3 CHEMICAL BONDING

Student Learning Outcomes [C-11-A-01 to C-11-A-25]

After studying this chapter, students will be able to:

- Analyze the formation of dative bond in CO, ozone and H_3O^+ ion (resonance structures are not required). (Understanding)
- Recognize that molecular ions/polyatomic ions can have expanded octets e.g., sulphate and nitrate. (Understanding)
- Use the differences in Pauling electronegativity values to predict the formation of ionic and covalent bonds. (Application)
- Use the concept of electronegativity to explain bond polarity and dipole moments of molecules. (Understanding)
- Explain the importance of VSEPR theory in the field of drug design by discussing how the shape and bond angles of the molecules help chemist predict their interactions in the body. (Understanding)
- Describe the shapes and bond angles in molecules using VSEPR theory (including describing sketching). (Understanding)
- Predict the shapes, and bond angles in molecules and ions. (Understanding)
- Explain valence bond theory. (Understanding)
- Describe covalent bonding in molecules using the concept of hybridization to describe sp, sp^2, and sp^3 orbitals. (Understanding)
- Explain hybridization and types of hybridization. (Understanding)
- Explain the salient features of molecular orbital theory. (Understanding)
- Explain the paramagnetic nature of oxygen molecule in the light of MOT. (Understanding)
- Calculate bond order of N_2, O_2, F_2, and He_2. (Understanding)
- Describe the types of van der Waals forces. (Understanding)
- Describe hydrogen bonding limited to molecules including ammonia and water. (Understanding)
- Use the concept of hydrogen bonding to explain the anomalous properties of water. (Understanding)
- Use bond energy values and the concept of bond length to compare the reactivity of covalent molecules. (Application)
- State that, in general, ionic, covalent, and metallic bonding are stronger than intermolecular forces. (Understanding)
- Define electronegativity as the power of an atom to attract electrons to itself. (Knowledge)
- Explain the factors influencing the electronegativities of elements in terms of nuclear charge, shielding by inner shells and subshells. (Understanding)
- Explain the trends in electronegativity across a period and down a group of the periodic table. (Understanding)

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A chemical bond is the force that holds together two or more atoms, molecules or ions. The properties of a substance depend on the type of the chemical bond between its atoms. The term chemical bond includes ionic, covalent, dative, metallic bonds, as well as inter-molecular forces, i.e. van der Waals forces. However, being weak enough, van der Waals forces are usually not termed as pure chemical bonds. In this chapter, we shall discuss the types of bonds in the light of electronegativity and its effect on the nature of bonding, dipole moment, and polarity. Then, the modern bonding theories such as VSEPR, VBT, Hybridization, and MOT will be discussed in detail. The intermolecular forces, i.e. van der Waals forces will also be taken into account. Finally, a comparison of the chemical bonds and intermolecular forces will be presented in terms of bond energies.

NaCl has ionic bond and is solid, but water is a covalent compound and liquid

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3.1 TYPES OF BONDING

Lewis concept of bonding gives a simple explanation of the formation of all types of bonds. According to this theory, atoms make bonds to complete their outermost shells to have noble gas-like configuration. This is mostly attained through the formation of an octet in the valence shell.

3.1.1 Ionic Bond

According to the Lewis theory, the ionic bond is formed by the complete transfer of electrons from an atom with low ionization energy to another atom with high electron affinity. The Na atom ($_{11}$Na = 2,8,1) tends to lose the outermost electron to form Na^+(2, 8) ion, which has the electronic configuration of $_{10}$Ne, a noble gas nearest to it. Chlorine atom Cl (2,8,7) gains one electron to form the chloride ion, Cl^- (2,8,8) , also gaining the next noble gas electronic arrangement. The oppositely charged Na^+ and Cl^- ions are held together by strong ionic bond in the crystal of NaCl.

A similar type of bond is expected between group 1and 2 metals and groups 16 and 17 elements.

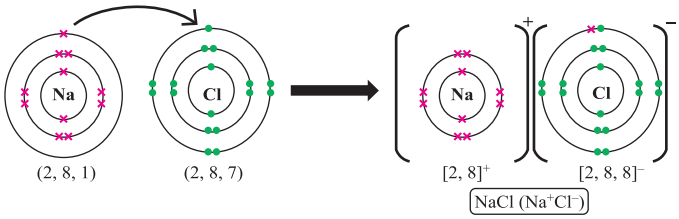

Figure 3.1 Ionic bond formation between Na and Cl

3.1.2 Covalent Bond (Electron Pair Bond)

A covalent bond is formed by the mutual sharing of electrons between two atoms. While sharing electrons, each atom completes its valence shell and attains the nearest noble gas configuration. The bond formation between two Cl atoms is shown below in **Figure 3.2**. A covalent bond may be non-polar or polar in character. The bond between two Cl atoms is purely covalent and non-polar. The electronegativity of the two atoms is exactly the same, due to which, the bonded atoms remain electrically neutral and there is no charge on either atom. The other such molecules are H_2 F_2, Br_2 and I_2 . Examples of polar covalent bonds are H–Cl, H-Br, H_2O, etc.

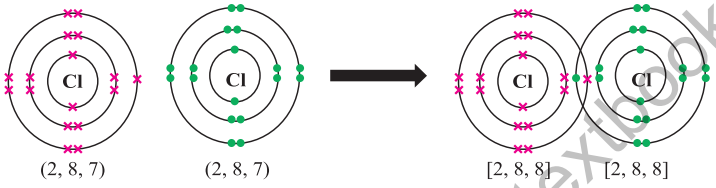

Figure 3.2 Formation of a covalent bond between two Cl atoms

3.1.3 Dative bond (Coordinate Covalent Bond)

A **dative bond** is formed between two atoms when the shared pair of electrons is donated by one of the bonding atoms. Let us consider the example of bond formation between H_2O and a proton (H^+). H_2O has two covalent bonds and there are two lone pairs of electrons on the oxygen atom. On the other hand, the proton is deficient in electrons. Therefore, the oxygen atom can donate its lone pair of electrons to the acceptor H^+, and this results in the formation of a dative bond as in the **Figure 3.3(a)**.

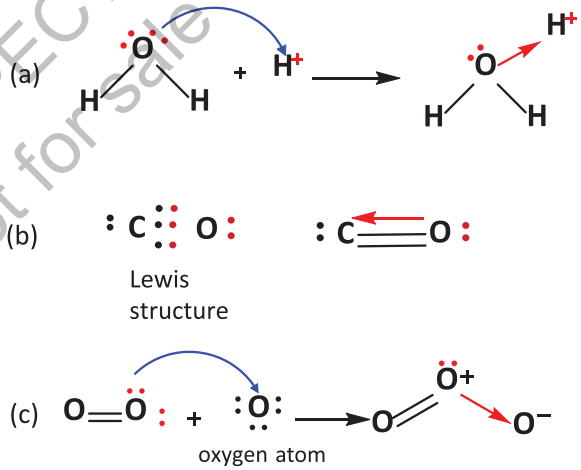

Figure 3.3 Dative bond formation (a) oxonium (hydronium) ion, (b) carbon monoxide, (c) ozone molecule

Carbon monoxide also contains a dative bond between oxygen and carbon atoms. Oxygen shares its two valence shell electrons with the carbon atom to make a normal double covalent bond. However, the valency of carbon is not satisfied with these bonds. It needs one more pair of electrons to complete its octet. Oxygen atom donates one of its lone pairs for the formation of a covalent bond, which is a dative bond as exhibited in **Figure 3.3(b)**. The structure of ozone molecule is presented in **Figure 3.3(c)**. It is formed by a reaction between the oxygen molecule with an oxygen atom (a free radical (O)). One of the oxygen atoms in the molecule donates a pair of electrons to make a coordinate covalent bond with this free radical. Therefore, the central atom has total three bonds including a double covalent bond

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on one side and a coordinate covalent bond on the other. It carries a positive charge, while the oxygen atom that accepts the lone pair carries a negative charge.

Quick Check 3.1

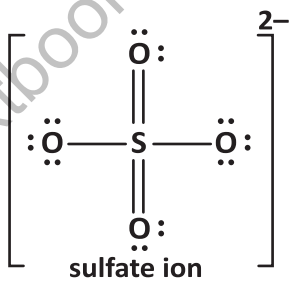
a) Draw the Lewis structures of N_2 and CS_2 molecules?

b) How many electrons are there in the valence shell of B in BF_3? Does it have the ability to accept a lone pair of electrons?

c) Show the formation of a dative bond between NH_3 and BF_3.

3.1.4 Expanded Octet in Polyatomic Ions

Polyatomic ions are the ions composed of more than one type of atoms. There formal charge is the net charge on them which is calculated based on the number of electrons in their valence shells after the formation of bonds. With the exception of ammonium ion (NH_4^+), these ions mostly carry a negative charge, for example the carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), and nitrate (NO_3^{3-}) ions. In some polyatomic ions, the central atom violates the octet rule by expanding its electron density to the higher orbitals. These are said to have **expanded octets**. Some prominent examples are SO_4^{2-}, ClO_4^-, PO_4^{3-}.



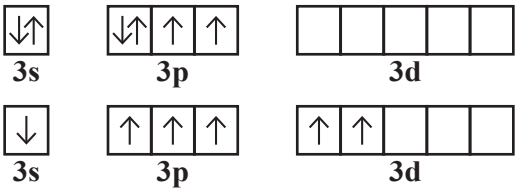
From the Lewis structures of SO_4^{2-}, we can calculate the number of electrons around the central S atom.

The number of electrons in the valence shell of S atom can be calculated as:

No of valence electrons = 2 × (no. of double bond electrons) + 2 × (no. of single bond electrons)

$$= 2(4) + 2(2) = 12$$

Thus, S has 12 electrons in its valence shell and it exceeds the octet by 4 electrons. The expansion of octet is caused by the involvement of the d orbital in bonding, which can accommodate the extra electrons. The following electronic configuration of native S(0) atom shows that it has two unpaired electrons in the p orbitals. The presence of d-orbital allows this configuration to extend to 4 unpaired electrons by the transfer of one electron from 3s and one from the 3p electron pair. It explains not only the variable oxidation states of S, but also the possibility of accepting extra electrons in its d orbital.



In the same way, we can calculate the number of valence electrons around the central iodine atom in the tri-iodide ion. The Lewis structure of the ion is given by:

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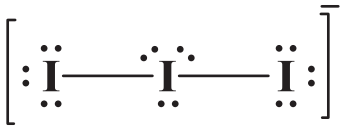

The number of valence electrons of the central atom can be calculated as follows,

No of valence electrons = 2 × (no. of single bond electrons) + 2 × (no. of lone pairs)

= 2 (2) + 2 (3)

= 10

The central iodine atom in tri-iodide ion (I_3^-) has 10 electrons in the valence shell and the octet expands by two electrons.

Quick Check 3.2

a) Can the elements of period 2 of the periodic table have expanded octet? Explain why or why not.

c) Predict and explain the expanded octets in the following ions: ClO_3^-, PO_4^{3-}.

3.2 ELECTRONEGATIVITY AND THE TYPE OF BOND

The concept of electronegativity has been discussed in detail in chapter 1. Here we will discuss the effect of electronegativity on the type of bonding. The difference in electronegativity of two bonded atoms provides an approximate measure of the bond polarity and an indication of the type of bond. When this difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The following figure diagrammatically depicts the change in the nature of bond with electronegativity difference. Two atoms having electronegativity difference less than 0.4 are said to make a pure covalent bond. An electronegativity difference between 0.4 and 1.8 corresponds to a polar covalent bond, whereas, above this value the bond between two atoms will be ionic in nature. The electronegativity differences between the atoms in the bonds such as H–H, H–Cl, and NaCl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. This is why H-H bond is purely non-polar, H-Cl a polar covalent bond, whereas NaCl is an ionic compound as shown in **Figure 3.4.**

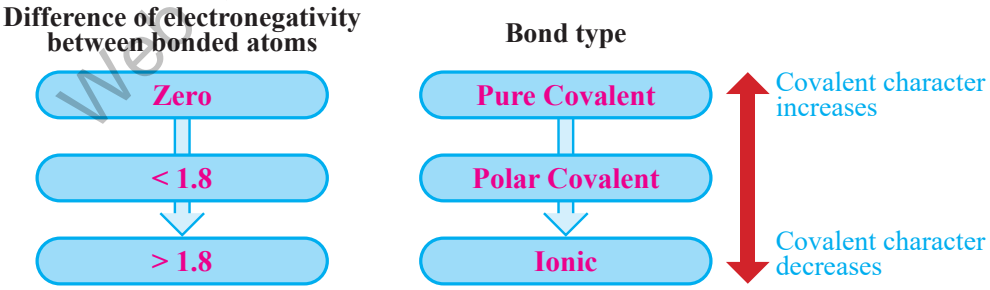

Figure 3.4 Variation of the nature of bond with the electronegativity difference

Quick Check 3.3

a) Predict with the help of electronegativity values whether the bonds in these compounds would be non-polar covalent, polar covalent, or ionic.

i) HF ii) KI iii) CaF_2 iv) ICl v) Br_2

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3.2.1 Dipole Moment and Polarity of Molecules

In compounds such as HF, where the bonded atoms are from different elements, the electronic distribution between the atoms is uneven. Due to this reason, one atom carries partial positive and the other partial negative charge. A molecule with δ+ charge on one part and δ- charge on the other part is called a **dipole** and such a molecule is said to have a **dipole moment**. It is a quantitative measurement of the polarity of a bond or a molecule. The dipole moments of diatomic molecules like HF, HCl, HBr, HI, NO, etc. are directed from the positive ends (δ+) to negative ends (δ-) as in **Figure 3.5**. Dipole moment is measured in Debye unit (D). Higher dipole moment indicates higher polarity in a molecule.

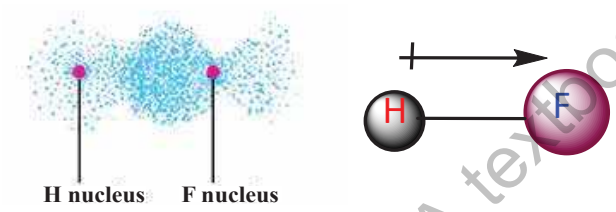
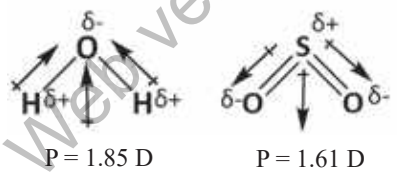
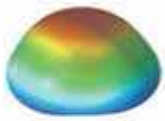


Figure 3.5 Electron density in HF is higher near the F atom and the dipole moment is directed from H to F

For compounds having more than two atoms, the dipole moment depends on the structure of the molecule. The dipole moment of water is 1.85 D which is directed from the end having two hydrogen atoms to the end with the oxygen atom as in the structure shown in **Figure 3.6**. A linear H_2O molecule (H-O-H) would have zero dipole moment. The non-zero dipole moment value shows that water is a non-linear molecule. Experiments reveal that the water molecule has a v-shaped structure. In contrast, SO_2 has a dipole moment of 1.61 D and in opposite direction to that in water. H_2S is also a non-linear molecule as the individual bonds are polar, but they don't cancel each other's dipole moment and the overall molecule has some dipole moment.





Electron density map of the water molecule. Red represents the rich oxygen region, and blue represents the electron-deficient hydrogen end. Dipole moment is from blue to red

Figure 3.6 Vector addition of individual bond moments in angular H_2O and SO_2 molecules

However, some molecules have net zero dipole moments as the symmetry in their structures causes the cancellation of the individual bond moments. For example, $BeCl_2$ is a linear molecule having two similar Cl atoms on both sides of the central atom at 180°. The individual Be-Cl bond moments are cancelled out as they are opposite in direction and equal in amount. Similarly, CCl_4 has four C-Cl bonds which are expected to have high polarity due to a large electronegativity difference between C and Cl atoms. The bond moments associated to the four C-Cl bonds are directed in such a way that they cancel each other. The net dipole moment of the CCl_4 molecule is zero making it a non-polar

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molecule. The CCl_4 molecule is perfectly tetrahedral. Similarly, BF_3 has a trigonal planar symmetrical structure and its dipole moment is also zero. As a rule, the molecules that have same ligands (atoms or groups of atoms with the central atom) in a regular geometry, the individual dipole moments may not be zero, but the molecule has net zero dipole moment as shown in **Figure 3.7**. Such molecules are said to be non-polar.

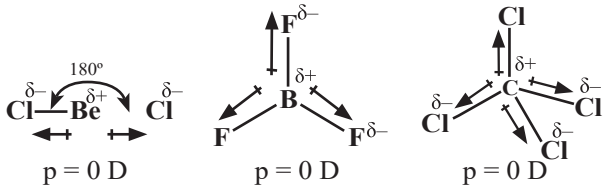

Figure 3.7 The individual bond moments in symmetrical molecules; $BeCl_2$, BF_3 and CH_4 are cancelled out to give zero net dipole moment.

Quick Check 3.4

a) Can you explain why CO has a dipole moment but CO_2 does not have any?

b) Do you think that individual bonds in CCl_4 are polar? Explain in terms of the electronegativity difference. What about the polarity of overall CCl_4 molecule?

c) Are the following molecules polar or non-polar? Briefly give reasons. HF, CH_2Cl_2, O_2, H_2S

3.3 INTERMOLECULAR FORCES

Intermolecular forces are also considered as binding forces just like chemical bonds. However, the attraction between the molecules is much weaker than the chemical bonds. These forces are believed to exist between all kinds of atoms and molecules when they are sufficiently close to each other. Such intermolecular forces are called van der Waals forces. These intermolecular forces bring the molecules close together and give particular physical properties to the substances in gaseous, liquid, and solid states.

Three types of such forces are mentioned here:

i) Instantaneous dipole-induced dipole forces or London dispersion forces

ii) Permanent dipole-permanent dipole forces

iii) Hydrogen Bonding

The detailed discussion on these forces will be made in the chapter on states and phases of matter (Chapter 5).

3.4 BOND ENERGY AND BOND LENGTH

The **bond energy** is the average amount of energy required to break all bonds of a particular type in one mole of a substance. It is determined experimentally by measuring the heat involved in a chemical reaction and its unit is kJ mol^{-1}. Bond energy is a measure of the strength of a bond and its reactivity. The strength of a bond depends upon the following factors.

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- Electronegativity difference of bonded atoms
- Size of atoms

The bond energies/enthalpies of some bonds are presented in **Table 3.1**.

Table 3.1 Average bond energies of some selected bonds in kJ mol^{-1}

Single bonds						Multiple bonds	
H-H	432	C-I	240	F-F	154	C=C	614
H-F	565	C-Cl	339	Cl-Cl	239	C≡C	839
H-Cl	427	C-N	305	Br-Br	193	O=O	495
H-Br	363	C-O	358	I-I	149	C=O	745
H-I	295	N-H	391	S-S	266	N≡N	941
C-H	413	N-O	201	Si-Si	340	C≡N	615
C-C	347	O-H	467	Si-O	452	N=O	607

Let us consider the role played by electronegativity difference. Look at the bond energies of H-X type of compounds, where X=F, Cl, Br, I. The data shows that the bond energy of a bond rises with the increasing electronegativity difference between the bonded atoms. As the difference in electronegativity increases, the bond polarity also becomes greater and this gives rise to additional attractive force for binding the atoms. This is why the bond energy for HF is higher (565 kJ mol^{-1}) than for HI (295 kJ mol^{-1}). It may be noted that energies of multiple bonds are greater than those of single bonds

C≡C > C=C > C-C

Bond length is the distance between the nuclei of two atoms forming a covalent bond. The bond lengths are experimentally determined by physical techniques, such as electron diffraction, X-ray diffraction, or spectral studies. The bond length of a bond is governed by many factors including electronegativity, size, and the nature of the covalent bond (single, double, or triple). Some selected bond lengths are given in **Table 3.2**.

Table 3.2 Bond lengths of some selected bonds

Bond	Bond length (pm)	Bond	Bond length (pm)
H-H	74	Si-F	155
H-Br	144	C-F	135
C-C	154	C-Cl	180
C=C	133	C-Br	196
C≡C	120	C-I	214
C=O	122	B-F	130
Si-H	146	B-Cl	175

With an increase in size of the atoms, the covalent bond length also increases. The C-Cl bond length is about 180 pm, whereas the C-F bond length is 135 pm. This is because the Cl atom is much larger. With the rise in electronegativity difference between the bonded atoms, the bond becomes shortened. For example, Si-F bond length in SiF_4 is found to be near 155 pm, whereas the calculation of Si-F bond from the covalent radii of Si and F (Si=117 pm and F=64 pm) is 181 pm.

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The electronegativity difference causes an ionic character in the covalent bond. The ionic character results in shortening of the bond length due to the additional attraction between the bonded atoms.

Quick Check 3.5

a) HI is a stronger acid and a robust reducing agent, whereas HF is a weaker acid. Explain.

b) Acetylene (HC≡CH) is more stable than ethene ($H_2C{=}CH_2$). Can you explain why?

3.5 A COMPARISON AMONG IONIC, COVALENT, METALLIC BONDS AND INTERMOLECULAR FORCES

Chemical bonds, i.e. ionic, covalent, and metallic bond are usually termed as true chemical bonds, as they affect the chemical properties of a substance. This is because of certain reasons. Firstly, chemical bonds result in the formation of new species through transfer and sharing of electrons. Whereas, intermolecular forces act to bring molecules closer and influence the physical properties. However, such a clear distinction between the chemical bonds and intermolecular forces is not possible. The distinctive feature of the chemical bonds and intermolecular forces is their bond strength. The strength of a force is measured by the bond energy. **Table 3.3** provides a comparison among different chemical bonds and intermolecular forces.

Table 3.3 Relative strengths of chemical bonds and intermolecular forces

Bond Type	Bond Energy ($kJ\ mol^{-1}$)
Ionic bond in NaCl	760
O-H bond in water	464
Hydrogen bonding	20-50
Permanent dipole- Permanent dipole force	5-20
Van der Waals forces	1-20

The bond energy of ionic bond (sodium chloride, 760 kJ mol$^-$) is highest, followed by covalent bond (O-H = 464 kJ mol$^-$), and average hydrogen bond energy (20-25 kJ mol$^-$). It shows that the ionic bond is the strongest form of chemical bonding. It also reveals that chemical bonds are generally much stronger than intermolecular forces. The permanent dipole-dipole forces (5-20 kJ mol$^-$) and London dispersion forces (1-20 kJ mol$^-$) are even weaker as indicated by their low bond energies. The metallic bond is mostly elaborated in terms of electrostatic forces, although some theories suggest that it may be of covalent nature. In any case, the metallic bond is weaker than both the ionic and covalent bonds. The average bond energy of the metallic bond is 100-150 kJ mol$^-$. A satisfactory argument for the low strength of metallic bond is extensive delocalization of electrons within the metallic crystal.

3.6 VALENCE BOND THEORY (VBT)

The VSEPR model predicts and explains the shapes of molecules but does not give reasons for the formation of bonds. VBT is concerned with both the formation of bonds and the shapes of molecules. This method of describing a covalent bond considers a molecule as a combination of atoms. The postulates of VBT are given below

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- A covalent bond is formed when half-filled orbitals in the valence shells of two atoms with similar energy overlap.
- A greater overlap of the orbitals results in a stronger bond.
- Covalent bonds are directional. The direction of the bond is determined by the shape and mode of the overlapping orbitals.

3.6.1 Formation of Sigma Bond

A sigma bond is formed by the linear overlap of two half-filled atomic orbitals on adjacent atoms. The orbitals approach each other on the nuclear axis. Both s and p orbitals can overlap head-on to form sigma bonds.

s-s Overlap

The 's' orbital of one atom overlaps with the s-orbital of the other to give a bond orbital. This type of overlap occurs during the formation of the H_2 molecule, where each hydrogen atom has a half-filled 's' orbital.

After the bond formation, the electrons are paired up and the electron density in this molecule is symmetrical around the two nuclei as in **Figure 3.8.**

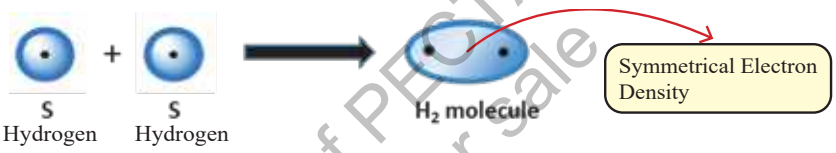

Figure 3.8 Overlap between s orbitals of two hydrogen atoms to form the H_2 molecule

s-p Overlap

The s orbital of one atom can overlap with the p orbital of the other to form a covalent bond (σ). For example, in HCl molecule, a half-filled s orbital of hydrogen overlaps with a half-filled p orbital of chlorine as shown in **Figure 3.9**. The electron density is higher close to the Cl atom due to its higher electronegativity value. This is why HCl is a polar molecule.

Fig. 3.9 Formation of σ bond by s-p overlap

p – p Overlap

An example of this type of overlap is the formation of the Cl_2 molecule where 'p' orbitals of two chlorine atoms overlap on the nuclear axis. The electron density is symmetrical around the nuclei of the two Cl atoms because both have same value of electronegativity.

Interesting Information!

The bond angle in H_2O is 104.5°, whereas in H_2S, it is 92°. This is because the orbitals of S are larger and the lone pair exerts a stronger repulsion.

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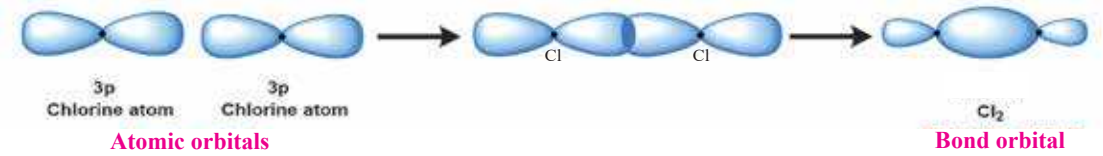

Figure 3.10 Overlap of p and p orbitals to form Cl_2 molecule according to VBT

The H_2S molecule is a non-linear molecule which is formed by the combination of one sulfur and two hydrogen atoms. The two 3p (say $3p_y$ and $3p_z$) orbitals of sulfur containing one electron each can overlap with the 1s orbitals of two hydrogen atoms. A V-shaped molecule is thus formed having a bond angle of 92° as in **Figure 3.11.**

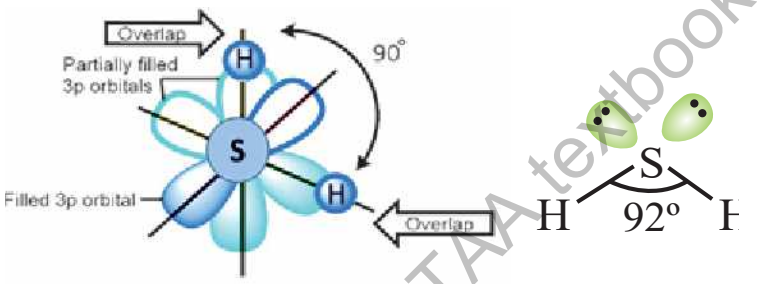

Figure. 3.11 The formation of H_2S molecule by H and S orbitals overlap

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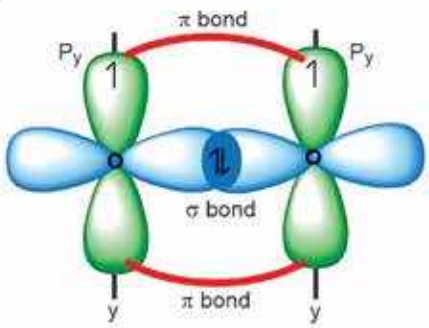
Formation of π bond

Consider the formation of a double covalent bond between oxygen atoms (O=O). There are two unpaired electrons on each atom in perpendicular p orbitals (say P_x and P_y). The p_x orbitals on the two oxygen atoms are oriented in such a way that they overlap end-to-end linearly. The linear overlap of the p_x orbitals gives a σ bond. However, the p_y orbitals on both atoms are aligned parallel to each other. They overlap in a parallel way so that the two p lobes overlap above the plane of the nuclei and the other two lobes below the plane as shown in **Figure 3.12**. This results in the formation of **π** bond. The oxygen atoms are doubly bonded through σ and **π bonds**.



O ═ O

Figure 3.12 Formation of double bond (σ and π) between oxygen atoms

Quick Check 3.6

a) Draw the orbital structures of H_2O and N_2 molecules.
b) Draw the orbital overlap to show the formation of F_2 and HF molecules

3.7 ATOMIC ORBITAL HYBRIDIZATION

A process in which atomic orbitals of slightly different energies and shapes are mixed together to form a new set of equivalent orbitals of same energy and same shape is called hybridization.

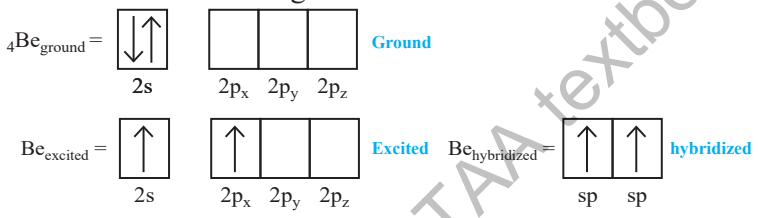
Keep in Mind

- Hybridization is a process of mixing of orbitals in a single atom (or ion).
- Only orbitals of comparable (relatively close) energies can be mixed to form hybrid orbitals.
- The number of mixing orbitals is always equal to the number of the resulting hybrid orbitals.

3.7.1 Types of Hybridization

sp Hybridization

In sp hybridization, one s (low energy and spherical) and one p orbital (high energy and dumb-bell shaped), intermix to give a new set of two orbitals of same energy and same shape called sp hybrid orbitals. These sp hybrid orbitals are arranged in linear geometry and oriented at 180º. The electronic configuration of the outermost shell of Be is as follows:



The two sp hybrid orbitals lie linearly as in **Figure 3.13**. The sp hybridization explains the geometry of linear molecules such as beryllium chloride, $BeCl_2$. It is formed when two sp hybrid orbitals of Be atom overlap with the half-filled p-orbitals of chlorine atoms.

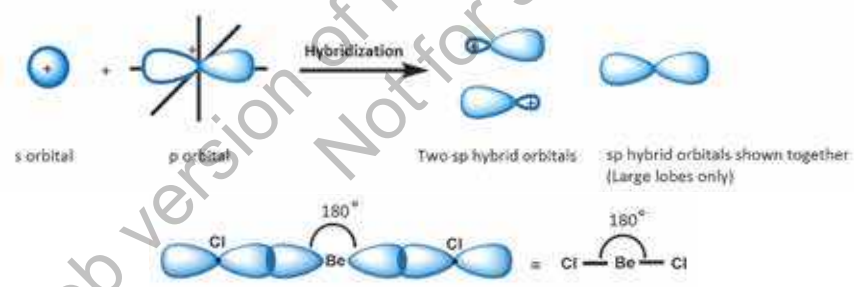


Figure 3.13 Mixing of s and p orbitals to give two hybrid sp orbitals and the formation of $BeCl_2$

sp^2 HYBRIDIZATION

In sp^2 hybridization, one s and two p atomic orbitals of an atom intermix to form three orbitals called **sp^2 hybrid orbitals**. The three half-filled sp^2 hybrid orbitals are arranged in a trigonal planar geometry with bond angles of 120° as in **Figure 3.14**.

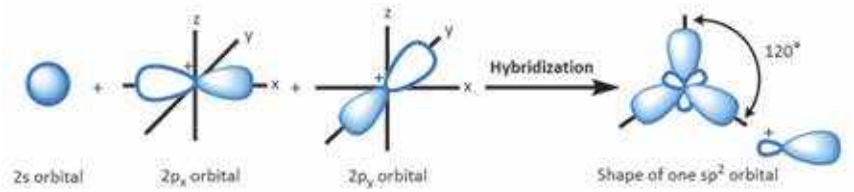


Figure 3.14 Formation of sp^2 hybrid orbitals from atomic orbitals

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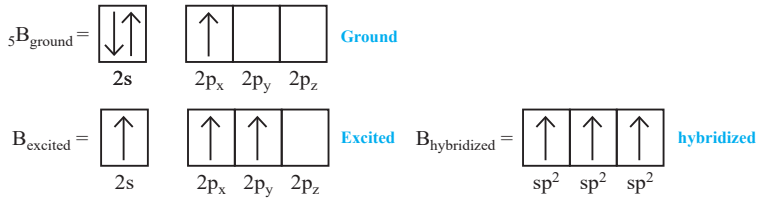
The sp^2 hybridization explains the geometry of planar molecules such as BF_3. Electronic configuration of $_5B$ is:



The three outermost orbitals of B mix together to give three sp^2 hybrid orbitals. On the other hand, one of the p orbitals of fluorine is half filled (e.g. $2p_z$). BF_3 is formed by the overlap of three half-filled sp^2 hybrid orbitals of boron with $2p_z$ orbitals of three fluorine atoms. The structure is trigonal planar with bond angles equal to 120°, each as in **Figure 3.15**.

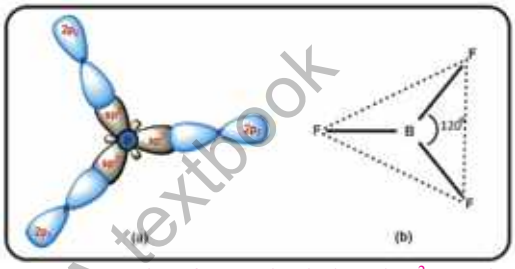
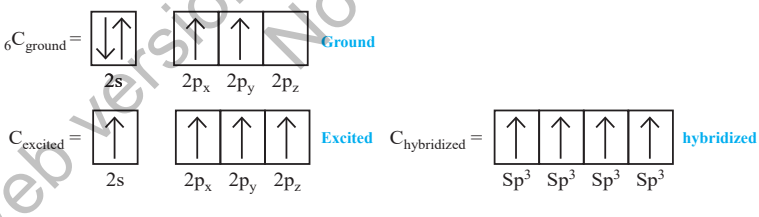


Figure 3.15 Formation of BF_3 molecule through sp^2-p overlap

sp^3 Hybridization

In sp^3 hybridization, one s-orbital (low energy and spherical) and three p-orbitals (high energy and dumbbell shaped), intermix to give a new set of four orbitals of same energy and same shape. Each of these hybrid orbitals is a sp^3 hybrid orbital. These hybrid orbitals are arranged in the tetrahedral geometry as shown in the example of CH_4 as in **Fig. 3.16.**

The electronic configurations of valence shell of $_6C$ in its excited and hybridized states are given as follows:



The energies of hybrid orbitals are lower than unhybrid orbitals. **Figure 3.13** shows the outermost four atomic orbitals of carbon mix up to give four hybrid orbitals of same energy and same shape.

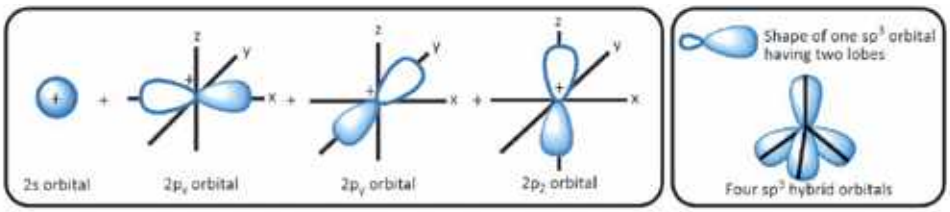


Figure 3.16 Formation of sp^3 hybrid orbitals of carbon in methane

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Did you Know?

Each sp^3 hybrid orbital consists of two lobes, one larger and the other smaller. For the sake of simplicity, the smaller lobe is usually not shown while representing sp^3 hybrid orbitals together.

The four new hybrid orbitals of equal energy have a tetrahedral geometry with carbon nucleus at the center. The methane molecule is formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms separately to form four sigma bonds. The four C-H bonds, which result from sp^3-s overlaps, are directed towards the corners of a regular tetrahedron.

3.8 VALENCE SHELL ELECTRON PAIR REPULSION MODEL (VSEPR)

The VSEPR model describes the shapes of molecules based on the electron pairs that surround the central atom. This model was presented by Sidgwick and Powell in 1940. It is based on the assumption that a molecule will take a shape such that the electronic repulsions among the valence electron pairs of that atom are minimum. In order to have the minimal repulsions, the electron pairs arrange themselves at farthest possible distances. This arrangement of the electron pairs determines the geometry of the resulting molecule.

Postulates

i. Both the lone pairs (non-bonded) as well as the bond pairs participate in determining the geometries of molecules.

ii. The electron pairs are arranged around the central atom so as to remain at maximum distance apart to avoid repulsions.

iii. The electrons of lone pairs occupy more space than the bond pairs. As a result, the non- bonding electron pairs exert greater repulsive forces on bonding electron pairs and, thus, tend to compress the bond pairs. The magnitude of repulsions between the electron pairs in a given molecule decreases in the following order:

Lone pair- lone pair (lp-lp) > lone pair -bond pair (lp-bp) > bond pair - bond pair (bp-bp)

An electron pair shared by two nuclei occupies less space than a lone pair bound by a single nucleus

iv. The two electron pairs of a double bond and three electron pairs of a triple bond, contain a higher electronic charge density, but they are regarded as single pairs.

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v. The presence of highly electronegative atoms with the central atom results in decreased electronic repulsions between the bond pairs, but stronger repulsion by the lone pair.

3.8.1 Predicting the Shapes of Molecules

In order to illustrate this model, the central atom is named 'A'. The electron pairs around 'A' are designated as 'B'. There may be different number of electron pairs around the central atom depending upon its valency. It gives rise to various types of molecules, such as AB_2, AB_3, AB_4, etc. The **electron pair geometry** of a molecule is determined by the total number of electron pairs around 'A'. Whereas, the actual **shape** of the molecule is determined by the atoms excluding the lone pairs. Following **Table 3.4** gives the possible shapes of different types of molecules having varying numbers of bond and lone pairs.

Table 3.4 Geometries and shapes of different systems of covalently bonded compounds

No. of electron pairs around central atom	No. of lone pairs	Electron pair geometry	Shape with respect to atoms	Angular separation of atoms	Examples
2	0	linear	linear	180°	CO_2, $BeCl_2$
3	0	trigonal	trigonal	120°	BCl_3, SO_3
3	1	trigonal	Angular, v- shaped	Less than 120°	SO_2 , $SnCl_2$
4	0	tetrahedral	tetrahedral	109.5°	CH_4, CCl_4
4	1	tetrahedral	pyramidal	Less than 109.5°	NH_3, H_3O^+
4	2	tetrahedral	Angular, v-shaped	Less than 109.5°	H_2O, OF_2
5	0	Trigonal bipyramidal	Trigonal bipyramidal	120°, 90°	PCl_5, I_3^-
6	0	octahedral	octahedral	90°	SF_6 , XeF_4

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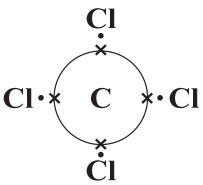
Steps to Determine the shapes of molecules.

The following steps are followed to predict the shape of a molecule.



- The least electronegative atom or the element with the least number of atoms is mostly selected as the central atom. For example, in CCl_4, the carbon atom is the central atom.
- The total number of electron pairs around the central atom are counted (including bond pairs and lone pairs). For example in CCl_4, the total number of bond pairs around the

C atom are 4 and it has no lone pair.

- The total number of electron pairs determines the electron pair geometry (as in the above table) of the molecule. For example, CCl_4 has total four electron pairs and its geometry is tetrahedral.
- Finally, the actual shape of the molecule is determined excluding the lone pairs (if any).

Keep in Mind

Number of electron pairs around the central atom are calculated as in the following example:

In NH_3,
Valence electrons in N = 5
Electrons shared by 3H = 3 x 1 = 3
Total number of electrons = 5 + 3 = 8
Total number of electron pairs = $\frac{8}{2} = 4$

Calculation for lone pairs on N
No. of lone pairs on N = Total no. of pairs – no. of bond pairs
No. of lone pairs on N = 4 – 3 = 1
Thus, N has 1 lone pair in NH_3.

AB_2 type Molecules (Linear geometry)

In such molecules, two electrons pairs around the central atom are arranged at an angle of 180º to minimize repulsions between them. Thus, they form a linear geometry as shown in **Figure 3.17**. $BeCl_2$ molecule is of AB_2 type with Be as the central atom and two bond pairs around it, but no lone pair. .

Figure 3.17 Linear shape of the $BeCl_2$ molecule

AB_3 type (Trigonal planar geometry)

In AB_3 type molecules, the central atom is surrounded by three electron pairs, which are arranged at maximum distance apart at an angle of 120° giving a trigonal geometry. For example, BF_3 molecule has a trigonal planar shape with each F-B-F bond angle of 120° **Figure 3.18**. The similar geometries are expected in the hydrides of group 3, i.e. AlH_3, GaH_3, BH_3, etc.

Figure 3.18 BF_3 is an AB_3 system having triangular planar geometry

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In $SnCl_2$, the Sn atom has 4 electrons in its outermost shell. It makes two bonds with two Cl atoms and the remaining two electrons exist as a lone pair **Figure 3.19**. One of the corners of the triangle is occupied by this lone pair, giving rise to a distorted trigonal electron pair geometry (in vapour phase). The actual shape of $SnCl_2$ is v-shaped and bond angle less than 120° due to the presence of a lone pair on Sn atom.

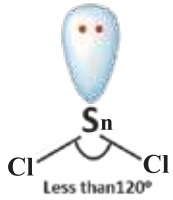

Figure 3.19 Shape of $SnCl_2$

AB_3-Type with Multiple Bonds

The molecule of SO_3 has all the three regions occupied by S=O bonds. The structure of SO_3 is perfectly trigonal with each angle equal to 120°. On the other hand, in SO_2, one corner of the triangle is occupied by a lone pair and the other two corners each by a double bond (S=O). Thus, it makes an angular or v-shaped structure just as $SnCl_2$ does as in **Figure 3.20**.

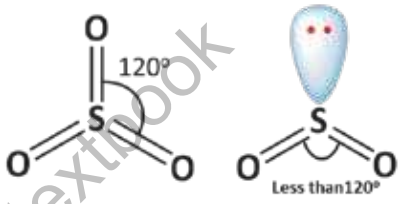

Figure 3.20 Shapes of multiply bonded SO_2 and SO_3

AB_4 Type (Tetrahedral geometry)

In this type of molecules the electron pair geometry is a regular tetrahedron. Each of the bond angles is of 109.5°. For instance, in methane, four bonded electron pairs are directed from the center towards the corners of a regular tetrahedron, as following **Figure 3.21**. On the same grounds, SiH_4, GeH_4, CCl_4 possess the similar shape.

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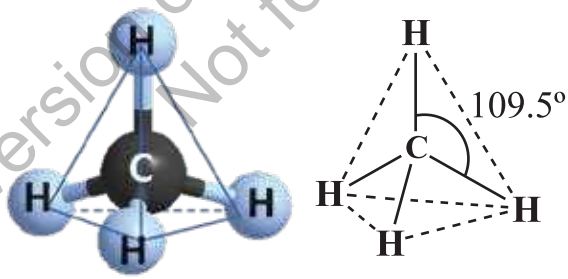

Figure 3.21 Regular tetrahedral shape of the CH_4 molecule

In the ammonia molecule (NH_3), there are three H atoms attached to the nitrogen atom having one lone pair. Due to a lone pair, the ideal angle 109.5° is reduced to 107° as in **Figure 3.22** Ammonia has triangular pyramidal shape. The substitution of hydrogen in NH_3 with electronegative atoms like F or Cl further reduces the bond angles.

In NF_3, three highly electronegative F atoms are bonded to the N atom.. The first reason being the strong polarity of N-F bond, due to which N atom pulls the lone pair closer to its nucleus. The lone pair exerts a stronger repulsion on bonding electrons. Moreover, the bond pairs (N-F bonds) are closer to F atoms than N atom. The increased distances in these bond pairs make their repulsions weaker and allow the bonds to come closer. The bond

angles are further compressed to 102.5°.

Figure 3.22 Distorted geometry and pyramidal shape of the NH_3 molecule

Experiments reveal that the water molecule (H_2O) is angular or v-shaped, although it has four electron pairs around the central atom. Two of the corners of the tetrahedron are occupied by two lone pairs and the remaining two by bond pairs. But, due to the greater repulsions of the lone pairs, the bond angle is reduced to 104.5° as in **Figure 3.23**.

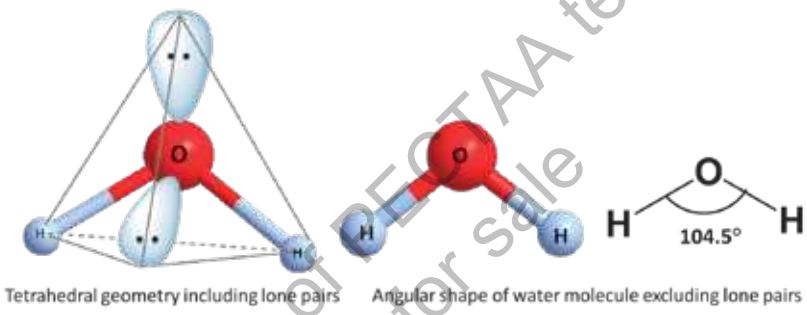

Figure 3.23 Water molecule has two lone pairs and is v-shaped with suppressed bond angle

The $[H_3O]^+$ ion is formed by the capture of a proton by a water molecule and it has the tetrahedral trigonal pyramidal shape. On the other hand, amid ion, $[NH_2]^-$, has a V–shaped structure as in **Figure 3.24.**

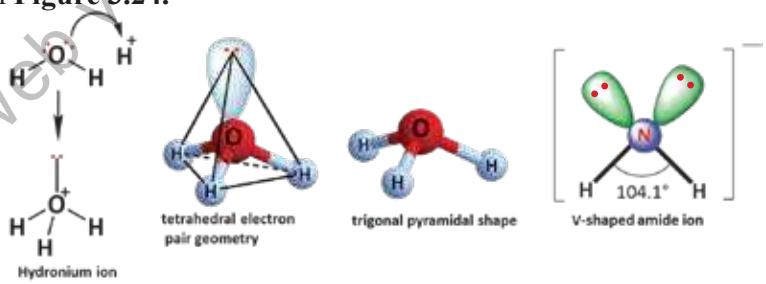

Figure 3.24 Shapes of hydronium (H_3O^+) and amide (NH_2^-) ions

Quick Check 3.7

a) Calculate the no. of lone pairs on the central atoms in the following: H_2O, ICl_3, I_3^-

b) Calculate the number of bond pairs and lone pairs in SiH_4, H_2Se, and PH_3.

c) Predict the shapes and angles in SiH_4, H_2Se, and PH_3.

d) Predict how the bond angle in H_2S would be different from that in H_2O.

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AB_5 type molecules (trigonal bipyramidal geometry)

AB_5 type molecules, have **trigonal bipyramidal** geometry. This is evident from the geometry of the PCl_5 molecule given in **Figure 3.25**. The angles within the plane are 120° and that between the axial atom and a planar atom is 90°.

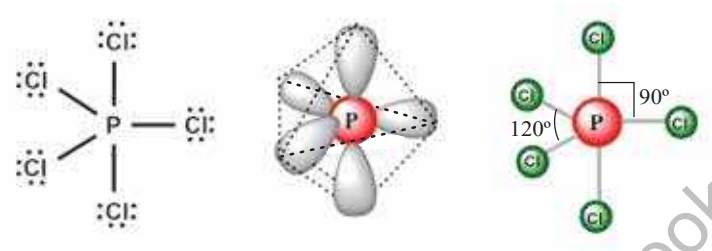

Figure 3.25 Lewis structure and shape of PCl_5 molecule

Tri-iodide ion $[I_3]^-$ is an AB_5 system. The central atom in this ion is the iodine atom. There are five electron pairs around the iodine atom including two bond pairs and three lone pairs. The lone pairs occupy the corners of the trigonal region and the iodine atoms occur vertically one being above and the second below the plane. The actual shape of the tri-iodide ion is linear and the iodine atoms are farthest apart at an angle of 180° as in **Figure 3.26.**

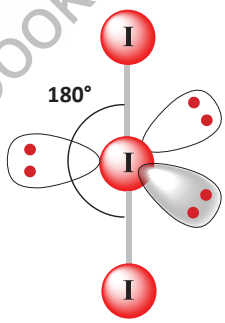

Figure 3.26 Shape of tri-iodide ion ($[I_3^-]$)

AB_6 type molecules (octahedral geometry)

AB_6 type molecules have 6 electron pairs around the central atom and the octahedral geometry. All the ABA angles in this type of geometry are of 90°. SF_6 is an AB_6 type molecule. The Lewis structure and the shape of SF_6 is given in **Figure 3.27**,

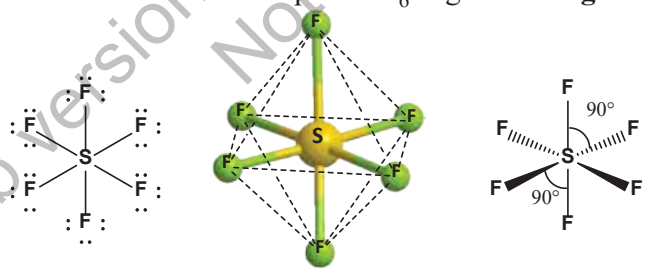

Figure 3.27 Lewis structure and octahedral shape of SF_6 with each angle of 90°

XeF_4 is an AB_6 type molecule with four bond pairs and two lone pairs. the two lone pairs remain at farthest distance at angle of 180°. Excluding the lone pairs, the actual shape of XeF_4 is square planar with all F-P-F angles equal to 90° as in **Figure 3.28**.

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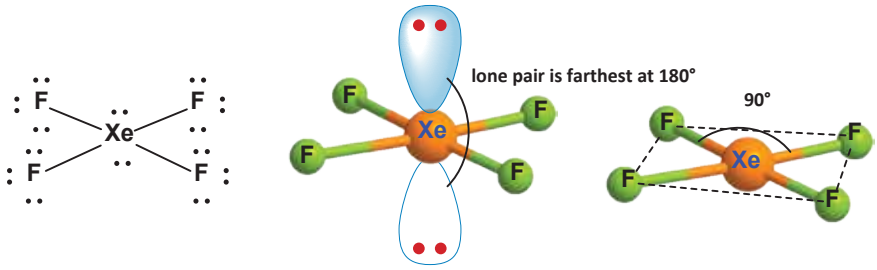


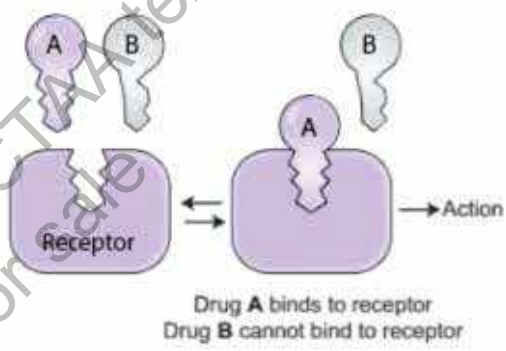
Figure 3.28 Lewis structure and square planar shape of XeF_4

Quick Check 3.8

Draw the Lewis structures for IF_3 and IF_5 and predict their geometry with reference to the VSEPR model.

3.8.2 Applications of VSEPR Model in Drug Designing

Drugs are chemical substances that prevent, diagnose, or treat a disease. Drugs interact with human body at specific points, or with specific processes called **targets** or **substrates**, through their bioactive molecules called **ligands**. A **receptor** is mostly a protein that receives and responds to a ligand through binding. The examples of targets in the body are receptors, such as enzymes, proteins, nucleic acids, and cellular pathways. Each drug interacts with a specific target in the body to a different degree, this feature is called **specificity** of a drug or a ligand.



Molecular shape is an important feature that determines how a drug interacts with a biological target. Only the ligands with suitable shape can fit in the active sites of a biological target as a specific key fits in a specific lock. VSEPR model is successfully applied in determining the shapes of various biological systems, such as substrate recognition, ligand specificity or selectivity, and antibody recognition. For example, Aspirin is an analgesic drug (painkiller) used for relief from pain as a primary medicine.

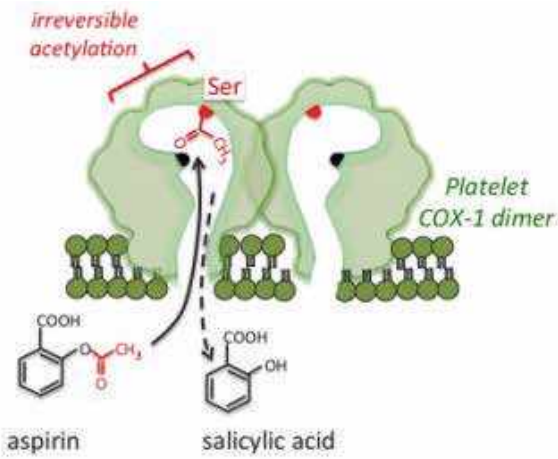


Figure 3.29 An interaction of Aspirin with COX (Published after permission from Tulane University Press)

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It interacts with an enzyme COX (cyclooxygenase) by binding to its active site through the acetyl group ($-OCCH_3$).

The shape of COX active site and that of acetyl group on Aspirin are compatible with each other as in **Figure 3.29** . Therefore, the binding is successful to block COX, which is a cause of the pain in the body.

3.9 MOLECULAR ORBITAL THEORY (MOT)

The molecular orbital approach explains the results of quantum mechanical calculations for covalent bonding. The postulates of this theory are:

- During the formation of a molecule, the atomic orbitals of the combining atoms overlap to form new orbitals called '**molecular orbitals'**, which are characteristic of the whole molecule.
- The atomic orbitals overlap with the lobe having suitable sign of the wave function of the orbital. For example, one lobe of a p orbital is given the '+' sign and the other is marked with '-' sign.
- Two atomic orbitals overlap to form two molecular orbitals. When same sign orbitals overlap, the **bonding molecular orbital** (σ or π) is formed that has lower energy than the parent atomic orbital, while with opposite signs, high energy **anti-bonding molecular orbital** (σ^* or π^*) is formed, that has higher energy than the parent atomic orbitals.
- The number of bonds formed between two atoms after the atomic orbitals overlap, is called the bond order and is taken as half of the difference between the number of bonding electrons (say a) and anti-bonding electrons (say b).

$$\text{Bond order} = \frac{a-b}{2}$$

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s-s Overlap

In the formation of H_2 molecule, two s orbitals of H atoms combine to give two molecular orbitals. The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (nuclear axis), while the anti-bonding molecular orbital has the electron density away from the nuclei of the overlapping atoms as in **Figure 3.30**.

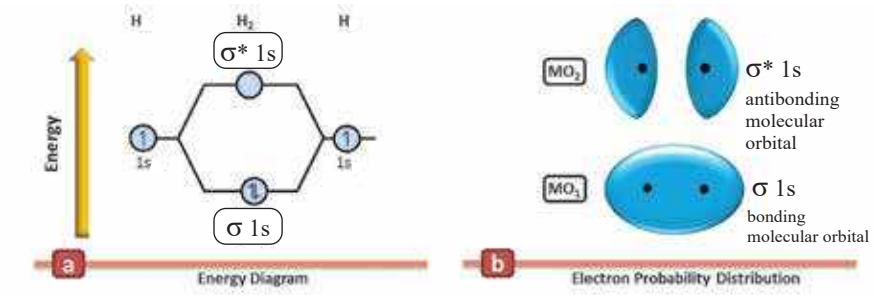

Figure 3.30 Formation of bonding and anti-bonding orbitals for the H_2 molecule

The p orbitals of an atom can combine to give σ bonds in the following ways:

a) Head on overlap

Here, the p-orbitals of the two atoms approach along the same axis (say x-axis) as shown in **Figure 3.31**. This combination of atomic orbitals gives rise to σ ($2p_x$) bonding and σ* ($2p_x$) antibonding molecular orbitals.

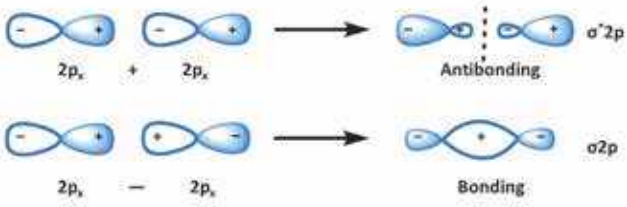

Figure 3.31 Head on overlap of p orbitals

b) Sideways overlap

When the axes of two p-orbitals (i.e p_y or p_z orbitals) are parallel to each other, they interact to form π molecular orbitals as shown in the diagram **Figure 3.32**. The bonding molecular orbitals π($2p_y$) or π($2p_z$) have zero electron density on the nuclear axis (called the nodal plane). On the other hand, anti-bonding molecular orbitals π * ($2p_y$) and π * ($2p_z$) have the least electron density in the inter-nuclear region as in **Figure 3.32**.

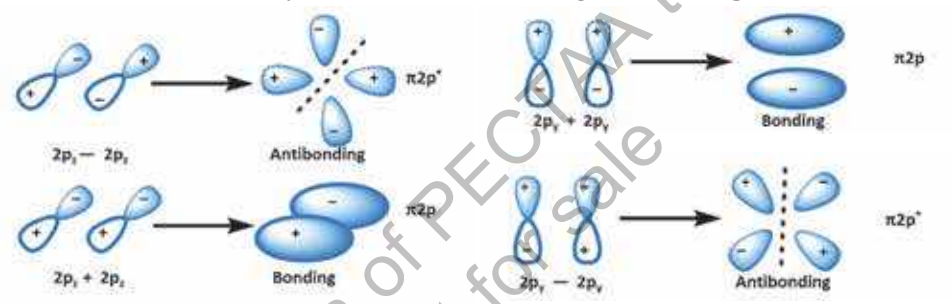

Figure 3.32 Formation of π MOs from p_y and p_z orbitals

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3.9.1 Molecular Orbital Diagrams of Some Diatomic Molecules

i) Helium

The electronic configuration of He is $1s^2$. For a successful formation of He_2 molecule, 1s orbitals of two He atoms must combine to form bonding (σ1s) and anti-bonding (σ*1s) orbitals as shown in **Figure 3.33**. Out of four electrons, two enter the bonding molecular orbital σ (ls) and the remaining two occupy the antibonding σ*(1s) molecular orbital. But on calculation we discover that the bond order for He_2 is zero. Hence, He_2 molecule is not formed.

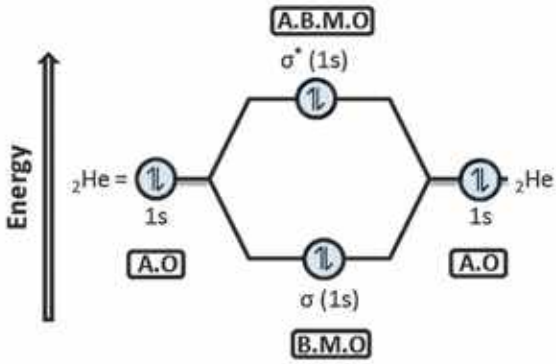

Figure 3.33 Molecular orbital diagram of He_2 molecule

$$\text{Bond order of } He_2 = \frac{2-2}{2} = \mathbf{0}$$

ii) Nitrogen (N_2)

Electronic configuration of N is,

$_7$**N:** $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

The molecular orbital diagram of N_2 based on this electron configuration is shown in **Figure. 3.34**. The valence shell 2s on both N atoms give σ2s and σ* 2s orbitals; whereas, 2p orbitals give six molecular orbitals which are arranged in the increasing order of energy as:

$$\sigma 2s < \sigma^* 2s < \pi 2p_y = \pi 2p_z < \sigma\, 2p_x < \pi^* 2p_y = \pi^* 2p_z < \sigma^*\, 2P_x$$

The bond order for N_2 can be calculated from its orbital diagram as:

$$\text{Bond order of } N_2 = \frac{6-0}{2} = 3$$

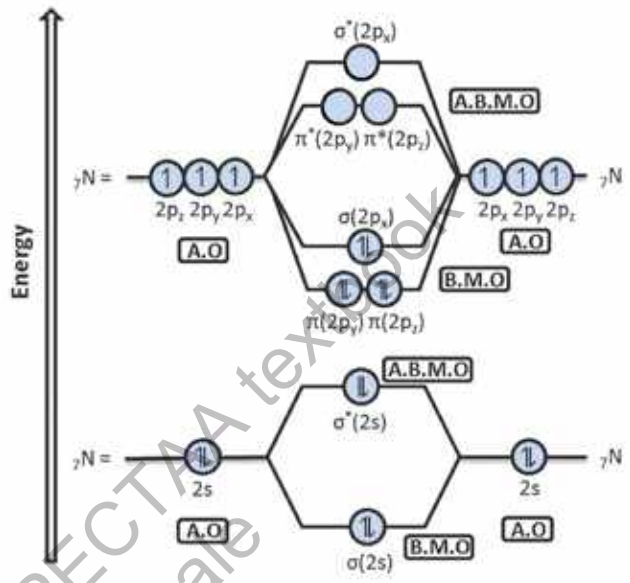

Figure 3.34 Molecular orbital diagram of N_2 molecule

Therefore, there are three covalent bonds between the nitrogen atoms in this molecule. One of these is a σ bond while the other two are π bonds.

iii) Oxygen, O_2

The formation of molecular orbitals in oxygen molecule is shown as follows in **Figure 3.35.**

The bond energy of the MOs can be arranged as

$$\sigma 2s < \sigma^*\, 2s < \sigma\, 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^*\, 2p_x$$

The bond order of oxygen is $2(\frac{6-2}{2})$, which shows the presence of one σ and one π bond between the oxygen atoms, i.e. they are linked by a double bond (O=O). Oxygen molecule is **paramagnetic** in nature, which means it is attracted by a magnetic field. Paramagnetic substances have one or more unpaired electrons in them. A substance with large number of

Liquid oxygen is attracted and gets suspended between the poles of a strong magnet

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unpaired electrons is strongly paramagnetic. MOT successfully explains the paramagnetic behavior of oxygen molecule.

The MO diagram of oxygen shows the presence of two unpaired electrons, one in $\pi^*(2p_y)$ and $\pi^*(2p_z)$ each. Due to the presence of these unpaired electrons, oxygen molecule has a net magnetic field, which interacts with the external magnetic field.

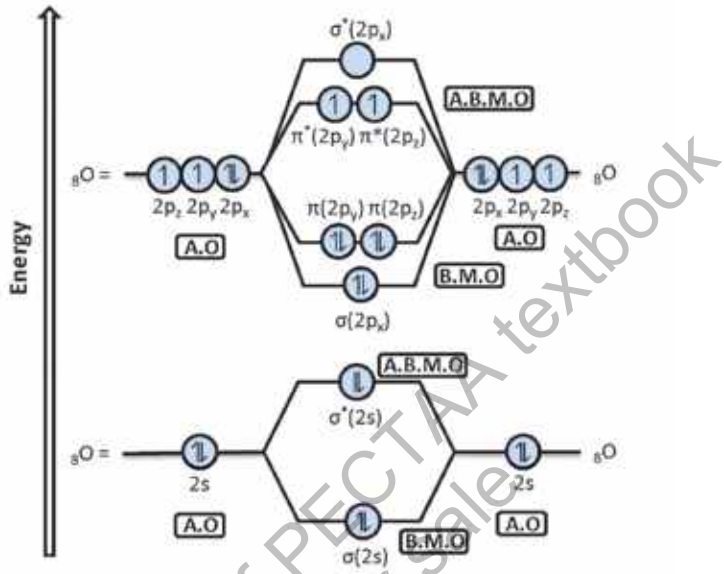

Figure 3.35 Molecular orbital diagram of O_2 molecule

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EXERCISE

MULTIPLE CHOICE QUESTIONS

Q.1 Four choices are given for each question. Select the correct choice.

I. Chemical bond formation takes place when

a) Force of attraction is equal to the force or repulsion

b) Force of repulsion is greater than force of attraction

c) Force of attraction overcomes force of repulsion

d) None of these

II. An ionic compound A^+B^- is most likely to be formed when

a) Ionization energy of A is high and electron affinity of B is low.

b) Ionization energy of A is low and electron affinity of B is high.

c) Both the ionization energy of A and electron affinity of B are high.

d) Both the ionization energy of A and electron affinity of B are low.

III. Which of the following molecules has zero dipole moment?

a) NH_3 b) $CHCl_3$

c) H_2O d) BF_3

IV. The numbers of σ and π bonds in the N_2 molecule are:

a) One σ and one π bonds b) One σ and two π bonds

c) Three σ bonds only d) Two σ and one π

V. Which of the following species has unpaired electrons in antibonding molecular orbitals?

a) O_2^{2+} b) N_2^{2-}

c) B d) F_2

VI. The shape of ICl_5 according to the VSEPR model is:

a) Tetrahedral b) Trigonal planar

c) Trigonal bipyramidal d) T-shape

VII. Which of the following molecules has a net dipole moment?

a) CO_2 b) CS_2

c) SO_2 d) CCl_4

VIII. How many electrons are present in the valence shell of P in PO_4^{3-}?

a) 8 b) 10

c) 12 d) 14

IX. How many extra electrons than a normal octet are there in the valence shell of I in ICl_5?

a) 2 b) 3

c) 4 d) 5

X. What is the type and shape of $[ICl_4]^-$ according to the VSEPR model?

a) AB_4, tetrahedral b) AB_4, pyramidal

c) AB_5, trigonal bipyramidal d) AB_6, square planar

XI. Which of the following molecules has a central atom with sp^3 hybridization and a tetrahedral electron pair geometry?

(a) BF_3 b) SO_2

(c) CCl_4 d) PCl_5

XII. Which of the following species contains a dative bond?

a) CH_4 b) NaCl

c) NH_4^+ d) O_2

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SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Define the following:

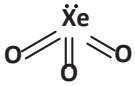
(i) Dipole (ii) Bond order (iii) Permanent dipole- permanent dipole force

(iv) London dispersion force

b. Draw the Lewis (electron dot) structures for the following species:

(i) HCN (ii) NCl_3 (iii) CO (iv) O_3 (v) NO_2

c. Xenon is a noble gas (group 18); xenon trioxide has the following structure:

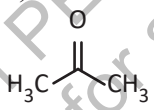


i. By counting electron pairs around the central atom, explain why xenon trioxide has this shape.

ii Draw a structure of xenon trioxide showing partial charges on the atoms and the direction of the dipole moment in the molecule.

d. Explain the difference between the formation of σ and π bonds in terms of VBT.

e. The structure of propanone (acetone) is:



i. Show how the central carbon atom forms σ and π bonds through hybridization.

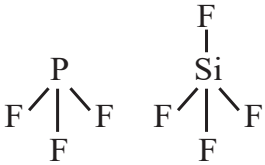
ii. Can propanone make a hydrogen bond with water when both are intermixed?

f. Predict the shapes of sulfate ($[SO_4]^{2-}$), borate ($[BH_4]^-$) and tri-iodide ions ($[I_3]^-$) according to the VSEPR model.

g. Sketch the molecular orbital pictures of π(2p) and π*(2p).

h. Sketch the hybrid orbitals and bond formation in PCl_3, $SiCl_4$, and NH_4^+.

i. The structures of PF_3 and SiF_4 are given below. Redraw these with partial charges and state which is polar and which is non-polar.



j. Draw the orbital structure of the CO_2 molecule in terms of VBT.

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k. Draw the Lewis structures and tell whether the following ions involve expanded octets.

i) ClO_4^- ii) ICl_4^- iii) NH_4^+ iv) I_3^-

l. The bond between K and Cl is ionic but that between Si and Cl is polar covalent. Explain why.

m. SO_2 is a polar molecule but SO_3 not. Justify.

n. Which of O_2^{2+}, and O_2^{2-} would be paramagnetic? Give reason in the light of MOT.

o. Which of the following bonds would be most polar?

i) C-Cl ii) Si-F iii) Se-F

p. Compare the bond energies of single, double, and triple bonds between the same two atoms (e.g., H-H, O=O, N≡N). Explain the trend in terms of the number of shared electrons.

DESCRIPTIVE QUESTIONS

Q.3 How the bonding in the following molecules can be explained with respect to valence bond theory?

i) Cl_2 ii) O_2 iii) N_2 iv) HF v) H_2S

Q.4 What are the postulates of VSEPR model? Discuss the structures of the following species with reference to this theory.

i) CH_4 ii) NH_3 iii) H_3O^+ iv) PCl_5 v) SO_2 vi) SF_6

Q.5 Explain the orbital hybridization for CH_4, NH_3, BF_3, and $BeCl_2$.

Q.6 Draw the molecular orbital diagrams of the following molecules. Calculate their bond orders.

i) H_2 ii) He_2 iii) N_2 iv) O_2

Q.7 Discuss the formation of F_2 molecule in the light of Lewis concept, VBT, and MOT.

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