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Engineering Chemistry-I (BS-109)

Chemical Bonding-2

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Valence Shell Electron Pair (VSEPR) Theory: Given by Gillespie-Nyholm in 1957

“Whenever there is a repulsion between the pairs of valence electrons in all atoms, the atoms will rearrange themselves in a geometric shape so as to minimize the electron pair repulsion.” (molecule must have minimum energy and maximum stability). This arrangement of the atom determines the geometry of the resulting molecule.

Postulates of VSEPR Theory:

- In polyatomic molecules (i.e. molecules made up of three or more atoms), one of the constituent atoms is identified as the central atom to which all other atoms belonging to the molecule are linked.
- The total number of valence shell electron pairs decides the shape of the molecule.
- The electron pairs have a tendency to orient themselves in a way that minimizes the electron-electron repulsion between them and maximizes the distance between them.
- If the central atom of the molecule is surrounded by bond pairs of electrons, then, the asymmetrically shaped molecule can be expected and if the central atom is surrounded by both lone pairs and bond pairs of electrons, the molecule would tend to have a distorted shape.
- The VSEPR theory can be applied to each resonance structure of a molecule.
- The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.

$$\text{l.p.-l.p.} > \text{l.p.-b.p.} > \text{b.p.-b.p.}$$

- If electron pairs around the central atom are closer to each other, they will repel each other. This results in an increase in the energy of the molecules. If the electron pairs lie far from each other, the repulsions between them will be less and eventually, the energy of the molecule will be low.
- The magnitude of repulsions between b.p. of electrons depends on the electronegativity difference between the central atom and other atoms.
- **Triple bond > double bond > single bond** : order of repulsion



Number of
valence electrons

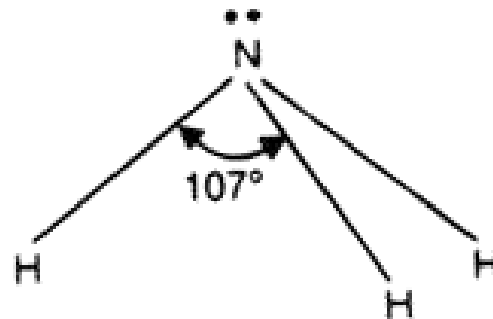
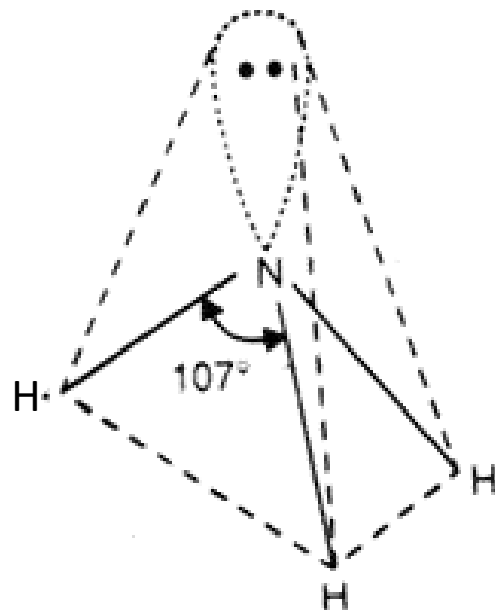
Steric No.	VSEPR Geometries				
	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

Number of electron pairs in outer shell	Shape of molecule	Bond angles
2	linear	180°
3	plane triangle	120°
4	tetrahedron	109°28'
5	trigonal bipyramid	120° and 90°
6	octahedron	90°
7	pentagonal bipyramid	72° and 90°



- **Structure of NH_3 :**

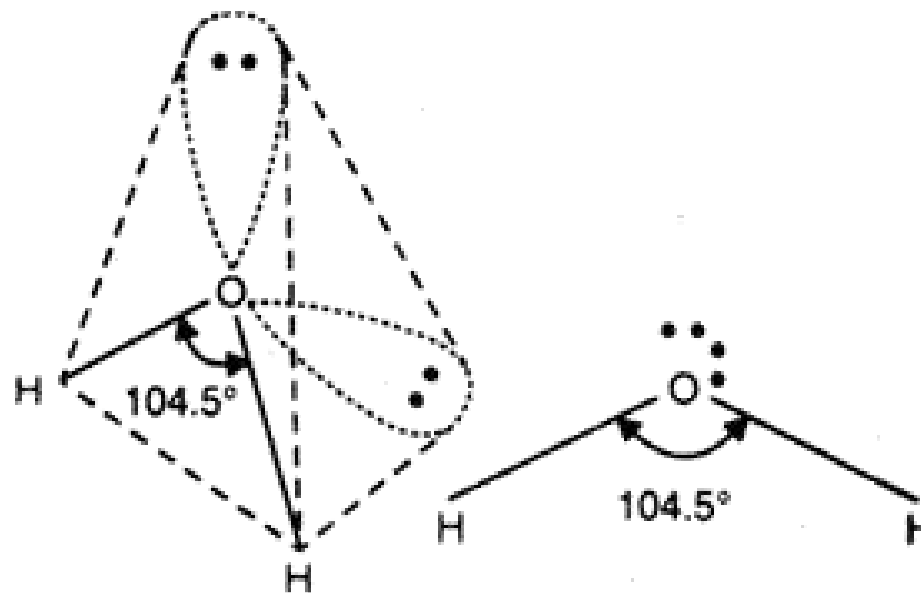
- N is the central atom having electronic configuration of $1s^2 2s^2 2p^3$ (**5** electrons in its valence shell)
- Three electrons participate in the bond formation with H while 2 electrons do not bond => **3 b.p. and 1 l.p.**
- Thus NH_3 has 4 valence electrons pairs, expected geometry: tetrahedral
- Presence of l.p. on N will repel the b.p. more than b.p.-b.p. repulsions. This leads to decrease in H-N-H bond angle from $109^\circ 28'$ to $107^\circ 48'$
- Final geometry: **Pyramidal**





- **Structure of H_2O :**

- O is the central atom having electronic configuration of $1s^2 2s^2 2p^4$ (6 electrons in its valence shell)
- Two electrons participate in the bond formation with H while 4 electrons do not bond => **2 b.p. and 2 l.p.**
- Thus H_2O has 4 valence electrons pairs, expected geometry: tetrahedral
- Due to the presence of two l.p. on O, the repulsion will occur between both the l.p.'s, l.p.-b.p and both the b.p.'s. Since the extent of repulsions between two l.p.'s is more, the water molecule is more deviated from the symmetrical tetrahedral geometry resulting in bent shape for the water molecule where the H-O-H angle is 104.5° .
- Final geometry: **Bent or angular or V-shaped**



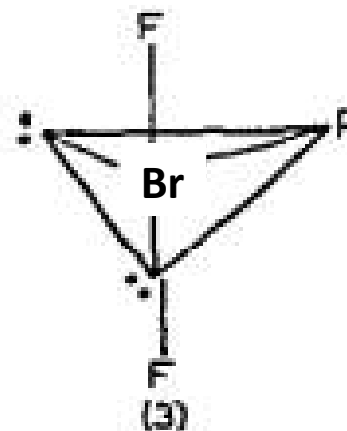
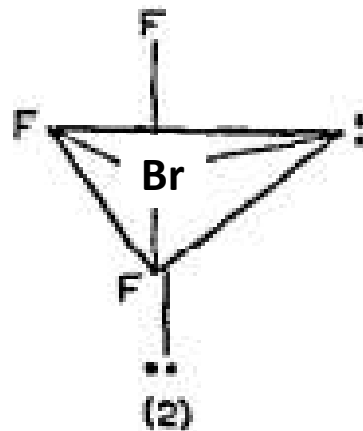
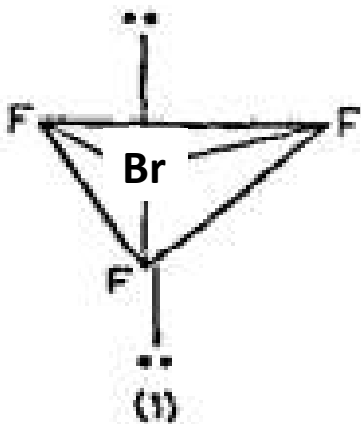
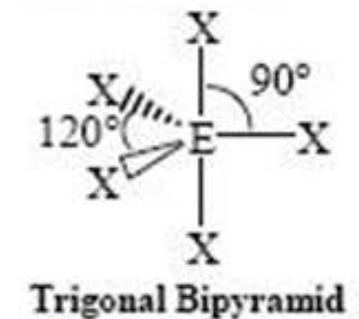
Distorted tetrahedral

V-shaped or bent



• Structure of BrF₃:

- Br is the central atom, which belongs to halogen group (17) having electronic configuration of 1s² 2s² 2p⁶ 3s² 3p⁶ 4s² 3d¹⁰ 4p⁵ (7 electrons in its valence shell)
- Three electrons participate in the bond formation with F while 4 electrons do not bond => **3 b.p. and 2 l.p.**
- Thus BrF₃ has 5 electrons pairs resulting into **trigonal bipyramidal geometry** (5 corners)
- TBP is not a regular shape since all the bond angles are not same (atoms at equatorial positions are at 120 ° while axial corners are at 90 ° with the equatorial atoms)
- Possible structures:



In tbp geometry the l.p. will be located at equatorial position rather than at apical position as this minimizes the repulsive forces

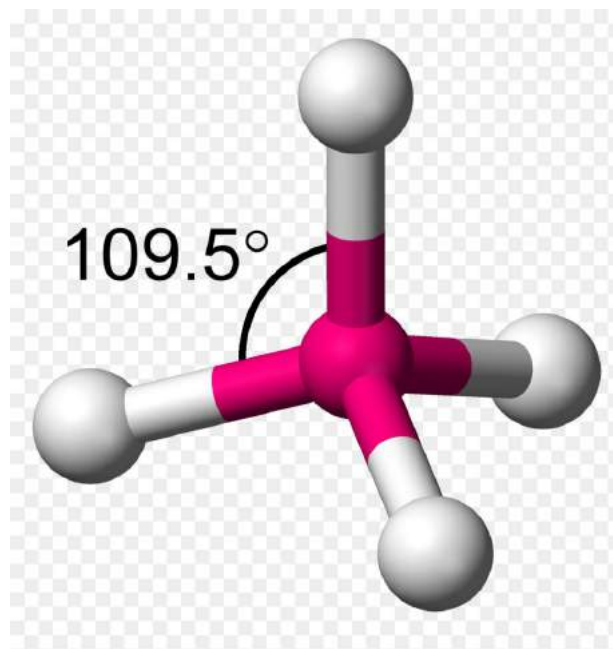
Structure 3 is most probable and the observed bond angles are 87 ° 40' (slight distortion to 90 ° is due to 2 l.p.)

- Most symmetrical, but six 90° repulsions between l.p-b.p
- No l.p.-l.p at 90 °
- Three 90 ° repulsions between l.p-b.p
- 1 l.p.-l.p. at 90 °
- Four 90 ° repulsions between l.p-b.p
- No l.p.-l.p. at 90 °



- **Structure of SiF_4 :**

- Si is the central atom having valence electronic configuration of $3s^2 3p^2$ (**4** electrons in its valence shell)
- All the four electrons participate in the bond formation with F \Rightarrow **4 b.p. and 0 l.p.**
- Thus SiF_4 has 4 valence electrons pairs.
- Geometry: **Tetrahedral**

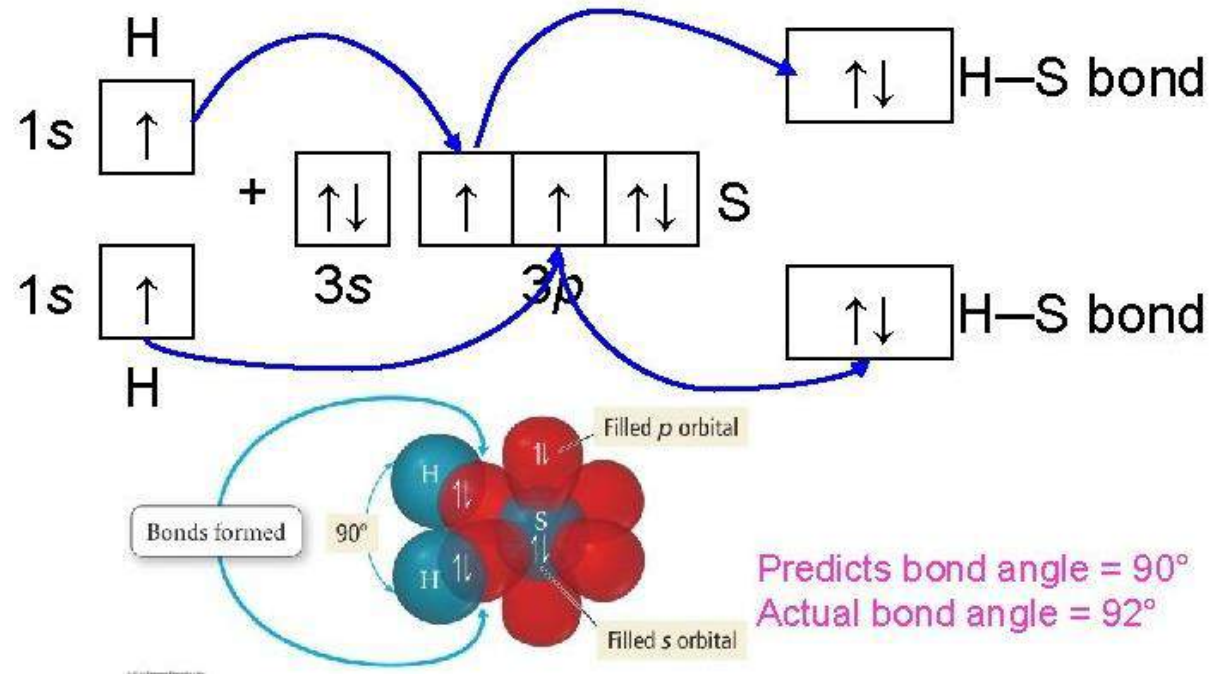




- **Valence Bond Theory (VBT):** describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms.
- According to valence bond theory, a covalent bond results when two conditions are met:
 1. an orbital on one atom overlaps an orbital on a second atom and
 2. the single electrons in each orbital combine to form an electron pair.
- Salient features:
 - Covalent bonds are formed when two valence orbitals (half-filled) belonging to two different atoms overlap on each other. The electron density in the area between the two bonding atoms increases as a result of this overlapping, thereby increasing the stability of the resulting molecule
 - The presence of many unpaired electrons in the valence shell of an atom enables it to form multiple bonds with other atoms. The paired electrons present in the valence shell do not take participate in the formation of chemical bonds as per the valence bond theory.
 - Covalent chemical bonds are directional and are also parallel to the region corresponding to the atomic orbitals that are overlapping.
 - the difference in the length and strength of the chemical bonds in H₂ and F₂ molecules can be explained by the difference in the overlapping orbitals in these molecules.
 - The covalent bond in an HF molecule is formed from the overlap of the 1s orbital of the hydrogen atom and a 2p orbital belonging to the fluorine atom, which is explained by the valence bond theory.



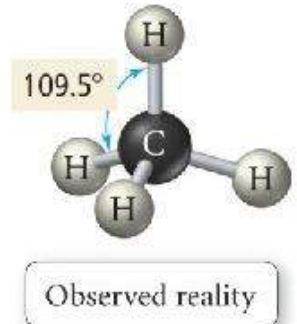
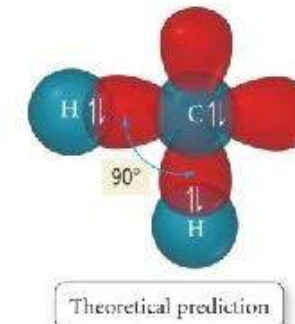
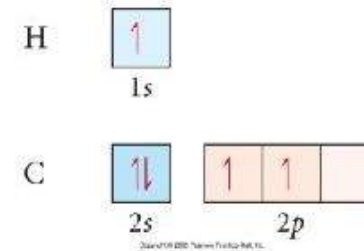
Atomic Orbital in the Bonding of H₂S



Limitation of VBT

Many molecules such as methane (tetrahedral, bond angle = 109.5°) can not be explained by half-filled atomic orbitals

✓ $C = 2s^2 2p_x^1 2p_y^1 2p_z^0$ would predict two or three bonds that are 90° apart





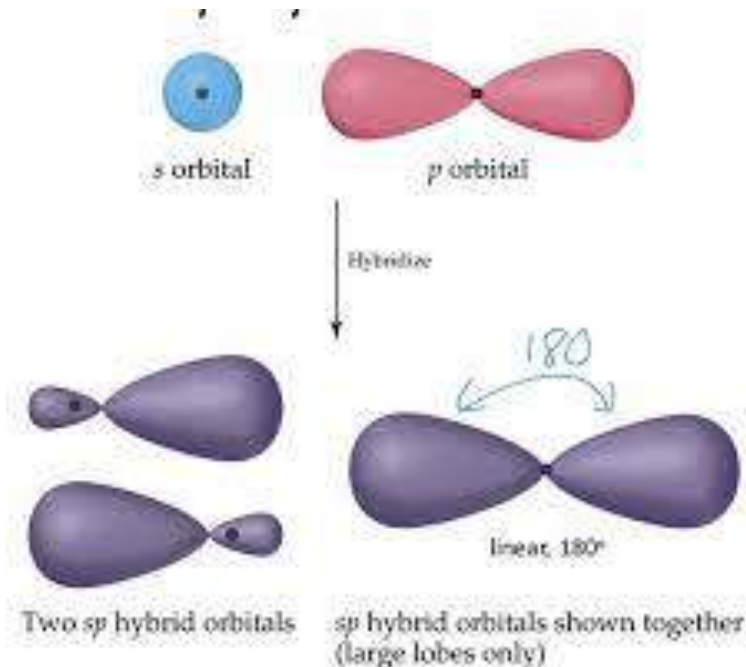
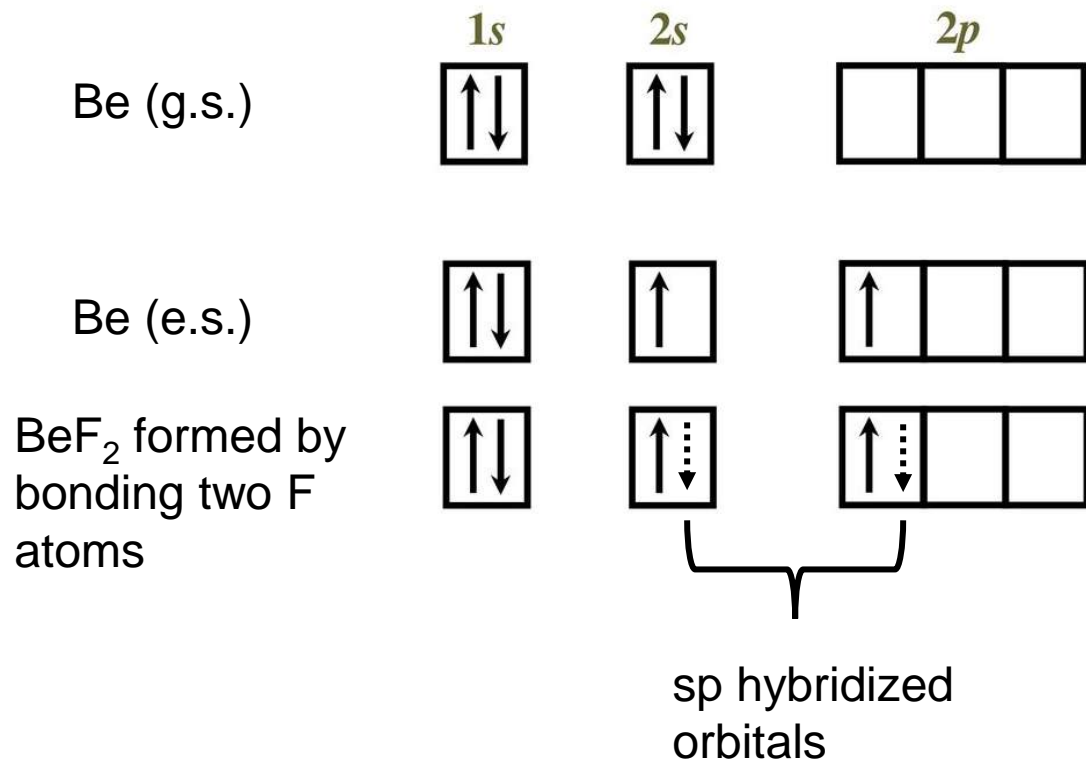
- **Hybridization:** Concept of mixing two atomic orbitals to give rise to a new type of hybridized orbitals. This intermixing usually results in the formation of hybrid orbitals having entirely different energies, shapes, etc.
- Redistribution of the energy of orbitals of individual atoms to give orbitals of equivalent energy happens when two atomic orbitals combine to form a hybrid orbital in a molecule. This process is called hybridization.
- Salient features:
 - Atomic orbitals of comparable energies are mixed together and mostly involves the merging of two 's' orbitals or two 'p' orbitals or mixing of an 's' orbital with a 'p' orbital as well as 's' orbital with a 'd' orbital. The new orbitals thus formed are known as hybrid orbitals.
 - Hybrid orbitals are quite useful in explaining atomic bonding properties and molecular geometry
 - Number of hybrid orbitals = number of pure orbitals
 - Hybridization happens only during the bond formation and not in an isolated gaseous atom.
 - Hybrid orbital generally form either sigma bond or contain a l.p. of electrons, but do not form pi bond



• **Types of hybridization:**

1) **sp hybridization:** mixing of one s and one p-orbital to form two new equivalent orbitals called sp hybridized orbitals.

- Each sp hybridized orbital has an equal amount of s and p character – 50% s and 50% p character.
- Shape: **Linear** (180°)
- Eg. **BeF₂**

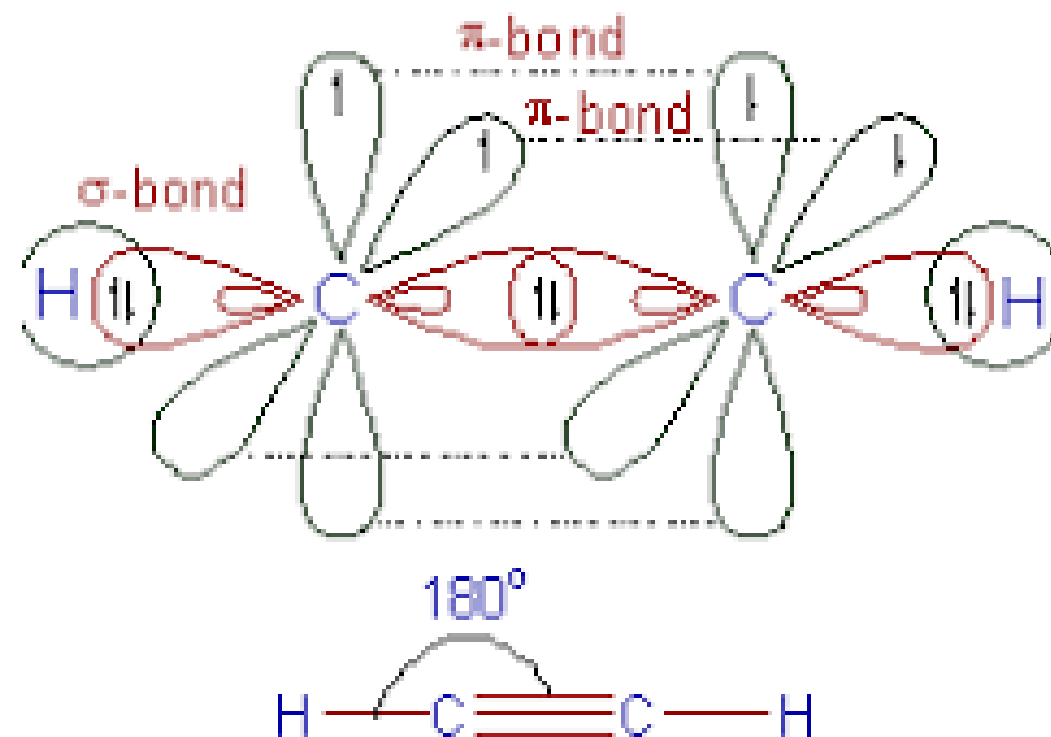
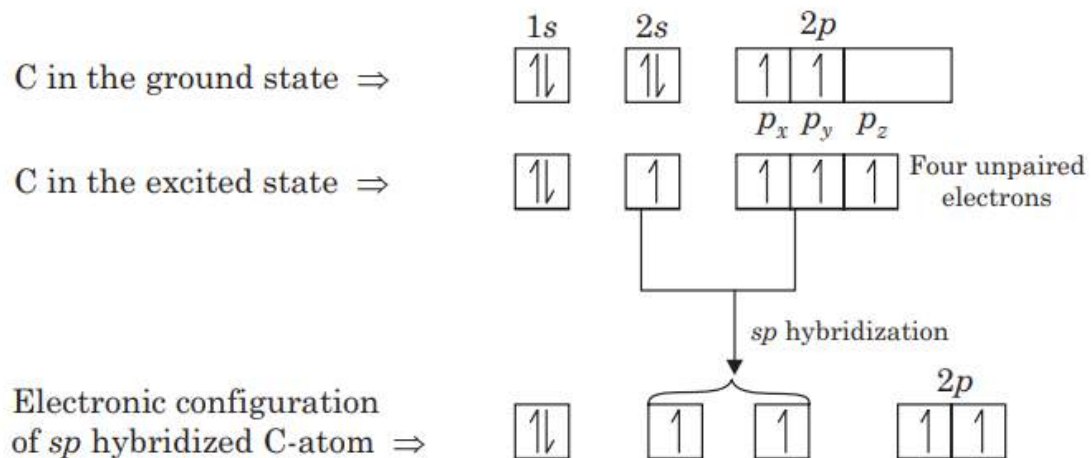


The two sp hybridized orbitals are oriented at 180° and the shape is linear



1) sp hybridization: Eg. Ethyne

Electronic configuration of:

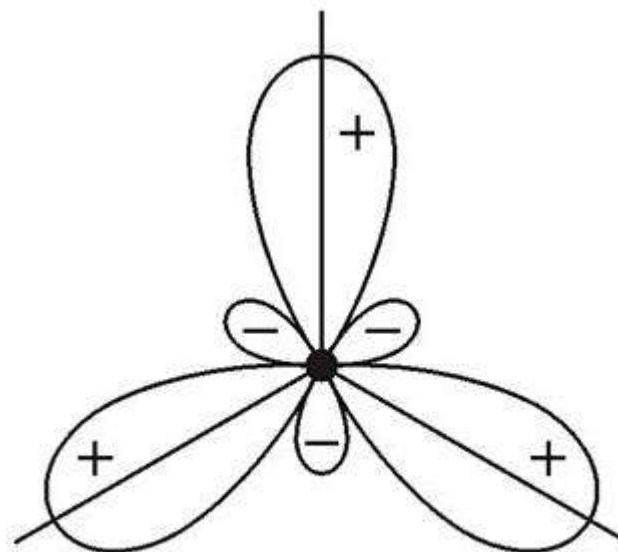
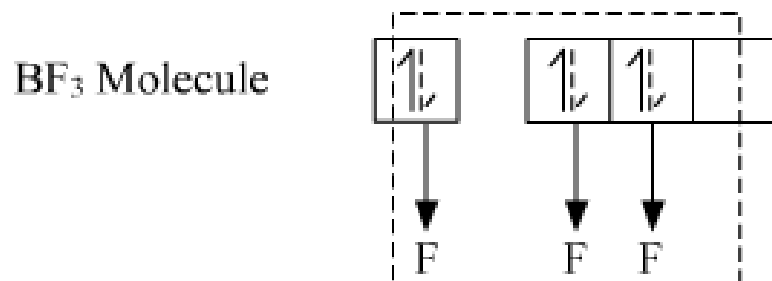
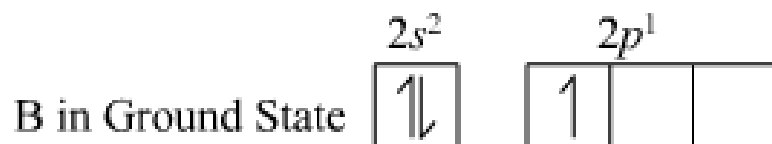


Linear structure of acetylene molecule

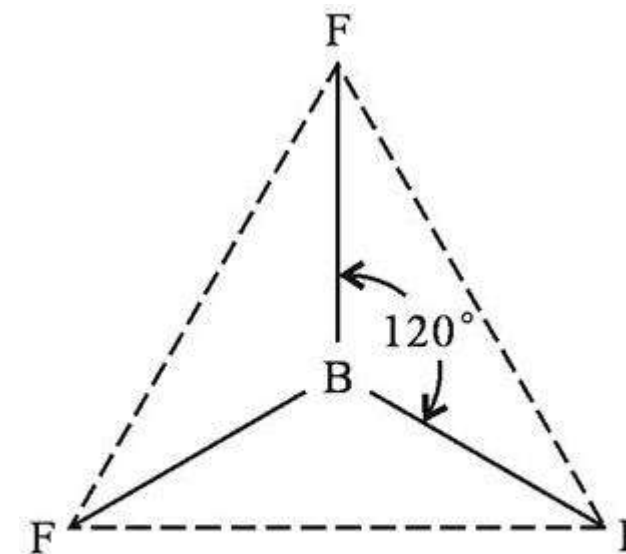


2) **sp^2 hybridization**: mixing of one s and two p-orbitals to form three new equivalent orbitals called sp^2 hybridized orbitals.

- Each sp^2 hybridized orbital has 33.3% s and 66.6% p character.
- Shape: **Trigonal planar** (120°)
- Eg. **BF_3**



Three sp^2 hybrid orbitals

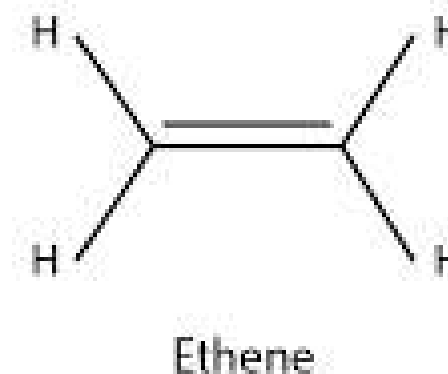
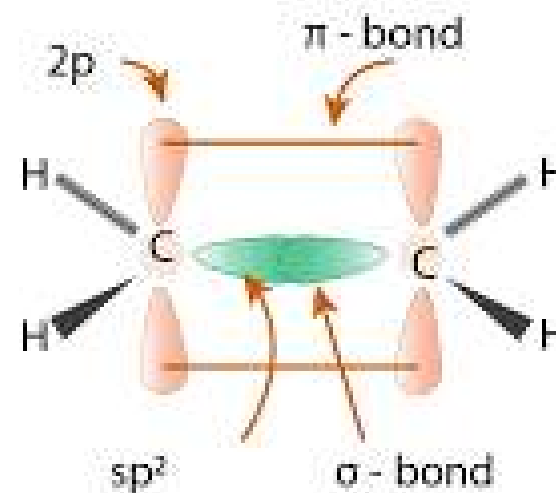
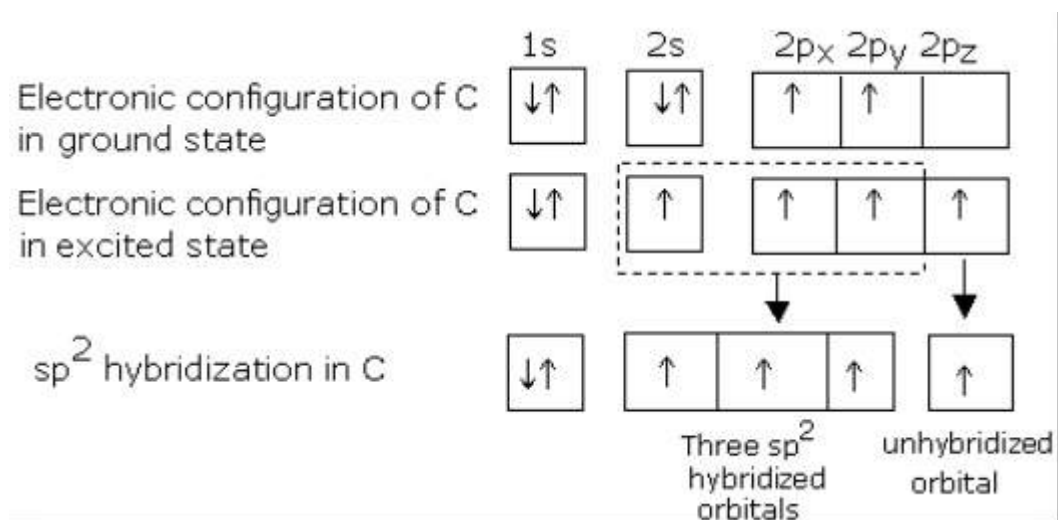


Trigonal planar

The three sp^2 hybridized orbitals are oriented at 120° and the shape is trigonal planar



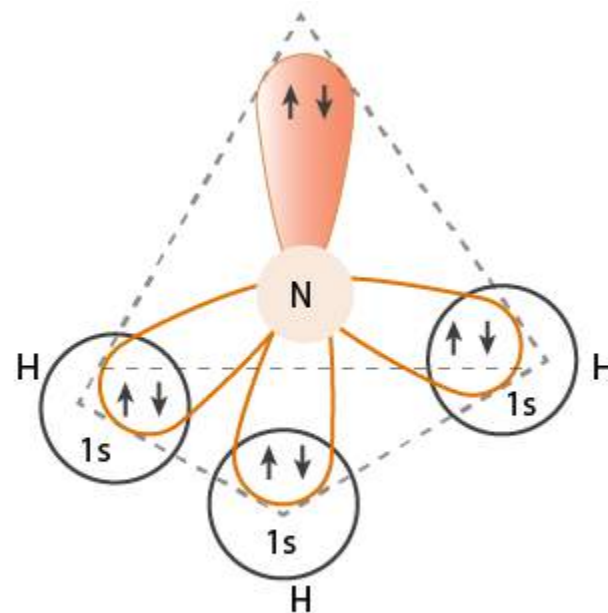
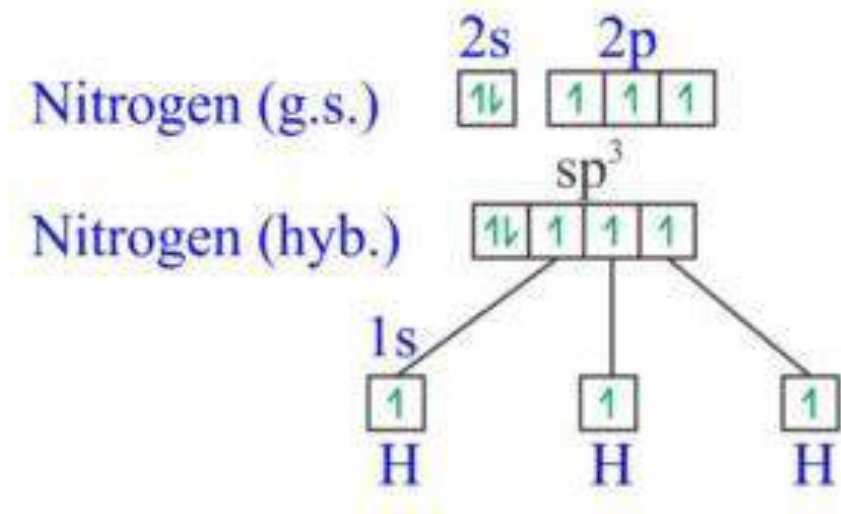
2) sp^2 hybridization: Eg. Ethene



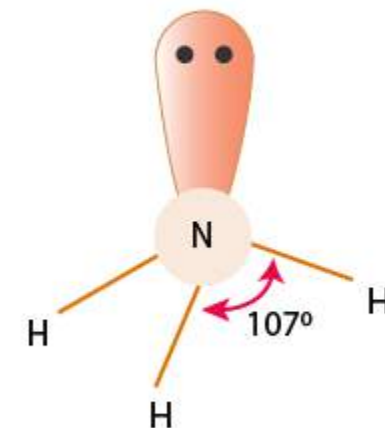


3) sp^3 hybridization: Eg. NH_3 (electronic config of N: $1s^2 2s^2 2p^3$)

- Three half-filled sp^3 orbitals of nitrogen form bonds to hydrogen's three atoms. However, the fourth sp^3 orbital that is present is a nonbonding pair of hybridized orbital and is normally used for holding the lone pair.



Orbital overlap in NH_3



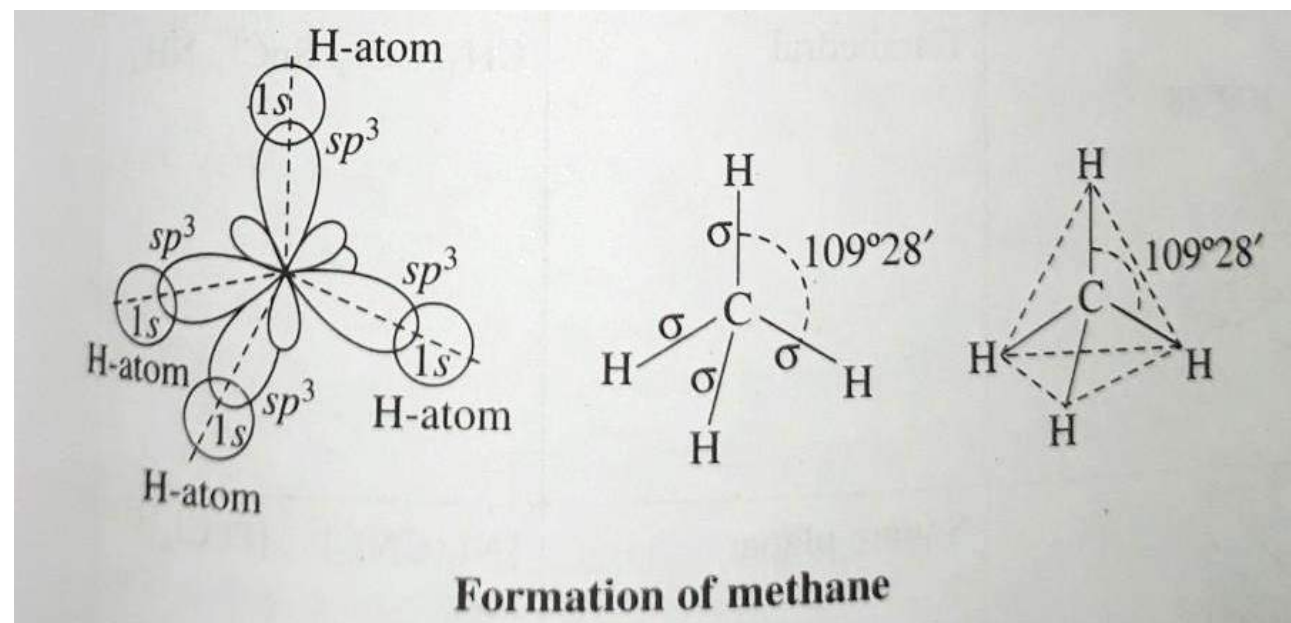
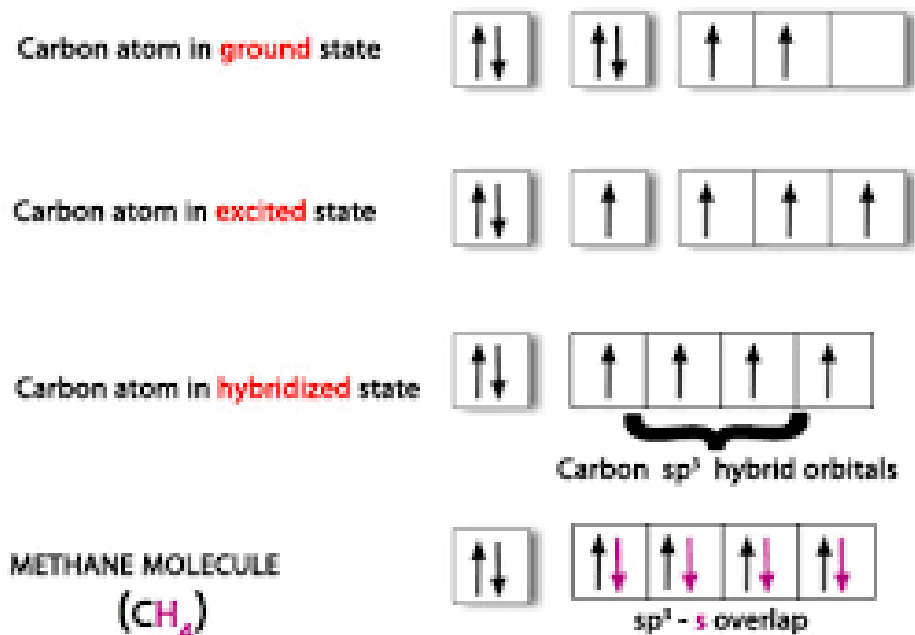
Pyramidal shape

The four sp^3 hybridized orbitals are oriented at $107^\circ 28'$ and the shape is pyramidal



3) sp^3 hybridization: mixing of one s and three p-orbitals to form four new equivalent orbitals called sp^3 hybridized orbitals.

- Each sp^3 hybridized orbital has 25% s and 75% p character.
- Shape: **Tetrahedral** ($109^\circ 28'$)
- Eg. **CH_4**

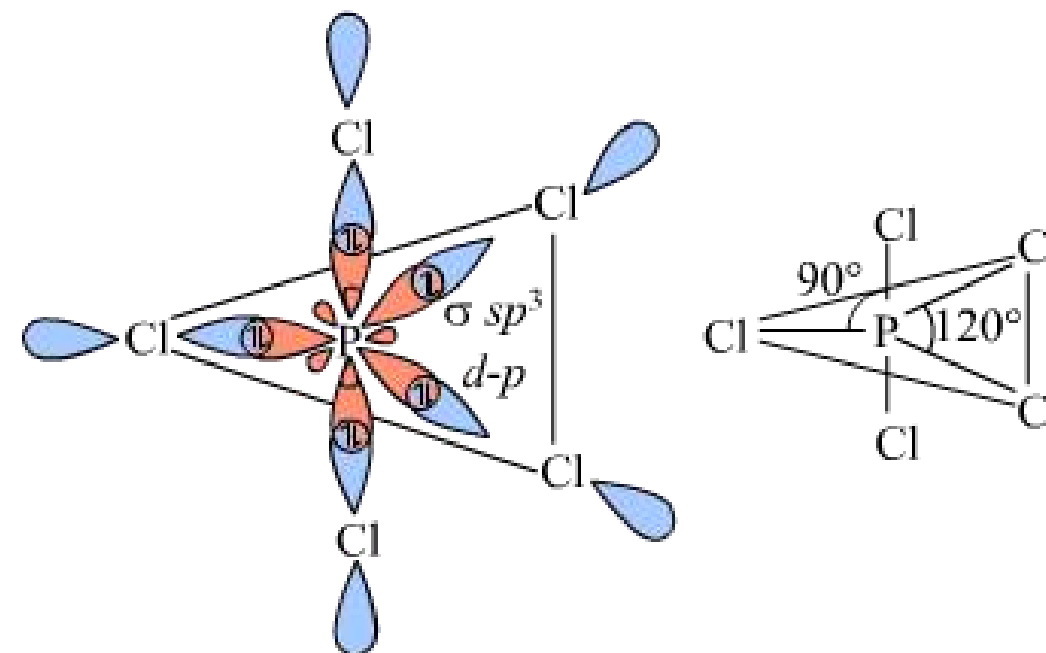
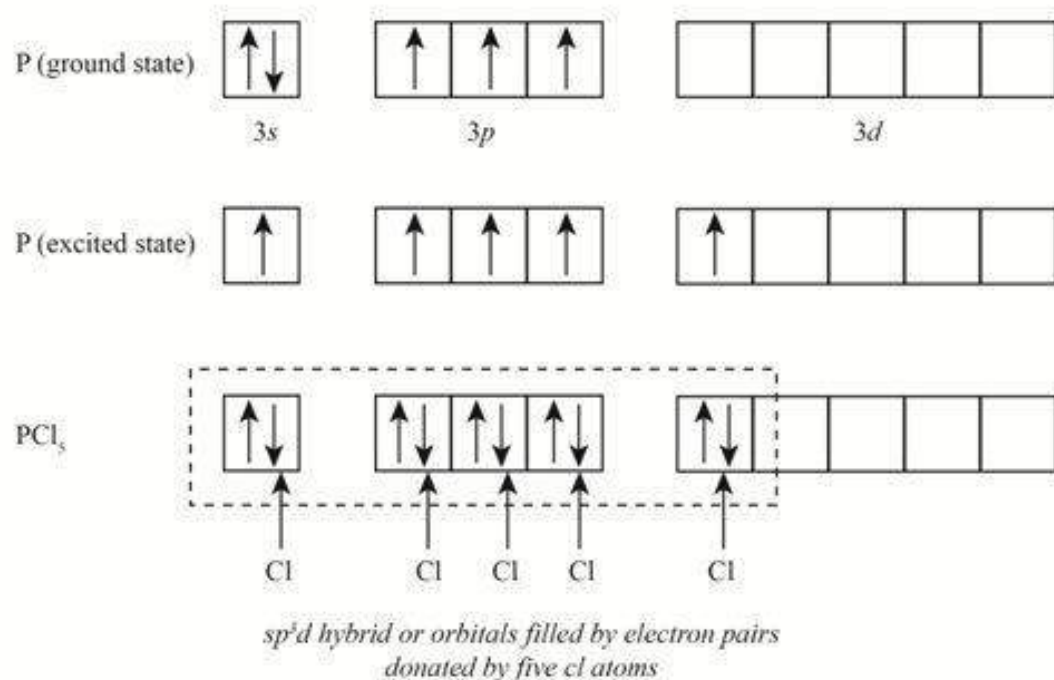


The four sp^3 hybridized orbitals are oriented at $109^\circ 28'$ and the shape is tetrahedral



4) **sp^3d hybridization:** mixing of 1s orbital, 3p orbitals and 1d orbital to form 5 sp^3d hybridized orbitals of equal energy

- Shape: **Trigonal bipyramidal**
- Three hybrid orbitals lie in the horizontal plane inclined at an angle of 120° to each other known as the equatorial orbitals.
- The remaining two orbitals lie in the vertical plane at 90 degrees plane of the equatorial orbitals known as axial orbitals.
- Eg. **PCl_5**

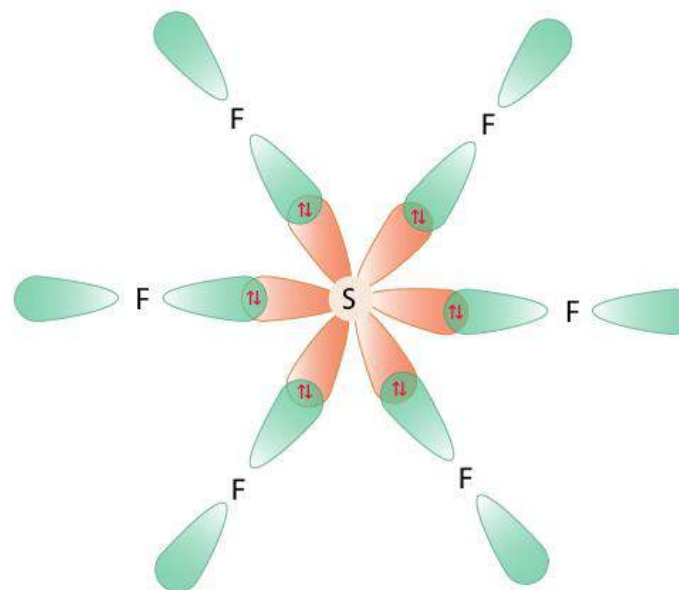
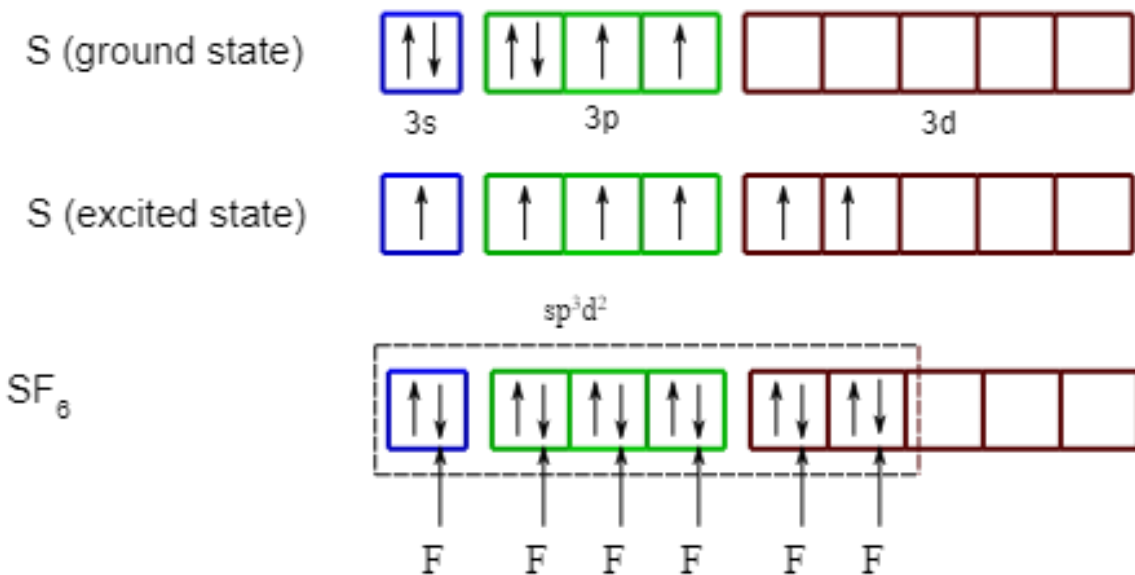


Trigonal bipyramidal structure of PCl_5

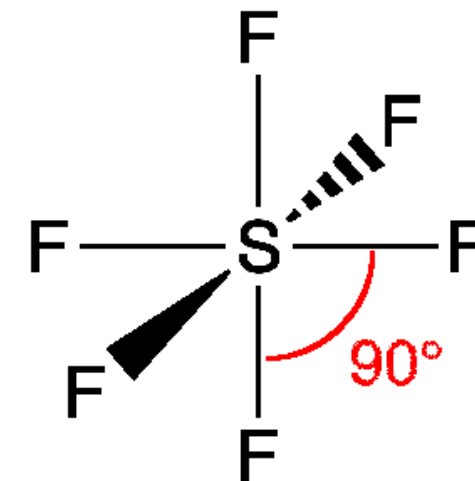


4) **sp^3d^2 hybridization:** has 1s, 3p and 2d orbitals, that undergo intermixing to form 6 identical sp^3d^2 hybrid orbitals.

- Shape: **Octahedral**
- Six hybrid orbitals are inclined at an angle of 90 degrees to one another.
- Eg. **SF_6**



Octahedral structure of sulphur hexafluoride



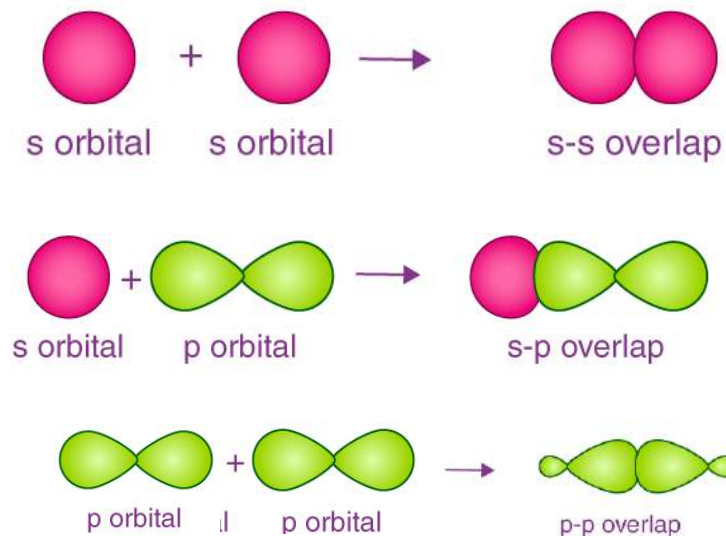
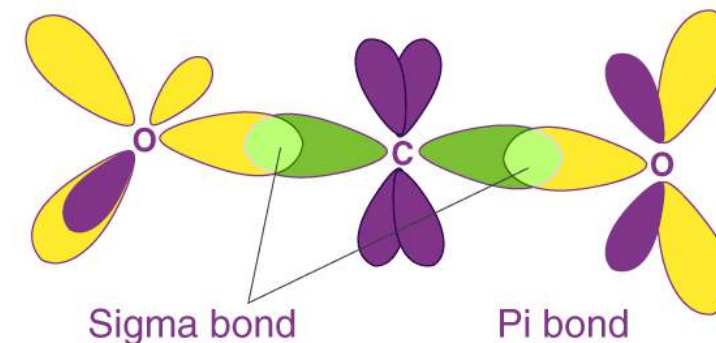


- **Sigma and Pi bonds:** Sigma and pi bonds are types of covalent bonds that differ in the overlapping of atomic orbitals. Covalent bonds are formed by the overlapping of atomic orbitals. **Sigma bonds are a result of the head-to-head overlapping of atomic orbitals whereas pi bonds are formed by the lateral overlap of two atomic orbitals.**

- **The Sigma (σ) Bond**

This type of covalent bond is formed by head-on positive (same phase) overlap of atomic orbitals along the internuclear axis. Sigma bonds are the strongest covalent bonds, owing to the direct overlapping of the participating orbitals. The electrons participating in a σ bond are commonly referred to as σ electrons. It can be formed by:

- a) s-s overlap: An s orbital must be half-filled before it overlaps with another.
- b) s-p overlap: one half filled s orbital overlaps with one half-filled p orbital along the internuclear axis, forming a covalent bond. This type of overlapping can be observed in ammonia. An NH_3 molecule features 3 sigma bonds, formed by the overlap of the $2p_x$, $2p_y$, and $2p_z$ orbitals belonging to the nitrogen atom and the 1s orbitals of the three hydrogen atoms.
- c) p-p overlap: one half-filled p orbital from each participating atom undergoes head-on overlapping along the internuclear axis.

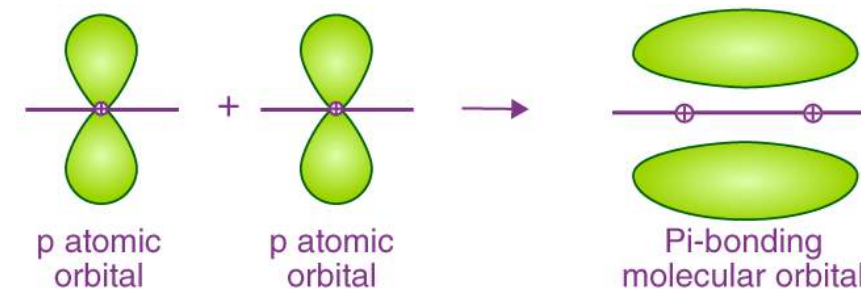




• The Pi (π) Bond

Pi bonds are formed by the sidewise positive (same phase) overlap of atomic orbitals along a direction perpendicular to the internuclear axis. During the formation of π bonds, the axes of the atomic orbitals are parallel to each other whereas the overlapping is perpendicular to the internuclear axis.

Pi Bonds are generally weaker than sigma bonds, owing to the significantly lower degree of overlapping. Generally, double bonds consist of one sigma and one pi bond, whereas a typical triple bond is made up of two π bonds and one σ bond. It is important to note that a combination of sigma and pi bonds is always stronger than a single sigma bond.



Sigma Bond	Pi Bond
The overlapping orbitals can be pure or hybrid	The overlapping orbitals must be unhybridized
These bonds are strong and have high bond energies.	These bonds are relatively weak.
Can exist independently	Must exist along with a sigma bond.
Has an impact on the shape of molecules	Has no role in determining the shape of molecules



- **Molecular Orbital Theory:** Given by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules. Each atom tends to combine together and form molecular orbitals. As a result of such arrangement, the valence electrons are considered to be associated with different nuclei in the molecule.
- Uses linear combination of atomic orbitals (LCAO) to form molecular orbitals concept.
- Salient features:
 - The atomic orbitals overlap to form new orbitals called **molecular orbitals**. When two atomic orbitals overlap they lose their identity and form new orbitals called molecular orbitals.
 - The electrons in the molecules are filled in the new energy states called the Molecular orbitals similar to the electrons in an atom being filled in an energy state called atomic orbitals. (Aufbau, Hund's and Pauli Exclusion)
 - There exist different types of molecular orbitals viz; bonding molecular orbitals, anti-bonding molecular orbitals, and non-bonding molecular orbitals. Of these, anti-bonding molecular orbitals will always have higher energy than the parent orbitals whereas bonding molecular orbitals will always have lower energy than the parent orbitals.
 - The probability of finding the electronic distribution in a molecule around its group of nuclei is given by the molecular orbital.
 - The two combining atomic orbitals should possess energies of comparable value and similar orientation. For example, 1s can combine with 1s and not with 2s.
 - The number of molecular orbitals formed is equal to the number of atomic orbitals combining.
 - The shape of molecular orbitals formed depends upon the shape of the combining atomic orbitals.



- **Linear Combination of Atomic Orbitals:** An atomic orbital is an electron wave; the waves of the two atomic orbitals may be in phase or out of phase. Suppose Ψ_A and Ψ_B represent the amplitude (or wavefunction) of the electron wave of the atomic orbitals of the two atoms A and B. Then wavefunction for the molecular orbital Ψ_{AB} obtained by linear combination of Ψ_A and Ψ_B is given as:

$\Psi_{AB} = c_1 \Psi_A + c_2 \Psi_B$ where, c_1 and c_2 are constants chosen to give a minimum energy for Ψ_{AB}
so, probability of finding an electron in a given volume space is Ψ^2

Therefore,

$$\Psi_{AB}^2 = (c_1 \Psi_A + c_2 \Psi_B)^2$$

$$\Psi_{AB}^2 = \underbrace{(c_1^2 \Psi_A^2)}_{\text{Prob of finding an electron on atom A}} + 2 \underbrace{c_1 c_2 \Psi_A \Psi_B}_{\text{Overlap integral}} + \underbrace{c_2^2 \Psi_B^2}_{\text{Prob of finding an electron on atom B}}$$

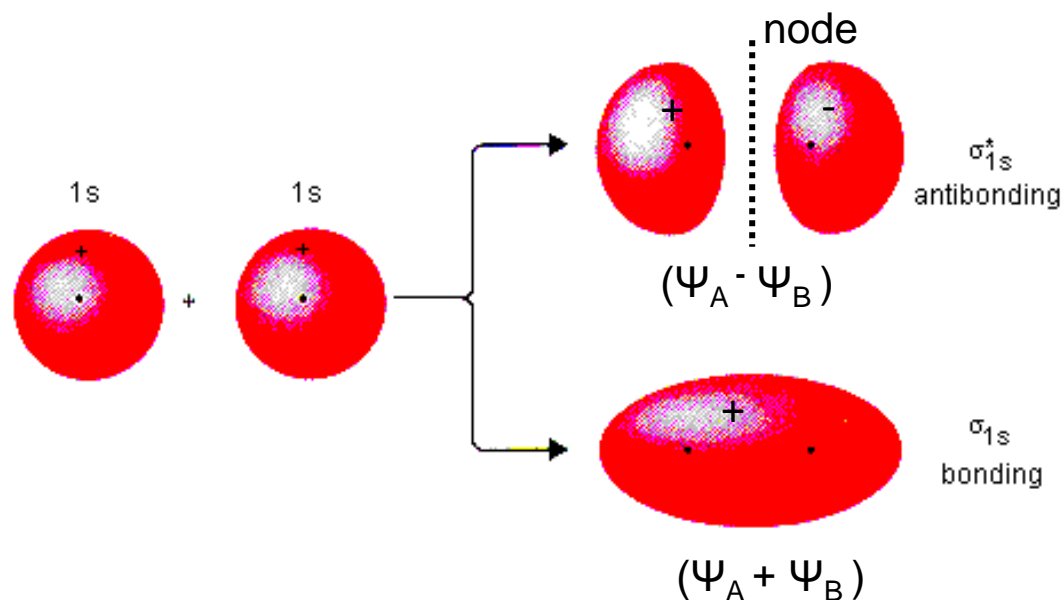
- Overlap integral represents the main difference between the electron clouds in individual atoms and in the molecule. Larger this term, stronger is the bond
- **Conditions for LCAO:**
 1. The atomic orbitals combining to form molecular orbitals should have comparable energy.
 2. The combining atoms should have the same symmetry around the molecular axis for proper combination, otherwise, the electron density will be sparse. For e.g. all the sub-orbitals of 2p have the same energy but still, 2pz orbital of an atom can only combine with a 2pz orbital of another atom but cannot combine with 2px and 2py orbital as they have a different axis of symmetry.
 3. The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms.



- **Combination of s-s orbitals:** Consider the H_2 molecule, for example. One of the molecular orbitals in this molecule is constructed by adding the mathematical wave functions for the two 1s atomic orbitals that come together to form this molecule (waves are in same phase). Another orbital is formed by subtracting one of these functions from the other (waves are out of phase). The two combinations can be written as:

$$\Psi_{AB} = N(\Psi_A + \Psi_B) \text{ where, } N \text{ is the normalizing constant}$$

and , $\Psi_{AB} = N(\Psi_A - \Psi_B)$



- Two lobes of opposite sign cancelling and therefore, zero electron density between the nuclei
- Anti-bonding molecular orbital
- Higher in energy than the original atomic orbitals
- Increased electron density between the nuclei
- Bonding molecular orbital
- Lower in energy than the original atomic orbitals

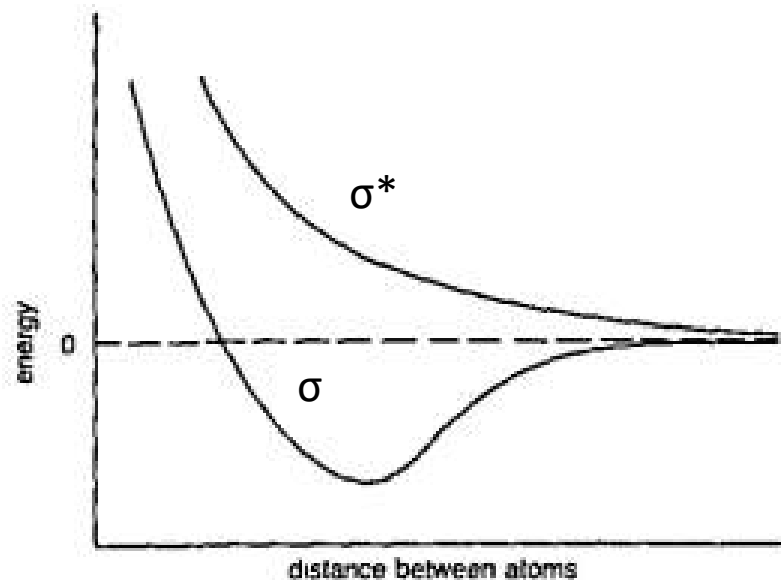


Figure 4 15 Energy of $\psi_{(g)}$ and $\psi_{(u)}$ molecular orbitals

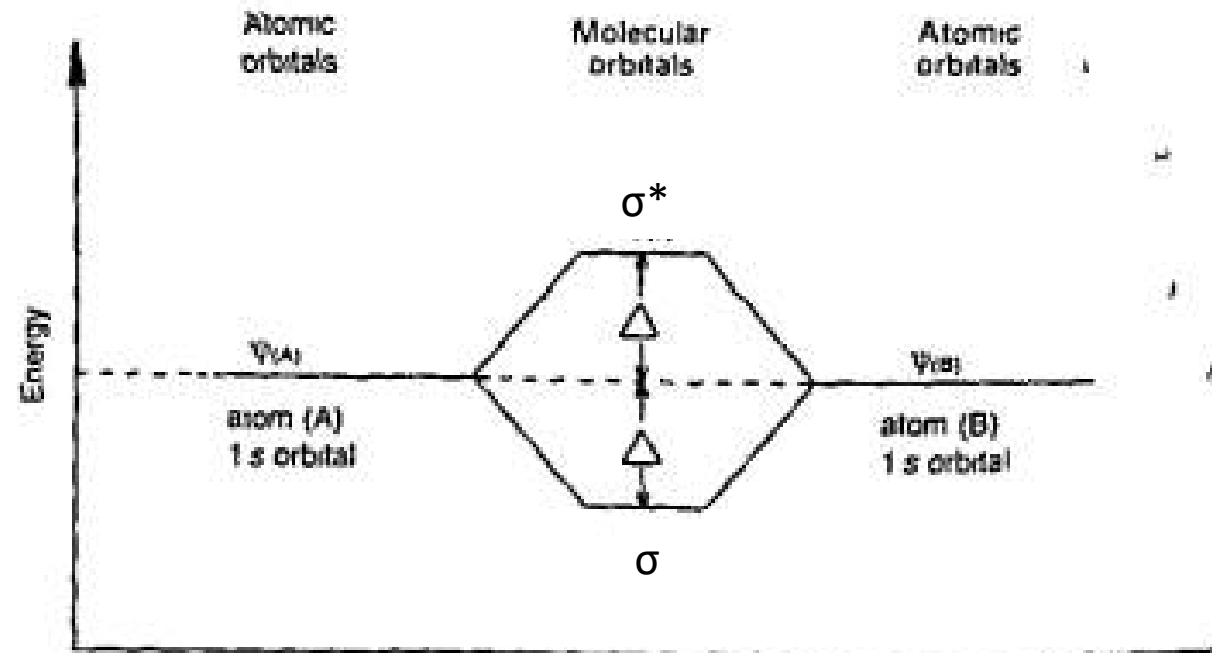


Figure 4 16 Energy levels of $s-s$ atomic and molecular orbitals

Δ = stabilization energy



- **Combination of s-p orbitals:** An s orbital **may** combine with a p orbital if the lobes of the p orbital are pointing along the axis joining the nuclei.

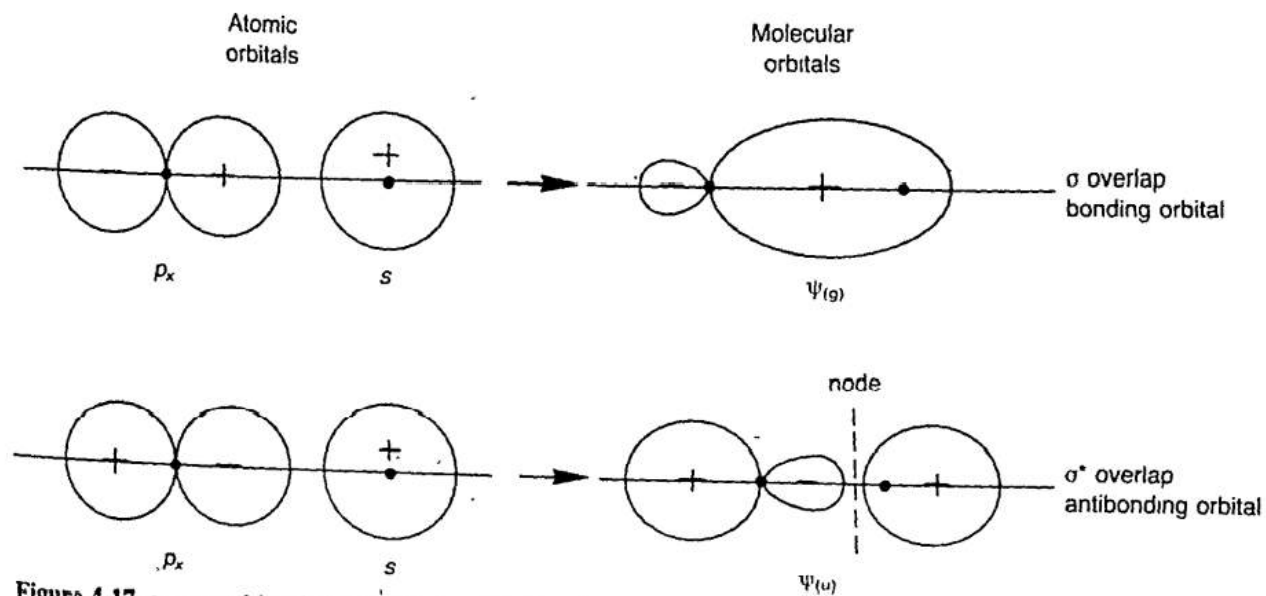
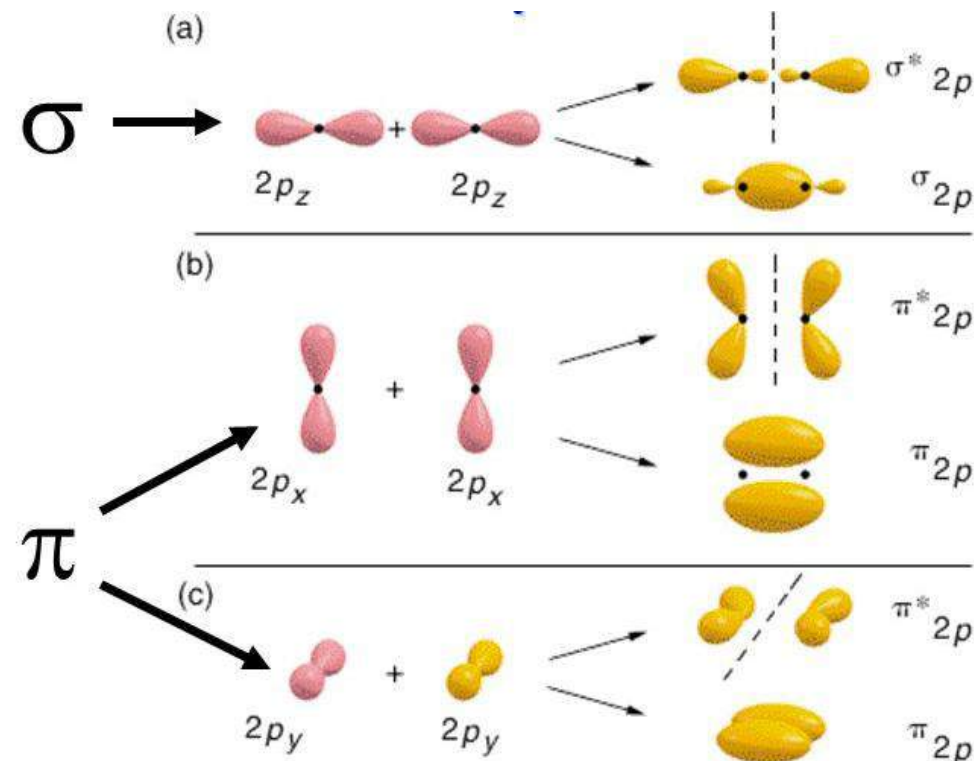


Figure 4.17 $s-p$ combination of atomic orbitals.



- **Combination of p-p orbitals:**

- a) overlap of two p orbitals along the internuclear axis results in the generation of σ_{2p} bonding and σ_{2p}^* antibonding orbitals.
- b) Overlap of two p orbitals with lobes perpendicular to the internuclear axis results in the formation of π_{2p} bonding and π_{2p}^* antibonding orbitals.



1) 1 sigma bond through overlap of orbitals along the internuclear axis.

2) 2 pi bonds through overlap of orbitals above and below (or to the sides) of the internuclear axis.



Molecular Orbital Theory	
Bonding Molecular Orbitals	Anti-Bonding Molecular Orbitals
Molecular orbitals formed by the additive effect of the atomic orbitals is called bonding molecular orbitals	Molecular orbitals formed by the subtractive effect of atomic orbitals is called anti-bonding molecular orbitals
Probability of finding the electrons is more in the case of bonding molecular orbitals	Probability of finding electrons is less in antibonding molecular orbitals. There is also a node between the anti-bonding molecular orbital between two nuclei where the electron density is zero.
The electron density, in the bonding molecular orbital in the internuclear region, is high. As a result, the nuclei are shielded from each other and hence the repulsion is very less.	The electron density in the antibonding molecular orbital in the internuclear region is very low and so the nuclei are directly exposed to each other. Therefore the nuclei are less shielded from each other.
The bonding molecular orbitals are represented by σ , π , δ .	The corresponding anti-bonding molecular orbitals are represented by σ^* , π^* , δ^* .



- **Order of energy of molecular orbitals:**

- The increasing order of energies of various molecular orbitals in simple homonuclear diatomic molecules is given below:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

where, $\pi 2p_x$ and $\pi 2p_y$; and $\pi^* 2p_x$ and $\pi^* 2p_y$ are of same energy and are therefore, degenerate

- For molecules like Li, Be, B, C and N, the order of energy changes as:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

Reason: This phenomenon is explained by **s-p mixing**. All the elements in the second period before oxygen have the small difference in energy between $2s$ and $2p_z$ orbitals, and they also have same symmetry. This results in s-p mixing (combination), which lowers the energy of the $\sigma(2s)$ and $\sigma^*(2s)$ and increases the energy of the $\sigma(2p_z)$ and $\sigma^*(2p_z)$ molecular orbitals. By moving towards right in a period, the s orbital gets more stabilized than the p orbital and the difference in their energies increases, making the s-p mixing for oxygen and higher atoms much smaller.



- **Bond Order:**

- Bond order is the number of chemical bonds between a pair of atoms.
- Bond order is an index of bond strength.
- Bond order is defined as half the difference between the number of bonding and antibonding electrons.

- **Bond Order = $\frac{1}{2} [N_b - N_a]$** where,

N_b is that the number of bonding electrons

N_a is that the number of antibonding electrons

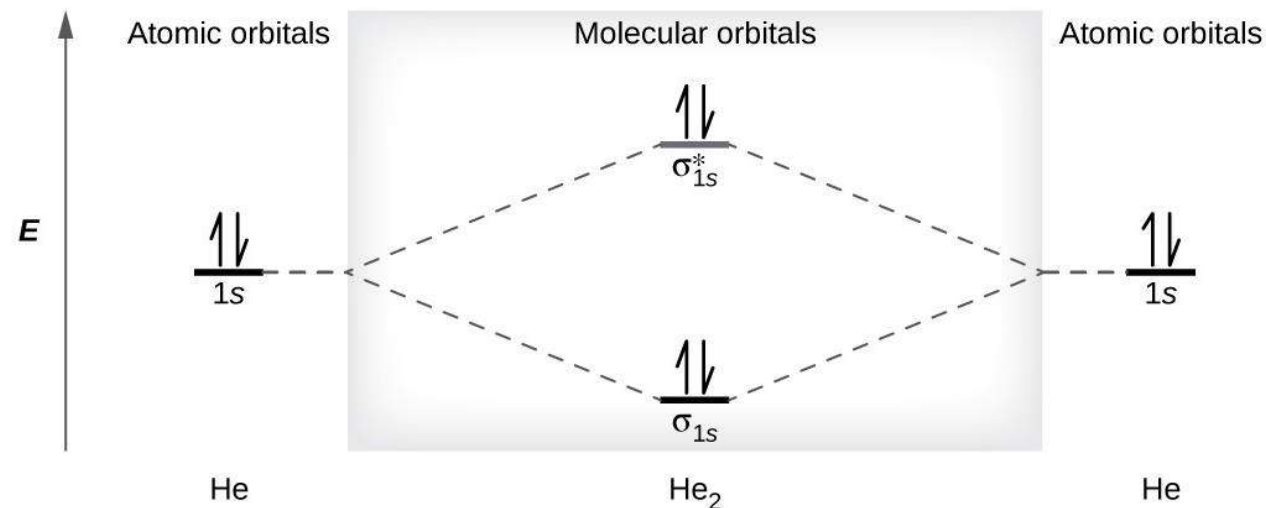
- Stable bonds have a positive bond order.
- If BO is 1, 2 or 3, it implies the presence of single, double or triple bond, respectively
- If BO is zero, it implies that there is no bond between two atoms i.e. molecule does not exist

- **Why He₂ does not exist?**

E.C. of He: $(\sigma 1s)^2$

BO: $\frac{1}{2} [2-2] = 0$

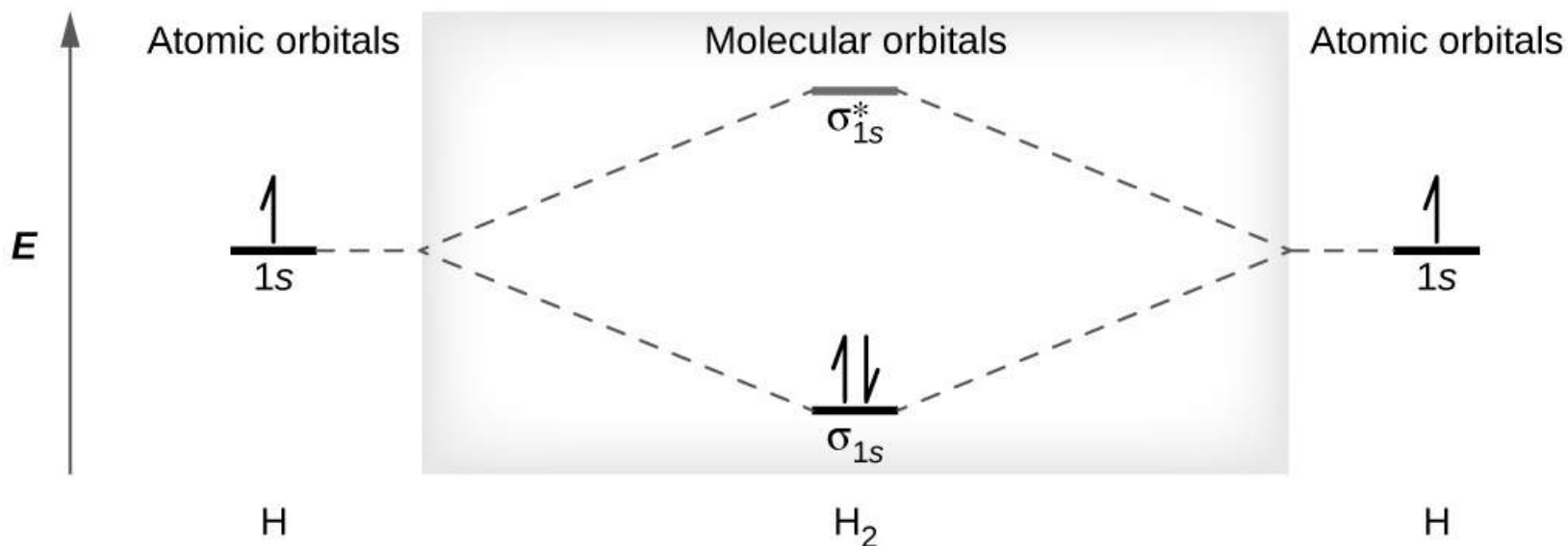
Two helium atoms do not combine to form a dihelium molecule, He₂, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule.





- **Molecular orbital diagram for simple homonuclear diatomic molecules:**

1. **Hydrogen molecule (H_2):** When the atomic orbitals of the two H-atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H_2 , readily forms, because the energy of a H_2 molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1s atomic orbitals. A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$.



A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$BO \text{ in } H_2 = (2-0)/2 = 1$$

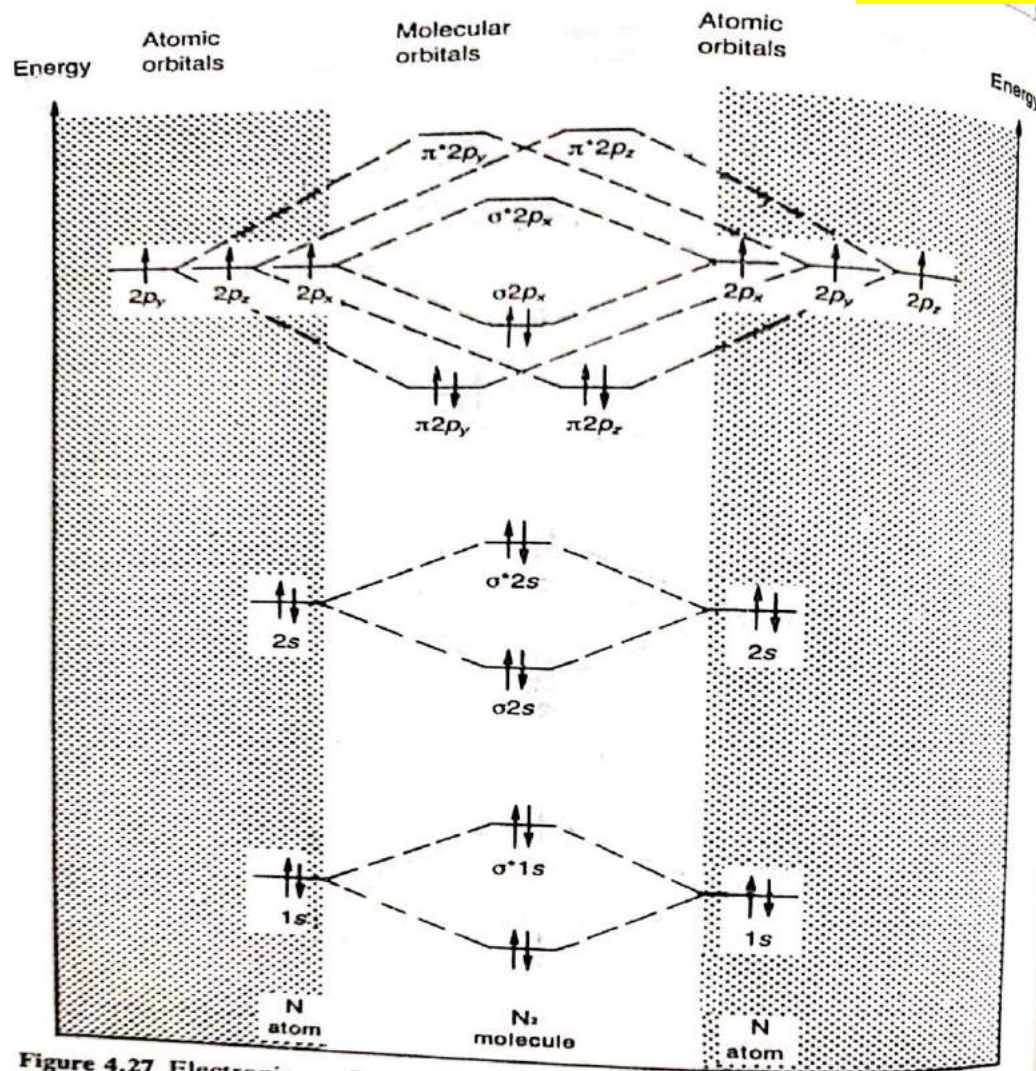
Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

Diamagnetic molecule (no unpaired electrons)



2. Nitrogen molecule (N_2):

7 electrons in N atom: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x^2, \pi 2p_y^2)(\sigma 2p_z)^2$



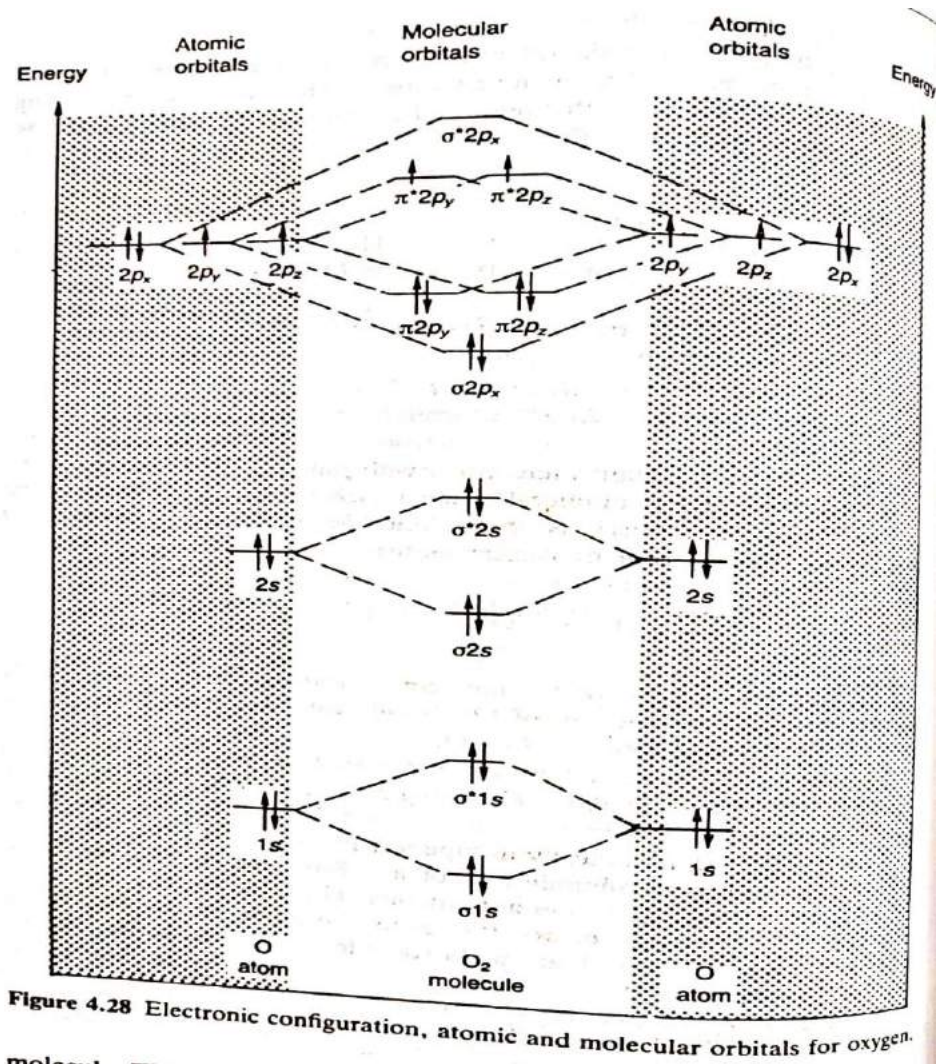
$$BO \text{ in } N_2 = (10 - 4) / 2 = 3$$

⇒ Triple bond between two N atoms

⇒ Diamagnetic molecule



3. Oxygen molecule (O_2): 8 electrons in O atom: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x^2, \pi 2p_y^2)(\pi^* 2p_x^1, \pi^* 2p_y^1)$



$$BO \text{ in } O_2 = (10 - 6) / 2 = 2$$

⇒ Double bond between two O atoms

⇒ Paramagnetic molecule



4.

Fluorine molecule (F_2):

9 electrons in F atom: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x^2, \pi 2p_y^2)(\pi^* 2p_x^2, \pi^* 2p_y^2)$

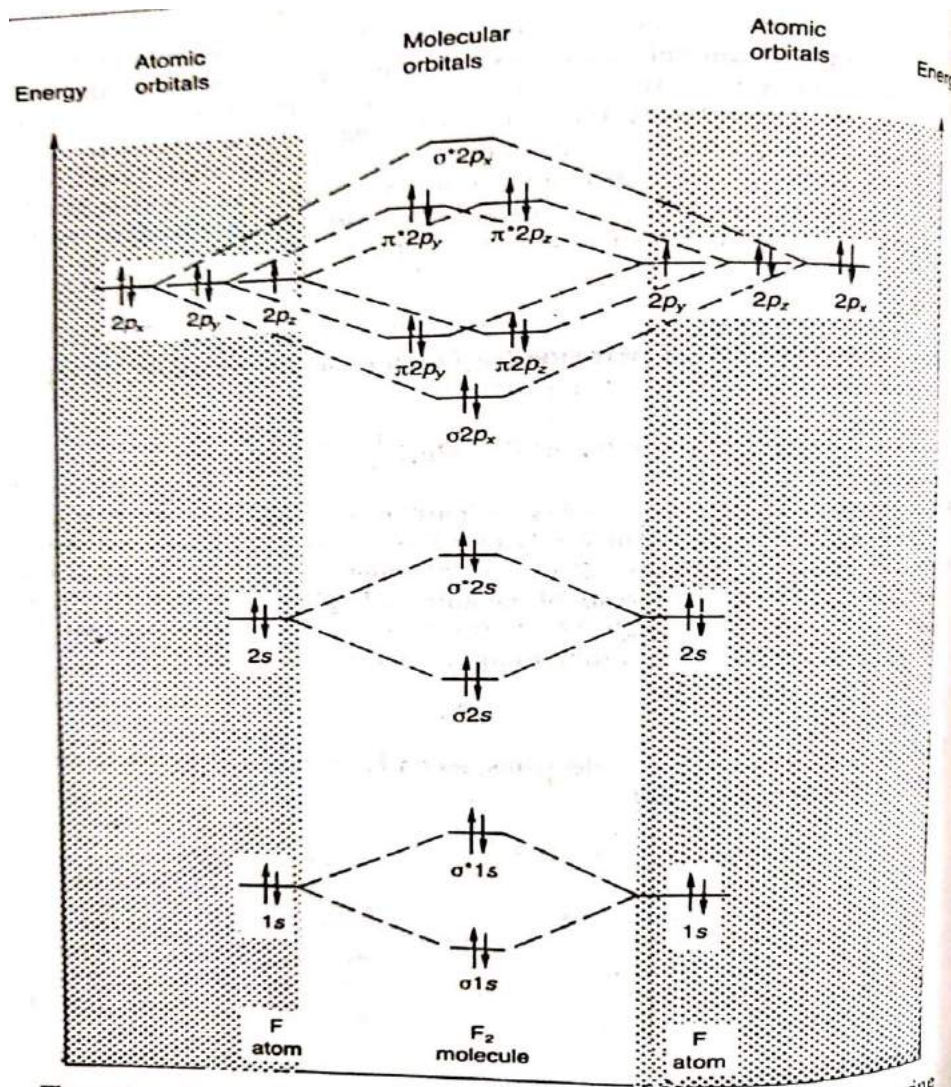


Figure 4.29 Electronic configuration, atomic and molecular orbitals for fluorine

$$BO \text{ in } F_2 = (10 - 8) / 2 = 1$$

⇒ Single bond between two F atoms

⇒ Diamagnetic molecule



Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements		
Molecule	Electron Configuration	Bond Order
Li ₂	($\sigma 2s$) ²	1
Be ₂ (unstable)	($\sigma 2s$) ² ($\sigma^* 2s$) ²	0
B ₂	($\sigma 2s$) ² ($\sigma^* 2s$) ² ($\pi 2p_x, \pi 2p_y$) ²	1
C ₂	($\sigma 2s$) ² ($\sigma^* 2s$) ² ($\pi 2p_x, \pi 2p_y$) ⁴	2
N ₂	($\sigma 2s$) ² ($\sigma^* 2s$) ² ($\pi 2p_x, \pi 2p_y$) ⁴ ($\sigma 2p_z$) ²	3
O ₂	($\sigma 2s$) ² ($\sigma^* 2s$) ² ($\sigma 2p_z$) ² ($\pi 2p_x, \pi 2p_y$) ⁴ ($\pi^* 2p_x, \pi^* 2p_y$) ²	2
F ₂	($\sigma 2s$) ² ($\sigma^* 2s$) ² ($\sigma 2p_z$) ² ($\pi 2p_x, \pi 2p_y$) ⁴ ($\pi^* 2p_x, \pi^* 2p_y$) ⁴	1
Ne ₂ (unstable)	($\sigma 2s$) ² ($\sigma^* 2s$) ² ($\sigma 2p_z$) ² ($\pi 2p_x, \pi 2p_y$) ⁴ ($\pi^* 2p_x, \pi^* 2p_y$) ⁴ ($\sigma^* 2p_z$) ²	0



Molecular Structure

Valence Shell Electron Pair Repulsion Theory

Number of electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone pairs	1 Lone pair	2 Lone pairs	3 Lone pairs	4 Lone pairs
	Linear					
	Trigonal Planar					
	Tetrahedral					
	Trigonal Bipyramidal					
	Octahedral					

Hybridization

Formula	Shape(Name)	Bond Angles	Hybridization
AX_2	Linear	180	sp
AX_3	Trigonal Planar	120	sp^2
AX_4	Tetrahedral	109.5	sp^3
AX_5	Triangular Bipyramidal	120, 90	sp^3d
AX_6	Octahedral	90	sp^3d^2
AX_2N	Bent	120	sp^2
AX_2N_2	Bent	109.5	sp^3
AX_3N	Trigonal Pyramidal	109.5	sp^3

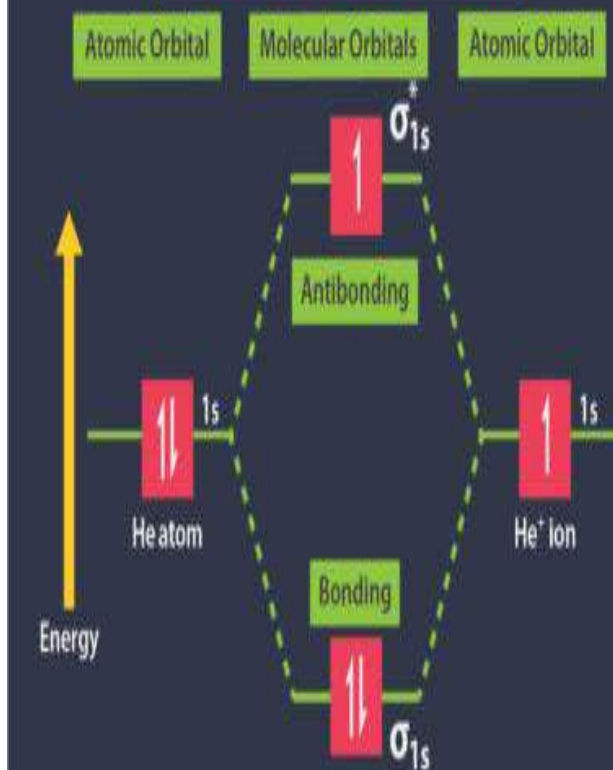
$$\text{Hybridization} = \frac{1}{2}[V+M-C+A]$$

V = Valence electrons
M = Monovalent atoms
C or A = Number of Cations or Anions

Example, NH_4^+
Hybridization = $\frac{1}{2}[5+4-1]$

H=2 $\rightarrow sp$
H=3 $\rightarrow sp^2$
H=4 $\rightarrow sp^3$
H=5 $\rightarrow sp^3d$
H=6 $\rightarrow sp^3d^2$

Molecular Orbital Theory



VSEPR

VSEPR theory is the theory that predicts the geometry of a molecule

Based on the repulsions between lone electron pairs and bond electron pairs

Does not give details about orbitals present in atoms of a molecule

Indicates the geometry of molecules

Does not indicate the types of bonds present between atoms

Valence Bond Theory

Valence bond theory is a theory that explains the chemical bonding in a covalent bond

Based on the overlapping of orbitals in order to form a chemical bond

Give details about orbitals present in atoms of a molecule

Does not indicate the geometry of molecules

Indicate the types of bonds present between atoms

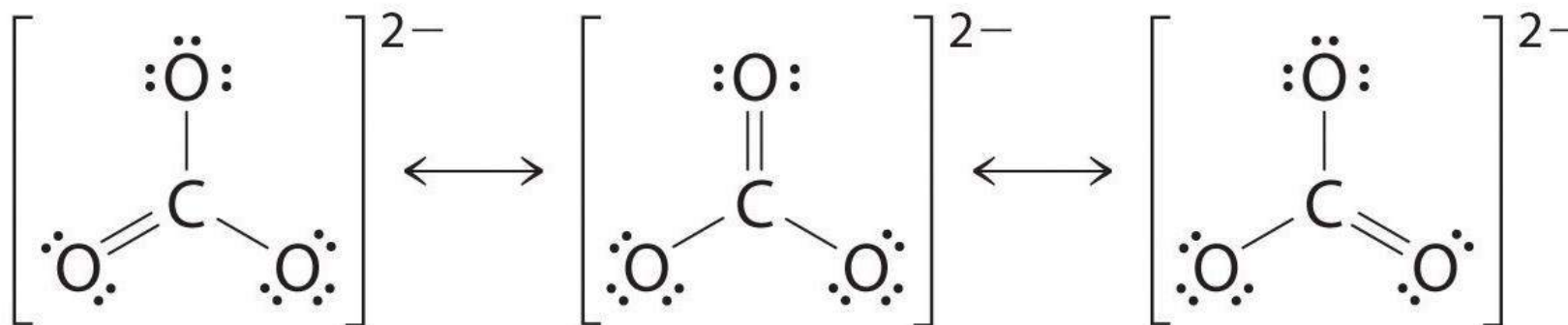
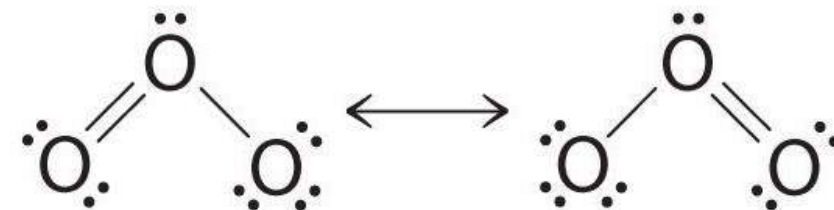
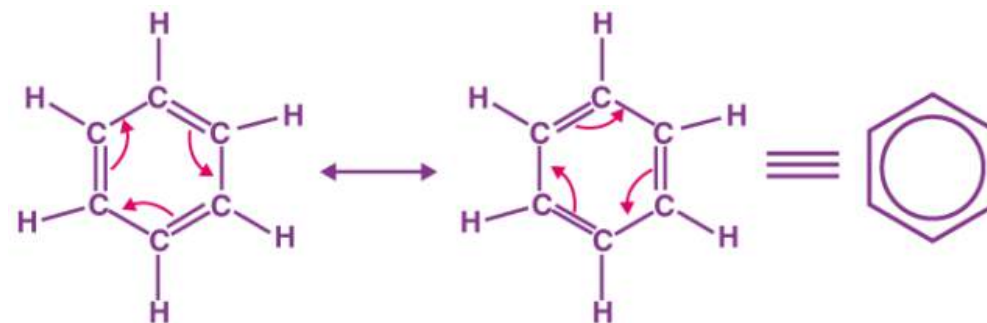


- **Resonance:** Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula.
- In many cases, a single Lewis structure fails to explain the bonding in a molecule/polyatomic ion due to the presence of partial charges and fractional bonds in it. In such cases, resonance structures are used to describe chemical bonding.
- It describes the bonding in particular molecules or ions by merging many contributory structures or forms, jointly called canonical structures or resonance structures within the theory of valence bonding into a hybrid resonance (or hybrid structure).
- Resonance structures are sets of Lewis structures that describe the delocalization of electrons in a polyatomic ion or a molecule.
- The combination of possible resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule.
- In general, molecules with multiple resonance structures will be more stable than one with fewer and some resonance structures contribute more to the stability of the molecule than others.



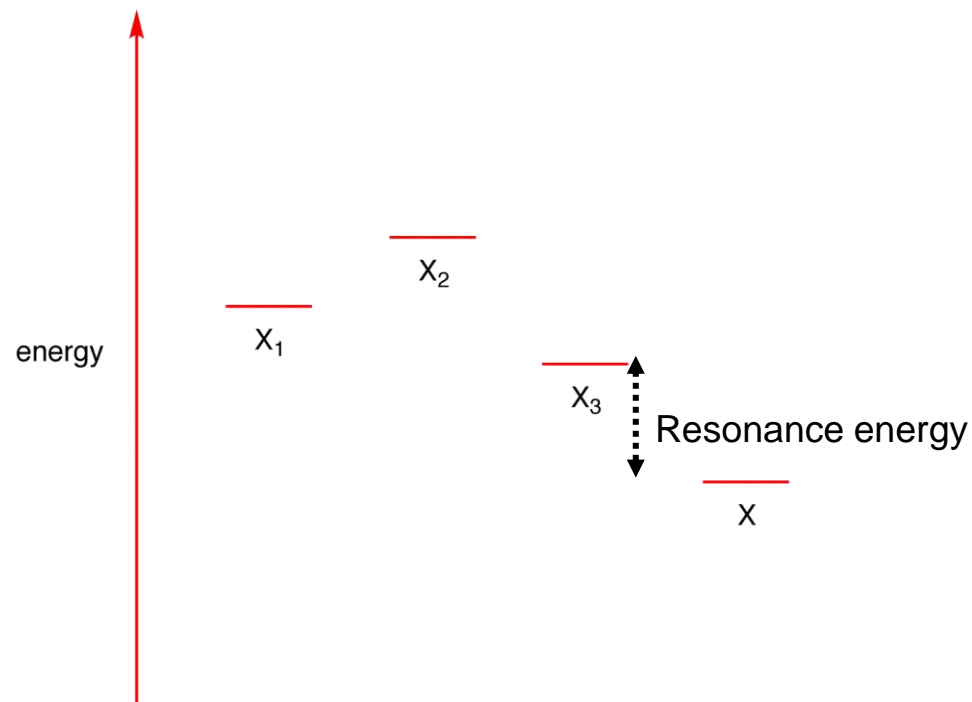
- **Examples:**

1. **Benzene:** The benzene molecule is stabilized by resonance, the pi electrons are delocalized around the ring structure. This delocalization causes each carbon-carbon bond to have a bond order of 1.5, implying that they are stronger than regular C-C sigma bonds.
2. **Ozone (O₃):** Both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O₂ (120.7 pm).
3. **Carbonate ion (CO₃)²⁻:** All C–O bond lengths are identical and shorter than C=O but greater than C–O

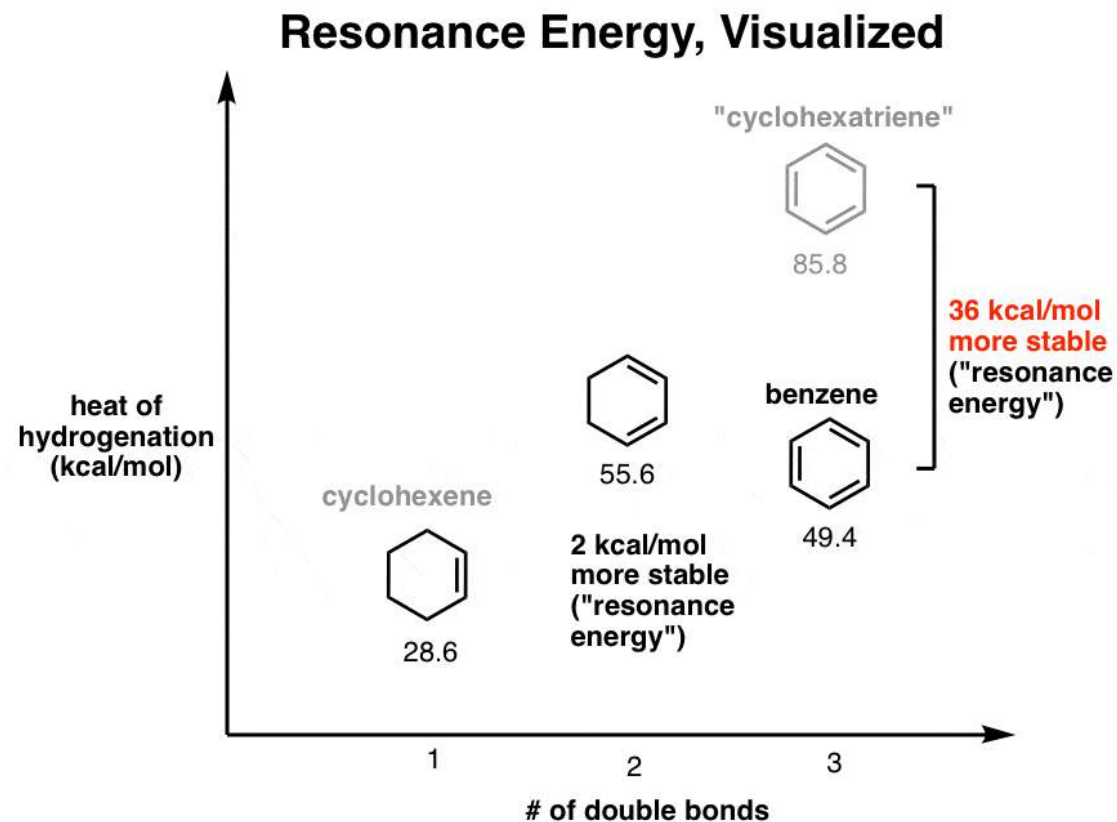




- **Resonance energy:** The difference in energy between the actual molecule and the canonical form of the lowest energy is called the Resonance Energy. The resonance energy of a molecule is expressed in kcal/mole or kJ/mole.



Resonance-stabilized molecule X (hybrid) has three resonance forms (X_1 , X_2 , and X_3)



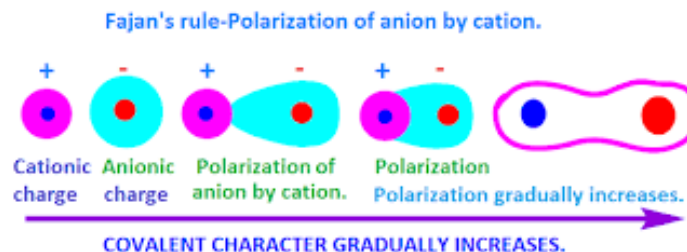
Resonance energy in benzene molecule as measured by heat of hydrogenation



- **Fajans' Rules:** by Kazimierz Fajans in 1923. These rules predict whether a chemical bond will be covalent or ionic.
- **Polarizing power:** It is the extent to which a cation can polarize an anion. It is proportional to charge density. Charge density is the ratio of charge to volume. Polarizing power \propto Charge density. More the charge density, greater is the polarizing power for that cation.
- **Polarizability:** It is the extent to which an ion can be polarized. Polarization is the distortion of a spherically symmetric electron cloud to an unsymmetric cloud.
- Rules summarizing the factors favoring polarization and hence covalency:
 1. *A small positive ion favors covalency.* In small ions the positive charge is concentrated over a smaller area. This makes the ion highly polarizing, and very good at distorting the negative ions.
 2. *Large negative ions favor covalency.* Large ions are highly polarizable, that is easily distorted by the positive ion, because the outermost electrons are shielded from the charge on the nucleus.
 3. *The charge of Cation:* Greater the charge of cation, greater is the covalent character of the ionic bond.
 4. Polarization and hence covalency is favored if the positive ion does not have a noble gas configuration. e.g. many transition metals
- Amongst the alkali chlorides, which one is the most covalent? Since the anion is the same, we have to compare the cations. According to Fajans' rules, smaller the cation, more is the covalency. Therefore, LiCl is the most covalent.



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- Amongst the anions, larger the size more would be the covalency. Therefore the order is: **NaF < NaCl < NaBr < NaI**
- Smaller the cation more is the covalency. Therefore, the order is: **CsF < RbF < KF < NaF < LiF**





Pauling's method for calculation of ionic radii:

- Pauling has calculated the radii of the ions on the basis of the observed internuclear distances in four crystals namely NaF, KCl, RbBr and CsI. In each ionic crystal the cations and anions are isoelectronic with inert gas configuration.
- Assumptions:
 - The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the inter nuclear distance between them.

$$r(C^+) + r(A^-) = d(C^+-A^-)$$

where, $r(C^+)$ = radius of cation, C^+ ; $r(A^-)$ = radius of anion, A^- ; and $d(C^+-A^-)$ = internuclear distance between C^+ and A^- ions in C^+A^- ionic crystal

- For a given noble gas configuration, the radius of an ion is inversely proportional to its effective nuclear charge.
i.e. $r(C^+) = 1/Z_{\text{eff}}(C^+)$ and $r(A^-) = 1/Z_{\text{eff}}(A^-)$

where, $Z_{\text{eff}}(C^+)$ & $Z_{\text{eff}}(A^-)$ are the effective nuclear charges of cation (C^+) and anion (A^-) respectively.

On combining,

$$r(C^+) / r(A^-) = Z_{\text{eff}}(A^-) / Z_{\text{eff}}(C^+)$$

we know $Z_{\text{eff}} = Z - \sigma$, where, Z = atomic number and σ = screening constant

$$r(C^+) / r(A^-) = Z(A^-) - \sigma(A^-) / Z(C^+) - \sigma(C^+)$$

- Find the radii of Na^+ and F^- in NaF crystal. Given: $d(\text{Na-F})$: 2.31 Å and σ for ions with $ns^2 np^6$: 4.5

Ans: $Z_{\text{Na}} = 11$ and $Z_{\text{F}} = 9$, $r(\text{Na}^+) / r(\text{F}^-) = 9 - 4.5 / 11 - 4.5 = 4.5 / 6.5$

$$\Rightarrow 6.5 r(\text{Na}^+) - 4.5 r(\text{F}^-) = 0$$

$$\text{and, } r(\text{Na}^+) + r(\text{F}^-) = 2.31$$

solving the above two equations,

$$r(\text{Na}^+) = 0.945 \text{ Å and } r(\text{F}^-) = 1.365 \text{ Å}$$