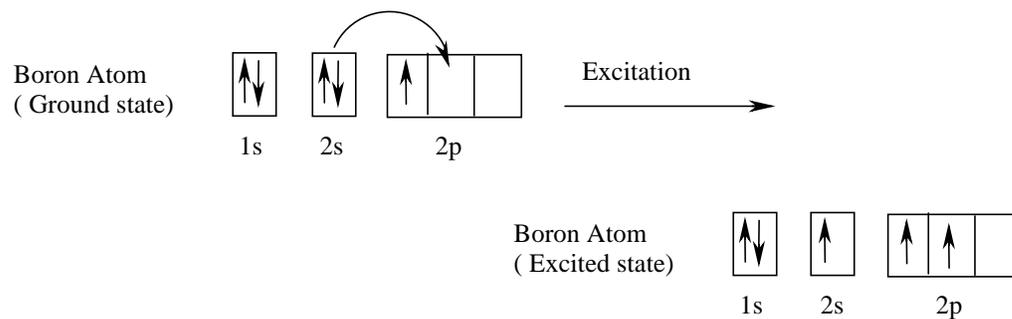
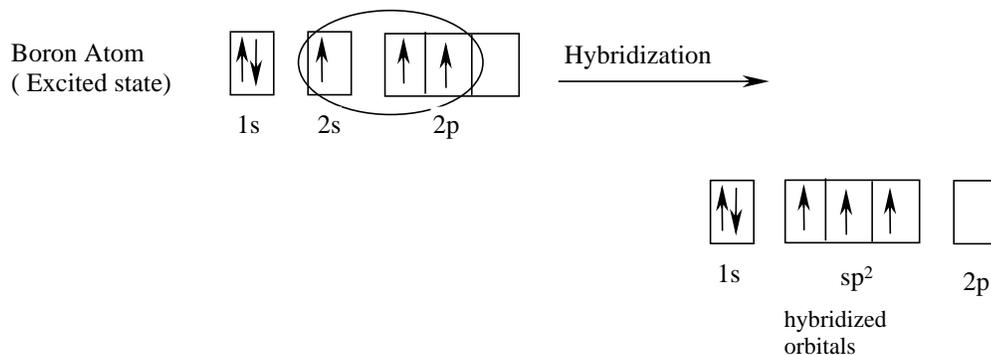


Fig. 5.2 : Formation of BeCl_2 ; sp hybridisation

Boron trichloride (sp^2 hybridisation) : In boron there are five electrons and the electronic configuration is $1s^2, 2s^2, 2p^1$. There are three electrons in the valence shell of boron atom. In order to form bonds with three chlorine atoms one of the electrons from the 2s orbital of boron atom is excited to its 2p orbital.



One 2s orbital and two 2p orbitals hybridise to give three sp^2 hybridized orbitals. This is called **sp^2 - hybridisation**.



The three hybridized orbitals are coplanar and directed towards the corners of an equilateral triangle. These **hybrid** orbitals then form bonds with the p-orbitals of chlorine atoms as shown below, fig. 5.3.

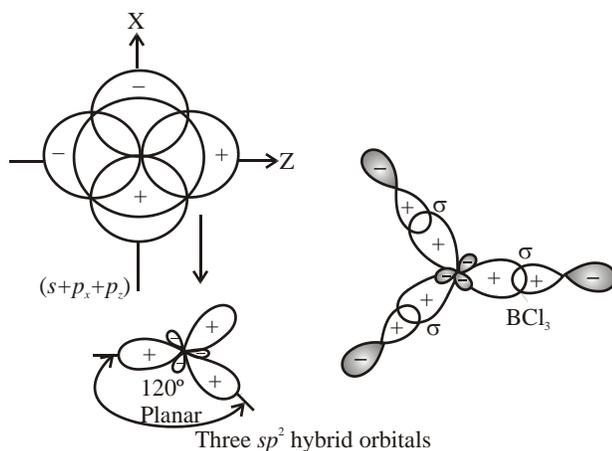
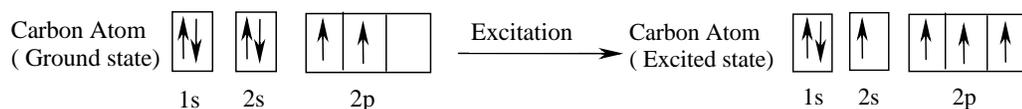
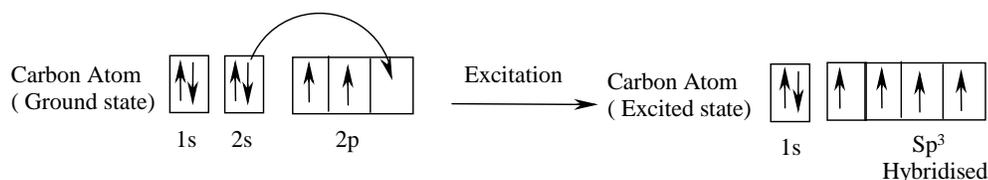


Fig. 5.3 : Formation of BCl₃ ; sp² hybridisation.

Bonding in Methane (sp³ hybridisation) : In case of methane the central atom, carbon, has an electronic configuration of 1s², 2s², 2p². In order to form bonds with four hydrogen atoms one of the electrons from the 2s orbital of carbon atom is excited to the 2p orbital.



One 2s orbital and three 2p orbitals of the carbon atom then hybridize to give four sp³ hybridized orbitals. This is called **sp³- hybridisation**.



These four sp³ hybrid orbitals are directed towards the corners of a regular tetrahedron. These **hybrid** orbitals then form bonds with the 1s orbitals of hydrogen atoms to give a methane molecule as shown below, Fig. 5.4.

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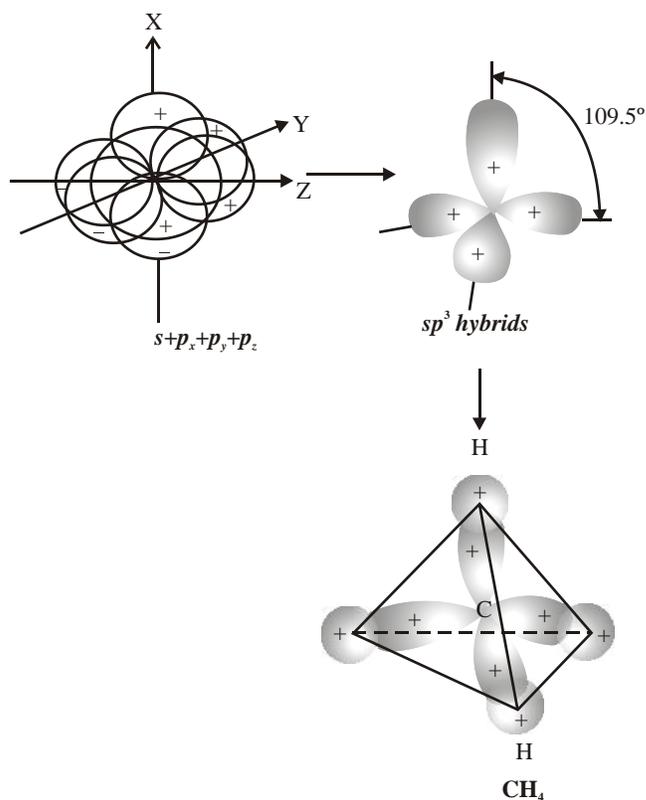
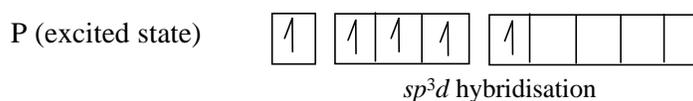


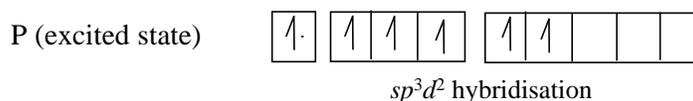
Fig. 5.4 : Formation of CH_4 ; sp^3 hybridisation.

Phosphorus pentachloride (sp^3d hybridisation):



Five sp^3d hybrid orbitals are formed which are directed towards the corners of a trigonal bipyramidal (Fig. 5.5a). These orbitals overlap with singly filled p -orbitals of five chlorine atoms and five σ bonds are formed. Thus PCl_5 molecule has a trigonal bipyramidal geometry. Three P–Cl bonds (equatorial) make an angle of 120° with each other and lie in one plane. The other two P–Cl bonds (axial) are at 90° to the equatorial plane, one lying above and the other lying below the plane.

SF_6 (sp^3d^2 hybridisation):





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Six sp^3d^2 hybrid orbitals are formed which are directed towards the corners of a regular octahedron. These orbitals overlap with singly filled orbitals of six F atoms and form σ bonds giving a regular octahedral geometry (Fig. 5.5 b)

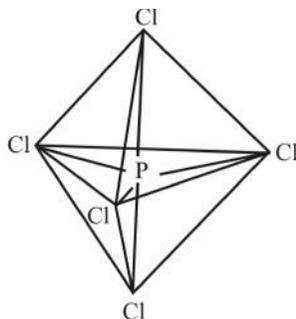


Fig. 5.5 (a) : Trigonal bipyramidal geometry of PCl_5 molecule.

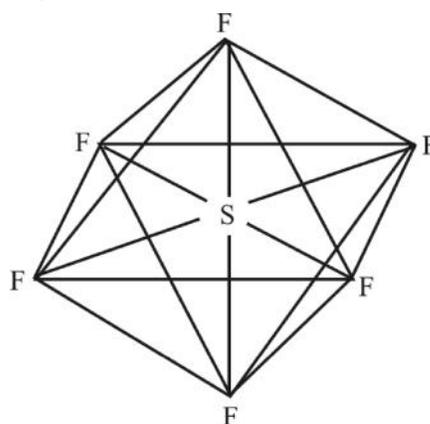


Fig. 5.5 (b) : Octahedral geometry of SF_6 molecule

5.5.1.2 Hybridisation and Multiple Bonds

So far we have discussed the bonding in those molecules in which the orbitals on a single central atom are hybridized. Let us see how does the concept of hybridisation help us in understanding bonding between pairs of such atoms. In the case of bonding in ethane (C_2H_6), two carbon atoms are bonded to each other and each carbon atom is bonded to three hydrogen atoms. You would recall that in the case of methane the valence orbitals of carbon atom undergo sp^3 hybridisation. In ethane each carbon atom undergoes sp^3 hybridisation to give four sp^3 hybridized orbitals. The two carbon atoms form a carbon – carbon bond by $sp^3 - sp^3$ overlapping. The remaining six sp^3 hybridized orbitals overlap with $1s$ orbitals of hydrogen atoms to give a molecule of ethane, C_2H_6 , as shown in fig. 5.6. The C-C bond so formed is along the internuclear axis. Such a bond is called a **bond**.

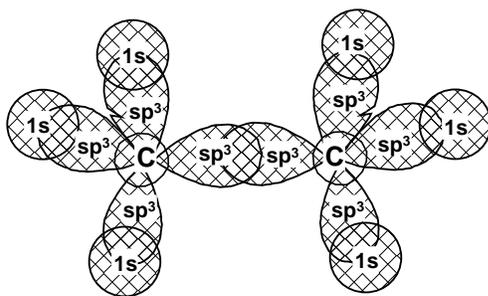


Fig. 5.6 : Formation of ethane molecule

Bonding in ethene: In case of ethene, the relevant orbitals of the carbon atoms undergo sp^2 hybridisation. Here, only two of the three p orbitals of the carbon atoms hybridize with the $2s$ orbital to form three sp^2 hybrid orbitals each. The remaining p -orbitals (one on each carbon atom) do not take part in hybridisation. A carbon – carbon bond is formed by overlapping of sp^2 orbital on the two carbon atoms [Fig 5.7(a)]. The remaining four sp^2 hybridized orbitals overlap with the $1s$ orbitals of hydrogen atoms to give the basic skeleton

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of the molecule. This leaves an un-hybridized p orbital each on both the carbon atoms [Fig 5.7(b)]. These are perpendicular to the molecular plane and undergo sideways overlap to give an electron cloud in the plane above and below the molecule [Fig 5.7(b and c)]. This is called a π -bond. In ethene there are two bonds between the carbon atoms (one sigma and one pi bond).

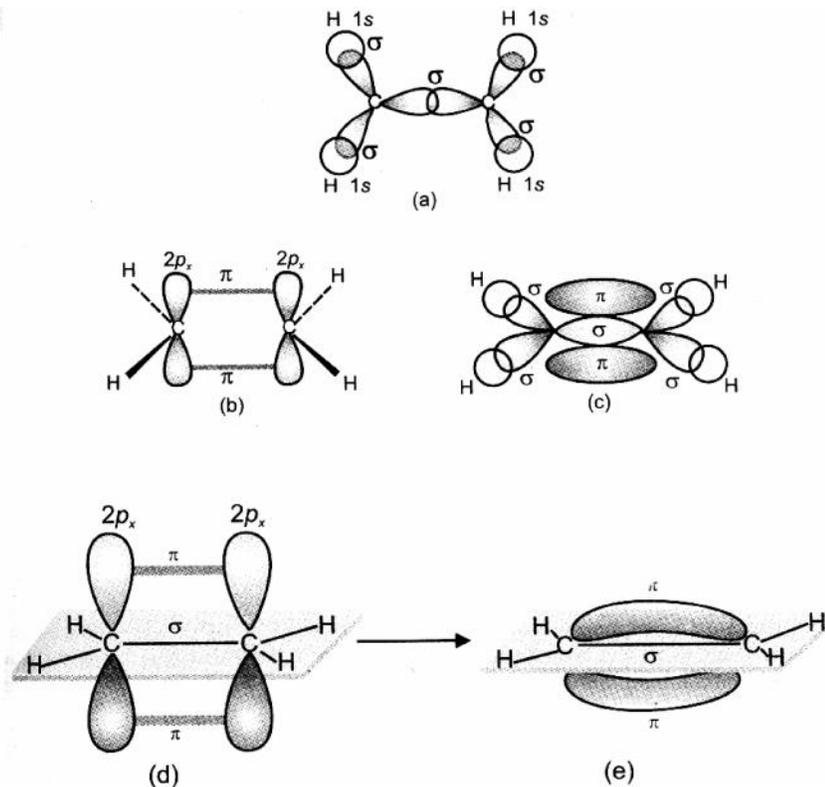


Fig. 5.7 : Formation of ethylene molecule: a) formation of the basic skeleton of the molecule b) sideways overlapping of the un-hybridized p orbitals and c) a f -bond (d) and (e) complete picture of ethylene molecule.

Bonding in ethyne (acetylene): In case of acetylene the bonding can be explained in terms of sp -hybridisation in carbon atoms. One $2s$ and one $2p$ orbitals hybridize to give two sp -hybridized orbitals. This leaves two mutually perpendicular unhybridised p orbitals each on both the carbon atoms. The carbon – carbon bond is formed by sp - sp overlapping with each other. The remaining sp orbital on each carbon overlaps with the $1s$ orbital of hydrogen to give C-H bonds (Fig. 5.8). The unhybridised p orbital each on both the carbon atoms overlap sideways to give two π -bonds.

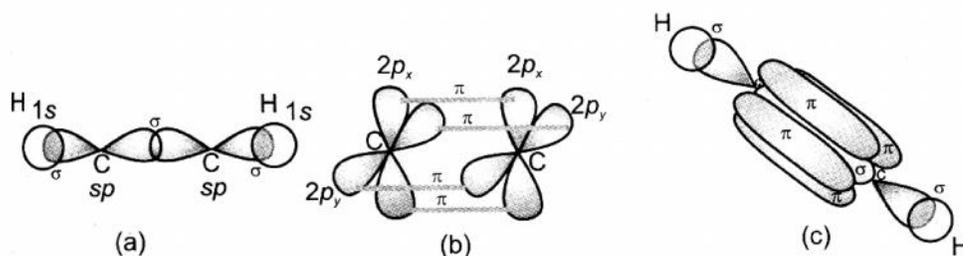


Fig. 5.8 : Formation of acetylene molecule : a) formation of the basic skeleton of the molecule b) sideways overlapping of two pairs of un-hybridized p orbitals and c) two mutually perpendicular f -bonds.



Notes



Intext Question 5.3

1. What do you understand by the term, 'hybridisation'?
.....
2. How would you explain the shape of ammonia molecule on the basis of hybridisation?
.....

5.5.2 Molecular Orbital Theory

You have just learnt about valence bond theory. It describes bond formation as a result of overlapping of the atomic orbitals belonging to the constituent atoms. The overlapping region responsible for bonding is situated between the two atoms i.e., it is localised. Molecular orbital theory (MOT) developed by F.Hund and R.S.Mulliken in 1932, is based on the wave mechanical model of atom. In contrast to the localized bonding in VBT, the molecular orbital theory visualises the bonding to be delocalised in nature i.e., spread over the whole molecule. According to MOT, in the process of bond formation

- **The atomic orbitals of the constituent atoms combine to generate new types of orbitals (called molecular orbitals).** These are spread over the whole molecule i.e., they are delocalised. In other words these new orbitals, do not “belong” to any one atom but extend over the entire region of the bonded atoms.
- These molecular orbitals are created by Linear Combination of Atomic Orbitals (LCAO) approach in which, **the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals.**
- The available **electrons then fill these orbitals in the order of increasing energy as in the Aufbau principle** used in the electron configurations of atoms.

Let us take the example of hydrogen molecule to understand the molecular orbital approach to chemical bonding. The two hydrogen atoms have an electron each in their respective 1s orbitals. In the process of bond formation the atomic orbitals of two hydrogen atoms can combine in two possible ways. In one, the MO wavefunction is obtained by addition of the two atomic wave functions whereas in the other the MO is obtained by subtraction of the atomic orbitals. The combination of the 1s orbitals on the two hydrogen atoms are shown in fig. 5.9.

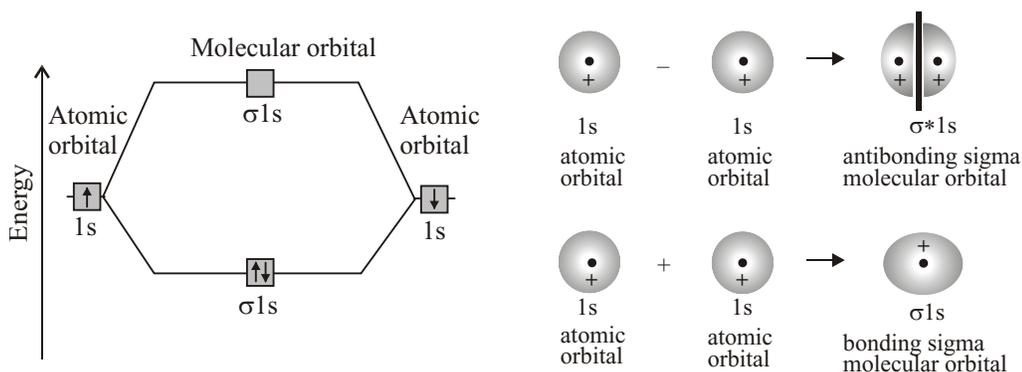


Fig. 5.9 : Formation of bonding (σ) and anti bonding (σ^*) molecular orbitals

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The molecular orbital obtained by the addition of atomic orbitals is of lower energy than that of the atomic orbitals and is called a **bonding orbital**. On the other hand, the orbital obtained by subtraction of atomic orbitals is of higher energy and is called an **anti-bonding orbital**. You can note here that the molecular orbitals obtained here are symmetric around the bond axis (the line joining the two nuclei). Such molecular orbitals are called **sigma** (σ) molecular orbitals. The bonding orbital obtained above is denoted as $\sigma 1s$ while the anti-bonding orbital is denoted as $\sigma^* 1s$. Here σ indicates the type of molecular orbital; $1s$ tells about the atomic orbital involved and $*$ is indicative of the anti-bonding nature of the MO. There are a total of 2 electrons in a hydrogen molecule, according to Aufbau principle these are filled into σ_{1s} orbital. Since the σ_{1s} orbital is a bonding orbital, its getting filled leads to stability or the bond formation.

Like electronic configuration of atoms we write MO electronic configuration for molecules. The MO configuration of hydrogen molecule is given as $(\sigma 1s)^2$. The molecular orbital energy level diagram are given in Fig. 5.10(a and b)

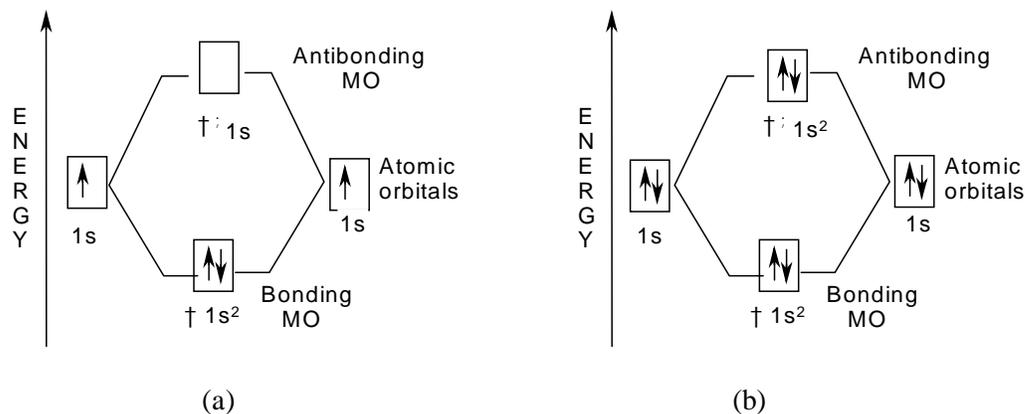


Fig. 5.10 : Molecular orbital energy level diagram for a) H_2 and b) He_2 molecules

Bond Order: we may define a new parameter called bond order as

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

Where, n_b and n_a refer to the number of electrons present in bonding and antibonding molecular orbitals respectively. For hydrogen molecule the bond order will be $\frac{1}{2}(2-0) = 1$, i.e., there is a single bond between two hydrogen atoms.

Helium (He_2) molecule

In case of He_2 , also there will be linear combination of $1s$ orbitals leading to the formation of $\sigma 1s$ and $\sigma^* 1s$ orbitals. The four electrons would be distributed as per the MO electronic configuration : $(\sigma 1s)^2 (\sigma^* 1s)^2$. The molecular orbital energy level diagram is given in fig. 3.10 (b). This gives a bond order of $\frac{1}{2}(2-2) = 0$, that is there is no bond between two helium atoms. In other words He_2 molecule does not exist.

Li_2 and Be_2 molecules

The bonding in Li_2 and Be_2 can be explained by combining the $1s$ and $2s$ orbitals to give appropriate MO's. The molecular orbital diagrams for Li_2 and Be_2 are given in Fig. 5.11.

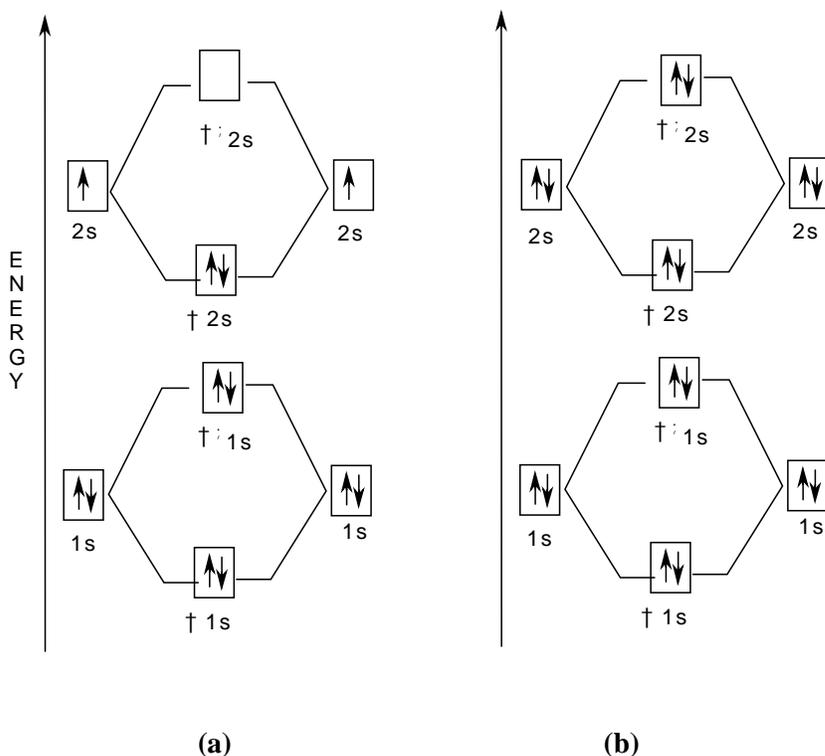


Fig. 5.11: Molecular orbital energy level diagram for a) Li_2 and b) Be_2 molecules

5.5.2.1 Molecular Orbital Bonding in Diatomic Molecules of Second Period

So far we have talked about bonding in the elements in which the MO's were obtained from the linear combination of s orbitals. In case of the atoms of second period (beyond Be) elements both s and p orbitals are involved in the formation of molecular orbitals. In such a case a number of different molecular orbitals are obtained depending on the type and symmetry of the atomic orbitals involved in the process. Let us try to understand the nature of MO's obtained in this case.

Here also the 1s and 2s orbitals of the two atoms would combine to give corresponding bonding and anti-bonding molecular orbital as shown in Fig.5.11 (b). Let us learn about the formation of MO's from the combination of p orbitals

As mentioned above, in LCAO, the atomic orbitals of **comparable energies** and of **suitable symmetry** combine to give molecular orbitals. A suitable symmetry means that the combining orbitals should have same symmetry about the molecular axis. It is normally assumed that the bond formation takes place along the z-direction. You have learnt in the first unit that the three p orbitals are directed towards three mutually perpendicular directions namely the x, y and z directions. Therefore the p_z orbitals of the two atoms would combine along the bond axis to give two molecular orbitals as shown below fig. 5.12. Since these molecular orbitals are symmetric around the molecular axis these are called σ orbitals. The designation of the orbitals would be σ_{2p_z} and $\sigma_{2p_z}^*$.

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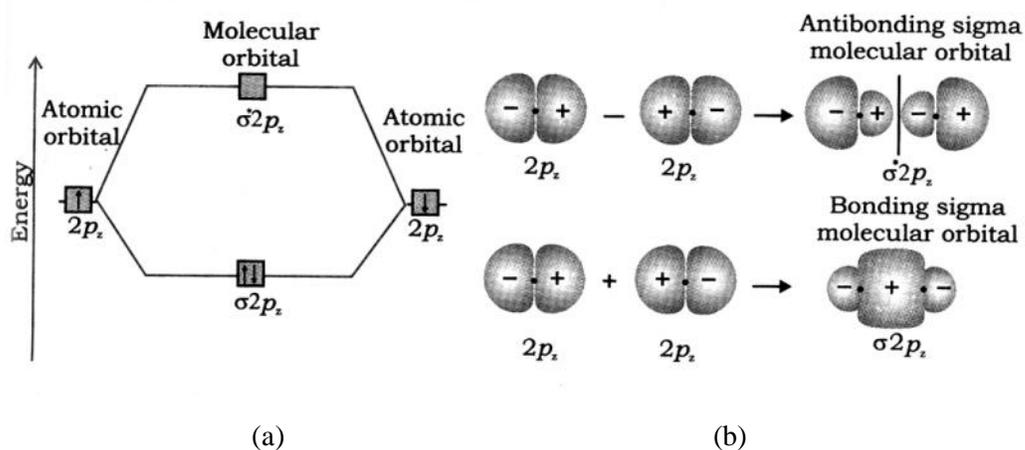


Fig.5.12: Overlapping of two $2p_z$ orbitals to give molecular orbitals

Combination of a p_z -orbital with either a p_x or a p_y orbital would not lead to any bonding. On the other hand a p_x orbital will combine with a p_x and the p_y with a p_y as shown in fig. 5.13.

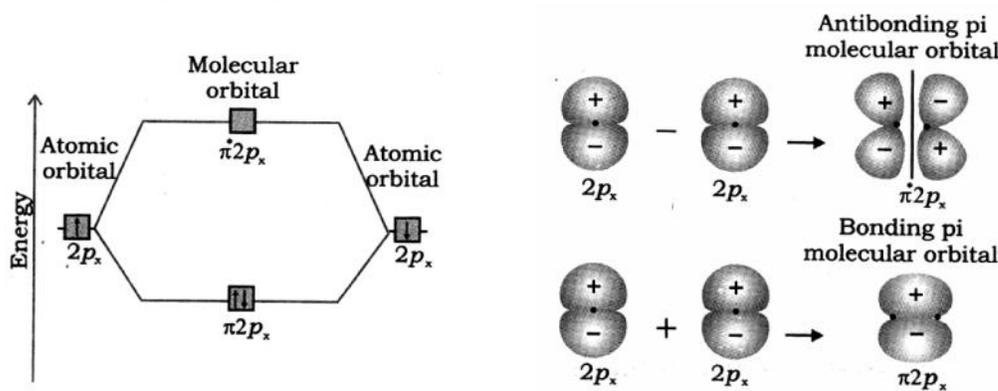


Fig 5.13 : Formation of molecular orbitals from two $2p_x$ atomic orbitals.

You may note here that these orbitals combine in a lateral fashion and the resulting molecular orbitals are not symmetric around the bond axis. These MO's are called π - molecular orbitals. These have large electron density above and below the internuclear axis. The anti-bonding π orbital, $\pi^* 2p_x$ (or $\pi^* 2p_y$) have a node (a region of zero electron density) between the nuclei.

The molecular orbitals obtained as a result of combination of respective AO's of two atoms can be represented in the form of following energy level diagram, Fig 5.14(a). The MO's obtained from the combination of 1s orbitals are not shown.(these belong to the inner core and are completely filled) The electrons in these molecular orbitals are filled in accordance with Aufbau principle and Hund's rule.

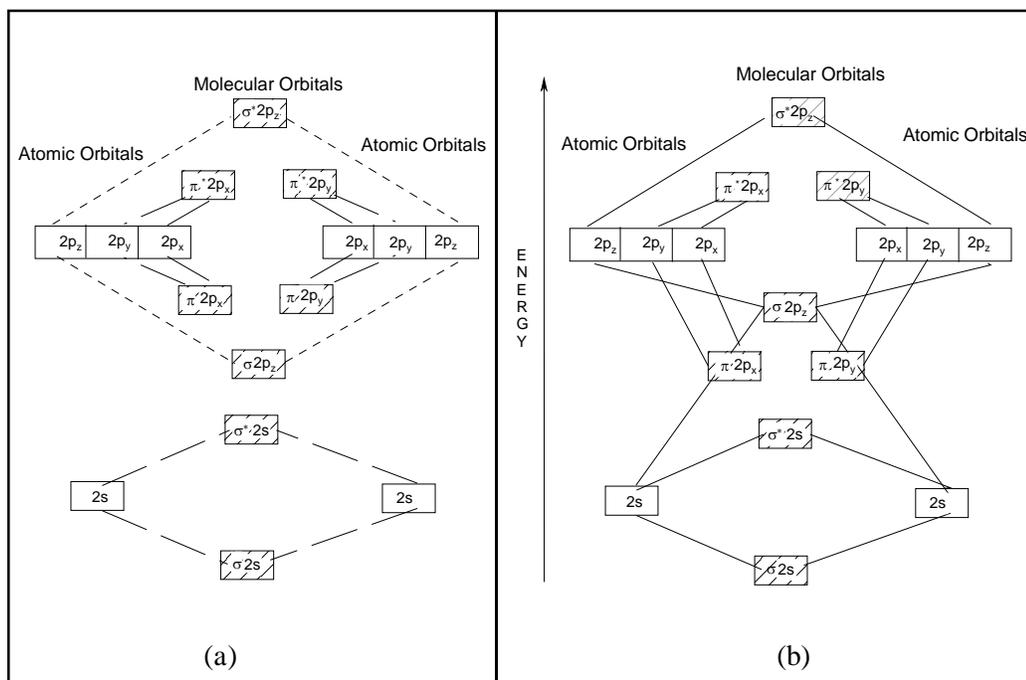


Fig.5.14: Molecular orbital energy level diagrams a) for O_2 and F_2 and b) for diatomic orbitals of lighter elements Li, Be, B, C and N

However, this energy level diagram is valid for the diatomic molecules O_2 and F_2 only; For the diatomic molecules of the lighter elements like, B, C and N this energy level diagram is somewhat modified. It is so because in case of lighter elements the difference in the energy of 2s and 2p orbitals is very low and s and p orbitals on the two atoms get mixed up. In place of normal pure 2s-2s or 2p-2p combinations we may have s-p combinations; for example 2s orbital of first atom can have a reasonable overlapping with $2p_z$ orbital of the second atom and vice versa. The modified energy level diagram is given in Fig 5.14 (b).

5.5.2.2 MO Electronic Configuration and Properties of the Molecule

The MO energy level diagram discussed above can be used to find out the MO electronic configuration of the molecule. This in turn provides the information about some properties of the molecule. Let us take the example of nitrogen molecule. An atom of nitrogen has five valence electrons; since there are two atoms, we have a total of ten valence electrons that need to be filled in the MO's. Using Fig.5.14, the MO electronic configuration can be written as $\sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2, \pi 2p_y^2, \sigma 2p_z^2$

Bond order : $\frac{1}{2} [n_b - n_a] = \frac{1}{2} [8 - 2] = \frac{1}{2} [6] = 3$; this means that in nitrogen molecule, a triple bond exists between the two nitrogen atoms.

Magnetic nature: molecules show magnetic behaviour depending on their MO electronic configuration. If all the MO's are **doubly occupied** the substance shows **diamagnetic** behaviour. In case one or more MO's are **singly occupied**, the substance shows **paramagnetic** behaviour. The MO electronic configuration of O_2 (with 12 valence electrons) is $\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^1, \pi^* 2p_y^1$; Since it contains

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unpaired electrons, oxygen shows paramagnetic behaviour. This has been found to be so experimentally also. In fact, the explanation of the paramagnetic behaviour of oxygen is an achievement of MOT.

The bond order and the magnetic behaviour of the molecular cations and anions can also be obtained in the same way. In such cases we add one electron for every negative charge and for every +ve charge we subtract an electron. For example, O_2^{2-} (oxygen molecule dianion) would have a total of 14 valence electrons (12 + 2) while oxygen molecule cation O_2^+ would have $12 - 1 = 11$ valence electrons.



Intext Question 5.4

1. What is the basic difference between the valence bond and molecular orbital theories?
.....
2. Calculate the bond orders for Li_2 and Be_2 molecules using the molecular orbital diagrams given in Fig. 5.12.
.....
3. Predict the magnetic behaviour of O_2 .
.....



What You Have Learnt

- A chemical bond may be visualised as an effect that leads to the decrease in the energy of the combination of two atoms when they come closer.
- The atoms combine in such a way so as to attain stable electronic configuration of noble gases.
- According to Kossel, transfer of an electron from one atom to the other achieves the stable configuration. This leads to formation of ions, which are held together by electrostatic interactions called ionic bond.
- According to Lewis, the stable configuration is achieved by sharing of electron pairs between the bonding atoms. This leads to the formation of a covalent bond.
- Bonding in simple molecules can be conveniently represented in terms of Lewis electron-dot structures.
- In some covalently bound atoms the shared pair of electron is more towards the atom with greater electronegativity and leads to partial ionic character in the molecule.
- Valence shell electron pair repulsion (VSEPR) theory is very helpful in predicting the shapes of simple molecules. It is based on the interactions between the electron pairs around the central atom in the molecule.
- Valence bond theory (VBT) and Molecular orbital theory (MOT) are two modern theories of chemical bonding. These are based on the wave mechanical model of atom.



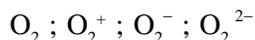
- According to the valence bond theory the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The overlap increases the electron charge density in the inter-nuclear region.
- In order to explain bonding in molecules containing more than two atoms, Pauling proposed the concept of hybridisation. In hybridisation, the atomic orbitals of the valence shell of the central atom 'hybridise' or merge and give newer orbitals with proper orientations, which explain the shape of the molecule.
- According to the Molecular orbital theory the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals. These molecular orbitals extend over the entire region of the molecule i.e., these are delocalised over the whole molecule.
- When two atomic orbitals combine it gives a pair of molecular orbitals; one is called bonding molecular orbital of lower energy and the other of higher energy is called anti-bonding orbital.
- The electrons present in the molecule are filled in these orbitals in the order of increasing energy (Aufbau principle) to give the MO electronic configuration.
- The number of bonds between the two atoms is called bond order and is defined as $\text{Bond order} = \text{b.o.} = \frac{1}{2}(n_b - n_a)$
- The MO electronic configuration can be used to predict the magnetic nature of the molecule. If all the MO's are doubly occupied the substance shows diamagnetic behaviour and if one or more MO's are singly occupied the substance shows paramagnetic behaviour.

**Terminal Exercise**

1. What do you understand by a chemical bond?
2. Explain the process of bond formation as a decrease in energy.
3. What do you understand by the term, 'bond length' ?
4. Describe the two possible ways in which the noble gas electronic configuration is achieved in the process of bond formation.
5. What are Lewis electron-dot symbols ? Show the formation of MgCl_2 in terms of Lewis symbols.
6. Define a coordinate bond and give some examples.
7. What is VSEPR theory ? predict the shape of SF_6 molecule using this theory.
8. Why do we need the concept of hybridisation ? How does it help in explaining the shape of methane ?
9. Give the salient features of molecular orbital theory.
10. Be_2 molecule does not exist. Explain on the basis of molecular orbital theory.



11. Write down the molecular orbital electronic configuration of the following species and compute their bond orders.



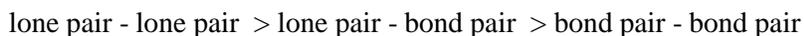
Answers to Intext Questions

5.1

- An electrovalent bond is formed when one or more electrons are transferred from one atom to another atom or atoms.
- $$:\ddot{\text{N}}\cdot + \cdot\ddot{\text{N}}: \longrightarrow :\ddot{\text{N}}:\ddot{\text{N}}: \longrightarrow :\text{N}\equiv\text{N}:$$
- In a covalent bond the shared pair of electrons is closer to the more electronegative atom. This leads to charge separation in the molecule and the bond becomes polar
- A bond in which both the bonding electrons are contributed by one atom only.

5.2

- The two postulates of VSEPR theory are
 - The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion
 - The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is stronger than that between two bond pairs. The order of repulsive force between different possibilities is as under.



- In methane the central carbon atom would have four pairs of electrons in its valence shell. According to VSEPR theory these would be placed tetrahedrally around the carbon atom. Hence the methane molecule would have a tetrahedral shape.

5.3

- Hybridisation is a concept which is quite useful in explaining the shapes of molecules. According to this two or more than two non equivalent orbitals with comparable energies and different shapes mix and give rise to an equal number of equivalent hybrid orbitals. The hybrid orbitals have identical energies and shapes.
- In ammonia the 2s and three 2p orbitals hybridize to give four sp^3 hybridized orbitals. Three of these overlap with the 1s orbitals of hydrogen and one remains nonbonding containing a lone pair. The sp^3 hybridized orbitals are directed towards the corners of a regular tetrahedron. But due to the difference in the repulsion between lone pair - bond pair and bond pair - bond pair the ammonia molecule has a distorted tetrahedral shape which is some what like a trigonal pyramid.

5.4

- Valence bond theory visualises the bond formation to be localized whereas according to MOT it is delocalised.

2. Bond order = b.o. = $\frac{1}{2}(n_b - n_a)$
for Li_2 ; Bond order = $\frac{1}{2} [4-2] = \frac{1}{2} [2] = 1$
for Be_2 ; Bond order = $\frac{1}{2} [4-4] = \frac{1}{2} [0] = 0$
3. MO configuration of O_2 is $\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2$
 $\pi^* 2p_x^1 = \pi^* 2p_y^1$
Due to 2 unpaired electrons O_2 molecule is paramagnetic.

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Notes