

Department of Mathematics and Natural Sciences

CHE101: Lecture 10 & 11

Contents:

- Valence Bond Theory
- Molecular geometry
- VSEPR Model
- Hybridization concepts

Geometries of Molecules

- all molecules containing three or more atoms are three-dimensional.
- The shape of a particular molecule is determined by the specific arrangement of atoms and the bond angles in it.
- Molecular shapes may be linear, bent (or angular), trigonal planar, pyramidal or tetrahedral.
- The shapes of molecules can be determined in the laboratory by modern methods such as X-ray and electron diffraction techniques.

Geometries of Molecules

- **Molecular shapes** are important because they are helpful in the investigation of molecular polarity, molecular symmetry or asymmetry.
- **Physical and chemical properties** of compounds depend on these factors.
- **VSEPR theory throws light on the three dimensional shapes of molecules**

VSEPR Theory

- The Lewis structure shows electron pairs in the valence shell of the central atom which experience electrostatic forces.
- On this basis, R.G. Gillespie (1970) proposed a theory called the Valence-Shell Electron Pair Repulsion or VSEPR (pronounced as 'Vesper') theory.
- It states that :

"The electron pairs (both lone pairs and shared pairs, surrounding the central atom will be arranged in space as far apart as possible to minimize the electrostatic repulsion between them"

VSEPR Theory

- Simplest atom with two electron pairs will be as far apart as possible so as to minimize repulsion between them.
- The arrangement in which the electron pair-central atom-electron pair angles is 180° , makes the electron pairs farthest apart.
- This arrangement is called linear because the electron pairs and the central atom are in a straight line.

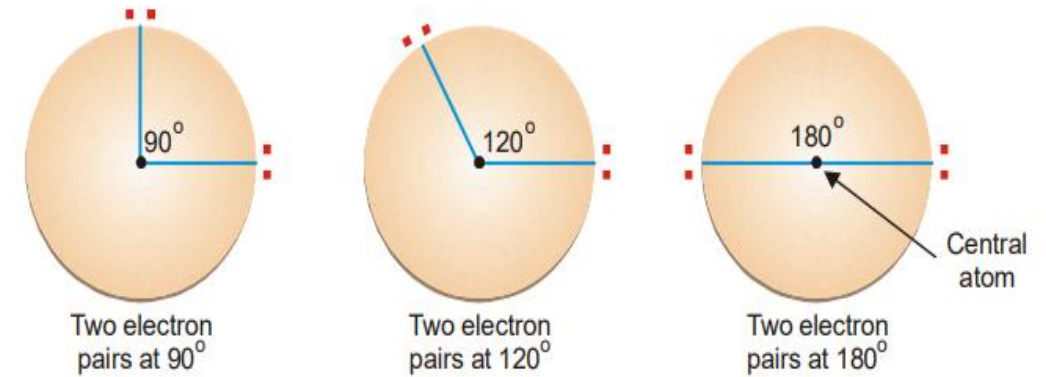


Figure 5.14

Arrangement of two electron pairs on circle at 90° , 120° and at 180° . Placement of electron pairs at 180° puts them the farthest apart, thereby minimising the electrostatic repulsion.

VSEPR Theory: Considerations

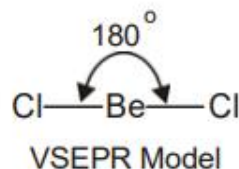
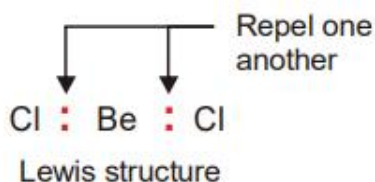
- **Multiple bonds behave as a single electron-pair bond** for the purpose of VSEPR. They represent a single group of electrons.
- **Order of repulsions** between lone pair and lone pair (lp-lp), lone pair and bonding pair (lp-bp), and bonding pair and bonding pair (bp-bp) is:
 $lp - lp > lp - bp > bp - bp$
- The bonding electron pairs of molecule that has lone pairs of electrons, are pushed closer and thus the bond angle is decreased.

VSEPR Theory: Considerations

- Now we proceed to work out the shapes of some common molecules with the help of VSEPR theory

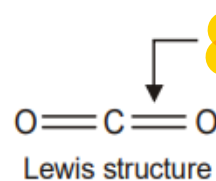
Linear Molecules

- Beryllium chloride, BeCl_2 . Figure shows its Lewis structure.
- The central atom Be has two bonding electron pairs and no unshared electron.
- According to VSEPR theory, the bonding pairs will occupy positions on opposite sides of Be forming an angle of 180° .
- An angle of 180° gives a straight line. Therefore, BeCl_2 molecule is linear.
- In general, all molecules as A-B-A which have only two bonds and no unshared electrons are linear

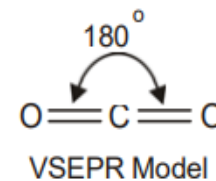
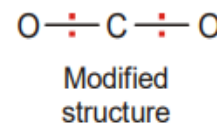


Geometry of CO molecule.

The central C atom has no unshared electron. We know that double bond counts the same as a single bond in VSEPR model. Thus CO_2 is a linear molecule



Counts the same as single bond



Linear Molecules

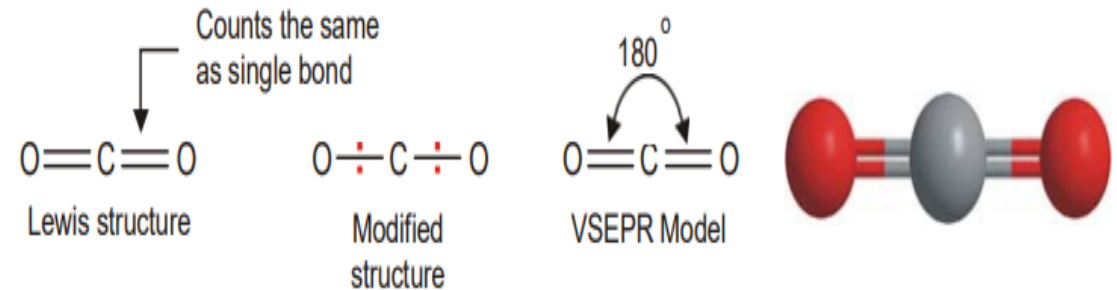
Geometry of CO molecule

- The central C atom has no unshared electron.
- Double bond counts the same as a single bond in VSEPR model.
- Thus CO₂ is a linear molecule

Do yourself:

Show the shape of

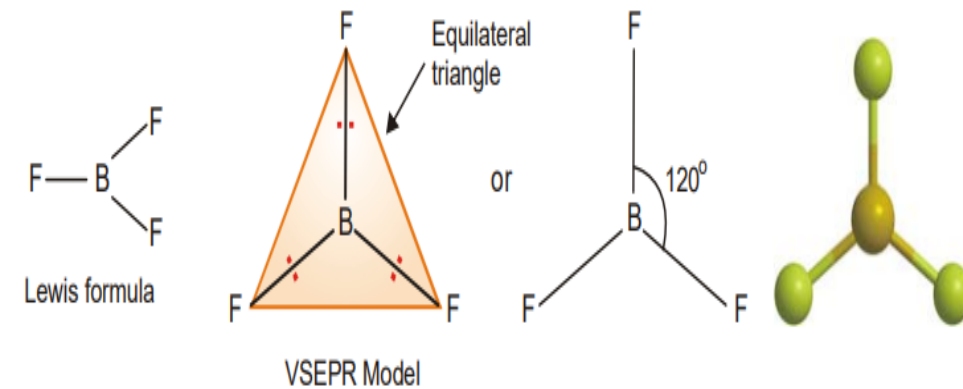
- Hydrogen cyanide ($\text{H} - \text{C} \equiv \text{N}$) and
- Acetylene ($\text{H} - \text{C} \equiv \text{C} - \text{H}$)



Trigonal Planar Molecules

Boron trifluoride, BF_3 .

- central atom B has three bonding electron pairs and no unshared electrons.
- VSEPR theory says that the three bonding electron pairs will be as far apart as possible.
- This can be so if these electron pairs are directed to the corners of an equilateral triangle.

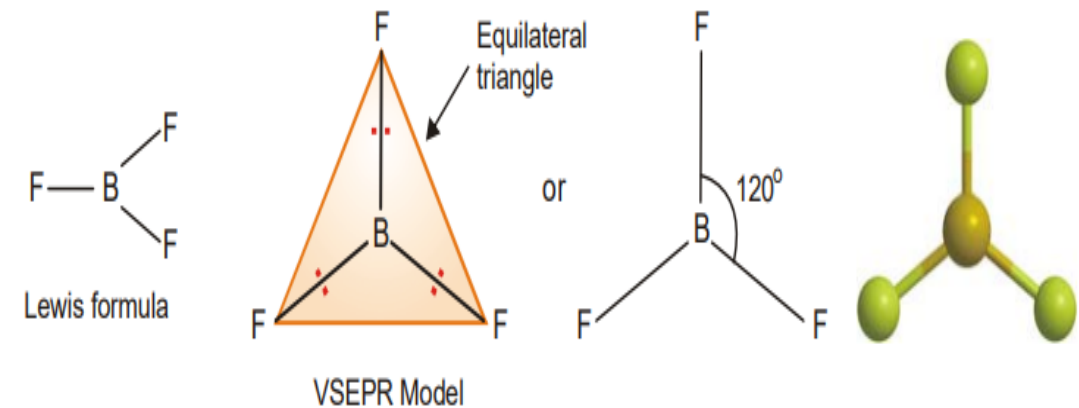


Trigonal Planar Molecules

- Thus VSEPR model of BF_3 molecule has **three F atoms at the corners of the triangle with B atom at its centre.**
- All the four atoms (three F and one B) **lie in the same plane.**
- Therefore, the shape of such a molecule is called **trigonal planar.** **The bond angle is 120° .**

Do yourself:

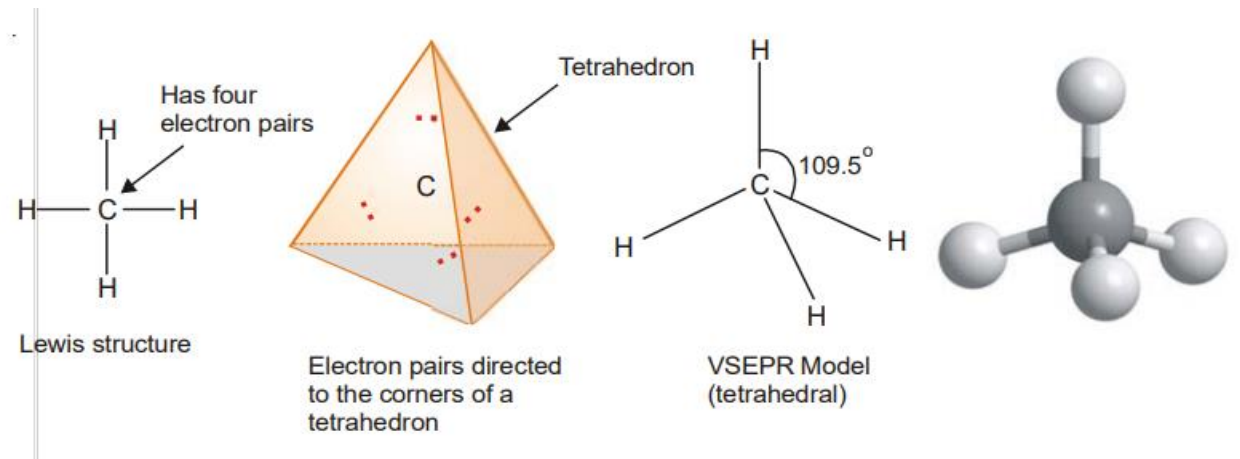
- Determine the structure of SO_3 molecule



Tetrahedral Molecules

Methane, CH₄:

- Lewis structure of methane shows that the central C atom has four bonding electron pairs.
- These electron pairs repel each other and are thus directed to the four corners of a regular tetrahedron.
- A regular tetrahedron is a solid figure with four faces which are equilateral triangles.
- All bond angles are 109.5°



Do yourself

Determine the structure of

- CCl_4
- Ammonium ion, NH_4^+ , and
- Sulphate ion, SO_4^{2-}

Pyramidal Molecules

Ammonia molecule:

- central N atom has three bonding electrons and one lone electron pair which are to be directed to the corners of a tetrahedron.
- Thus, predicted H-N-H bond angle is 109.5° .
- But the shape of a molecule is determined by the arrangement of atoms and not the unshared electrons.
- Thus, if we see only at the atoms, NH_3 molecule as a pyramid with the N atom located at the apex and H atoms at the three corners of the triangular base.

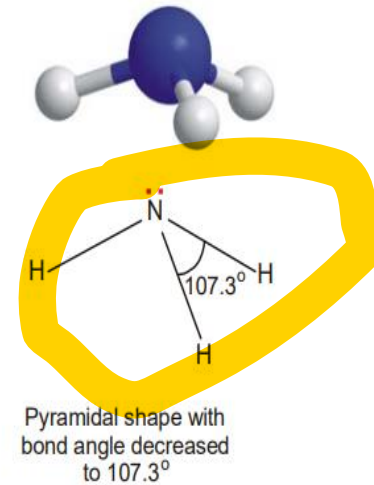
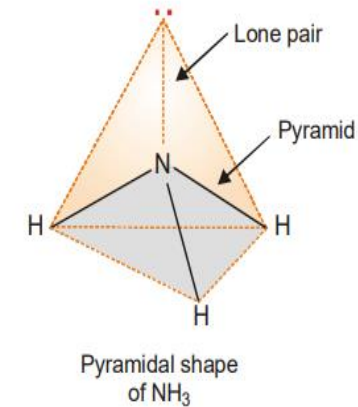
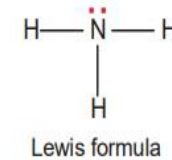


Figure 5.21

Pyramidal Molecules

- According to VSEPR theory, a lone pair exerts greater repulsion on the bonding electron pairs than the bonding pairs do on each other.
- As a result, the bonds of NH_3 molecule are pushed slightly closer.
- This explains why the observed bond angle H-N-H is found to be 107.3° instead of 109.5° predicted from tetrahedral geometry
- All molecules in which the N atom is joined to three other atoms by covalent bonds, have pyramidal shape. For example, amines RNH_2 , R_2NH and R_3N have pyramidal shape.

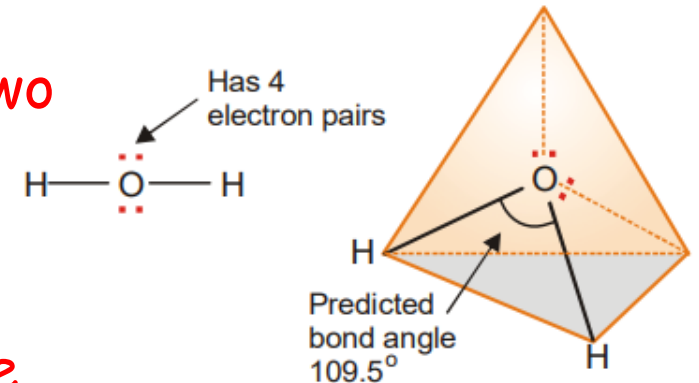
Do yourself:

- Determine the structure of Phosphorus trichloride, PCl_3

Bent or Angular Molecules

Water, H_2O :

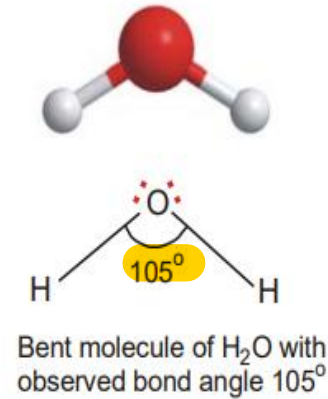
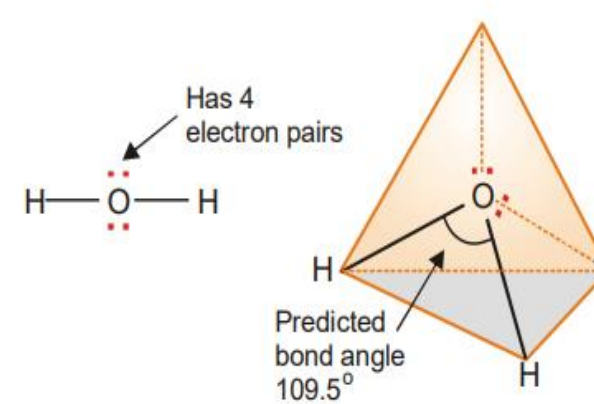
- The central O atom is bonded to two H atoms by covalent bonds and has two lone pairs.
- Thus O is surrounded by two bonding electron pairs and two unshared electron pairs.
- VSEPR theory says that in order to secure maximum separation between them, the four electron pairs are to be directed to the corners of a tetrahedron.
- If we look at the three atoms (and ignore the unshared pairs), the atoms HOH lie in the same plane and the predicted bond angle is 109.5° .



Bent or Angular Molecules

Water, H_2O :

- But with two unshared pairs repelling the bonding pairs, the bond angle is compressed to 105° , the experimental value.
- Thus the H_2O molecule is flat and bent at an angle at the O atom. Such a molecule is called a bent molecule or angular molecule.



Bent or Angular Molecules

Sulphur dioxide, SO_2

- The S atom is bonded to one O by a double bond and to the other O by a single bond. It has an unshared electron pair.
- So, S atom is surrounded by three electron pairs, two bonding pairs and one unshared pair.
- For maximum separation the three electron pairs are directed to the corners of an equilateral triangle with a bond angle 120° .
- But with the unshared electron pair repelling the bonding electron pairs, the bond angle is actually reduced somewhat.
- Thus SO_2 has a planar bent molecule with the observed bond angle 119.5° .

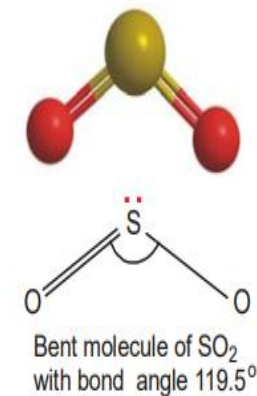
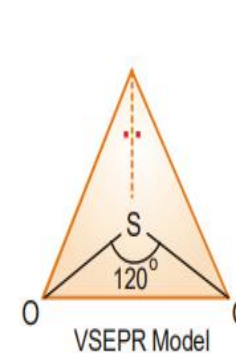
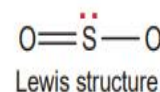


Figure 5.25

How to work out the shape of a Molecule

- First find the number of bonding pairs of electrons in the molecule.
- Find the number of valence electrons (electrons in the outer energy level) on an atom of the central atom (The one of which there is only one.)
- Find the number of lone pairs on the central atom by subtracting the number of bonding pairs (3) from the valence electrons (5)
- Distribute all the electron pairs around the central atom and learn the angles they will make from molecules with no lone pairs
- Learn that the repulsion between lone pairs of electrons is greater than the repulsion between bonding pairs, and subtract 2° from the bond angles for every lone pair
- Learn the names of the shapes. The shapes are named from the position of the atoms and not the position of the orbitals.


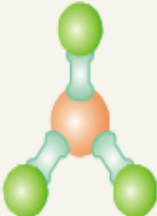
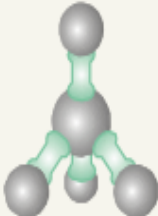

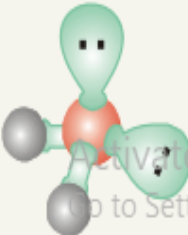
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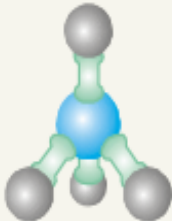
For polyatomic ions:

- subtract 1 from the number of valence electrons for every + charge on the ion and
- add 1 to the valence number for every - charge, then proceed as before.

TABLE OF SHAPES

Formula	BeCl_2	BCl_3	CH_4	NH_3	H_2O
	Beryllium chloride	Boron trichloride	Methane	Ammonia	Water
Bonding Pairs	2	3	4	3	2
Valence Electrons	2	3	4	5	6
Lone Pairs	0	0	0	1	2
Angles between bonding pairs	180°	120°	109.5°	107°	105°
Name of shape	Linear	Trigonal Planar	Tetrahedral	Trigonal Pyramid	Bent
					

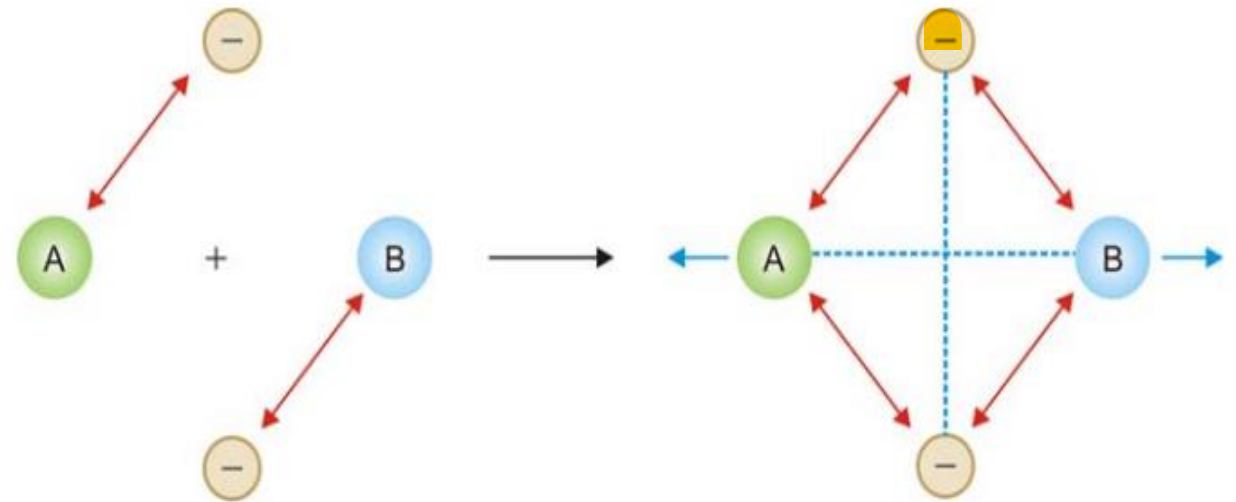
Polyatomic ions

Formula	NH_4^+
Bonding Pairs	4
Valence Electrons	5
Rule 2(a)	$5 - 1 = 4$
Lone Pairs	0
Angles between bonding pairs	109.5°
Name of shape	Tetrahedral
	

Valence Bond Theory

Valence Bond Theory

- a stable chemical union or bond between two (or more) atoms comes into existence only if the energy is lowered when the atoms come in close proximity
- 'Energy' means the sum of the kinetic and potential energies.
- The potential energy of a system in which atoms A and B approach each other can be due to
 - Electron-electron repulsions
 - Nucleus-nucleus repulsions
 - (Nucleus-electron attractions.)



■ Figure 6.1

Illustration of potential energy of the system consisting of approaching atoms A and B; the double headed arrows (\leftrightarrow) indicate attraction and dotted lines indicate repulsion.

Bond Formation (Valence Bond Theory)

- Bond formation between atoms to give chemical compounds can be interpreted admirably in terms of the orbital theory of atomic structure.
- Heitler and London believed that electron cloud of the valence orbital on one atom 'overlaps' the electron cloud of the other bonding atom to form a covalent linkage.
- The theory of 'maximum overlap', affords an excellent interpretation of covalent bond formation.

The essential conditions for the overlap of electron waves of orbitals:

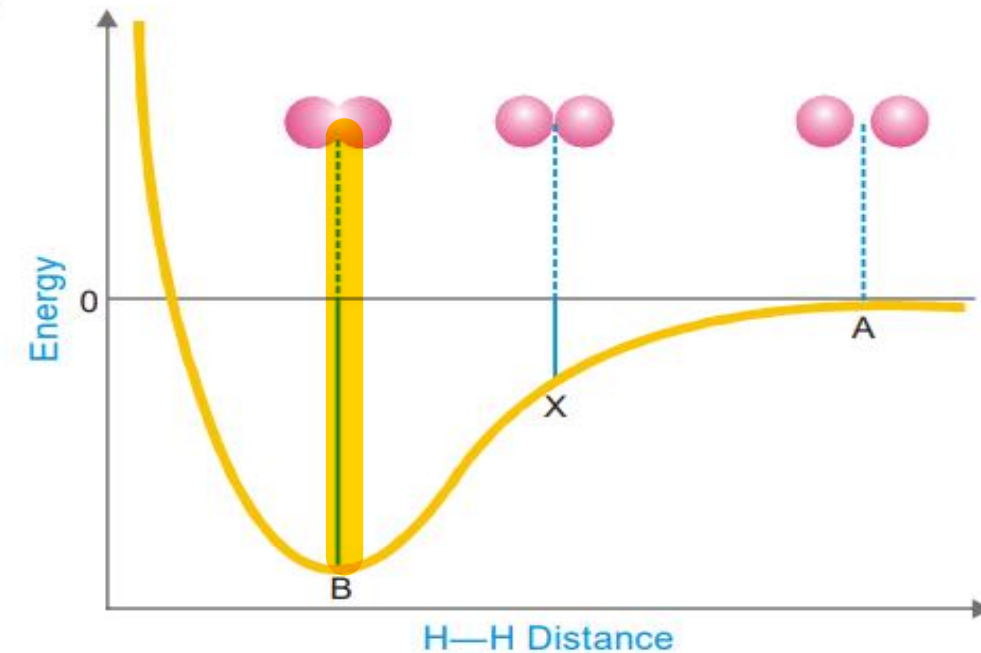
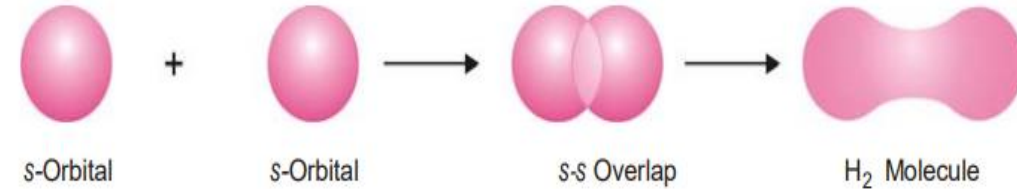
- The orbitals entering into combination must have only one electron
- The atoms with valence or bonding orbital (half-filled) should approach sufficiently close to one another with the axis of their orbitals in proper alignment.

Bond Formation (Valence Bond Theory)

- The new arrangement has lesser energy than the isolated atoms and, is therefore, more stable.
- The amount of energy given off or released per mole at the time of overlapping of atomic orbitals to form a bond is termed as Bond Energy or Stabilisation Energy..
- Since the overlapping involves a release of energy, it must produce a stabilizing effect on the system.
- Overlapping of the atomic orbitals halts at a stage when the atomic nuclei have come close enough to exercise a repulsive force on one another, which exactly balances the force of merger.
- This equilibrium distance at which the two atomic nuclei are now held is called the Bond length

Formation of H_2 molecule

- 1s orbitals of two H atoms overlap, resulting in the formation of a bigger electron cloud known as **molecular orbital**.
- This new molecular orbital having both the electrons holds the two H atoms together in the form of Hydrogen molecule (H-H)
- As the two atoms approach closer and closer for the overlap of half-filled 1s orbitals on them, the energy of the system goes on decreasing till it registers a minimum
- Beyond this point the energy of repulsion predominates and there is a steep rise in the energy curve with a further decrease of internuclear distance.



■ **Figure 6.3**
Energy diagram of s-s overlap.

Types of overlapping & Covalent Bond Nature

- A covalent bond is of two types depending on the type of overlapping between the two atoms:

Sigma (σ) bond

- When there is end to end overlapping of atomic orbitals along the internuclear axis, the bond resulted is called sigma (σ) bond. (also called "head-on" overlapping or "axial" overlapping)

Pi (π) Bond

- This type of covalent bond is formed by the sidewise overlap of the half filled atomic orbitals. It is also called lateral or sidewise overlap.
- This type of overlapping takes place perpendicular to the internuclear axis

Sigma (σ) bond

- Results when one of the following types of overlapping takes place :

s – s overlapping:

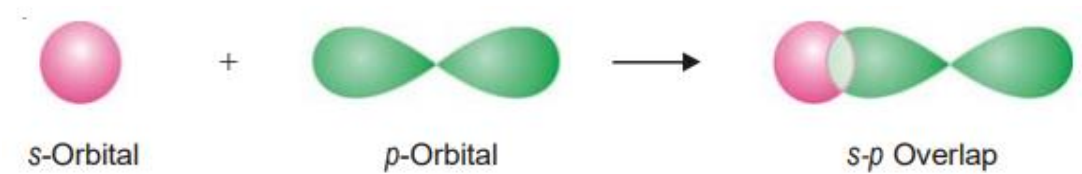
- Here s-orbital of one atom overlaps with the s-orbital of other atom. An example of this type of overlapping is the formation of hydrogen molecule from two H-atoms.

Sigma (σ) bond

s - p overlapping

- In this type of overlap s-orbital of one atom overlaps with the half filled p-orbital of the other atom as shown below :

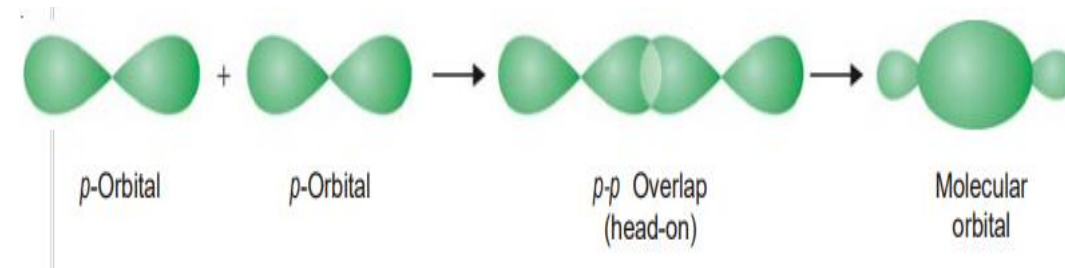
Examples : HF, HCl etc.



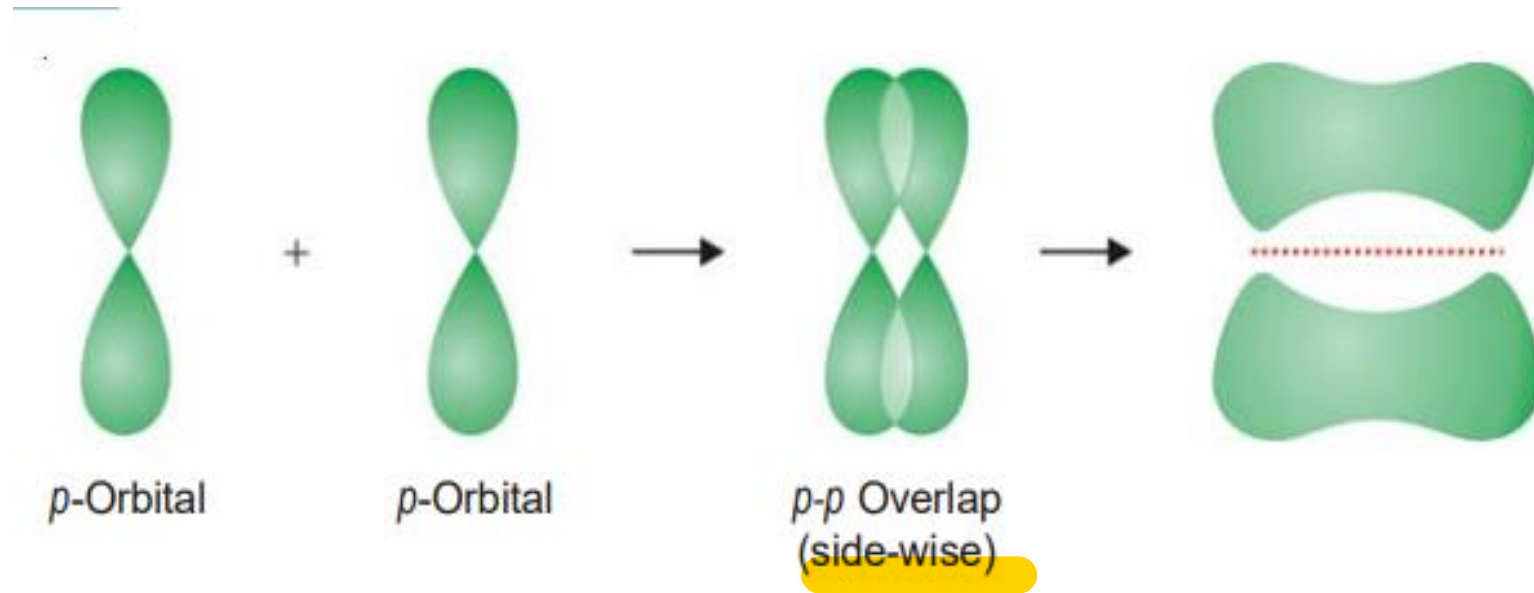
p - p overlapping

- Here p-orbital of one atom overlaps with the p-orbital of the other atom on internuclear axis. It is shown below

Examples: F_2 , Cl_2 , Br_2 etc



Pi (π) Bond



Strength of σ and π bonds

- the strength of a covalent bond depends upon the extent of overlapping between the atomic orbitals of participating atoms.
- During the formation of σ bond the extent of overlapping is more and hence a Sigma bond is stronger than Pi bond

Differences Between Sigma and Pi bonds

Sigma (σ) bond

1. It is formed by *end to end* overlapping of half filled atomic orbitals.
2. Overlapping takes place *along internuclear axis*.
3. The *extent of overlapping is large* and *bond formed is stronger*.
4. The molecular orbital formed as a result of overlapping is *symmetrical about the internuclear axis*.
5. There is *free rotation about σ bond* and no geometrical isomers are possible.
6. *The bond can be present alone*.
7. *s and p orbitals* can participate in the formation of σ bond.

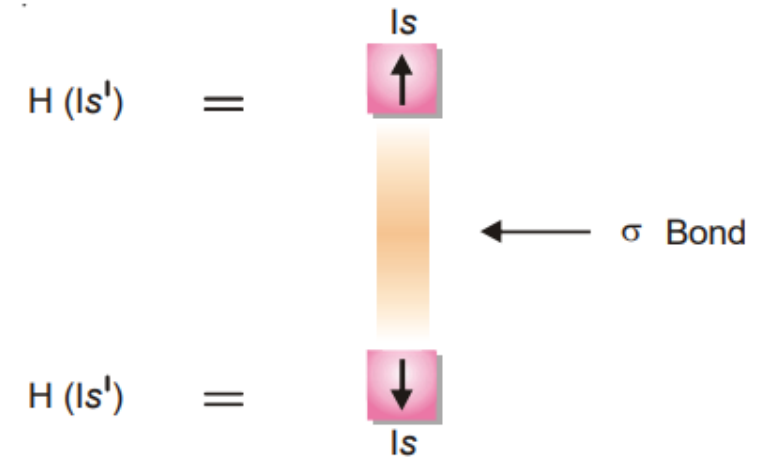
Pi (π) Bond

1. It is formed by the *sidewise* overlapping of half filled *p-orbitals* only.
2. Overlapping takes place *perpendicular to internuclear axis*.
3. The extent of overlapping is *small* and *bond formed is weaker*.
4. The molecular orbital formed as a result of overlapping consists of two *lobes above and below the internuclear axis*.
5. There is *no free rotation about π bond* and geometrical isomers are possible.
6. The bond is always formed *in addition to sigma (σ) bond*.
7. *Only p-orbitals* participate in the formation of π bond.

Orbital Representation Of Molecules

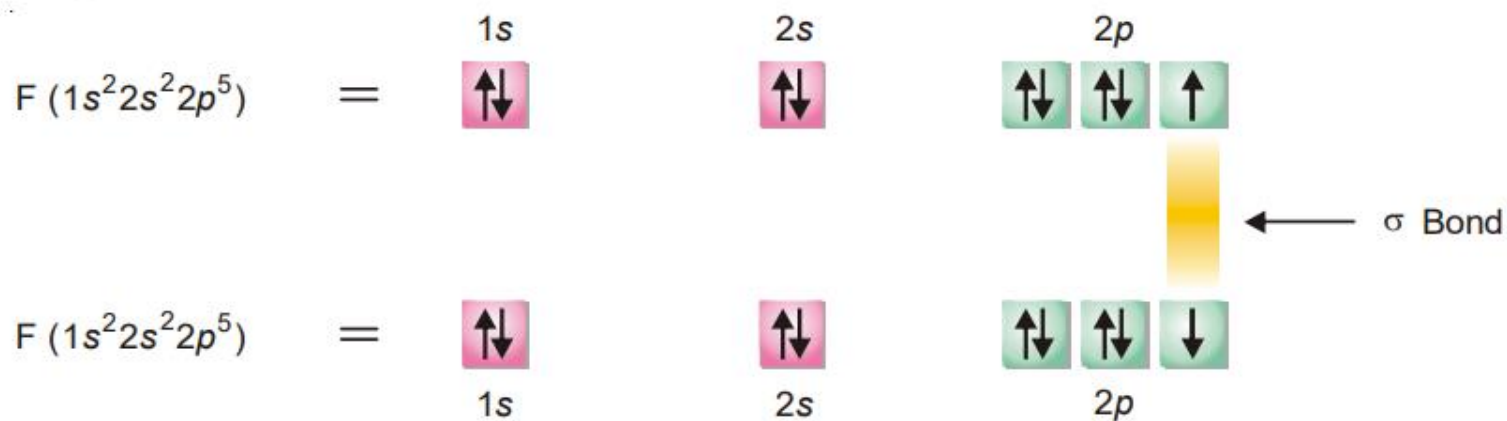
Formation of H₂ molecule

- Each hydrogen atom has **one electron in 1s-orbital**.
- Two such atoms join to **form a molecule** of hydrogen.
- In this case **s-s overlapping between two 1s-orbitals** of hydrogen atoms takes place resulting in the formation of hydrogen molecule



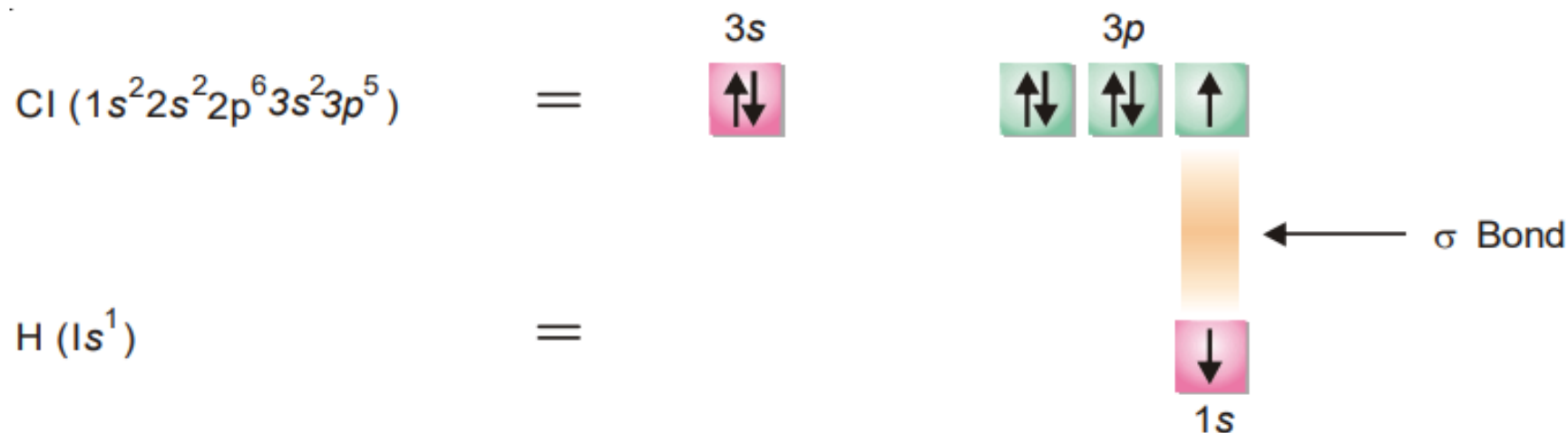
Formation of F₂ molecule

- Fluorine (at. no. 9) atom has electron configuration $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$.
- The unpaired electron in $2p_z$ orbital of one atom overlaps with similar orbital of other Fluorine atom along internuclear axis leading to the formation of σ bond



Formation of HCl molecule

- During the formation of HCl molecule, **1s orbital of Hydrogen atom having an unpaired electron overlaps** with
- 3p_z orbital of chlorine atom** having electronic configuration $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$.
- This **overlapping takes place along internuclear axis** leading to the formation of σ bond as shown below :



Do yourself

- Formation of Nitrogen molecule
- Formation of H_2O molecule
- Formation of Oxygen molecule

Challenges of existing concepts

- Formation of molecules of Be, B and C present problems of greater magnitude having no solution with the previous theory.
- To explain fully the tendency of these atoms to form bonds and the shape or geometry of their molecules, **another concept is required**

Concept Of Hybridization

- According to this concept, we may mix any number of atomic orbitals of an atom, which differ in energy only slightly, to form new orbitals called Hybrid orbitals.
- The mixing orbitals generally belong to the same energy level (say 2s and 2p orbitals may hybridize).
- The total number of hybrid orbitals formed after mixing, is invariably equal to the number of atomic orbitals mixed or hybridized.
- An important characteristic of hybrid orbitals is that they are all identical in respect of energy and directional character

Concept Of Hybridization: Definition

- They, however, differ from the original atomic orbitals in these respects. They may also differ from one another in respect of their arrangement in space. i.e., orientation.
- Like pure atomic orbitals, the hybrid orbitals of an atom shall have a maximum of two electrons with opposite spin.
- Thus hybridization may precisely be defined as
"the phenomenon of mixing up (or merging) of orbitals of an atom of nearly equal energy, giving rise to entirely new orbitals equal in number to the mixing orbitals and having same energy contents and identical shapes."

Rules Of Hybridization

For hybridization to occur, the atom needs to satisfy the following conditions :

- Orbitals on a single atom only would undergo hybridization
- There should be very little difference of energy level between the orbitals mixing to form hybrid orbitals.
- Number of hybrid orbitals generated = the number of hybridizing orbitals
- The hybrid orbitals assume the direction of the dominating orbitals
- It is the orbitals that undergo hybridization and not the electrons.
- The electron waves in hybrid orbitals repel each other and thus tend to be farthest apart.

Types of Hybridization

- Hybridization lends an entirely new shape and orientation to the valence orbitals of an atom
- It has a significant importance in determining the shape and geometry of the molecules formed from such orbitals.
- Depending upon the number and nature of the orbitals undergoing by hybridization, we have various types of hybrid orbitals. For instance s, p, and d orbitals of simple atoms may hybridize
 - sp Hybridization
 - sp^2 Hybridization
 - sp^3 Hybridization
 - sp^3d hybridization
 - sp^3d^2 hybridization

sp Hybridization

- The mixing of an s and a p orbital only leads to two hybrid orbitals known as sp hybrid orbitals after the name of an s and a p orbital involved in the process of hybridization.
- The process is called sp hybridization.
- Each sp orbital has 50% s-character and 50% p-character.
- Orbitals thus generated are the seat of electrons which have a tendency to repel and be farther apart.

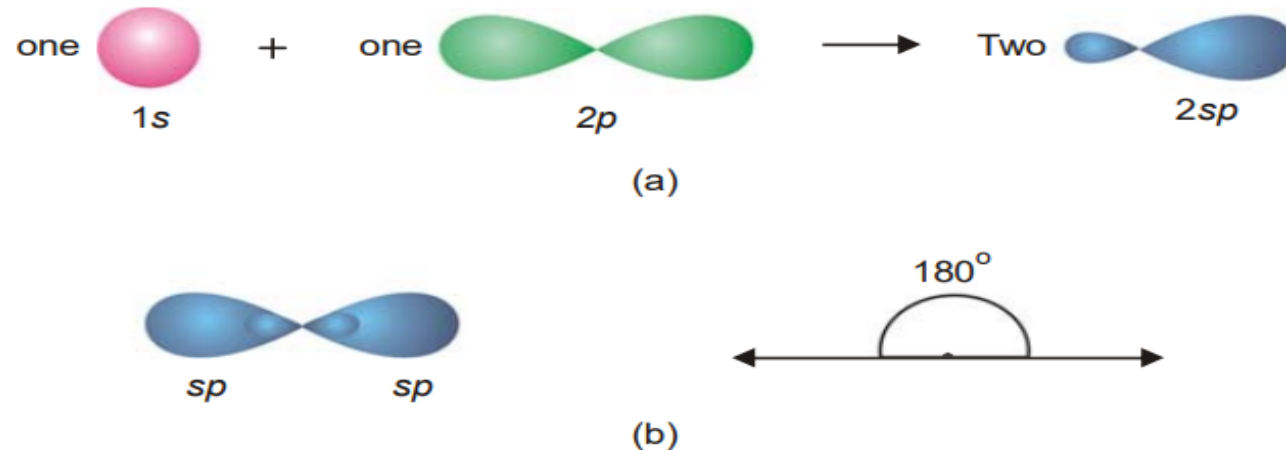


Figure 6.6

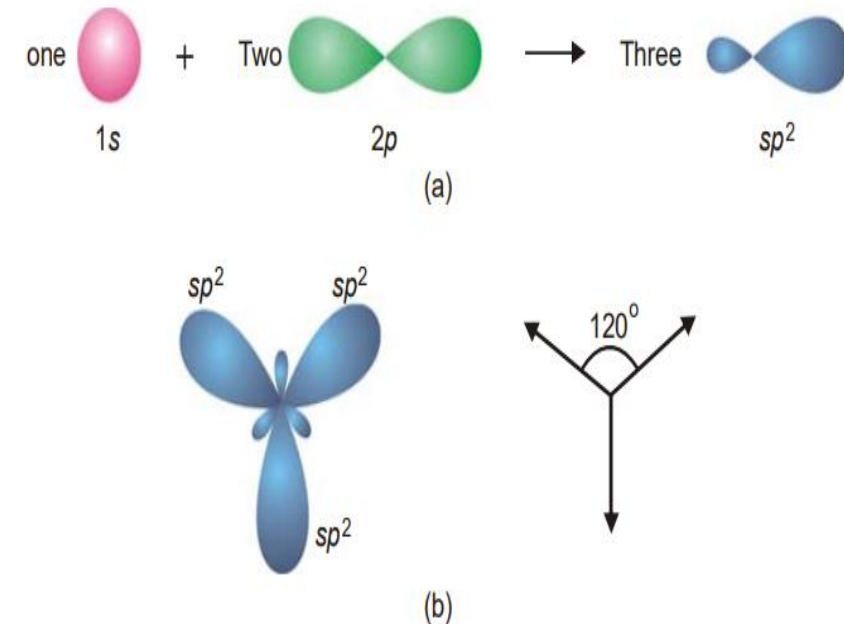
(a) sp Hybridization. (b) Disposition of hybrid orbitals along a line.

sp Hybridization

- In order to do so the new orbitals arrange themselves along a line and are, therefore, often referred to as Linear hybrid orbitals.
- This gives an angle of 180° between the axes of the two orbitals.
- an sp orbital has two lobes (a character of p orbital) one of which is farther than the corresponding s or p orbitals and also protrudes farther along the axis.
- It is this bigger lobe that involves itself in the process of an overlap with orbitals of other atoms to form bonds.
- Examples : BeF_2 , BeCl_2 , etc.

sp² Hybridization

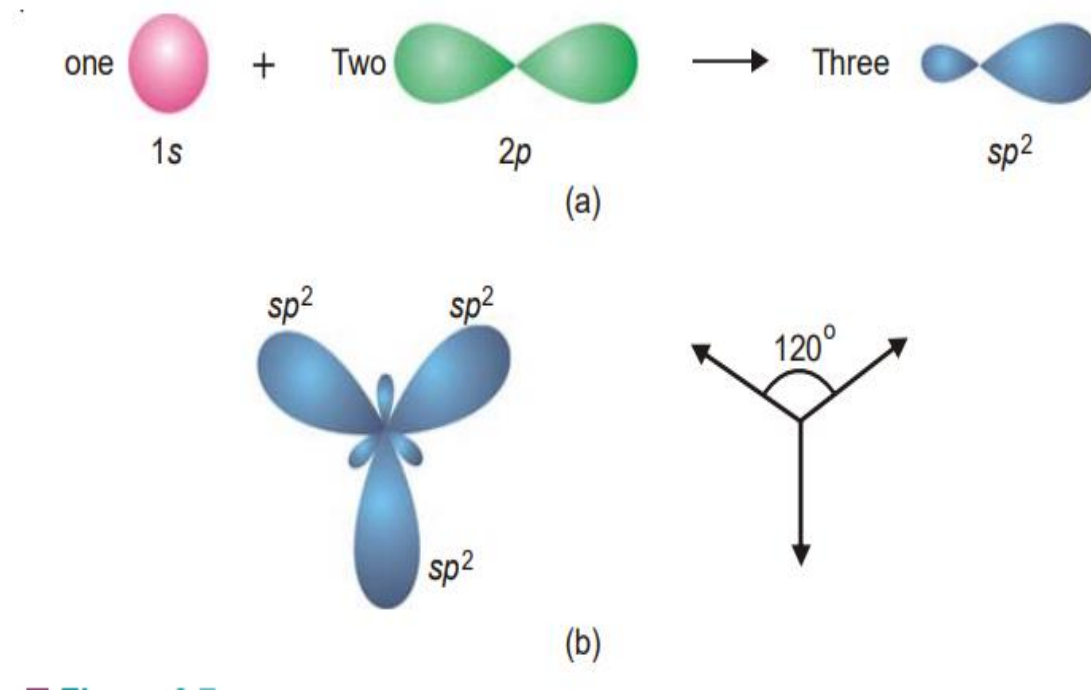
- When an s and two p orbitals mix up to hybridize, there result three new orbitals called sp² hybrid orbitals (spoken as 'sp two').
- Each sp² hybrid orbital has 33% s-character and 67% p-character.
- Like unhybridized orbitals, new hybrid orbitals lie in a plane
- They have to lie farthest apart in a plane which can happen if they are directed at an angle 120° to one another



sp^2 Hybridization

- It is for this reason that sp^2 hybrid orbitals are also called Trigonal hybrids, the process being referred to as Trigonal hybridization.
- The sp^2 hybrid orbitals resemble in shape with that of sp hybrid orbitals but are slightly fatter

Examples : BF_3 , NO_3^- , etc

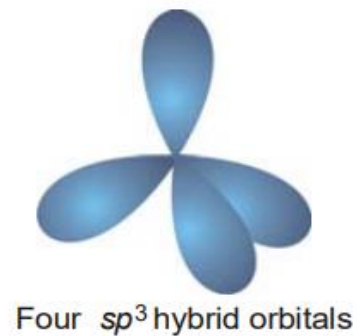


sp^3 Hybridization

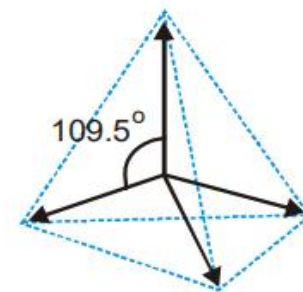
- The **four new orbitals** formed by mixing **an s** and **three p orbitals** of an atom are known as sp^3 hybrid orbitals.
- Each sp^3 hybrid orbital has **25% s-character** and **75% p-character**.
- Since mixing of orbitals takes place **in space**, **the four hybrid orbitals** would also lie in space.
- **An arrangement in space** that keeps them farthest apart is that of a **tetrahedron**.



(a)

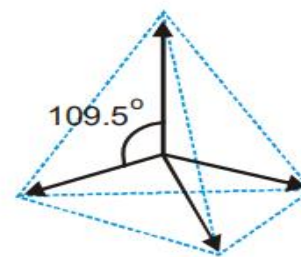
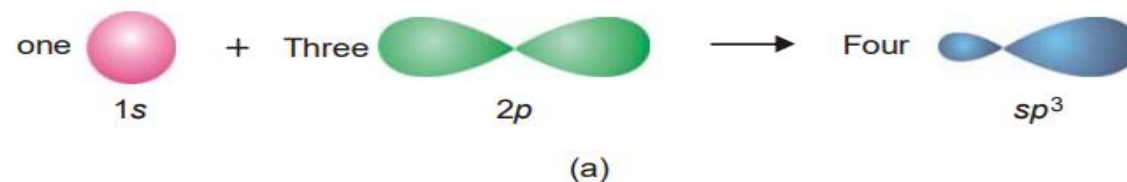


(b)



sp^3 Hybridization

- Thus each of the four **hybrid orbitals are directed towards the four corners** of a regular tetrahedron.
- Because of their tetrahedral disposition, this type of hybridization is also called **Tetrahedral hybridization**.
- They are of the **same shape** as that of the previous two types **but bigger in size**.



(b)

Hybridization involving d orbitals

- Out of several types of hybridization involving d orbitals., sp^3d , sp^3d^2 and sp^2d hybridization are the most important ones.

sp^3d hybridization:

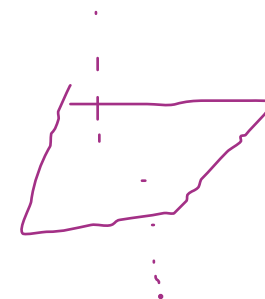


- one of s type, three of p type and one of d type orbitals involve.
- The five new orbitals will be farthest apart by arranging three of them in a plane at an angle of 120° to one another and
- the other two in a direction perpendicular to the plane. The figure obtained by joining the ends assumes the shape of a trigonal bipyramid
- This type of hybridization is, therefore, called Trigonal bipyramidal hybridization.

Hybridization involving d orbitals

sp^3d^2 hybridization:

- two d type of orbitals take part in hybridization with one s type and three p type orbitals,
- six hybrid orbitals called sp^3d^2 hybrid orbitals are created.
- To be away from one another four of them are dispersed in a plane at an angle of 90° each and the rest two are directed up and below this plane in a direction perpendicular to it.
- On joining their corners, an octahedron results and this type of hybridization also gets the name Octahedral hybridization.



Hybridization involving d orbitals

sp^2d hybridization:

- So far we have been considering the hybridization of orbitals belonging to the same energy level (say 3s, 3p, and 3d orbitals) of an atom.
- But this may not necessarily be so always. In fact, **there is very little energy difference between 3d, 4s and 4p orbitals which may undergo sp^2d hybridization.**
- The d orbital involved in this type of hybridization has the same planar character as the two p orbitals have and the hybrid orbitals will also be planar, dispersed in such a way so as to be farthest apart i.e., subtending an angle of 90° between them.
- This gives a square planar arrangement for them and the hybridization is, therefore, **called Square planar hybridization.**



Hybridization And Shapes Of Molecules

- Diatomic molecules must all be invariably linear but tri-and tetra-atomic molecules have several possible geometrical structures.

Shape of BeF_2 molecule

- An isolated Be atom in its ground state has the electronic configuration $1s^2, 2s^2$, like He
- But Be behaves differently because its 2s orbital though complete, possesses another empty 2p level lying in the same shell. This is not so for He ($1s^2$)
- The Be atom, gets excited & one of its $2s^2$ electrons is 'promoted' to the next available $2p_x$ orbital before the atom participates in chemical bonding.
- the excited atom acquires the structure $1s^2, 2s^1, 2p_x^1$.
- If at this stage the atom forms two bonds by suitable overlaps with two fluorine atoms, these bonds will not be identical, one involving the s and the other p orbital

Shape of BeF_2 molecule

- Thus the s and p orbitals first hybridize to form two new and completely equivalent sp hybrid orbitals.
- The two sp hybrid orbitals overlap two 2p orbitals from two fluorine atoms in the 'head on' manner to form two σ bonds.
- The two sp orbitals being linear, lend a linear shape to BeF_2 molecule with Be atom lying in the center and two F atoms on its either side
- so that $\text{F}-\text{Be}-\text{F}$ angle is equal to 180°

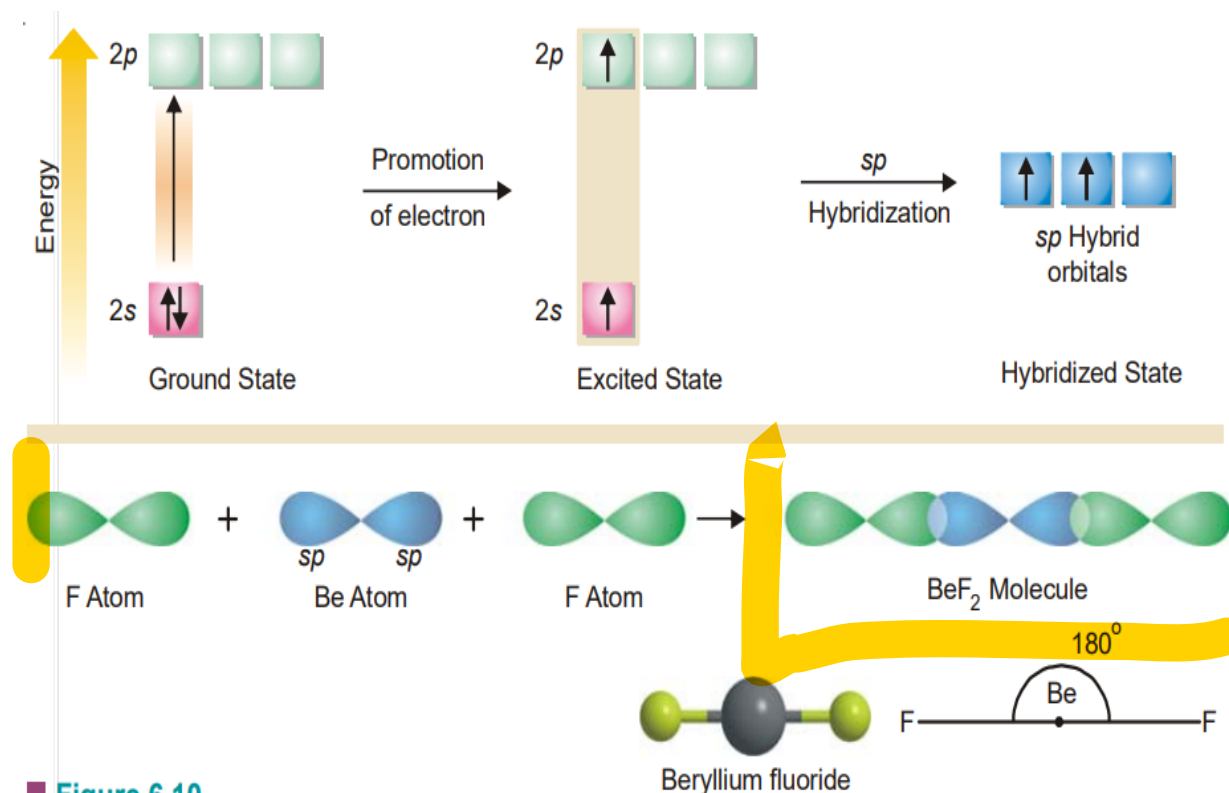


Figure 6.10

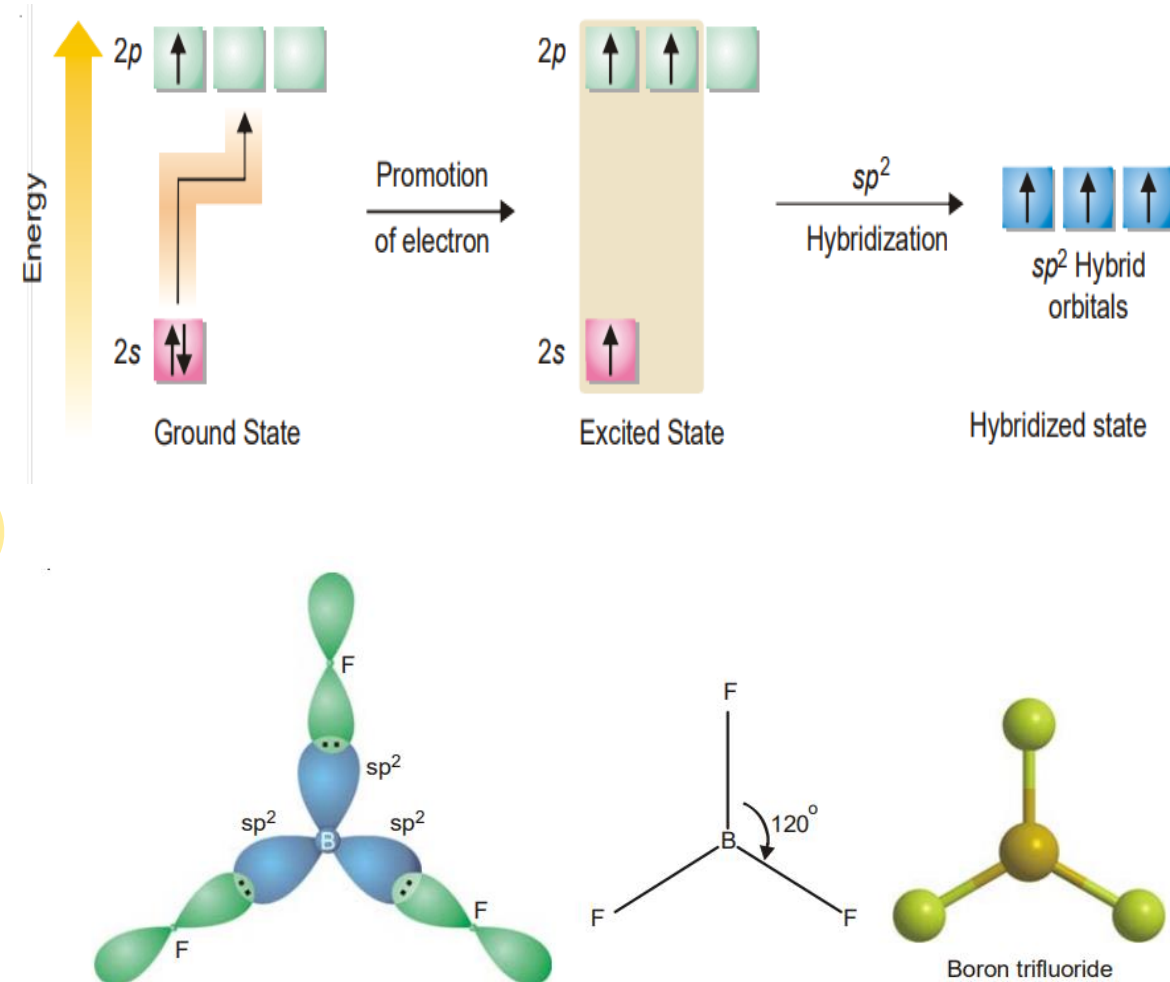
Various states of Be atom. Its orbitals undergo sp hybridization in the excited state. Overlaps and geometry of BeF_2 are also shown.

Shape of BF₃ molecule

- The orbital electronic configuration of Boron (B) is $1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0$.
- As there is only one bonding orbital $2p_x$, B is expected to form only one bond.
- Boron, in fact, is known to form compounds such as BCl₃, BF₃, BH₃ etc., indicating its capacity to form three bonds.
- What actually happens is that the two electrons of $2s$ orbital get unpaired when it is excited just like Be. One of these unpaired electrons thus gets promoted to the vacant $2p_y$ orbital lying close to it.
- Thus in the excited state of Boron there are three half-filled orbitals available for bonding.
- If as such it were to form bonds by overlap, the nature of these bonds would be different owing to their different types.

Shape of BF₃ molecule

- One 2s and two 2p orbitals undergo sp^2 hybridization giving three sp^2 hybrid orbitals lying in one plane i.e., xy, and subtending an angle 120° .
- The equivalent hybrid orbitals can now enter into bond formation by overlapping with three 2p orbitals of three fluorine atoms
- Thus BF₃ molecule is planar and each F—B—F angle is equal to 120°



Shapes Of Carbon Compounds

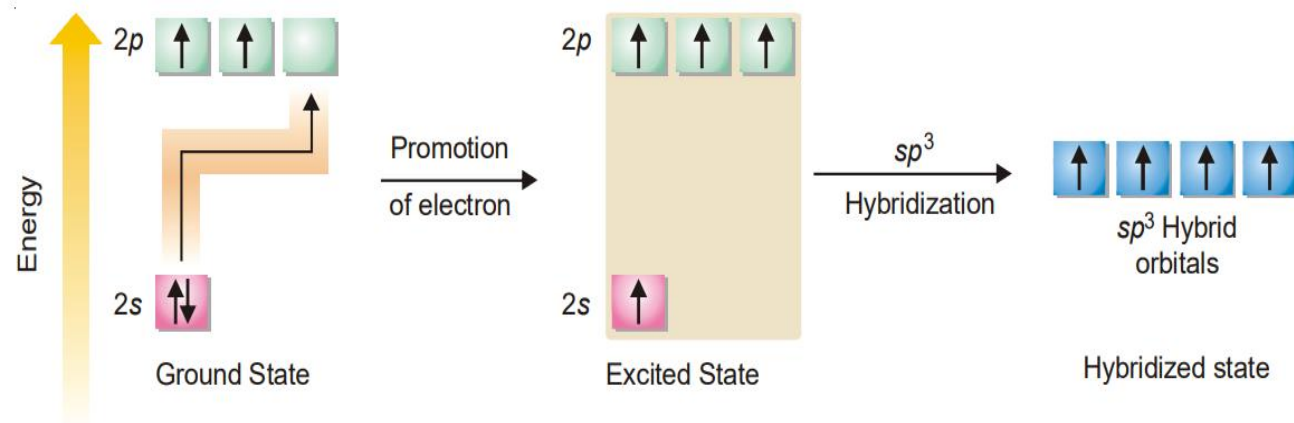
- The carbon atom ($1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$) possesses two 2p bonding orbitals i.e., $2p_x$ and $2p_y$
- can be expected to form only two bonds ordinarily.
- But in common practice carbon behaves as tetra-covalent.
- To remove the clash between the expected and the actual, the concept of hybridization comes to our rescue.
- Carbon can undergo three types of hybridization.

sp³ Hybridization of Carbon

- One electron from 2s orbital, being quite near in energy can be promoted to the vacant 2p_z orbital thus obtaining the excited atom.
- At this stage the carbon atom undoubtedly has four half-filled orbitals and can form four bonds.
- But orbitals of carbon atom first undergo hybridization before forming bonds.
- In the excited atom all the four valence shell orbitals may mix up to give identical sp³ hybrid orbitals also four in number.
- Each of these four sp³ orbitals possesses one electron and overlaps with 1s orbitals of four H-atoms

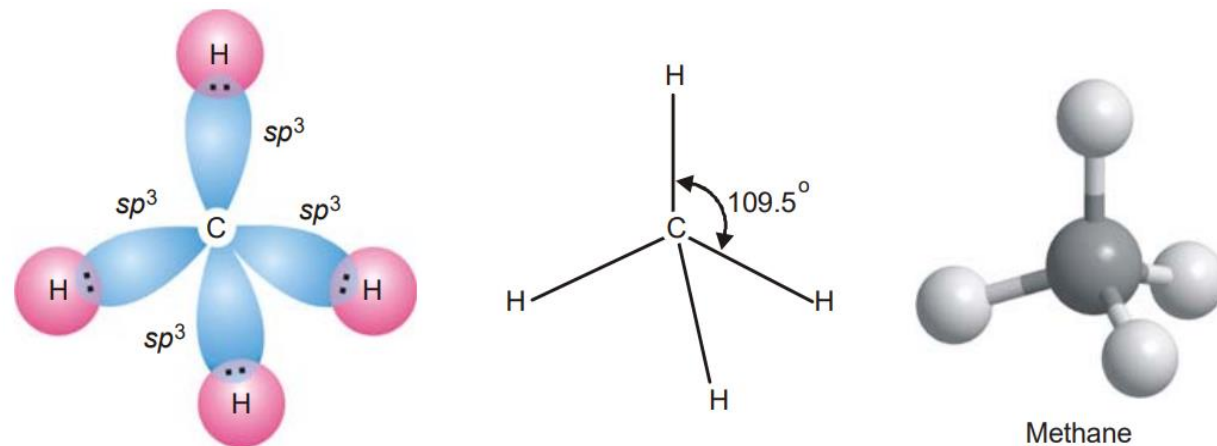
sp³ Hybridization of Carbon

- Thus forms four equivalent bonds in methane molecule.
- Due to the **tetrahedral disposition** of sp³ hybrid orbitals, the orbitals are inclined at an angle of 109.5°.
- Thus all the HCH angles are equal to 109.5°



■ Figure 6.13

Various states of carbon atom; the orbitals here are undergoing sp³ hybridization.



■ Figure 6.14

Shape and formation of methane molecule.

sp² Hybridization of Carbon

- Three out of the four valence orbitals hybridize (2s, 2p_x and 2p_y orbitals)
- Three sp² hybrid orbitals are generated lying in a plane and inclined at an angle of 120°.
- The new orbitals lie in the xy plane while the fourth pure 2p_z orbital lies at right angles to the hybridized orbitals with its two lobes disposed above and below the plane of hybrid orbitals.
- Two such carbon atoms are involved in the formation of alkenes (compounds having double bonds).
- In the formation of ethene two carbon atoms (in sp² hybridization state) form one sigma bond by 'head-on' overlap of two sp² orbitals contributed one each by the two atoms.

sp² Hybridization of Carbon

- The remaining two sp² orbitals of each carbon form σ bonds with H atoms.
- The unhybridized 2p_z orbitals of the two carbon atoms undergo a side-wise overlap forming a π bond.
- Thus the carbon to carbon double bond in ethene is made of one σ bond and one π bond.

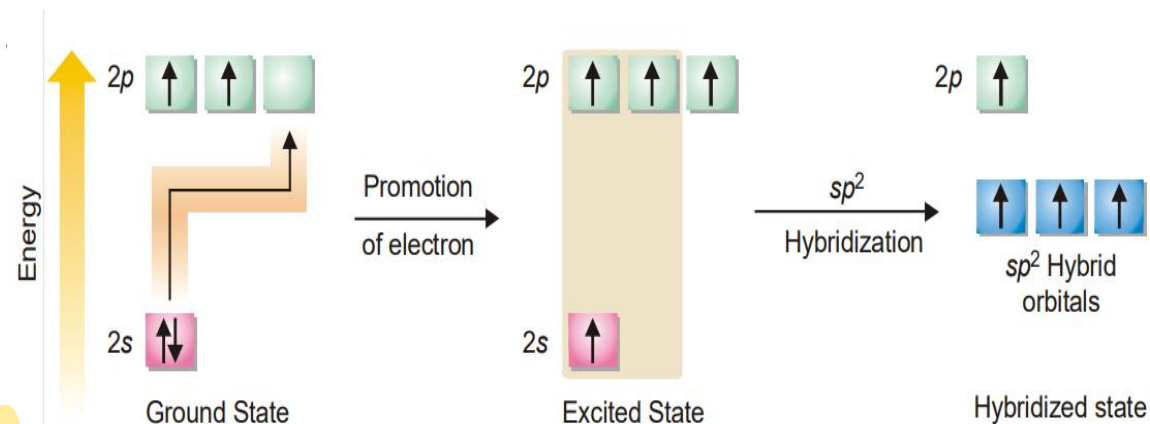
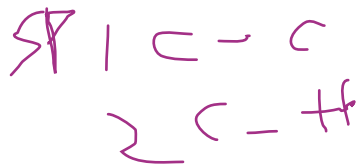
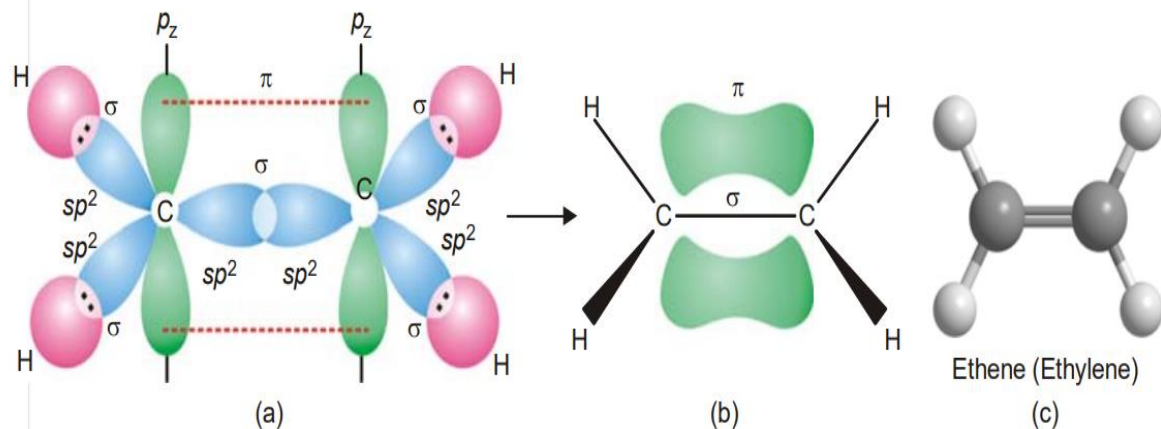


Figure 6.15

Excited carbon atom undergoing sp² hybridization leaves a pure 2p_z orbital.



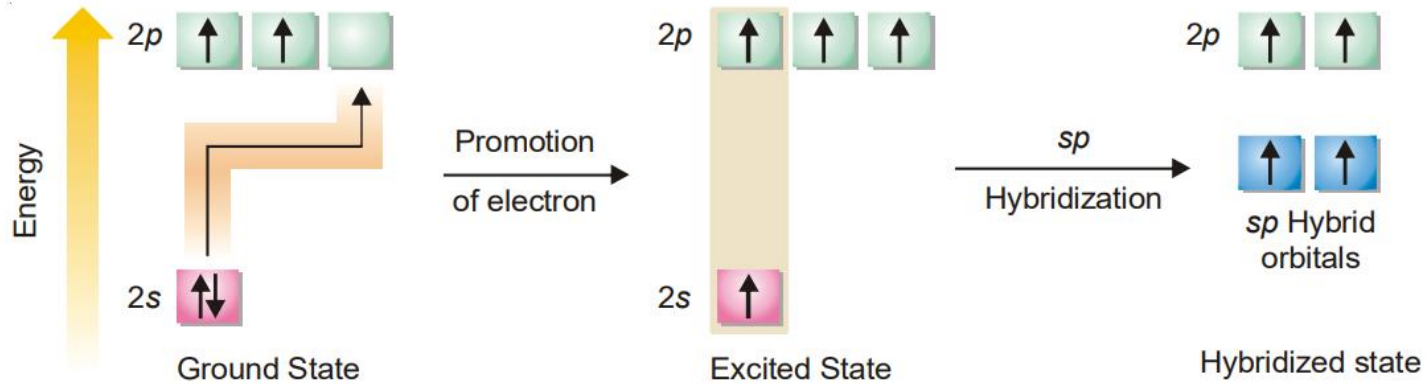
sp Hybridization of Carbon

- Here one 2s and only one 2p orbital hybridize to form two equivalent colinear orbitals;
- the other two 2p orbitals remain undisturbed, both being perpendicular to the axis of hybrid orbitals.
- One of the two sp hybrid orbitals on each of the two carbons in ethyne molecule, may be used in forming a σ bond between them.

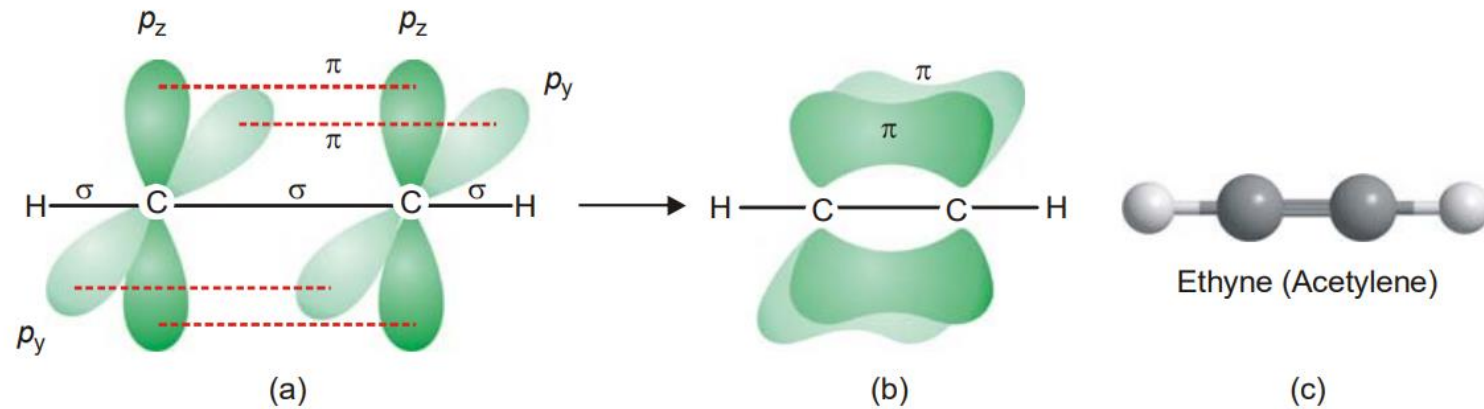
sp Hybridization of Carbon

- This leaves two pure 2p orbitals ($2p_y$ and $2p_z$) on each carbon atom being perpendicular to H-C-C-H nuclear axis
- These pure 2p orbitals are capable of forming two π bonds by side-wise overlaps.
- Thus ethyne molecule contains one σ and a two π bonds between the two carbons and each carbon is linked with one H-atom through σ bonds

sp Hybridization of Carbon



■ **Figure 6.17**
sp Hybridization of the orbitals of excited carbon.



Shape of Ammonia molecule, NH_3

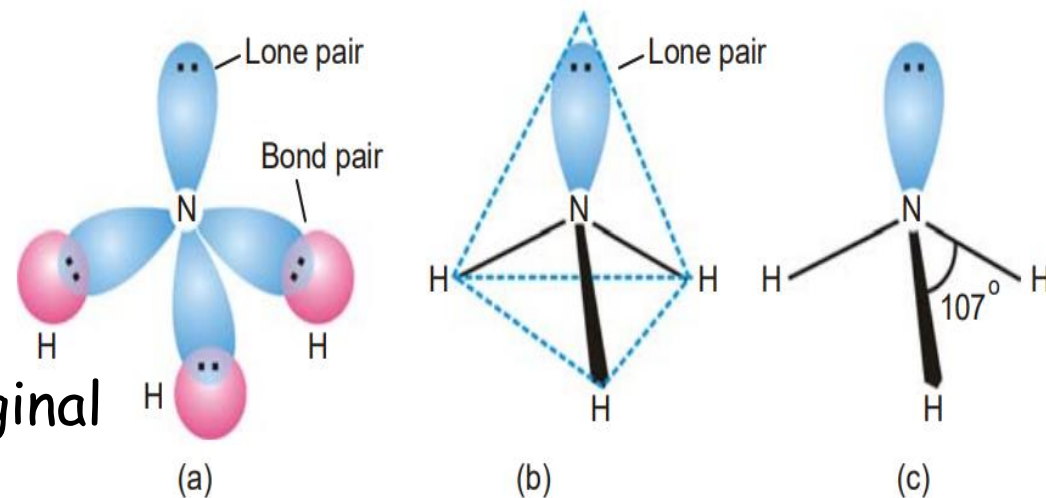
- The orbital structure of NH_3 has three orbital overlap axes inclined at an angle of 90° with N-atom as the origin.
- The four atoms in the molecule of NH_3 do not lie in the same plane but form a pyramid at whose base are the three H-atoms and the N-atom is at the apex of the pyramid.
- predicted H-N-H bond angles is 90° , the angle between the axes, which does not agree with the experimental value of 107° .
- The anomaly can be explained satisfactorily employing
 - (a) the concept of hybrid orbitals and
 - (b) the electron pair interactions.

1s² 2s² 2p_x¹ 2p_y¹ 2p_z¹

Shape of Ammonia molecule, NH_3

sp^3 Hybridization in ammonia molecule:

- Orbitals of the second energy level of N-atom ($2s^2, 2p_x^1, 2p_y^1, 2p_z^1$) undergo sp^3 hybridization,
- Four new hybrid orbitals result.
- One of these will have two electrons (like the original atom) and is non-bonding
- The other three have one electron each and can form bonds by overlap.
- Now these hybrid orbitals are tetrahedrally dispersed with an angle of 109.5° between them



Shape of Ammonia molecule, NH_3

Electron pair repulsion

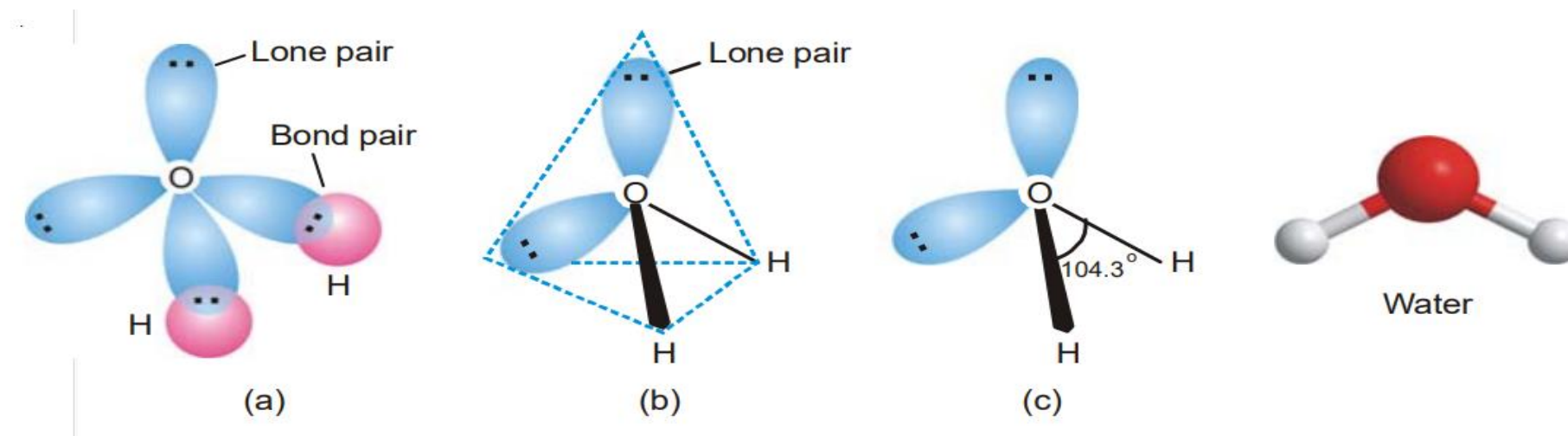
- The three bond pairs and one lone pair may get arranged tetrahedrally about the central atom.
- The lone pair is attracted more towards the N-atom than the bond pairs which belongs to the H-atoms and N-atom jointly.
- This is because of the fact that the lone pair belongs only to the N-atom and hence its electron cloud is more concentrated near the N-atom.
- The lone pair is, therefore, capable of exerting a greater repulsion on a bond pair than a bond pair can repel another bond pair.
- As a result three bonds of ammonia molecule are forced slightly closer than in the normal tetrahedral arrangement. Therefore each of the HNH bond angles is 107.3° .

Shape of Water molecule, H₂O

- In the central oxygen atom of the molecule, there are two bonding orbitals ($2p_y^1$ and $2p_z^1$).
- $1s^2 \ 2s^2 \ 2p_x^2 \ 2p_y^1 \ 2p_z^1$
- These may overlap with $1s$ orbitals of two H atoms of opposite spins.
 - Results in the formation of a σ MO, giving two σ bonds in the molecule as a whole
 - The molecule involves two $2p$ orbitals at right angles and the bond established by an orbital retains the directional character of the bonding orbital
 - It is reasonable to expect the bond angle to be equal to 90° .

Shape of Water molecule, H₂O

- But careful experiments reveal the HOH angle to be 104.3° rather than the predicted 90°
- The discrepancy between the expected and the experimental values of the bond angle is best explained with the help of hybridization concept.



Shape of Water molecule, H₂O

- The valence orbitals of the second energy shell of oxygen atom all hybridize giving four tetrahedrally dispersed sp³ hybrid orbitals.
- Two of these four hybrid orbitals are non-bonding,
- the rest two having one electron each are capable of bonding by overlaps with orbitals of two H atoms.
- Predicted HOH angle would be 109.5°, tetrahedral angle
- there are two lone pairs in the vicinity of the central O-atom which has two bond pairs also.
- The repulsive forces operating results in 104.3°

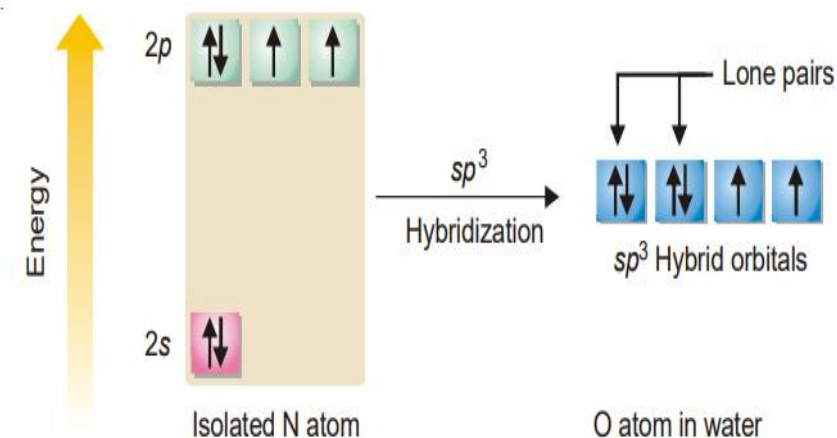


Figure 6.22

sp³ Hybridization of orbitals of oxygen atom.

Do yourself

- In the light of the above discussions try to explain the molecular geometry of PH_3 , PCl_3 , NF_3 , H_2S .

Thank you