1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 1)
Module Name/Title	Chemical bonding and molecular structure: Part 3, The Valence Shell Electron Pair Repulsion (VSEPR) Theory and Hybridisation
Module Id	kech_10403
Pre-requisites	Nature of bonding in molecules, covalent
Objectives	After going through this lesson, the learners will be able to understand the following: • Postulates of VSEPR theory • Shapes of molecules containing bond pair only • Shapes of molecules containing lone pair and bond pair • Valence bond theory • Orbital Overlap Concept • Directional properties of bonds • Overlapping of atomic orbitals • Hybridisation
Keywords	VSEPR, shapes of molecules, valence bond theory, hybridisation

2. Development Team

Role	Name	Affiliation
National MOOC Coordinator (NMC)	Prof. Amarendra P. Behera	CIET, NCERT, New Delhi
Program Coordinator	Dr. Mohd. Mamur Ali	CIET, NCERT, New Delhi
Course Coordinator (CC) / PI	Prof. R. K. Parashar	DESM, NCERT, New Delhi
Course Co-Coordinator / Co-PI	Dr. Aerum Khan	CIET, NCERT, New Delhi
Subject Matter Expert (SME)	Preeti Kiran	Kendriya Vidyalaya No1, AFS, Hindan, GZB
Review Team	Dr. Sulekh Chandra	Zakir Hussain College, New Delhi
	Dr. Aerum Khan	CIET, NCERT

Table of Contents:

1. Introduction: The Valence shell electron pair repulsion (VSEPR) theory

As already explained, Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalentmolecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957) Table 1.

Table 1: Dipole Moments of Selected Molecules

Type of Molecule	Example	Geometry
Molecule (AB)	HF	linear
	HCl	linear
	HBr	linear
	HI	linear
	H_2	linear
Molecule (AB_2)	H_2O	bent
	H_2S	bent
	CO_2	linear
Molecule (AB_3)	NH_3	trigonal-pyramidal
	NF_3	trigonal-pyramidal
	BF_3	trigonal-planar
Molecule (AB_4)	CH_4	tetrahedral
	$CHCl_3$	tetrahedral
	CCl_4	tetrahedral

The main postulates of VSEPR theory are as follows:

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.

- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.

- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.

- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsions. These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as **(i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs.**

Table 2 shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB. Table 3 shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Table 4 explains the reasons for the distortions in the geometry of the molecule.

As depicted in Table 2, in the compounds of AB_2, AB_3, AB_4, AB_5 and AB_6, the arrangement of electron pairs and the B atoms around the central atom A are: **linear, trigonal planar,**

tetrahedral, trigonal-bipyramidal and octahedral, respectively. Such arrangement can be seen in the molecules like $BF_3(AB_3)$, $CH_4(AB_4)$ and $PCl_5(AB_5)$ as depicted below (Fig. 1) by their ball and stick models.
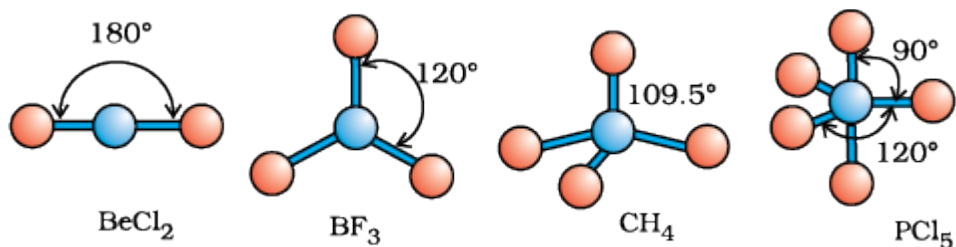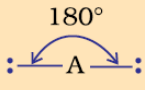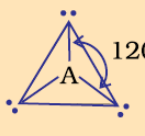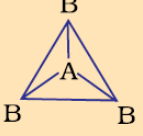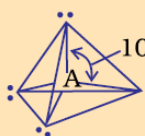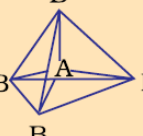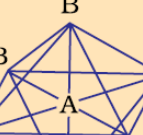

Fig 1: The shapes of molecules in which central atom has no lone pair
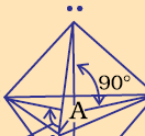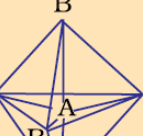
The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds ofp-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small. The theoretical basis of the VSEPR theory regarding the effects of electron pair repulsions on molecular shapes is not clear and continues to be a subject of doubt and discussion.

Table 2. Geometry of Molecules in which the Central Atom has No Lone Pair of Electrons

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	180° :←A→: Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	120° A Trigonal planar	B A B B Trigonal planar	BF_3
4	109.5° A Tetrahedral	B A B B B Tetrahedral	CH_4, NH_4^+
5	90° A 120° Trigonal bipyramidal	B B A B B B Trigonal bipyramidal	PCl_5
6	90° A 90° Octahedral	B B A B B B Octahedral	SF_6

2. Shapes of molecules containing bond pairs only

Shape of BeF₂ molecule: Linear

In BeF$_2$, the central Be atom (Z=4; $1s^2$ $2s^2$) has two electrons in the valence shell. In the formation of BeF$_2$ each of these valence electrons is shared by two fluorine atoms. As a result

the Be atom is surrounded by two bond pairs of electrons. Therefore the geometry of BeF_2 is linear and bond angle is $180°$.

Other molecules such as $BeCl_2$, $ZnCl_2$, $HgCl_2$, have linear shape.

Shape of BF$_3$ molecule : Trigonal Planar

In BF_3 ,the central B atom (Z=5; $1s^2 2s^2 2p^1$) has three electrons in the valence shell. In the formation of BF_3 each of these valence electrons is shared by three fluorine atoms. As a result the B atom is surrounded by three bond pairs of electrons. Therefore the geometry of BF_3 is trigonal planar and bond angle is $120°$.
This geometry is planar because the three F atoms and B atom lie in the same plane.

Molecules such as BCl_3 , $AlCl_3$ etc have same shape.

Shape of CH$_4$ molecule : Tetrahedral

In CH_4 , the central C atom (Z=6; $1s^2 2s^2 2p^2$) has four   electrons in the valence shell. In the formation of CH_4 each of these valence electrons are bonded to four hydrogen atoms forming four bond pairs around the central C atom.. As a result the C atom is surrounded by four bond pairs of electrons. Therefore the geometry of CH_4 is tetrahedral as these four electron pairs try to remain as far apart as possible, and bond angle is $109.5°$.
Molecules such as CCl_4 , SiH_4 , NH_4^+ adopt tetrahedral geometry.

Shape of PCl$_5$ molecule: Trigonal Bipyramidal

In PCl_5 , the central P atom (Z=15; $1s^2 2s^2 2p^6 3s^2 3p^3$) has five electrons in the valence shell. In the formation of PCl_5 each of these valence electrons are bonded to five chlorine atoms forming five bond pairs around the central P atom.. As a result the P atom is surrounded by five bond pairs of electrons. Therefore the geometry of PCl_5 is trigonal bipyramidal as these five electron pairs try to remain as far apart as possible, and all bond angles are not equal. Three electrons are in the same plane at an angle of $120°$, while other two are perpendicular to the plane, both making an angle of $90°$ with the plane.

In this geometry ,all five P-Cl bonds are not equal. The three bonds lying in the trigonal plane are called equatorial bonds. Of the remaining two bonds , one lies above and the other below the equatorial plane both making an angle of 90° with the plane. These bonds are called axial bonds.

It has been observed that axial bonds are slightly longer than equatorial bonds . Since the structure is unsymmetrical as a result it is less stable and highly reactive.

Molecule such as PF_5 adopts same geometry.

Shape of SF_6 molecule : Octahedral

In SF_6 , the central S atom (Z=16; $1s^2 2s^2 2p^6 3s^2 3p^4$) has six electrons in the valence shell. In the formation of SF_6 each of these valence electrons are bonded to six chlorine atoms forming six bond pairs around the central S atom.. As a result the S atom is surrounded by six bond pairs of electrons. Therefore the geometry of SF_6 is octahedral as these six electron pairs try to remain as far apart as possible, and all bond angles are equal of 90 ° .

TeF_6, SeF_6 molecule has same shape.

Shape of IF_7 molecule : Pentagonal Bipyramidal

In IF_7 , the central I atom (Z=53; ....$5s^2 5p^3$) has seven electrons in the valence shell. In the formation of IF_7 each of these valence electrons are bonded to seven fluorine atoms forming seven bond pairs around the central I atom.. As a result the I atom is surrounded by seven bond pairs of electrons. Therefore the geometry of IF_7 is pentagonal bipyramidal as these seven electron pairs try to remain as far apart as possible, and all bond angles are not equal. Five electron pairs are in the same plane at an angle of 72° , while other two are perpendicular to the plane, both making an angle of 90° with the plane.

Table 3: Shape (geometry) of Some Simple molecules/Ions with Central Ions having One or More Lone Pairs of Electrons(E)
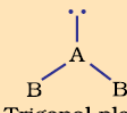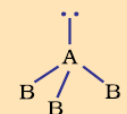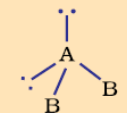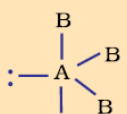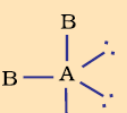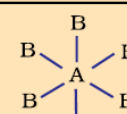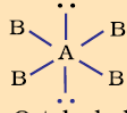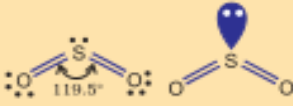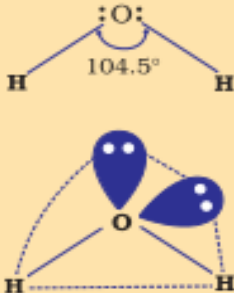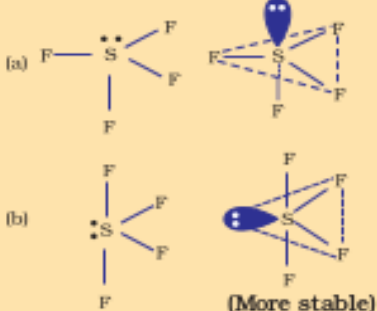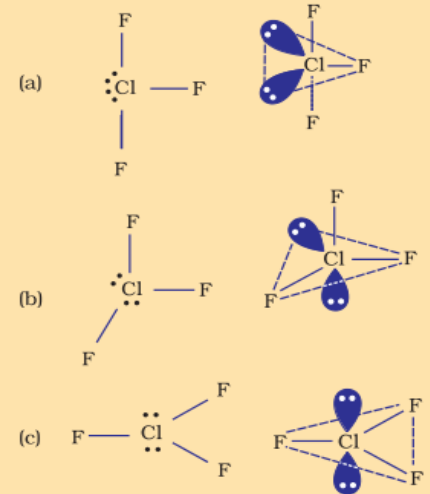
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	Tetrahedral	Trigonal pyramidal	NH_3
AB_2E_2	2	2	Tetrahedral	Bent	H_2O
AB_4E	4	1	Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	Trigonal bi-pyramidal	T-shape	ClF_3
AB_5E	5	1	Octahedral	Square pyramid	BrF_5
AB_4E_2	4	2	Octahedral	Square planar	XeF_4

Table 4: Shapes of Molecules containing Bond Pair and Lone Pair

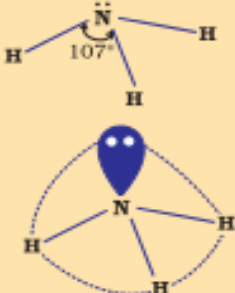| Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_2E	4	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more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

Table 4: Shapes of Molecules containing Bond Pair and Lone Pair (continue......)

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_3E_2	3	2	(a) (b) (c)	T-shape	In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped).

Key Note:

It may be noted that the central atoms (C,N and O) in three molecules CH_4, NH_3, H_2O have four electon pairs around the central atom. Therefore these molecules adopt tetrahedral geometries. But in methane there is no lone pair, ammonia molecule has one lone pair and water has two lone pair of electrons. Due to the presence of lone pairs ammonia and water molecules have distorted geometries while methane molecule has regular geometry of tetrahedron. Due to larger lone pair – bond pair repulsion than bond pair – bond pair in NH_3 the bond angle is reduced from $109.5°$ to $107°$. The geometry of ammonia is pyramidal.

In case of water two lone pairs force the O-H bonds closely than the N-H bond in NH_3.So the bond angle decreases to a larger extent i.e to $104.5°$.The geometry of water is V-shaped or angular.

3. Valence Bond Theory

As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H_2(435.8 kJ mol^{-1}, 74 pm) and F_2(155 kJ mol^{-1}, 144 pm), although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules.

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

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on theknowledge of atomic orbitals, electronic configurations of elements (Units 2), the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. A rigorous treatment of the VB theory in terms of these aspects is beyond the scope of this book. Therefore, for the sake of convenience, valence bond theory has been discussed in terms of qualitative and non-mathematical treatment only. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules.

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

Attractive forces arise between:

(i) nucleus of one atom and its own electron that is $N_A–e_A$ and $N_B– e_B$.

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

Similarly repulsive forces arise between

(i) electrons of two atoms like $e_A– e_B$,

(ii) nuclei of two atoms $N_A– N_B$.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig. 2).

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases.
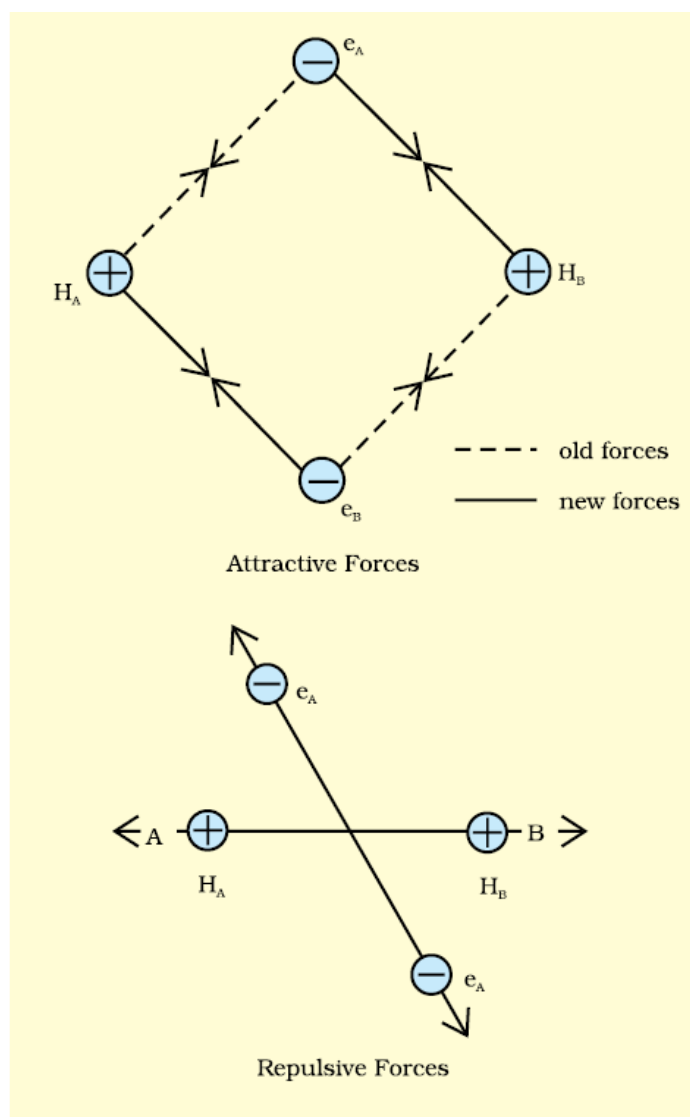
Fig. 2: Forces of attraction and repulsion during the formation of H_2 molecule

Ultimately an stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as **bond enthalpy**, which is corresponding to minimum in the curve depicted in Fig. 3. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

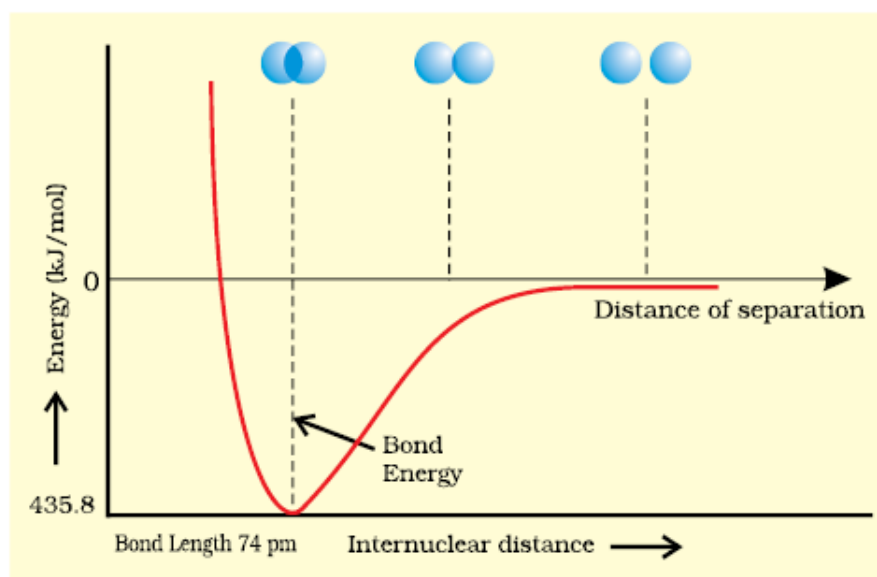$$H_2(g) + 435.8 \text{ kJ mol}^{-1} \rightarrow H(g) + H(g)$$
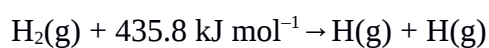
Fig. 3: The potential energy curve for the formation of H_2molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.

3.1 Orbital Overlap Concept

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

3.2 Directional Properties of Bonds

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

In case of polyatomic molecules like CH_4, $NH_3$and H_2O, the geometry of the molecules is also important in addition to the bond formation. For example why is it so that CH_4molecule has tetrahedral shape and HCH bond angles are 109.5°? Why is the shape of NH_3molecule pyramidal ?

The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like CH_4, $NH_3$and H_2O, etc. in terms of overlap and hybridisation of atomic orbitals.

3.3 Overlapping of Atomic Orbitals

When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space (Fig. 4.9). Positive and negative sign on boundary surface diagrams in the Fig. 4.9 show the sign (phase) of orbital wave function and are not related to charge. Orbitals forming bond should have same sign (phase) and orientation in space. This is called positive overlap. Various overlaps of s and p orbitals are depicted in Fig. 4.
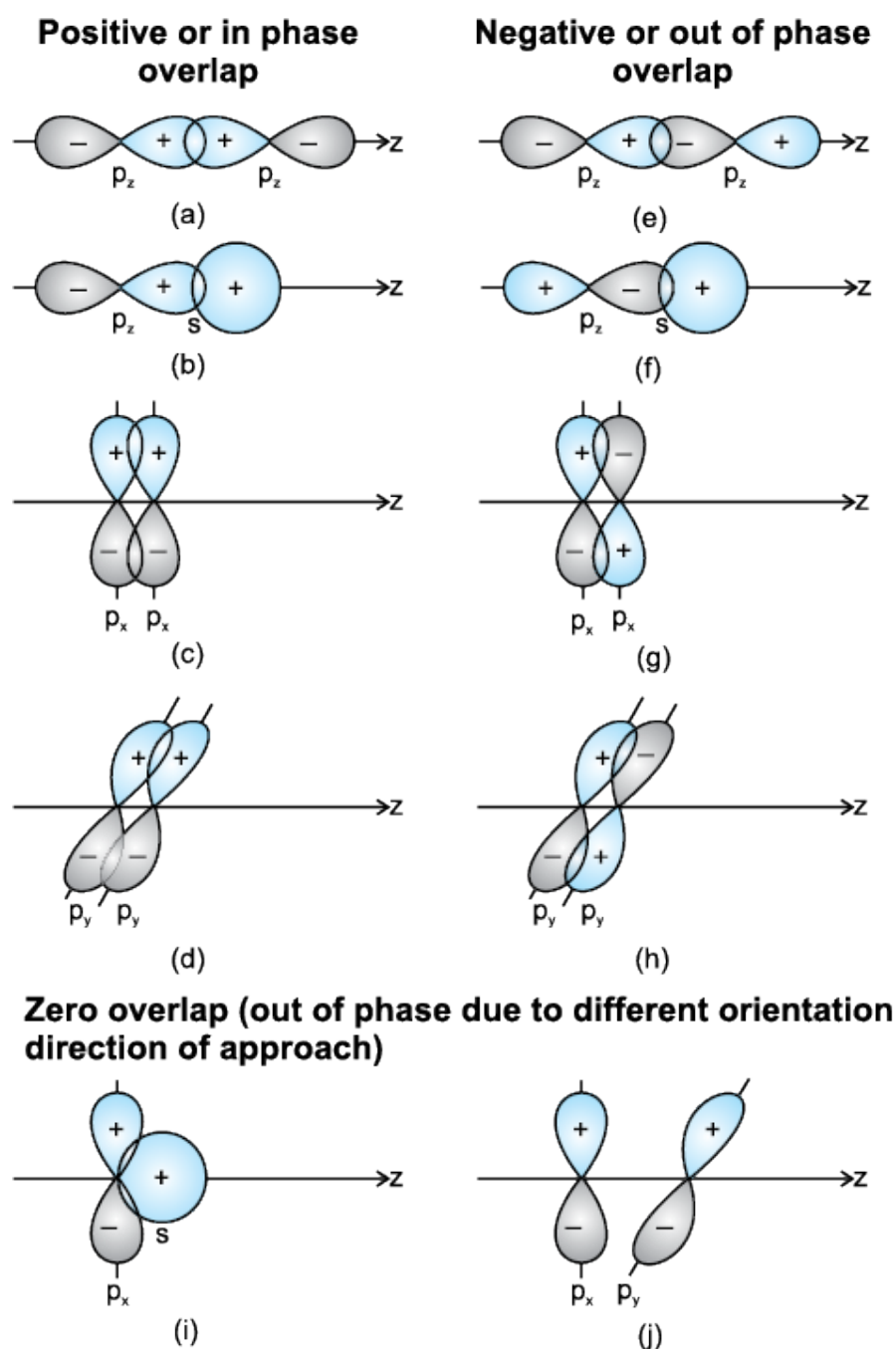

Fig. 4 Positive, negative and zero overlaps of s and p atomic orbitals

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. We know that the shapes of CH_4, NH_3, and H_2O molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to use VB theory to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

Let us first consider the CH_4(methane) molecule. The electronic configuration of carbon in its ground state is $[He]2s^2 2p^2$ which in the excited state becomes $[He] 2s^1 2p_x^1 2p_y^1 2p_z^1$. The energy required for this excitation is compensated by the release of energy due to overlap between the orbitals of carbon and thehydrogen.The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1sorbitals of the four H atoms which are also singly occupied. This will result in the formation of four C-H bonds. It will, however, be observed that while the three p orbitals of carbon are at $90°$to one another, the HCH angle for these will also be $90°$. That is three C-H bonds will be oriented at $90°$to one another. The 2sorbital of carbon and the 1sorbital of H are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond cannot be ascertained. This description does not fit in with the tetrahedral HCH angles of $109.5°$. Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in CH_4. Using similarprocedure and arguments, it can be seen that in the case of $NH_3$and H_2Omolecules, the HNH and HOH anglesshould be $90°$. This is in disagreement with the actual bond angles of $107°$and $104.5°$in the $NH_3$and H_2O molecules respectively.

4. Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping:
(i) Sigma(σ) bond, and (ii) pi(π) bond

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

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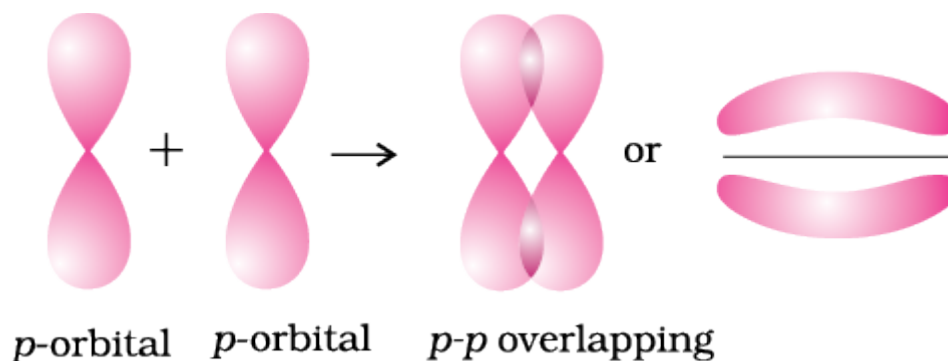

s-orbital   s-orbital   s-s overlapping

- ***s-p* overlapping:**This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.
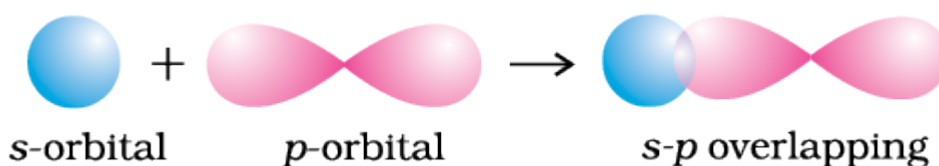
- ***p–p* overlapping :**This type of overlap takes place between half filled p-orbitals of the two approaching atoms.
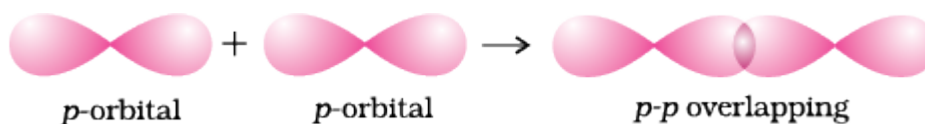
(ii) **pi (π) bond :**In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.

5. Strength of Sigma and pi Bonds

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

6. Hybridisation

In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3 and H_2O etc., Pauling introduced the concept of hybridisation.

According to him the atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation which can be defined as "The process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape". For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

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

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation

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

Types of Hybridisation

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

(I) *sp hybridisation:* **This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals**. The suitable orbitals for sp hybridisation are s and p_z, if the hybrid orbitals are to lie along the z-axis.

- Each sp hybrid orbitals has 50% s-character and 50% p-character.
- Such a molecule in which the central atom is sp-hybridised and linked directly to two other central atoms possesses **linear geometry**. This type of hybridisation is also known as **diagonal hybridisation**.

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

Example of molecule having *sp* hybridisation

BeCl₂: The ground state electronic configuration of Be is $1s^2 2s^2$. In the exited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its bivalency. One 2s and one 2p-orbital gets hybridised to form twosphybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an **angle of 180°.** Each of thesphybridised orbital overlaps with the 2p-orbital of chlorine axially and form two Be-Cl sigma bonds. This is shown in Fig 5.
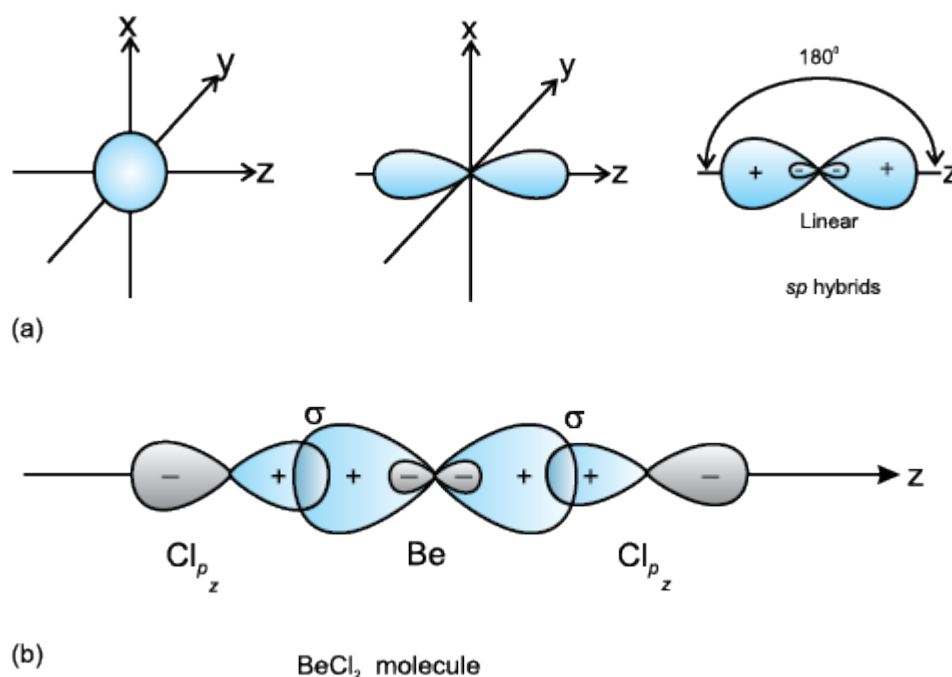

(a)

(b)   BeCl₂ molecule

Fig. 5 (a) Formation of sp hybrids from s and p orbitals; (b) Formation of the linear BeCl₂ molecule

(II) *sp² hybridisation:* In this hybridisation there is involvement of ones and two p-orbitals in order to form three equivalent sp^2 hybridised orbitals. For example, in BCl_3 molecule, the ground state electronic configuration of central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital as a result boron has three unpaired electrons. These three orbitals (one 2s and two 2p) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B-Cl bonds. Therefore, in BCl_3 (6), the geometry is trigonal planar with ClBCl bond angle of 120°.
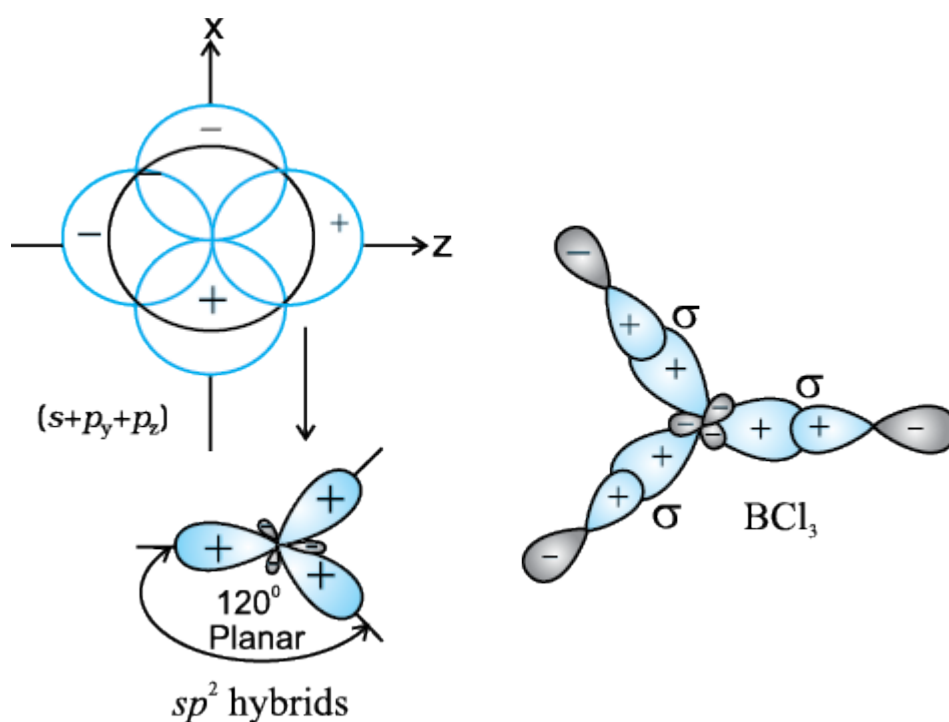

Fig.6. Formation of sp² hybrids and the BCl₃ molecule

(III) *sp³ hybridisation:* This type of hybridisation can be explained by taking the example of CH_4 molecule in which there is mixing of ones-orbital and three p-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp^3 hybrid orbital is 109.5° as shown in Fig. 7.
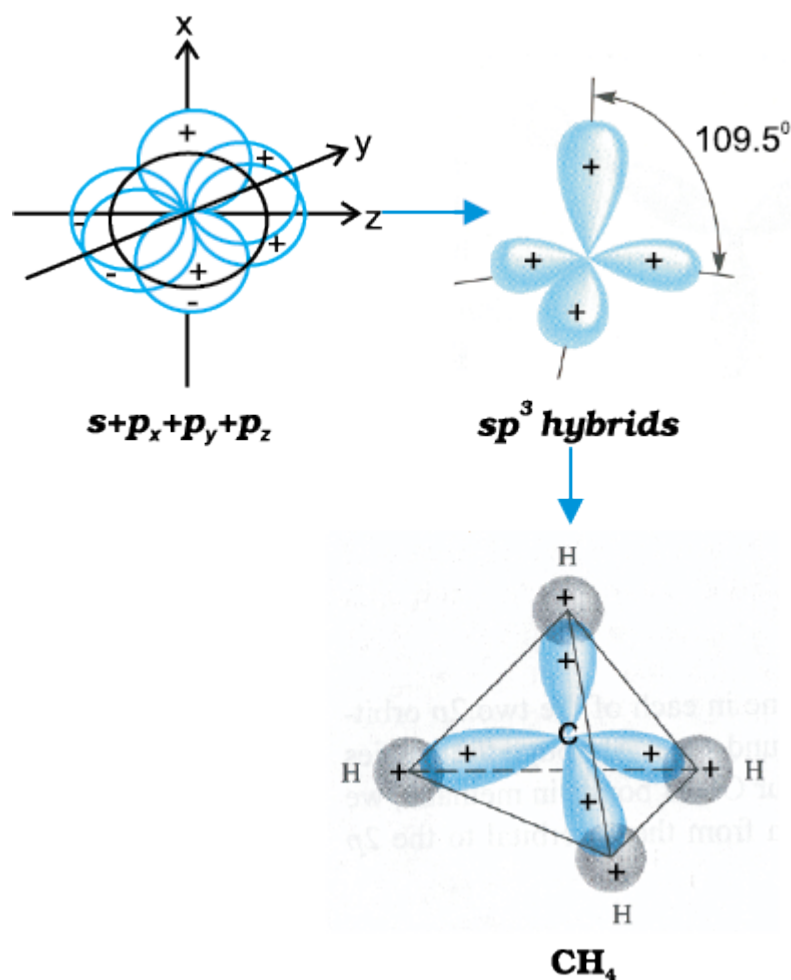
Fig. 7 Formation of sp^3 hybrids by the combination of s , p_x, p_y and p_z atomic orbitals of carbon and the formation of CH_4 molecule

The structure of NH_3 and H_2O molecules can also be explained with the help of sp^3 hybridisation. In NH_3, the valence shell (outer) electronic configuration of nitrogen in the ground state is $2s^2 2p_x^1 2p_y^1 2p_z^1$ having three unpaired electrons in the sp^3 hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with 1s orbitals of hydrogen atoms to form three N–H sigma bonds. We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to 107° from 109.5°. The geometry of such a molecule will be pyramidal as shown in Fig. 8.

Ammonia, NH₃
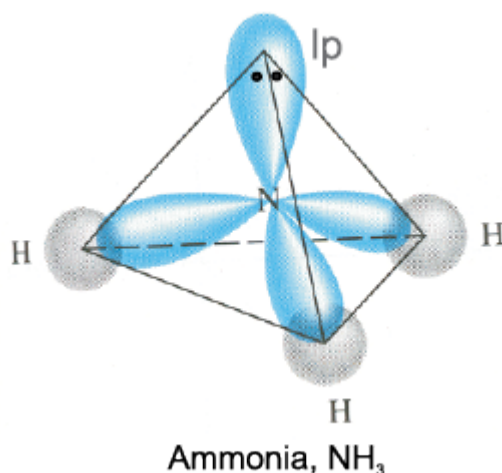
Fig. 8 Formation of NH_3 molecule

In case of H_2O molecule, the four oxygen orbitals (one 2s and three 2p) undergo sp^3 hybridisation forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp^3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5° from 109.5° (Fig. 9) and the molecule thus acquires a V-shape or angular geometry.
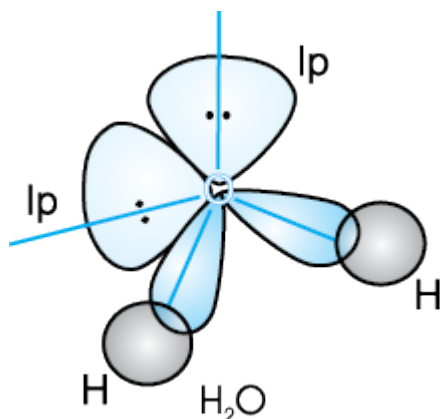

Fig.9: Formation of H_2O molecule

Other Examples of sp^3, sp^2 and sp Hybridisation

sp^3 Hybridisation in C_2H_6 molecule: In ethane molecule both the carbon atoms assume sp^3 hybrid state. One of the four sp^3 hybrid orbitals of carbon atom overlaps axially with similar orbitals of other atom to form sp^3-sp^3 sigma bond while the other three hybrid orbitals of each carbon atom are used in forming sp^3–s sigma bonds with hydrogen atoms as discussed in section 6 (iii). Therefore in ethane C–C bond length is 154 pm and each C–H bond length is 109 pm.

sp²Hybridisation in C₂H₄: In the formation of ethene molecule, one of the sp^2 hybrid orbitals of carbon atom overlaps axially with sp^2 hybridised orbital of another carbon atom to form C–C sigma bond. While the other two sp^2 hybrid orbitals of each carbon atom are used for making sp^2–s sigma bond with two hydrogen atoms. The unhybridised orbital ($2p_x$ or $2p_y$) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form weak π bond, which consists of two equal electron clouds distributed above and below the plane of carbon and hydrogen atoms.

Thus, in ethene molecule, the carbon-carbon bond consists of one sp^2–sp^2 sigma bond and one pi (π) bond between p orbitals which are not used in the hybridisation and are perpendicular to the plane of molecule; the bond length 134 pm. The C–H bond is sp^2–s sigma with bond length 108 pm. The H–C–H bond angle is 117.6° while the H–C–C angle is 121°. The formation of sigma and pi bonds in ethene is shown in Fig. 10.
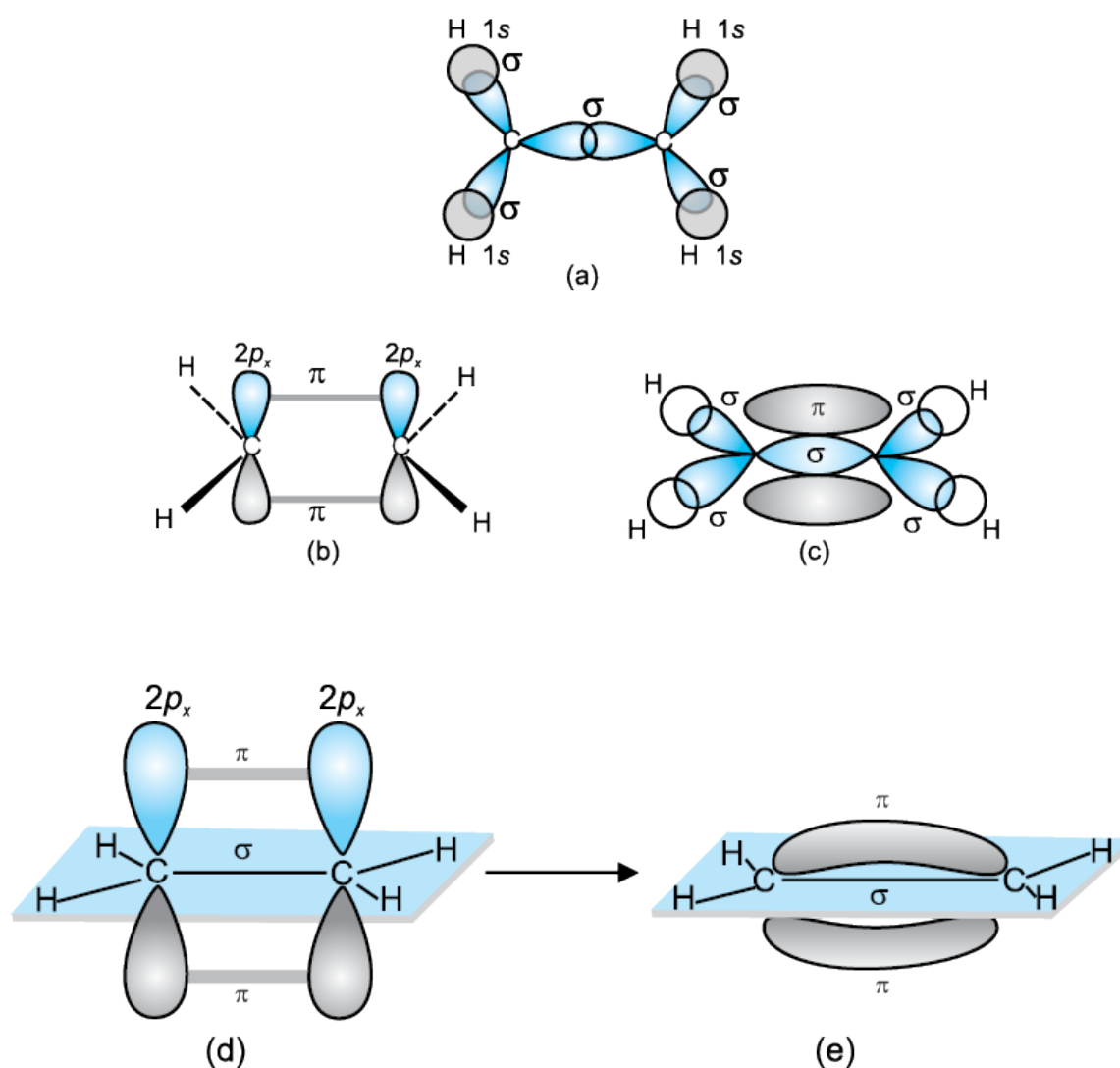

Fig. 10 Formation of sigma and pi bonds in ethane

sp Hybridisation in C₂H₂: In the formation of ethyne molecule, both the carbon atoms undergo sp-hybridisation having two unhybridised orbital i.e., $2p_y$ and $2p_x$. One sp hybrid orbital of one carbon atom overlaps axially with sp hybrid orbital of the other carbon atom to form C–C sigma bond, while the other hybridised orbital of each carbon atom overlaps axially with the half filled s orbital of hydrogen atoms forming σ bonds. Each of the two unhybridised p orbitals of both the carbon atoms overlaps sidewise to form two π bonds between the carbon atoms. So the triple bond between the two carbon atoms is made up of one sigma and two pi bonds as shown in Fig. 11.

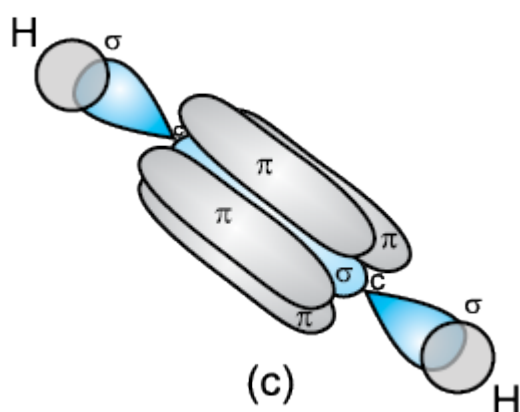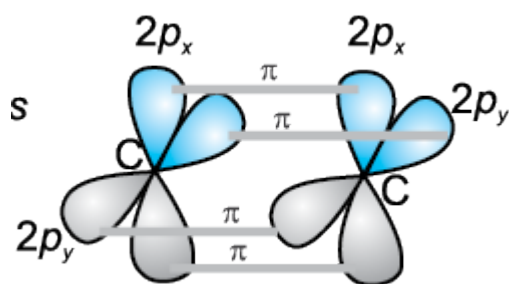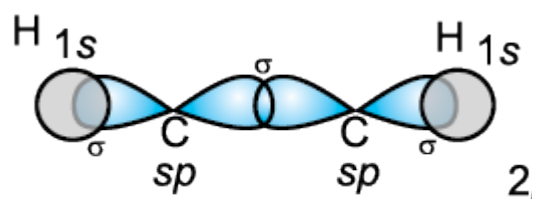Fig. 11 Formation of sigma and pi bonds in ethyne

**Hybridisation of Elements involving d Orbitals**

The elements present in the third period contain d orbitals in addition to s and p orbitals. The energy of the 3 d orbitals are comparable to the energy of the 3s and 3p orbitals. The energy of 3d orbitals are also comparable to those of 4s and 4p orbitals. As a consequence the hybridisation involving either 3s, 3p and 3d or 3d, 4s and 4p is possible. However, since the difference in energies of 3p and 4s orbitals is significant, no hybridisation involving 3p, 3d and 4s orbitals is possible.

The important hybridisation schemes involving s,p and d orbitals are summarised below:

Shape of molecules/ ions	Hybridisation type	Atomic orbitals	Examples
Square planar	dsp^2	$d+s+p(2)$	$[Ni(CN)_4]^{2-}$, $[Pt(Cl)_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s+p(3)+d$	PF_5, PCl_5
Square pyramidal	sp^3d^2	$s+p(3)+d(2)$	BrF_5
Octahedral	sp^3d^2 d^2sp^3	$s+p(3)+d(2)$ $d(2)+s+p(3)$	SF_6, $[CrF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$

(i) Formation of PCl₅ (sp³d hybridisation): The ground state and the excited state outer electronic configurations of phosphorus (Z=15) are represented below.

sp³d hybrid orbitals filled by electron pairs donated by five Cl atoms.
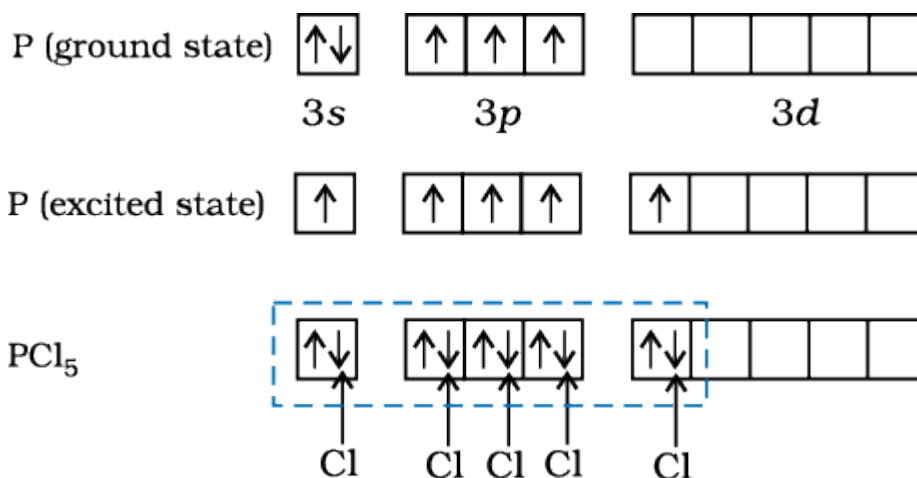
sp³d hybrid orbitals filled by electron pairs donated by five Cl atoms.

Now the five orbitals (i.e.,ones, threepand onedorbitals) are available for hybridisation to yield a set of five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as depicted in the Fig. 12.
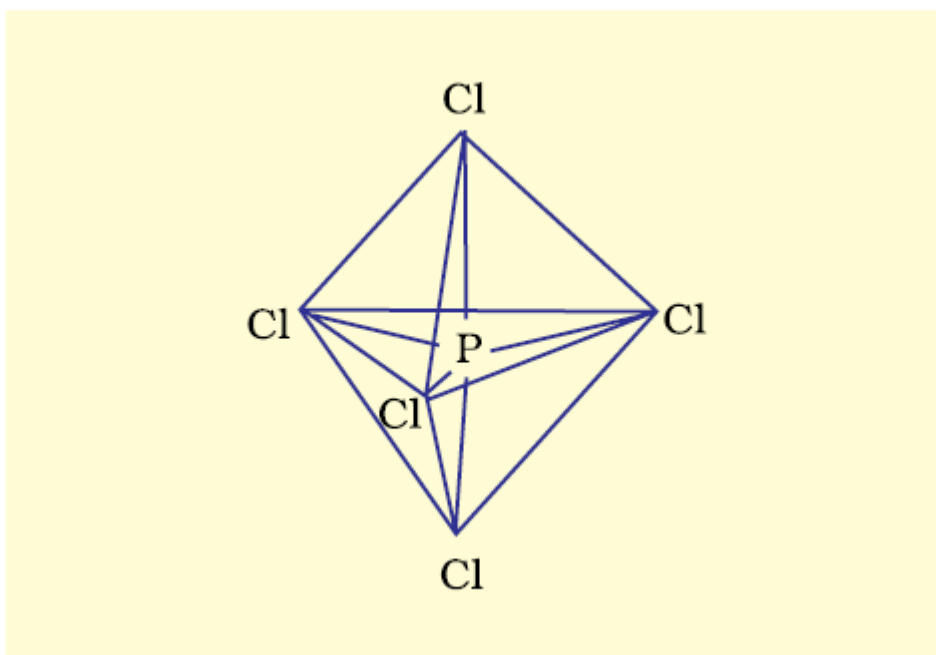

Fig. 12 Trigonal bipyramidal geometry of PCl_5 molecule

It should be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent.In PCl_5 the fivesp^3dorbitals of phosphorus overlap with the singly occupied$p$orbitals of chlorine atoms to form five P–Cl sigma bonds. Three P–Cl bond lie in one plane and make an angle of 120° with each other; these bonds are termed as equatorial bonds.The remaining two P–Cl bonds–one lying above and the other lying below the equatorial plane, make an angle of 90° with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes PCl_5molecule more reactive.

(ii) Formation of SF$_6$ (sp^{3}d^2 hybridisation): In SF_6 the central sulphur atom has the ground state outer electronic configuration $3s^2\ 3p^4$. In the exited state the available six orbitals i.e.,ones, three p and two d are singly occupied by electrons. These orbitals hybridise to form six new sp^3d^2 hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF_6. These six $sp^3\ d^2$ hybrid orbitals overlap with singly occupied orbitals of

fluorine atoms to form six S–F sigma bonds. Thus SF_6 molecule has a regular octahedral geometry as shown in Fig. 13.
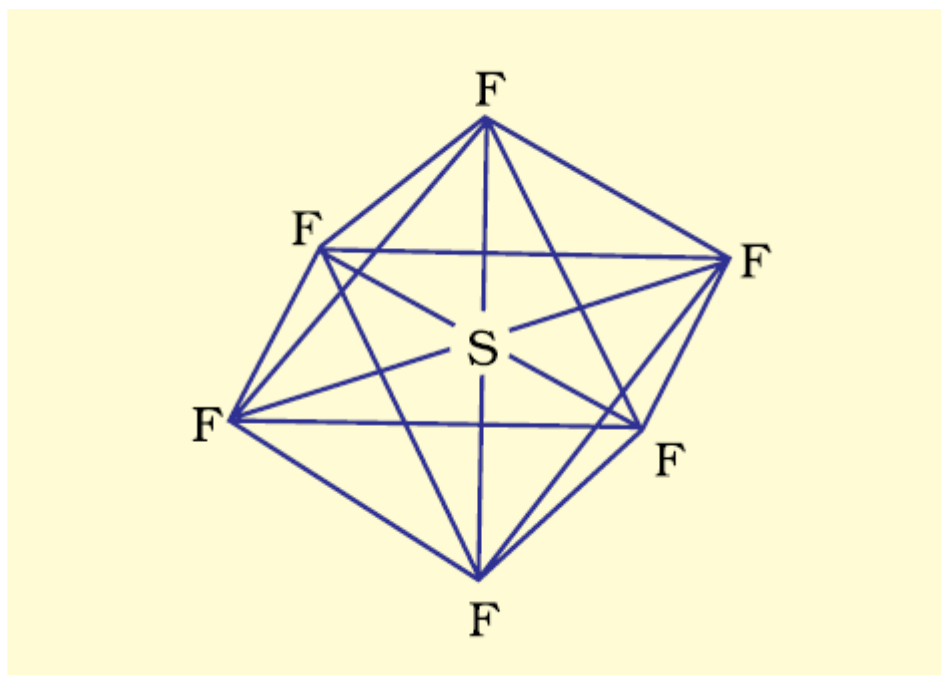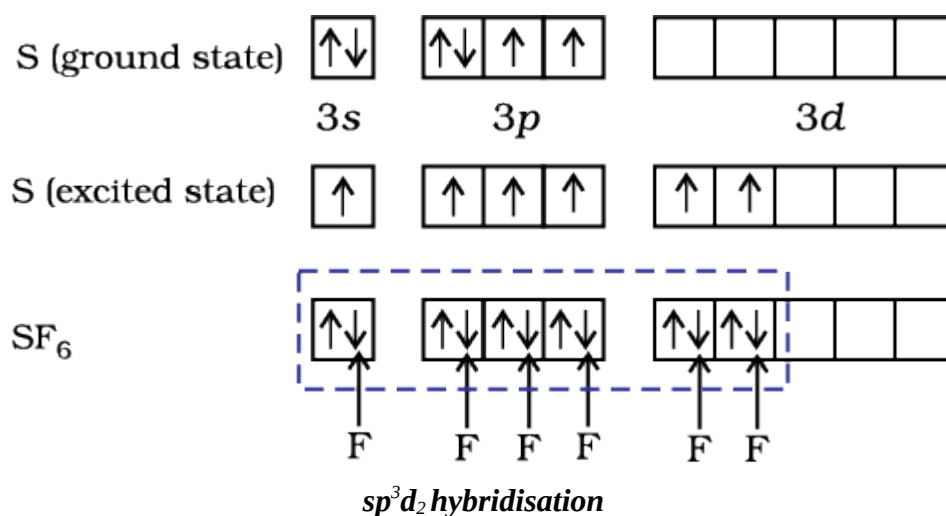

sp^3d_2 *hybridisation*

Fig. 13 Octahedral geometry of SF_6 molecule

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

The valence bond (VB) approach to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically the VB theory discusses bond formation in terms of overlap of orbitals. For example the formation of the H 2 molecule from two hydrogen atoms involves the overlap of the 1s orbitals of the two H atoms which are singly occupied . It is seen that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium inter-nuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilization of the molecule. Beacuse of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. It is however seen that the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account.

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