CHEMICAL BONDING - I

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COVALENT BONDING

- Formed by sharing of electrons between combining atoms.

- Sharing of electrons between atoms occur so that each atom can acquire the nearest noble gas electronic configuration

- Combining atoms may be same (**Homo atomic:** H_2 , N_2 , Cl_2 etc.) or they can be different (**Hetero atomic:** HCl , NH_3 , H_2O etc.)

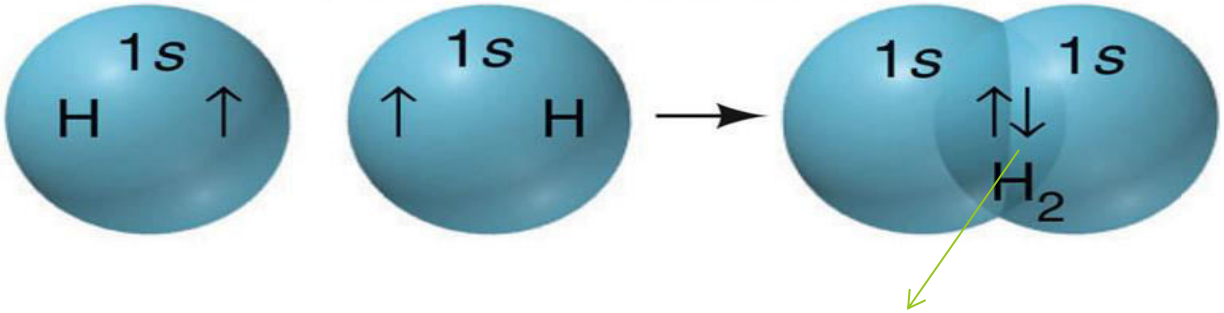
- Depending on the number of electron pairs shared, the compounds can have
- Single bond
- Double bond
- Triple bond

SINGLE BONDS

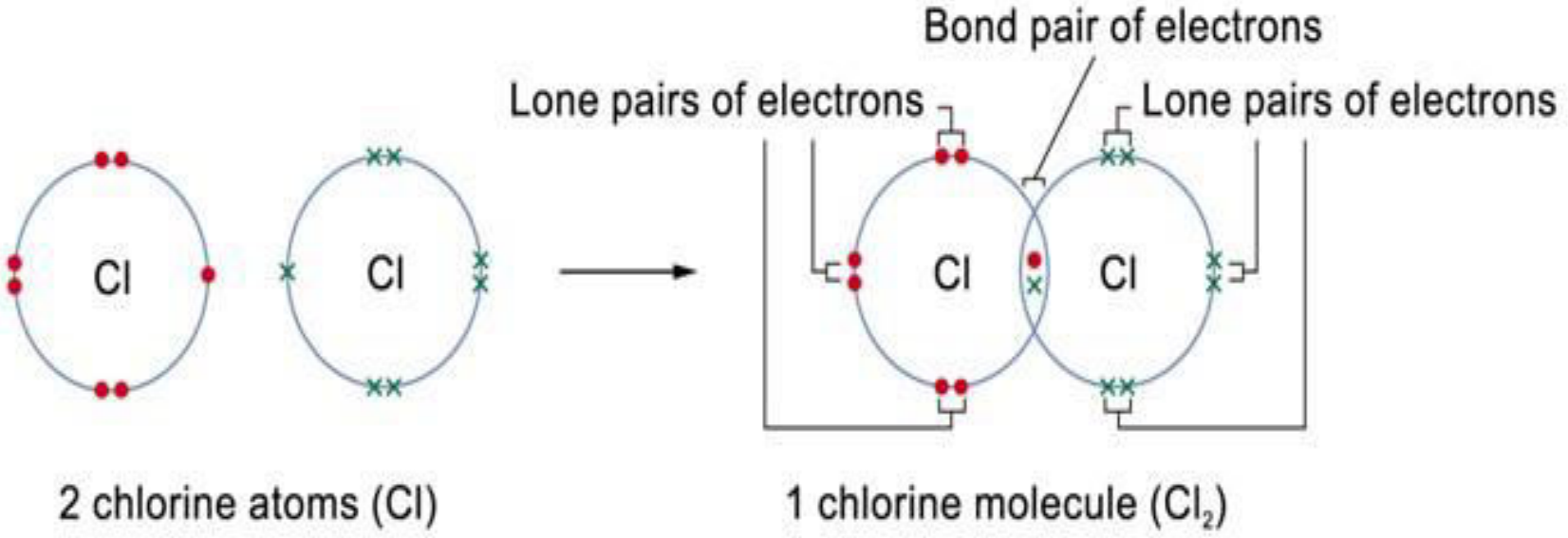
A covalent bond results from the overlap of orbitals of two atoms.

The shared space is occupied by two electrons, which have opposite spins.

ORBITAL OVERLAP AND SPIN PAIRING IN H_2 & Cl_2

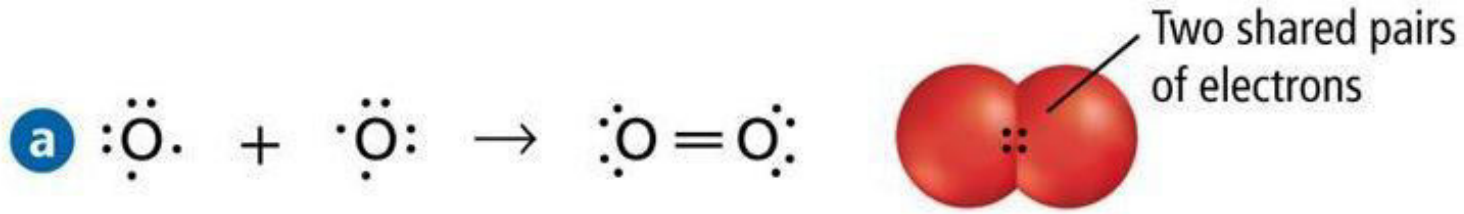


Shared Electrons

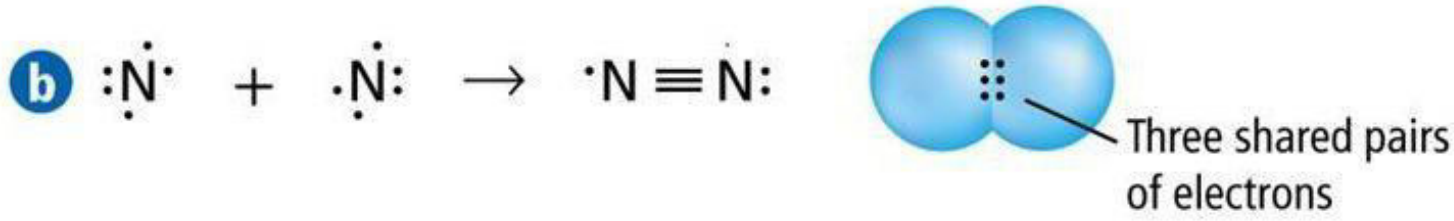


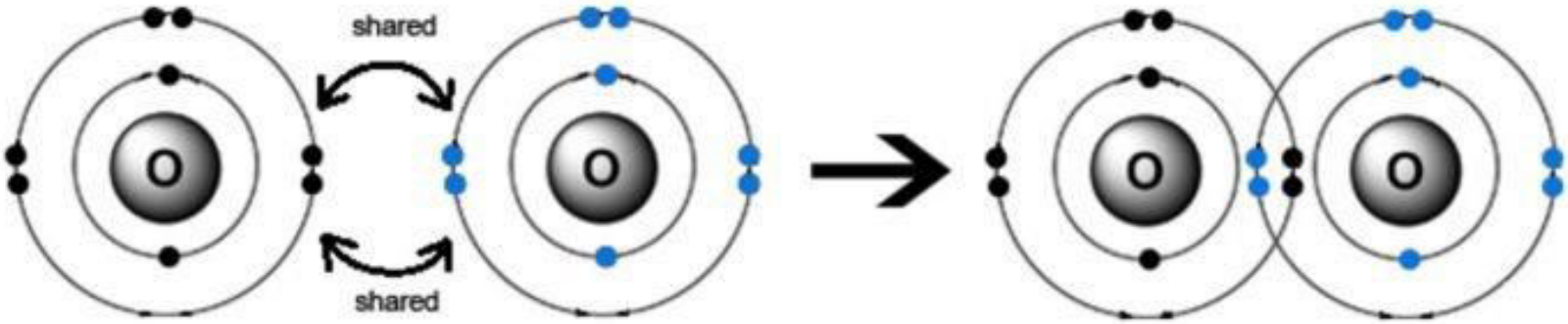
Multiple Covalent Bonds

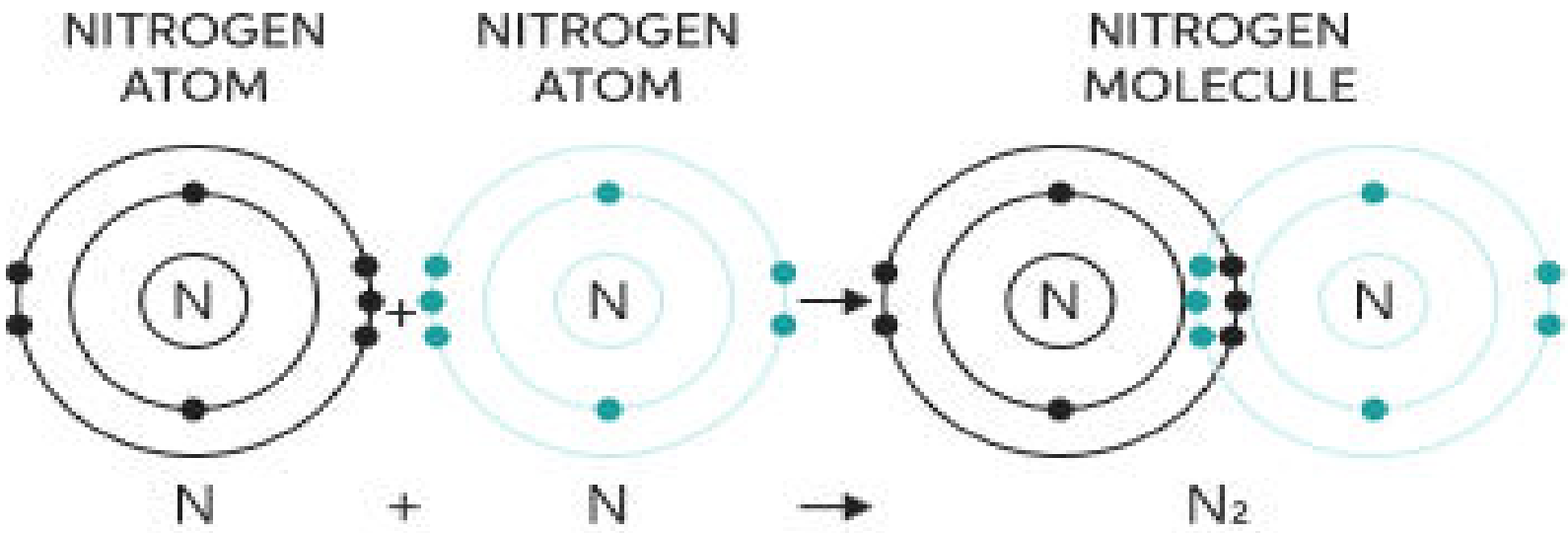
- Double bonds form when two pairs of electrons are shared between two atoms.



- Triple bonds form when three pairs of electrons are shared between two atoms.

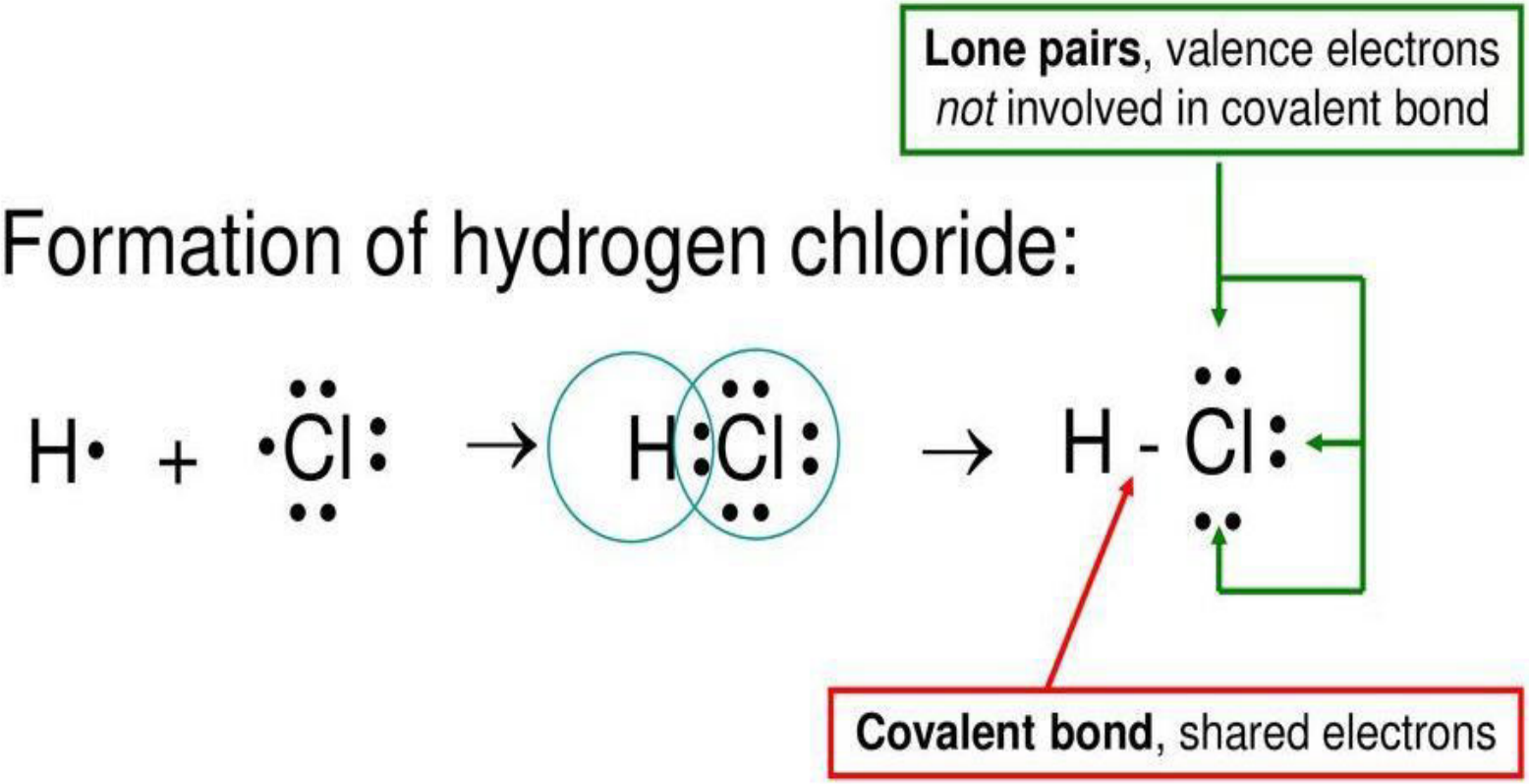



shared
shared
O
O
O
O
2.6
Oxygen atom, O
2.6
Oxygen atom, O
2.8
2.8
Oxygen molecule, O_2
(stable)


NITROGEN ATOM
NITROGEN ATOM
NITROGEN MOLECULE
N
N
N
N
+
N + N → N_2

HETEROATOMIC COVALENT BOND

- Formation of hydrogen chloride:



Structural Formula: H-Cl (lone pairs are not drawn)

THEORETICAL TREATMENT OF COVALENT BOND

- Schrodinger wave equation can be used to describe the behaviour and energies of electrons in atoms as well as molecules.
- Solving Schrodinger wave equation for molecules is very difficult as molecules have more variables.
- Solutions can however be obtained by using certain approximations.
- Two different methods of approximation are used to explain chemical bonding.

- They two methods / theories of approximation are

1. Valence bond theory
2. Molecular orbital theory

- Both of these theories are based on **variation principle.**

- **Variation principle** is a mathematical technique used to calculate the lowest energy state / ground state energy of the system.

- The basic idea of variation principle is that the energy **(E_0)** for the wave function **(ψ_0)** of the ground state must **always be less** than the energy of any other proposed wave function of the system.

Schrodinger wave equation in simplified form can be written as

$$\mathbf{H\psi = E\,\psi}$$

where **H** is the Hamiltonian operator which performs on wave function **ψ** to give **E,** the total energy of the system.

Multiplying both sides of the above equation by **ψ*** and integrating over the space **∂T**

$$\mathbf{\int \psi^* H\,\psi\,\partial T = \int \psi^* E\,\psi\,\partial T}$$

$$\mathbf{\int \psi^* H\,\psi\,\partial T = E \int \psi^*\,\psi\,\partial T}$$ as **E** is constant

Rearranging the above equation,

$$E = \frac{\int \psi^* H \psi \, \partial T}{\int \psi^* \psi \, \partial T}$$

By the above relation energy of the system can be calculated by knowing the value of true / exact wave function **ψ.**

It is very difficult to know the true / exact wave function **ψ.**

So how does this principle work if true / exact wave function ψ is not known?

- A guess is taken that a wave function ψ_1 (which may not be correct) is close to the true wave function .

- Applying the variation principle, its energy E_1 can be determined.

- Similarly another wave function ψ_2 is guessed, whose energy is taken as E_2.

- According to variation principle, the energies E_1 **and** E_2 should always be greater than E_0 , the ground state energy of the system.

- The wave function which gives the lowest value of energy is considered to be a better approximation.

- If $\mathbf{E_2 < E_1}$, then the wave function $\boldsymbol{\psi_2}$ having energy $\mathbf{E_2}$ is considered to be a better approximation than $\boldsymbol{\psi_1}$ having energy $\mathbf{E_1}$

- The best possible wave function is the one which gives the value of energy **closest to** the ground state energy of the system.

- **A wave function having value of energy less than the ground state energy of the system is not possible.**

VALENCE BOND THEORY (VBT)

- Proposed by Heitler and London in 1927.
- Refined and extended by Pauling and Slater in 1931.
- ***Basic assumptions of the theory :***

1) Atom share its electrons with other atoms to form bonds resulting in the formation of molecule.

2) Atoms do not lose their identity even after the formation of molecule.

3) Only the valence electrons are involved in bond formation.

4) Inner electrons do not participate in bond formation.

5) During bond formation, only the valence electrons of the bonded atoms lose their identity whereas the inner electrons are unaffected.

6) The stability of a bond is given in terms of release in energy during bond formation.

7) Greater the energy released, stronger is the bond.

VBT is based on two theorems :

❖ *Theorem 1*

If ψ_A and ψ_B are two wave functions of isolated independent atoms A and B having energies E_A and E_B, then the total wave function for the system of two atoms can be given as

$$\psi = \psi_A \cdot \psi_B \quad ; \quad E = E_A + E_B$$

❖ *Theorem 2*

If a system is represented by a number of wave functions ψ_1, ψ_2, ψ_3, ... ψ_n, then the true wave function ψ is given by taking the linear combination of all the wave functions.

$$\psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + \ldots\ldots\ldots + C_n\psi_n$$

where $C_1, C_2, C_3, \ldots\ldots C_n$ are the contribution of the each wave function towards true wave function.

APPLICATION OF VBT TO THE FORMATION OF H_2 MOLECULE

- Applying the concept of VBT to the formation of hydrogen molecule from two hydrogen atoms say **H_A and H_B**.

- When the two atoms are very far from one another, there is no interaction between them.

- The wave function for such system is given as

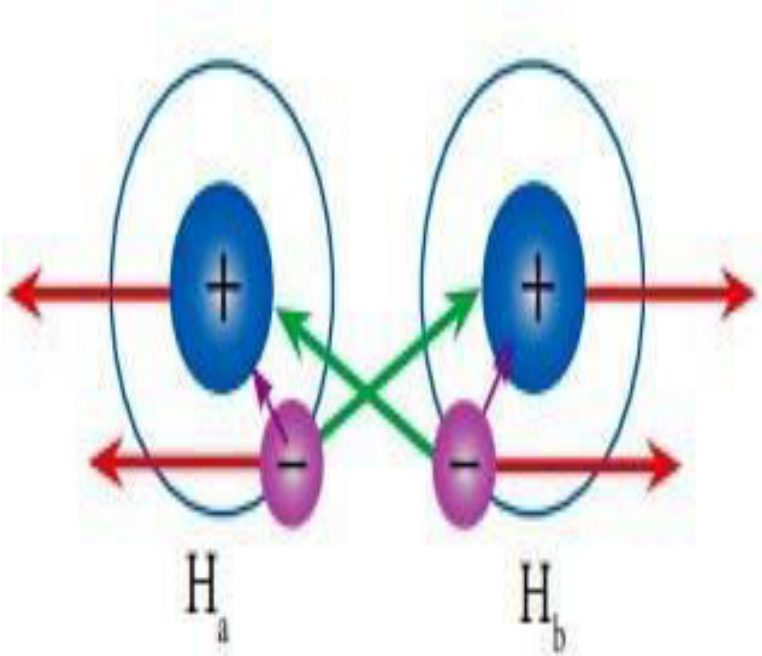
$$\psi = \psi_A \psi_B \quad \text{.....(eqn.1)}$$

where ψ_A is the wave function of H_A
and ψ_B is the wave function of H_B

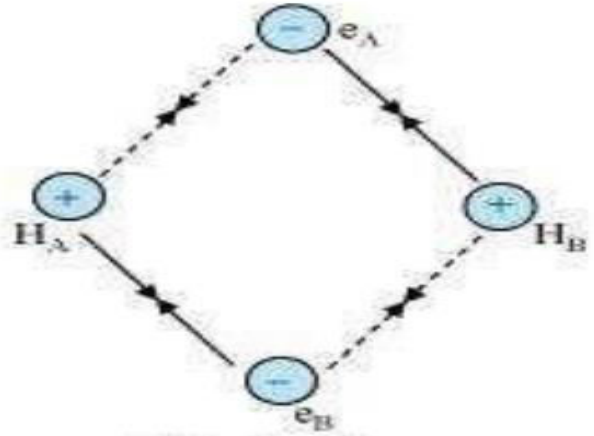
- As the two hydrogen atoms come close to one another, attractive and repulsive interactions occur/ start between them.

- The attractive interactions occur between nucleus of one and electron of other i.e. $\mathbf{H_A - e_2}$, $\mathbf{H_B - e_1}$.

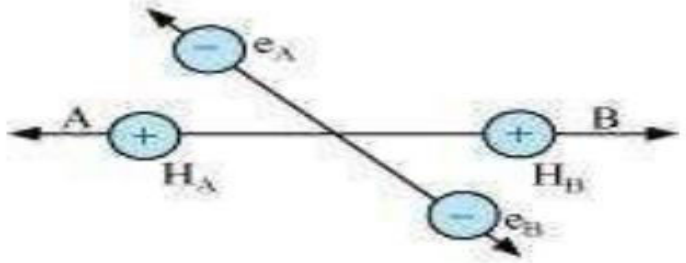
- The repulsive interactions occur between the two nuclei ($\mathbf{H_A - H_B}$) and the electrons ($\mathbf{e_1 - e_2}$) of both the atoms.



Green arrows : Attractive interactions
Red Arrows : Repulsive interactions



Attractive Forces



Repulsive Forces

- The system can now be represented as

$$\mathbf{H_A^{\,1}\,H_B^{\,2}}$$

where **1** represents electron associated with $\mathbf{H_A}$
and **2** represents electron associated with $\mathbf{H_B}$

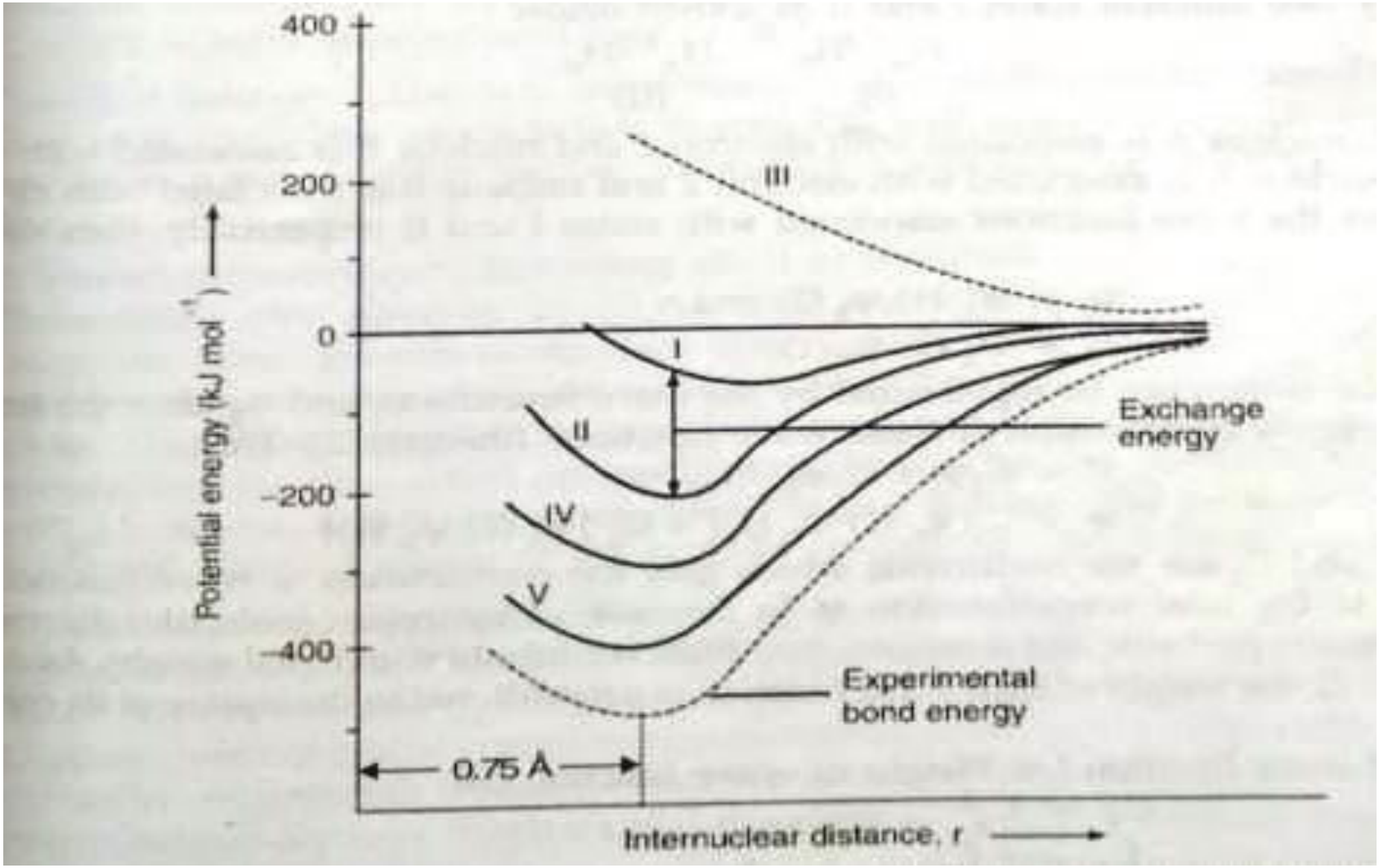
- The combined wave function ψ can be given as

$$\boldsymbol{\psi_1 = \psi_A(1)\,\psi_B(2)} \quad \textbf{.....(eqn. 2)}$$

where $\boldsymbol{\psi_A}$ and $\boldsymbol{\psi_B}$ are the wave functions of the interacting hydrogen atoms **A** and **B.**

- With the help of the wave function $\boldsymbol{\psi_1}$, energy of the H_2 molecule can be calculated as a function of internuclear distance (r).

The energy change of the system as a function of internuclear distance can be graphically depicted as **Curve I** shown below



- The total energy of two isolated hydrogen atoms is taken to be **zero by convention.**

- As the two hydrogen atoms come close to one another, due to attractive forces coming into play, the energy of the system goes on decreasing.

- This value of energy goes on decreasing till a certain minimum value is reached.

- This point corresponds to the formation of hydrogen molecule (shown as minima in the curve I)

- If the two atoms are still brought closer after attaining a minima , then repulsive forces between the two atoms come into play. This results in the increase in potential energy

- The fall in potential energy is called the **Bond energy** and it comes out to be only **24 KJ/ mol.**

- **The experimental bond energy of hydrogen molecule has been found to be 458 KJ/mol** (shown by dotted line).

- Comparison of the experimental bond energy and bond energy given by curve I shows very poor agreement.

- Also the minimum is found at an internuclear distance of **about 0.90 Å (curve I)** whereas the experimental minimum is found at a distance **of 0.74 Å .**

- **It means that the wave function ψ_1 is not correct.**

- It requires further improvement to be in agreement with the experimental data.

IMPROVEMENTS

Three of the improvements are discussed. They are

- **Exchange of electrons**
- **Screening effect of electrons**
- **Ionic character of H – H bond**

1st Improvement : Exchange of electrons

- The equation 2 was obtained on the assumption that the **electrons of the two hydrogen atoms could be distinguished** from one another.

- So, the electron around **nucleus A was labelled 1** and the electron around **nucleus B was labelled 2.**

- This assumption is incorrect.
- When a bond is formed the two atomic orbitals overlap and the electrons become **indistinguishable** i.e. we cannot tell which electron is associated with which nucleus.
- It means a state when **electron 1 is near nucleus B** and **electron 2 is near nucleus A** is possible.
- In such case, the system of the two hydrogen atoms can be represented by two different states I and II

$\mathbf{H_A^1 H_B^2}$ **(State I)**

$\mathbf{H_A^2 H_B^1}$ **(State II)**

- Assuming $\boldsymbol{\psi_I}$ and $\boldsymbol{\psi_{II}}$ to be the wave functions associated with

state I and II, then the wave functions for the two states can be given as

$$\psi_I = \psi_A(1)\,\psi_B(2)$$
$$\psi_{II} = \psi_A(2)\,\psi_B(1)$$

- As both the wave functions are equally probable, the true wave function is given as the linear combination of the above two wave functions (Theorem 2)

$$\psi = C_1\psi_I + C_2\psi_{II} \quad \text{.....(eqn. 3)}$$

or

$$\psi = C_1[\psi_A(1)\,\psi_B(2)] + C_2[\psi_A(2)\,\psi_B(1)] \text{.....(eqn. 4)}$$

where C_1 and C_2 are the mixing coefficients and give the **contribution** of the two wave functions I and II towards the total wave function.

- As both the wave functions are equally probable, their contribution to the total wave function should also be equal.

- According to theorem 2 of VBT, the weight of each wave function is proportional to the square of its coefficients.

- So Weight of ψ_I = Weight of ψ_{II}

$$C_1^2 = C_2^2$$

$$C_1 = \pm C_2$$

- For simplicity, it is assumed that

$$C_1 = 1 \text{ and } C_2 = \pm 1$$

- Substituting the values of C_1 and C_2 in **eqn. 4,** two new combinations are obtained

$$\psi_+ = \psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1) \text{.....(eqn. 5)}$$
$$\psi_- = \psi_A(1)\,\psi_B(2) - \psi_A(2)\,\psi_B(1)$$

- The wave function ψ_+ is called the symmetric combination whereas the wave function ψ_- is called the antisymmetric combination.

- The energies associated with these wave functions ψ_+ and ψ_- as a function of internuclear distance are given by curve II and III respectively.

- The energy curve II corresponding to wave function ψ_+ shows significant lowering of energy.

- The bond energy corresponding to is 303 KJ/mol and the

Internuclear distance is 0.80Å.

- This value of bond energy (303KJ/mol.) **is much better** than that calculated from eqn. 2 (24KJ/mol.)
- This additional lowering in energy (303 – 24 = 279KJ/mol.) is due to the concept of exchange of electrons between two hydrogen atoms. **So, it is called exchange energy.**
- The wave function ψ_+ is also called **covalent wave function** and is written as $\psi_{covalent}$
- It is so called because there is **no charge separation** as one electron is associated with one nucleus and the other electron is associated with other nucleus.

- The energy curve III corresponding to wave function ψ_- shows an increase in energy as the two hydrogen atoms approach each other.

- This represents **repulsive or non bonding state. It means bonding is not possible in antisymmetric combination.**

2nd Improvement : Screening effect of electrons

- The wave function shown by **eqn. 5** can further **be improved** by taking into consideration **screening effect of electrons**.

- When the two atoms come close to one another, the electrons of one atom shield the other electron of other atoms from nucleus.

- So the electrons do not feel the full charge of the nucleus.
- The charge felt by the electrons is less than the actual nuclear charge and is called the **effective nuclear charge (Z_{eff})**
- If **effective nuclear charge (Z_{eff})** is taken into consideration instead of actual nuclear charge, then the wave function given by **eqn. 5** can be further improved.
- It has been found that on taking screening effect into consideration, **bonding energy of 365 KJ/mol. is obtained.**
- This is shown by **curve IV.**

3rd Improvement : Ionic character of H – H bond

- The bond energy of 365KJ/mol is still quite less than the experimental bond energy of 458 KJ/mol obtained for hydrogen molecule.
- It indicated that still improvement have to done .
- In the 1st improvement, simultaneous exchange of electrons was allowed.
- However, there is a possibility that both the electrons may be present close to one nucleus or other at the same time.
- It means that both the electrons 1 and 2 are present on atom $\mathbf{H_A}$ or $\mathbf{H_B}$ at the same time.

- These may be represented by states as shown

$H_A^{1,2}\ H_B$ **State III** **and** $H_A\ \ H_B^{1,2}$ **State IV**

- The corresponding wave function may be written as

$$\psi_{III} = \psi_A(1)\,\psi_A(2)$$

and

$$\psi_{IV} = \psi_B(1)\,\psi_B(2)$$

- Both the above states can be thought as ionic $H_A^-\ H_B^+$ and $H_A^+\ H_B^-$ respectively.

- These ionic interaction tend to increase the force of attraction between the two hydrogen atoms.

- This will lead to decrease in the bond energy of the system.
- The resulting ionic wave function can be given as

$$\psi_{ionic} = \psi_A(1)\,\psi_A(2) + \psi_B(1)\,\psi_B(2) \ldots\ldots\ldots\ldots \text{(eqn. 6)}$$

as ψ_{III} and ψ_{IV} are equally probable and their contribution will be the same.

- From above it is concluded that H – H bond is not purely covalent.
- It has some ionic character as well.
- On **combining the covalent and ionic wave functions** together, the real wave function can be written as

$$\psi = \psi_{covalent} + \lambda\psi_{ionic}$$

$$\psi = [\psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1)] + \lambda[\psi_A(1)\,\psi_A(2) + \psi_B(1)\,\psi_B(2)$$

…….(eqn. 7)

where λ is called the mixing constant. It gives the extent to which ionic wave function contribute to the total wave function.

- By knowing λ ,the extent to which the bond is ionic in nature can be found out.
- In case of hydrogen molecule, the value of **λ is 0.17.**

- The plot of energy corresponding to wave function given by **eqn. 7** is shown by **curve V**
- The bonding energy represented by curve V is 388 KJ/mol.
- This is closer to the experimental value of 458 KJ/mol.
- Also with these three improvements in the wave function, the internuclear distance between hydrogen atoms has been found to be 0.75Å (75pm).
- This value is in close agreement with the experimental value of 0.74Å (74pm).

- The differences that still persist/ remain are due to some complicated electronic interactions.

- A number of improvements have been suggested to get the wave function which gives the bond energy closer to the experimental value.

- **James and Coolidge** used a wave function which had **13 terms** and got a bond energy of **455 KJ/mol**.

- **Kolos and Roothan** suggested a wave function of **50 terms** and got the bond energy equal to the experimentally calculated value of 458 KJ/mol.

TABLE 5.1. Bond energies and bond lengths for H_2 molecule with the corresponding wave functions.

Wave function	Bond energy (kJ mol^{-1})	Bond length pm
$\psi = \psi_A(1)\psi_B(2)$	24	90
$\psi_{covalent} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$	302	80
$\psi_{covalent}$ + Screening effect	365	76
$\psi_{covalent} + \lambda\psi_{ionic}$	388	75
James and Coolidge (13 terms polynomial)	455	74
Kolos and Roothan (50 terms polynomial)	458	74
Experimental value	458	74

LIMITATIONS OF VALENCE BOND THEORY

The main limitations of VBT are

- Successful only in case of a few simple systems.
- Mathematical treatment involved is complicated and involves approximations.
- Formation of coordination valency (coordinate bond) could not be explained by this theory as it involves bond formation by sharing of electrons equally by the two atoms.
- This theory could not explain bonding in electron deficient compounds.
- According to VBT, it is not possible to write a single structure which explains all the structural features of a molecule or ion under consideration.
- It fails to explain paramagnetism in case of O_2 molecule.

Despite all the limitations, VBT is used as a qualitative guide in predicting the geometry of ions and molecules.

DIRECTIONAL CHARACTER OF COVALENT BOND

- A covalent bond is formed by sharing of unpaired electrons of the combining atoms.
- The electrons are localised between the nuclei of the atoms.
- The spin of the electrons must be opposite to each other.
- The strength of the covalent bond is proportional to the amount of overlap of the atomic orbitals of the participating electrons.

- The bond formed will be strong if there is maximum overlap of the atomic orbitals .

- Maximum interpenetration of charge densities of the electrons involved also increases the strength of the bond.

- Two s – s orbitals cannot overlap strongly because they are spherically symmetrical in all directions. This means that s – s bond is weak.

- The three p – orbitals are directed along the x, y and z axes. So they have directional nature.

- Also the lobes of the p – orbitals are longer then the radius of the corresponding s – orbitals, leading to more effective overlap with other s and p orbitals than s – s orbital overlap.

- d and f orbitals also have directional nature.

- In other words, the directional nature of the p, d and f orbitals is responsible for the directional character of covalent bond.

- This directional nature of the covalent bond leads to definite shapes and geometries of the molecules.

- The shapes and geometries of the molecules can be explained on the basis of two theories :

1. Hybridisation
2. Valence shell electron pair repulsion (VSPER) theory

HYBRIDISATION

- A covalent bond is formed by sharing of unpaired electrons.
- The number of bonds formed by an atom depends on the number of unpaired electrons in that atom.
- This is called the covalency of an element.

Element	H	He	Li	Be	B	C	N	O	F	Ne
Number of unpaired electrons	1	0	1	0	1	2	3	2	1	0
Co - valency	1	0	1	2	3	4	3	2	1	0

Table of covalency of 1st ten elements of the periodic table

Exceptions in the above table are Be, B and C

- In terms of unpaired electrons, Be is expected to be inert as it does not has any unpaired electrons.

- Also, B with one unpaired electron and C with two unpaired electrons are expected to be monovalent and divalent respectively.

Element	1s	2s	$2p_x$	$2p_y$	$2p_z$
Beryllium (Be : $1s^2$,$2s^2$)	↑↓	↑↓			
Boron (B : $1s^2$, $2s^2$, $2p^1$)	↑↓	↑↓	↑		
Carbon (C: $1s^2$, $2s^2$, $2p^2$)	↑↓	↑↓	↑	↑	

- But, Beryllium has been found to form divalent compounds like BeH_2 , BeF_2 , $BeCl_2$.
- Boron has been found to form trivalent compounds like BH_3 , BF_3 , BCl_3 .
- Whereas Carbon has been found to form tetravalent compounds like CH_4 , CF_4 , CCl_4.
- So, simple theory of bonding is insufficient to account for the increase in valency of Be, B, C.
- To explain these anomalies, **Linus Pauling introduced a new concept called Hybridisation.**

According to **Linus Pauling theory of hybridisation**:

- Some of the paired electrons get unpaired before the participation of the atom in bond formation.
- The process of unpairing of electrons require energy.
- This energy requirement is met from the energy released during bond formation.
- This can be explained by taking example of a **carbon compound**

- The ground state electronic configuration of Carbon (Z =6) is **$1s^2$, $2s^2$, $2p^2$** and can be represented as

Carbon (G.S)

- As seen there are only two unpaired electrons in the valence shell of carbon. So, Carbon should form only two bonds.

- However carbon is known to form four bonds in its compounds i.e. Carbon shows a bonding capacity of four.

- This can be explained by **promoting** one of the **2s** electron to the empty **$2p_z$** orbital, which is of higher energy.

- This is known as promotion effect.
- The arrangement of electrons after promotion is called the excited state and is represented as

Carbon (E.S.)

- The excited state has four unpaired electrons, suggesting that carbon can now form four bonds.
- The above configuration shows that all four bonds will not be identical.
- For e.g. in the formation of Methane (CH_4) molecule,

- one C – H bond will be formed by overlapping of 2s - orbital of carbon and 1s orbital of hydrogen.
- Whereas the remaining three bonds will be formed between different 2p orbitals of carbon and 1s orbital of hydrogen.
- The energies of the bonds formed will be different as different set of orbitals (s – s and s – p) overlap.
- However, experimentally it has been found that all the four C – H bonds are having exactly same energy.
- The equivalent character of the bonds can be explained by the concept of Hybridisation.

HYBRIDISATION

The phenomenon of inter - mixing of atomic orbitals of slightly different energies so that redistribution of energies occur between them, resulting in the formation of new orbitals having identical shape and equal energy.

- The new orbitals formed as a result of inter mixing are called **Hybrid orbitals.**

- Hybridisation is not a real physical process but a mathematical concept which has been introduced to explain the structural properties of molecules.

SALIENT FEATURES OF HYBRIDISATION

- The number of hybrid orbitals formed is **equal to** the number of atomic orbitals that inter mix.
- All the hybrid orbitals are **degenerate** i.e. they have the same energy.
- All the hybrid orbitals have the **same shape and size**.
- Hybrid orbitals are **more efficient/effective** in forming stable bonds as compared to the pure atomic orbitals.
- The hybrid orbitals **orient themselves** in some fixed direction in space and thus decide the geometry of the molecule.

CONDITIONS FOR HYBRIDISATION

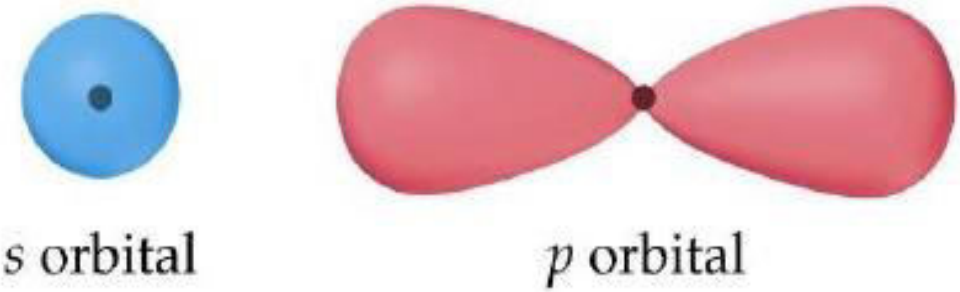
- Only the orbitals in the valence shell of the atom are involved in hybridisation.
- The energy difference between the orbitals involved in hybridisation should be very less.
- Promotion of electron from one orbital to another is not essential before undergoing hybridisation.
- Both half filled and completely filled orbitals of the valence shell can participate in hybridisation.

TYPES OF HYBRIDISATION

There are many types of hybridisation depending on the type of orbitals involved.

sp - hybridisation

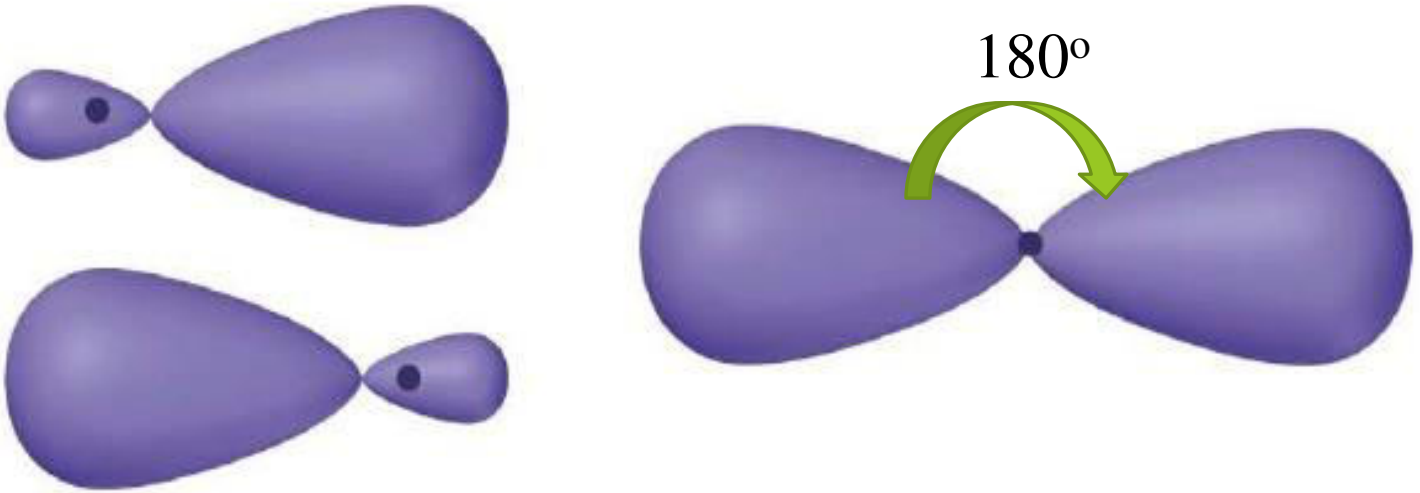
- sp – hybridisation involves the inter – mixing of one s and one p orbital to give rise to two equivalent hybrid orbitals.
- These two hybrid orbitals formed are called **sp hybrid orbitals**.
- These two sp hybrid orbitals try to remain as far as possible from one another, thus adopting a linear geometry.
- The two sp hybrid orbitals make an angle of 180^{o} .



s orbital

p orbital

Hybridize



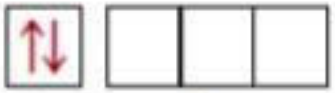
Two *sp* hybrid orbitals

sp hybrid orbitals shown together (large lobes only)

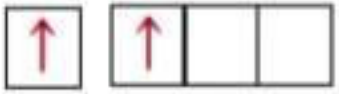
sp Hybridization

e.g. beryllium chloride ($BeCl_2$)

G.S

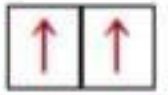


promotion

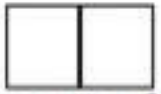


E.S

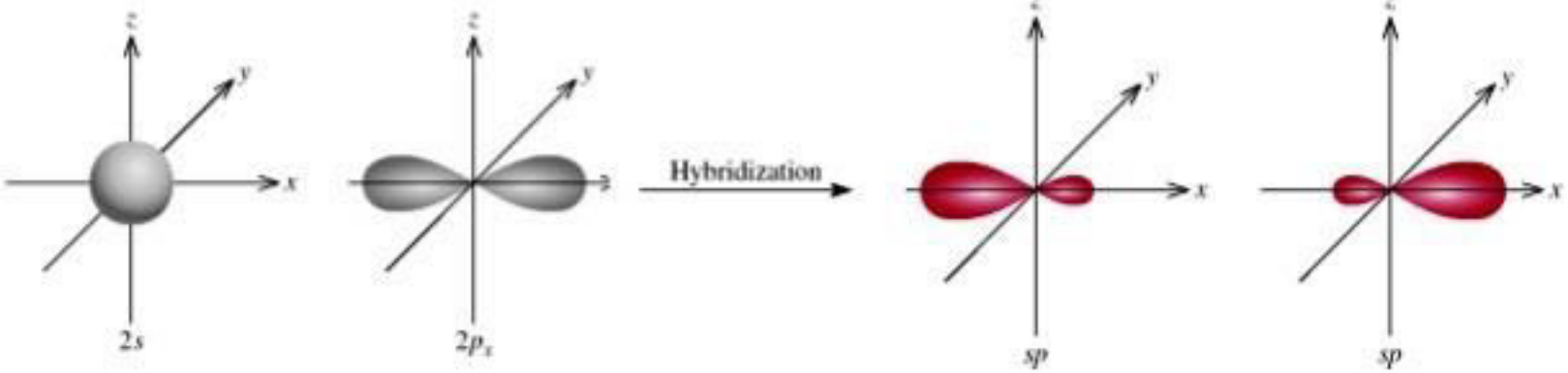
hybridization



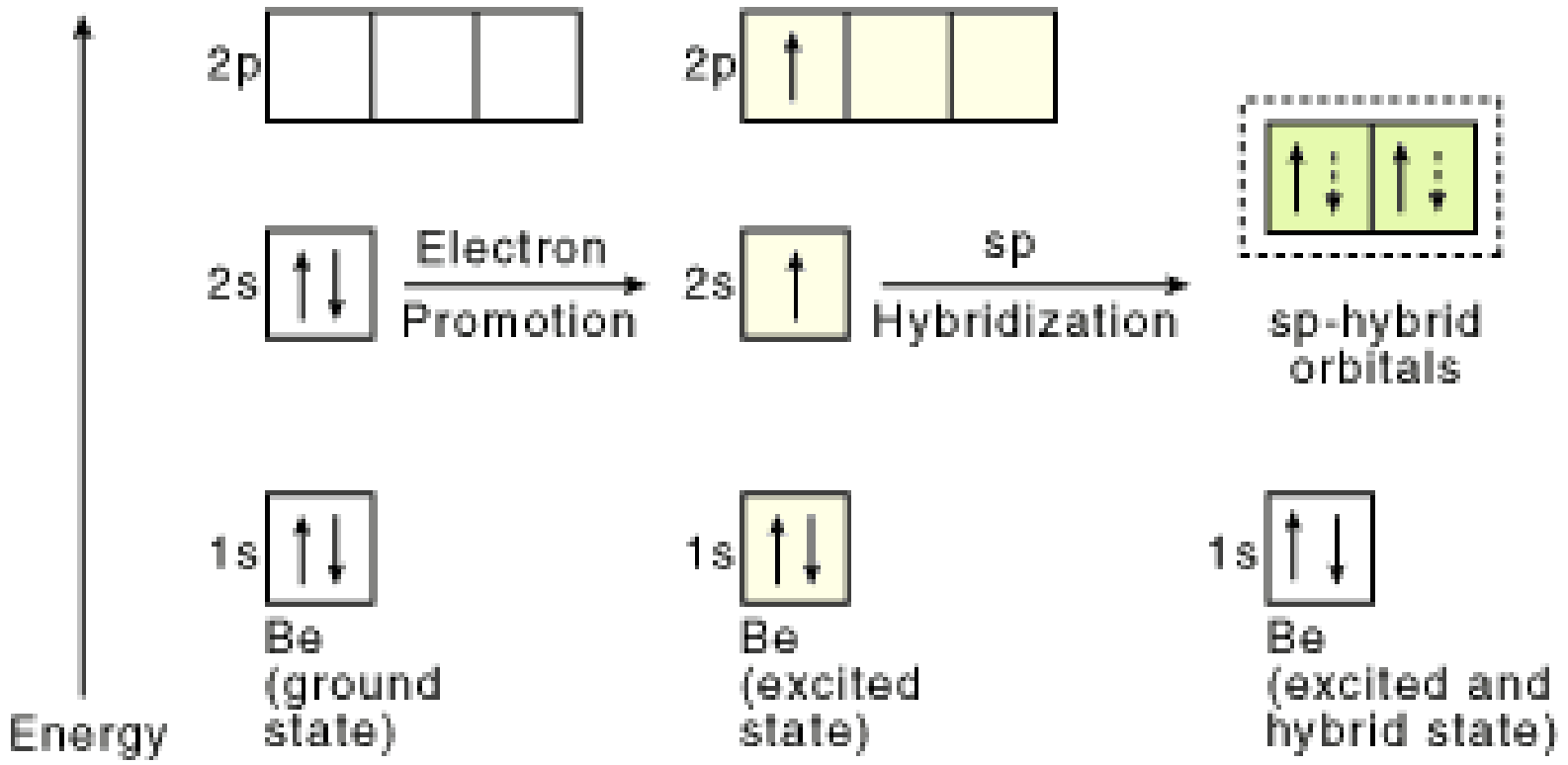
sp orbitals



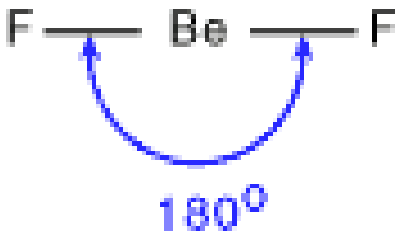
empty 2*p* orbitals



sp – hybridisation : BeF_2



sp-hybrid orbitals



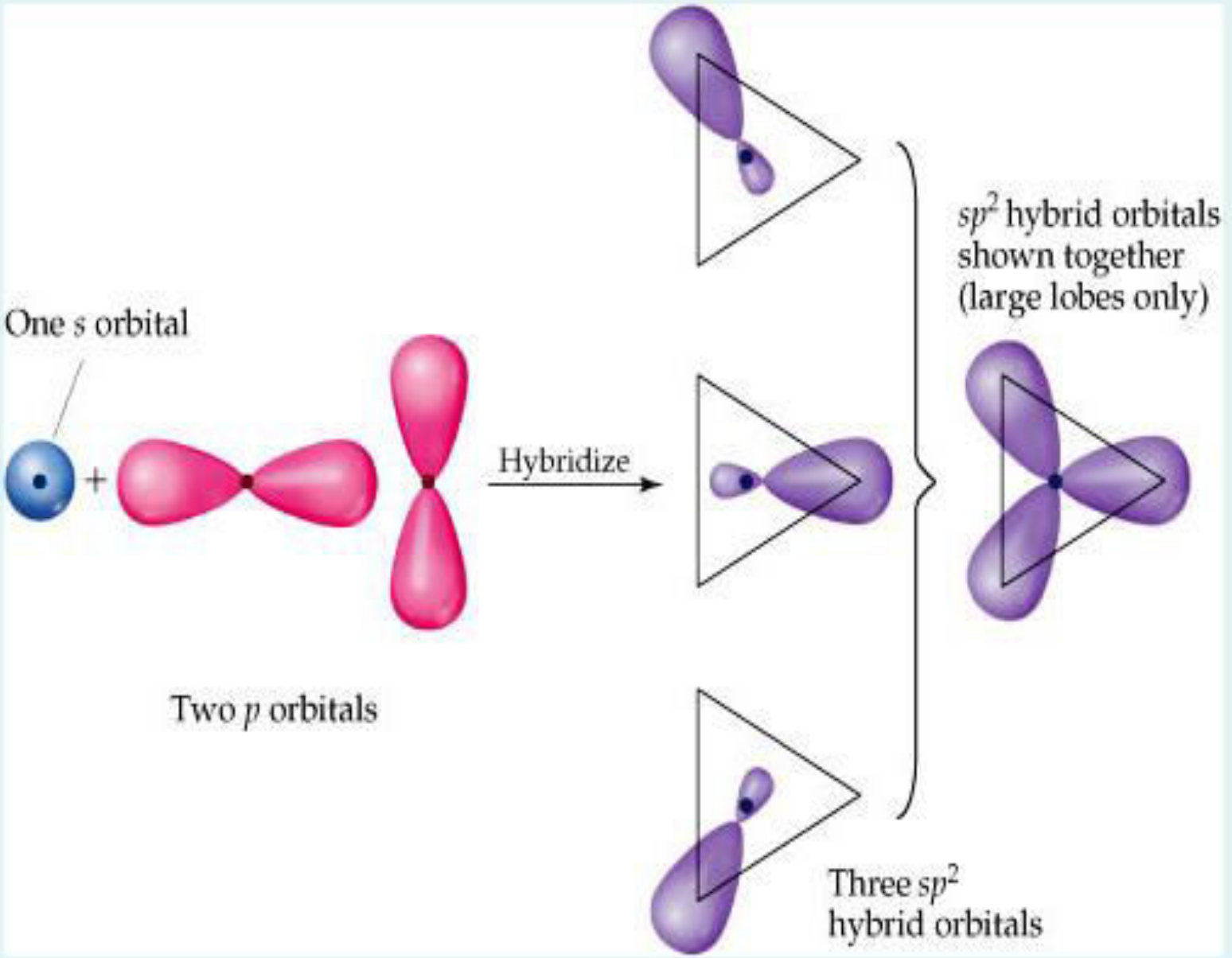
sp^2 - hybridisation

- sp^2 – hybridisation involves the inter – mixing of one s and two p orbital to give rise to three equivalent hybrid orbitals.

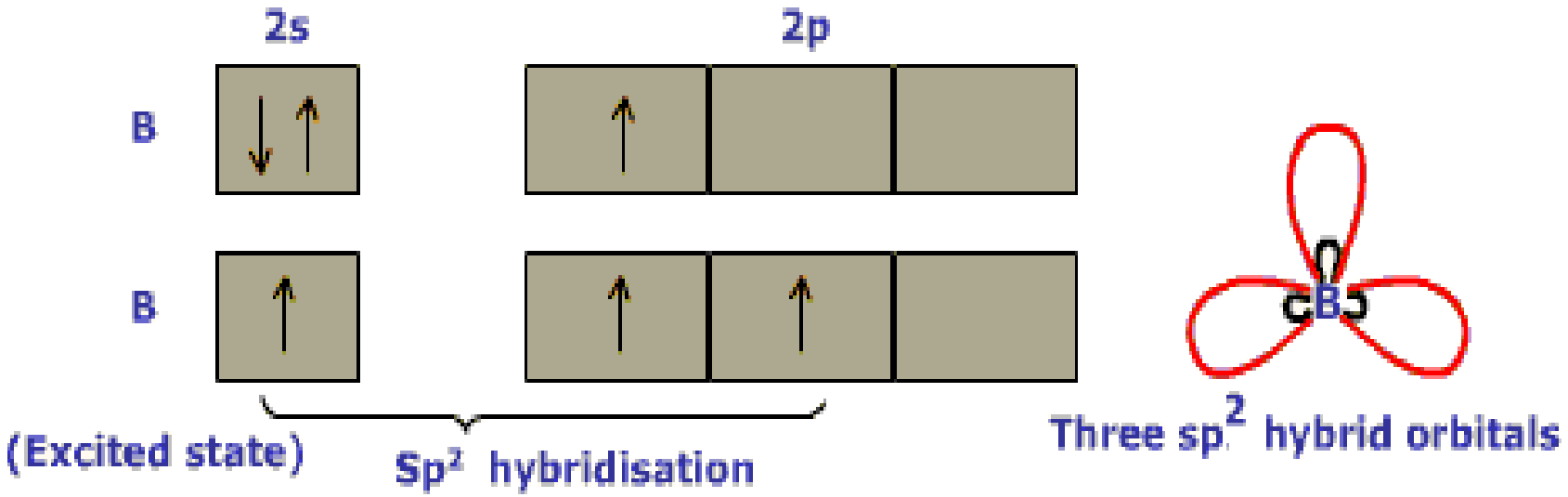
- These three hybrid orbitals formed are called **sp^2 hybrid orbitals.**

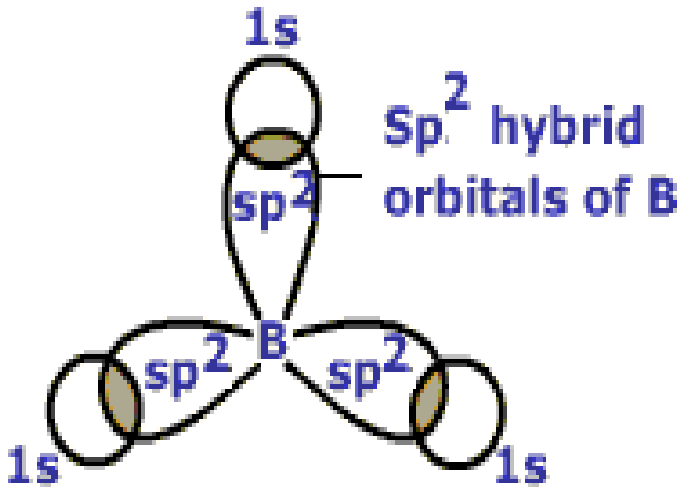
- These three sp^2 hybrid orbitals try to remain as far as possible from one another, thus adopting a **trigonal planar geometry.**

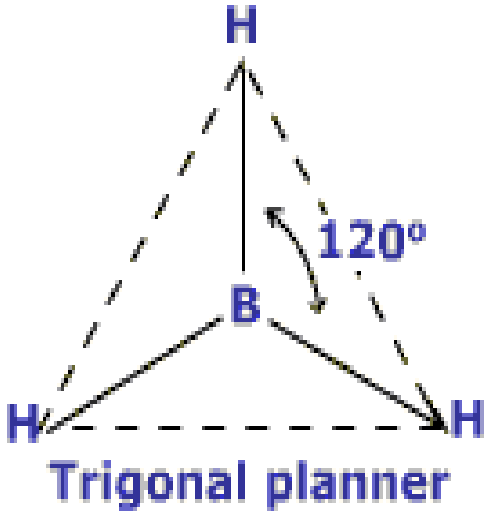
- The three sp^2 hybrid orbitals make an angle of **120^o** with each other.

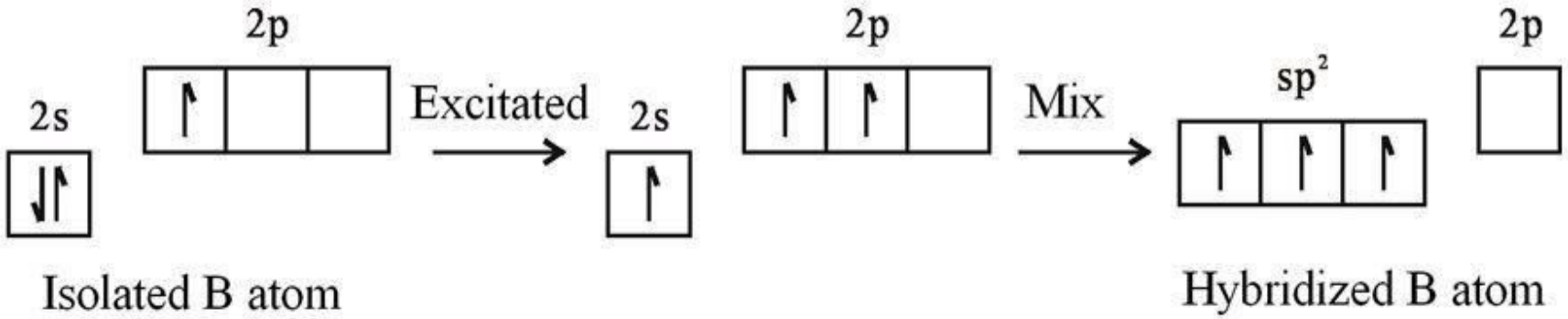

One s orbital
+
Two p orbitals
Hybridize
sp2 hybrid orbitals
shown together
(large lobes only)
Three sp2
hybrid orbitals

Boron trihydride molecule (BH_3)



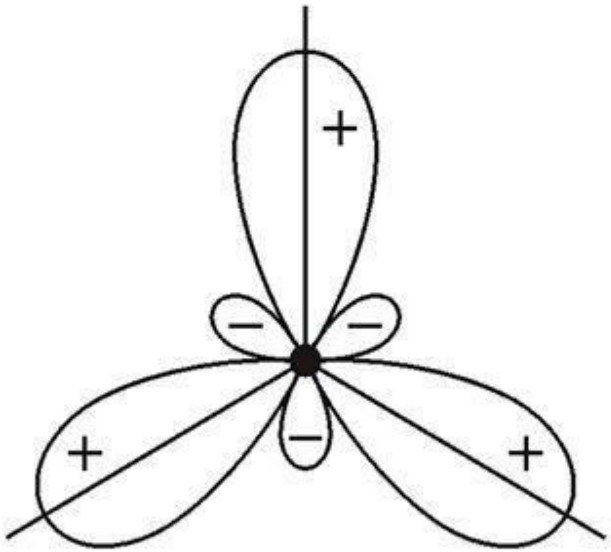




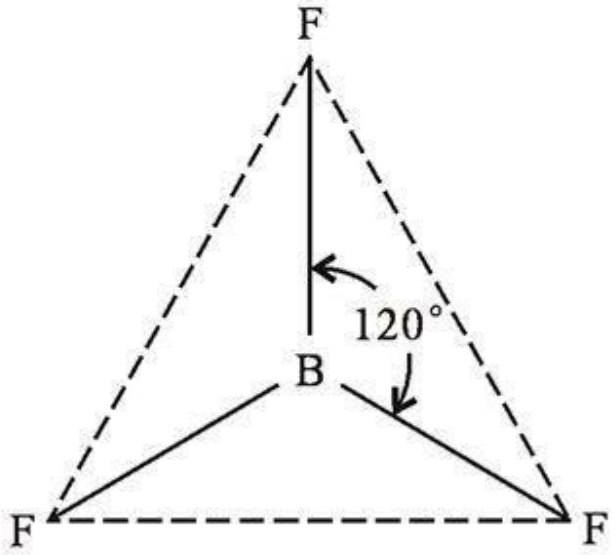


Isolated B atom

Hybridized B atom

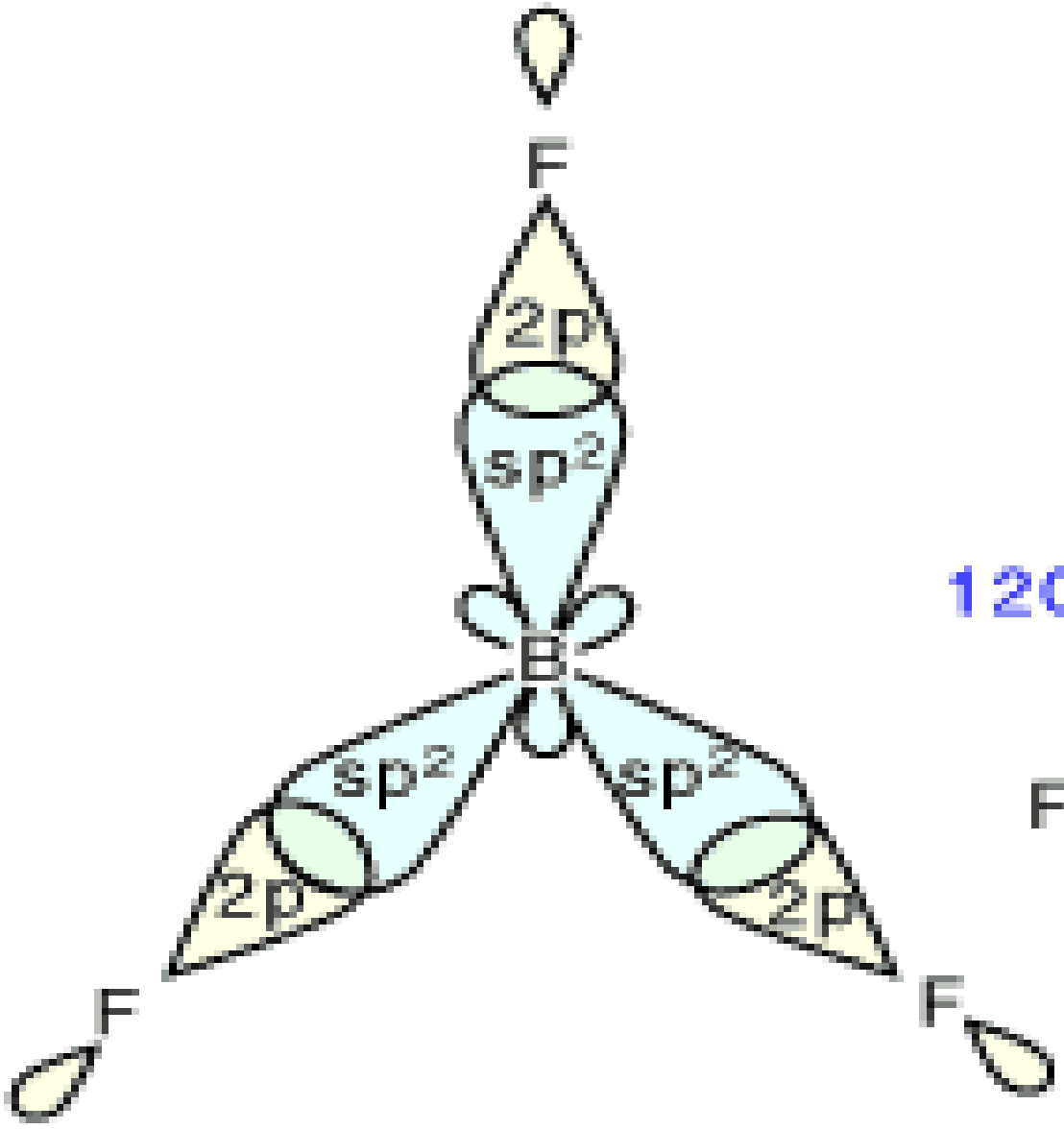


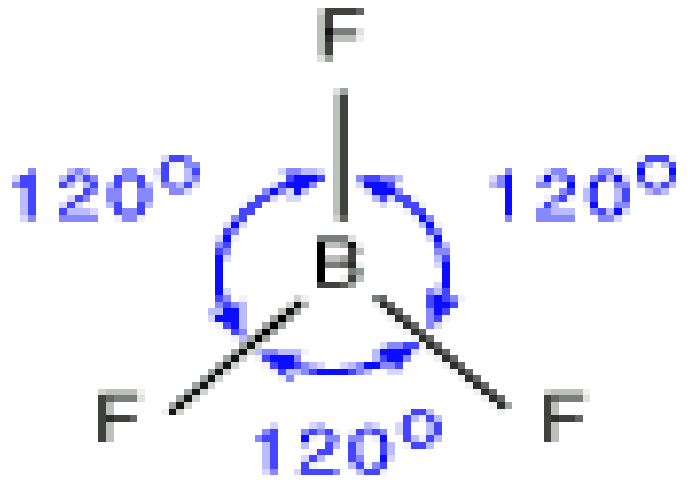
Three sp^2 hybrid orbitls



Trigonal planar

Figure: The sp^2 hybrid orbitals in BF_3


F
2p
sp2
B
sp2
sp2
2p
2p
F
F


F
120°
120°
B
F
F
120°

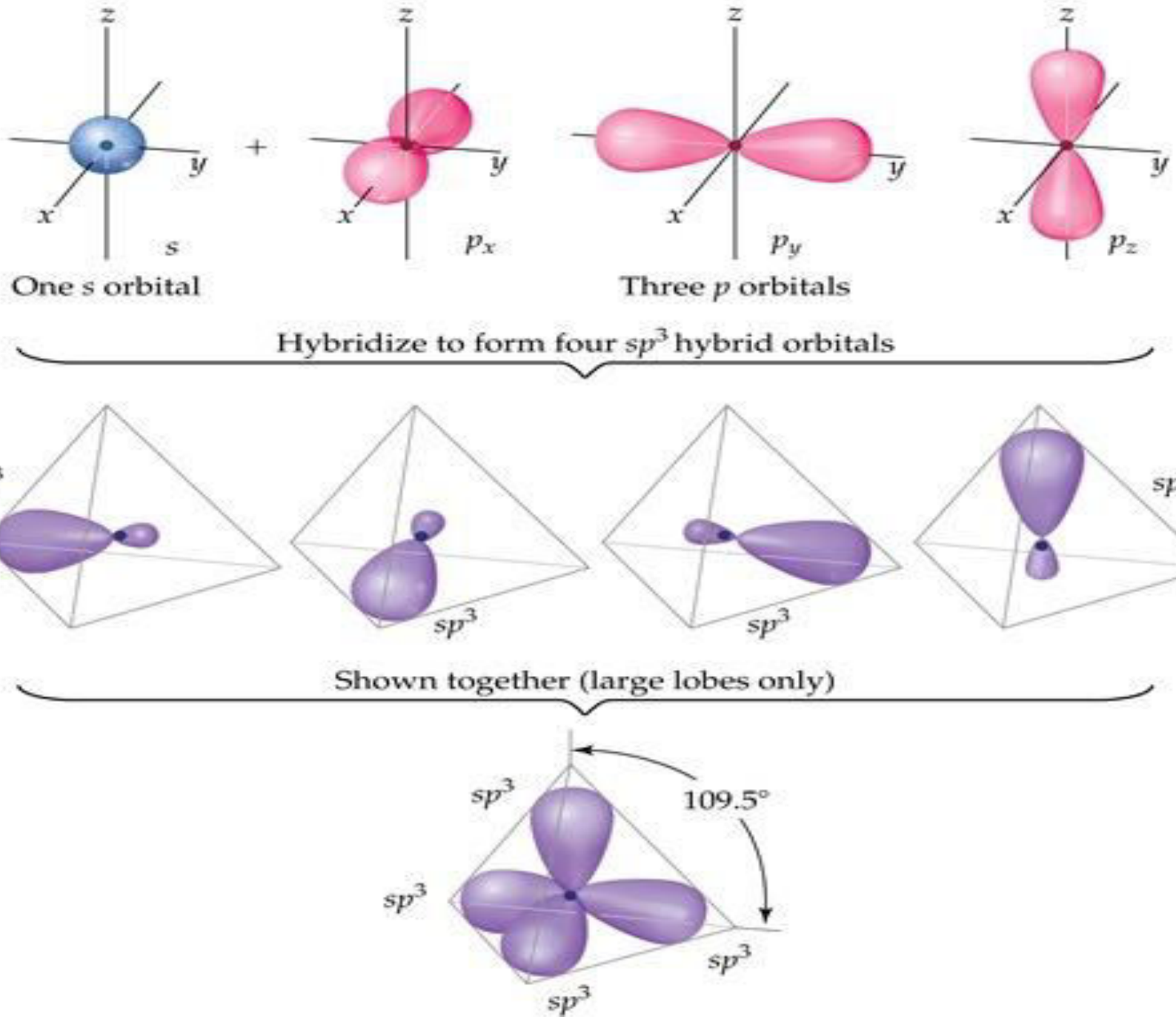
sp^3 - hybridisation

- sp^3 – hybridisation involves the inter – mixing of one s and three p orbital to give rise to four equivalent hybrid orbitals.

- These four hybrid orbitals are called **sp^3 hybrid orbitals**.

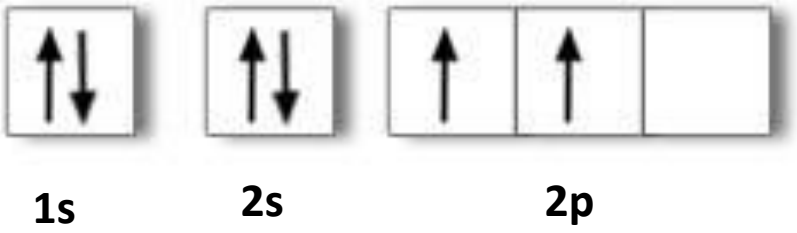
- These four sp^3 hybrid orbitals try to remain as far as possible from one another, thus adopting a tetrahedral geometry.

- The four sp^3 hybrid orbitals make an angle of 109.28^o with each other.


z
y
x
s
+
p_x
p_y
p_z
One s orbital
Three p orbitals
Hybridize to form four sp^3 hybrid orbitals
sp^3
Shown together (large lobes only)
109.5°

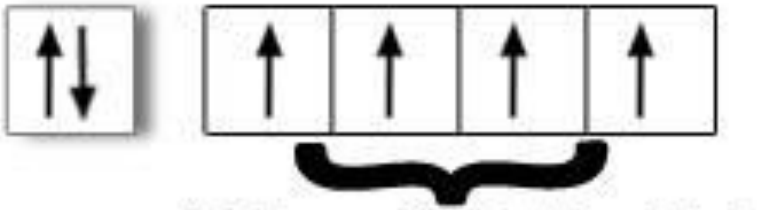
Methane molecule (CH_4)

Carbon atom in ground state



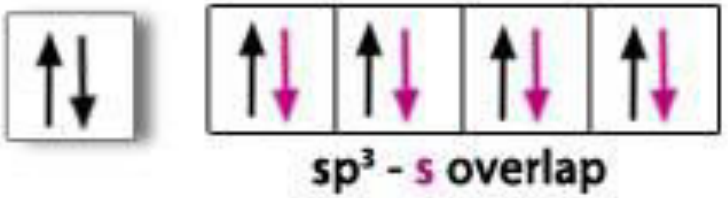
Carbon atom in excited state

Carbon atom in hybridized state



METHANE MOLECULE

(CH_4)



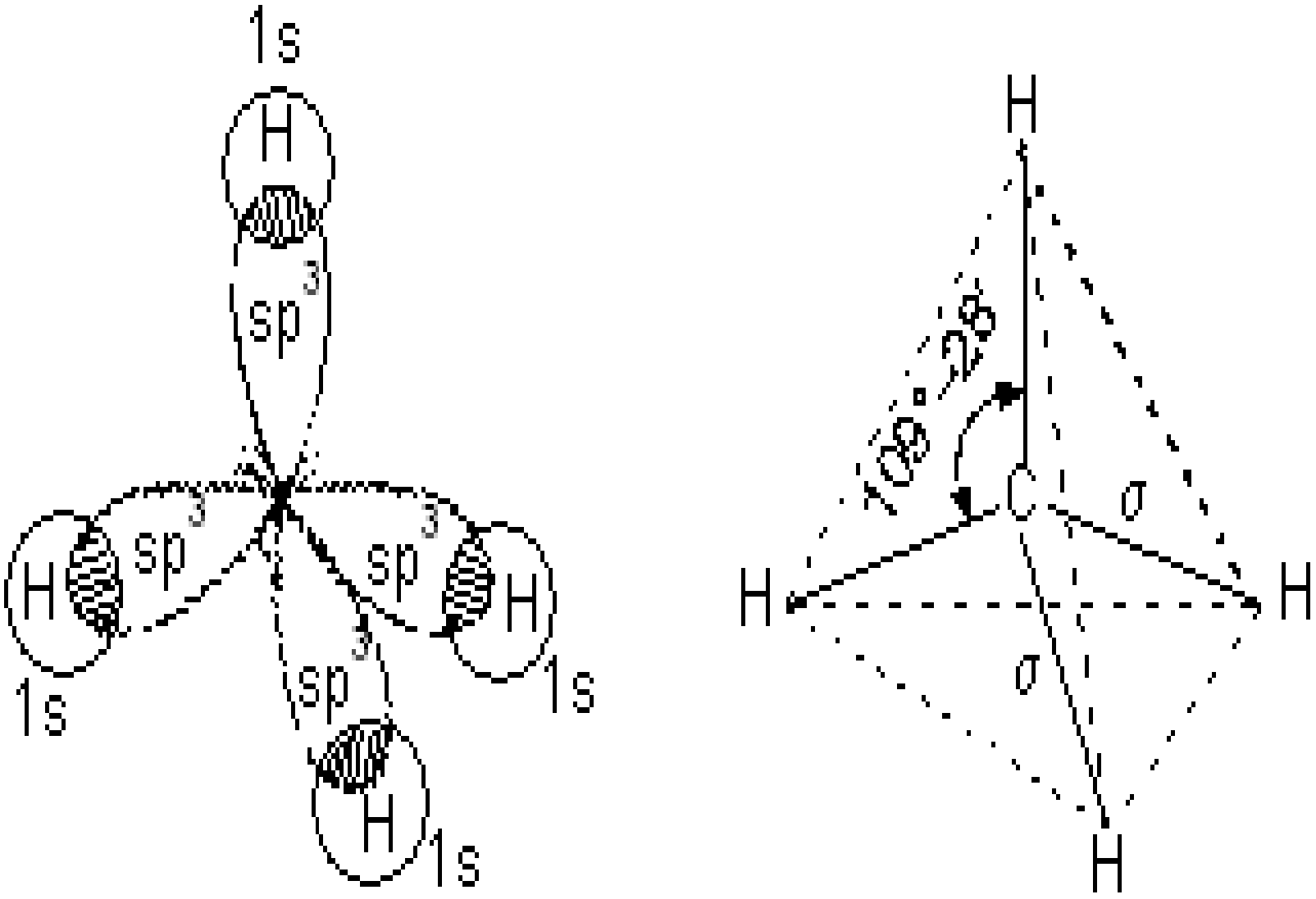


Figure. Orbital picture of methane.

sp^3d / dsp^3- hybridisation

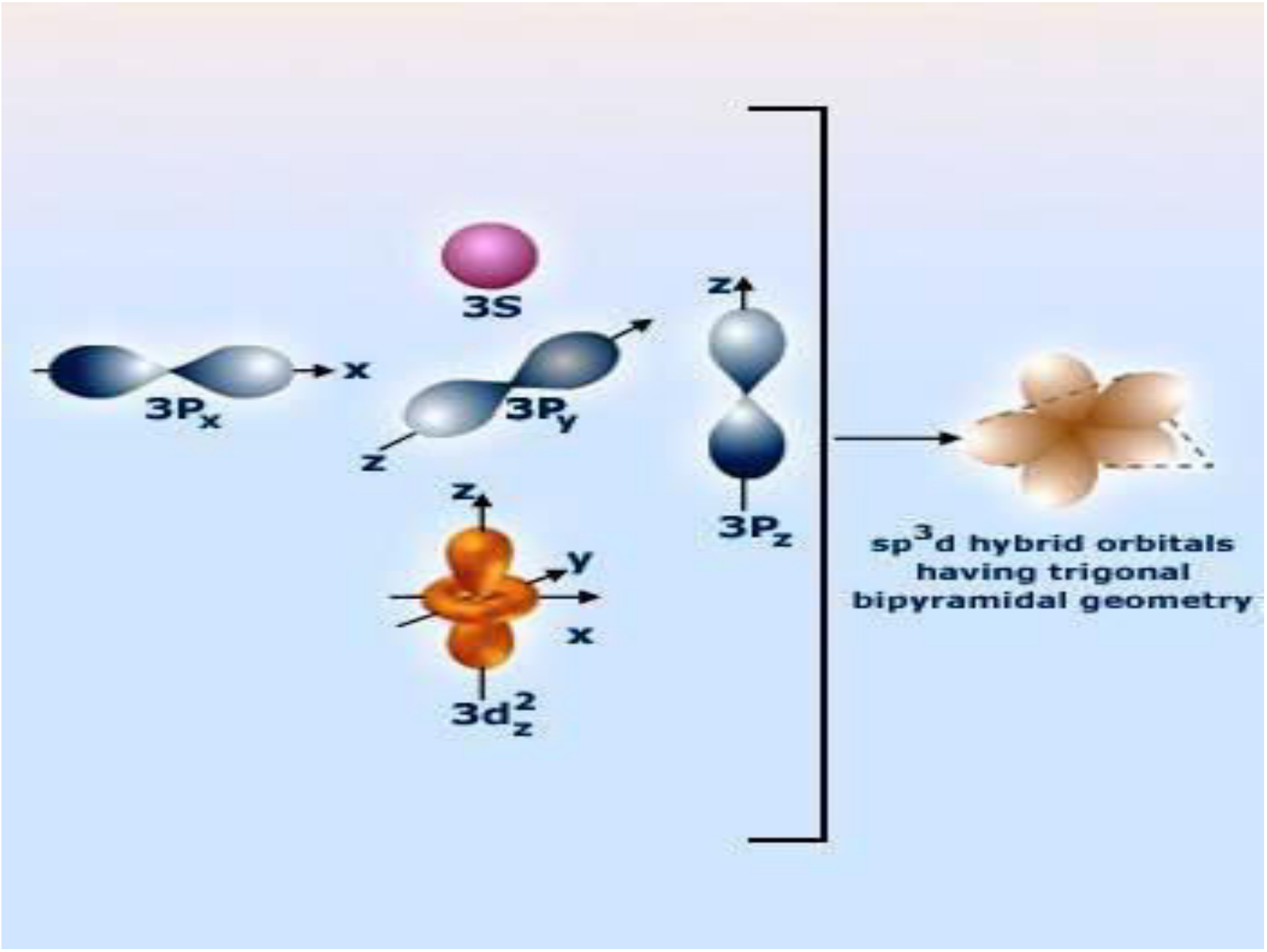
- **sp^3d** – hybridisation involves the inter – mixing of one s, three p and one d orbitals to give rise to five equivalent hybrid orbitals of same energy.
- These five hybrid orbitals are called **sp^3d** hybrid orbitals.
- These five hybridised orbitals in **sp^3d** hybridisation are not equivalent.
- They are divided into two sets of equivalent hybridised orbitals.
- One set of **three** and other set of **two** sp^3d hybrid orbitals

- First set consists of three **sp^3d** hybrid orbitals which are directed towards the corner of an equilateral triangle making an angle of **120^o** with each other.

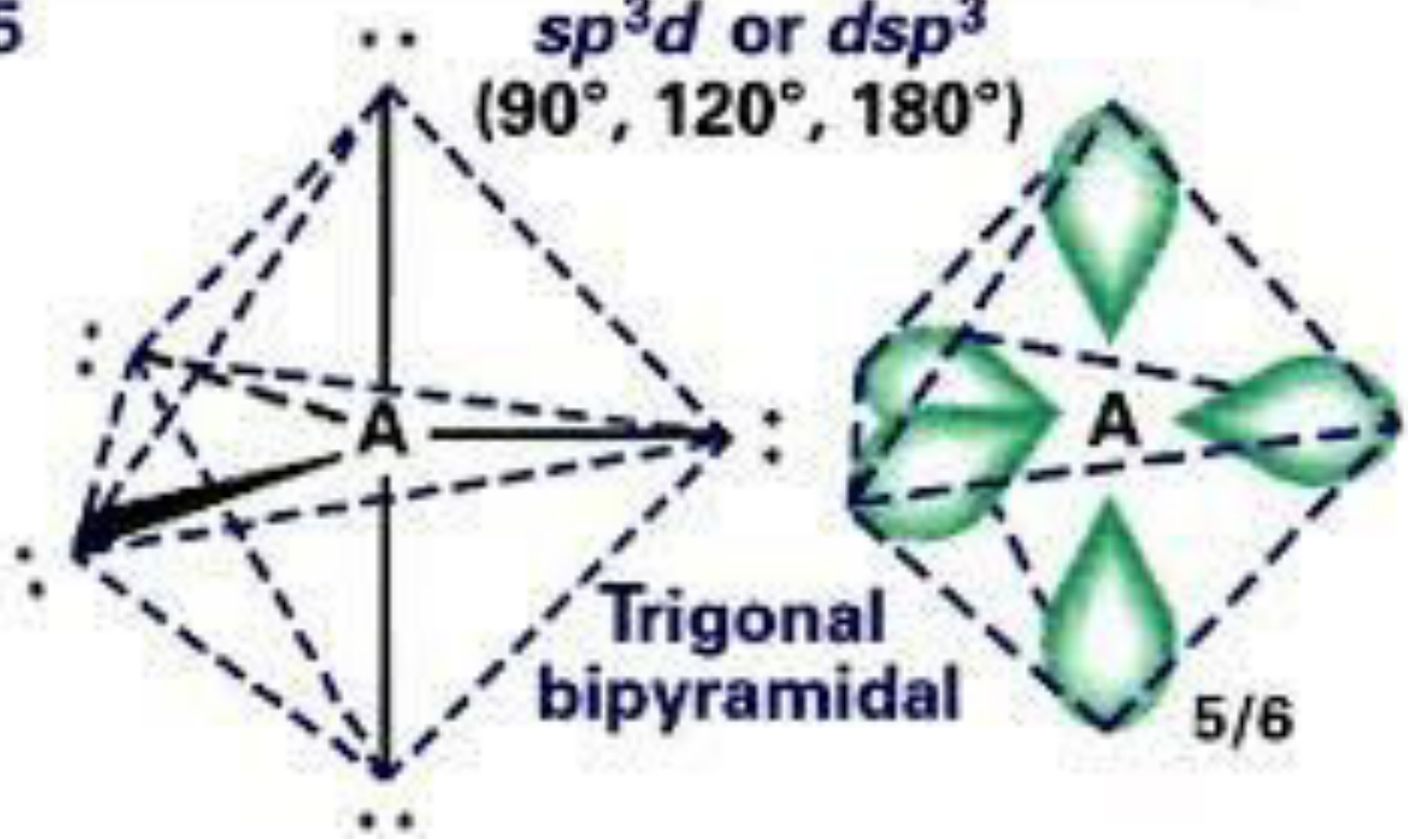
- The bonds formed by the overlap of these orbitals are called **equitorial bonds** .They are denoted by **'e'**.

- The second set consists of two **sp^3d** hybrid orbitals. They are at **right angles** to the plane of first set of hybridised orbitals i.e. above and below the plane of the equilateral triangle making a angle of **90^o** with the first set of orbitals.

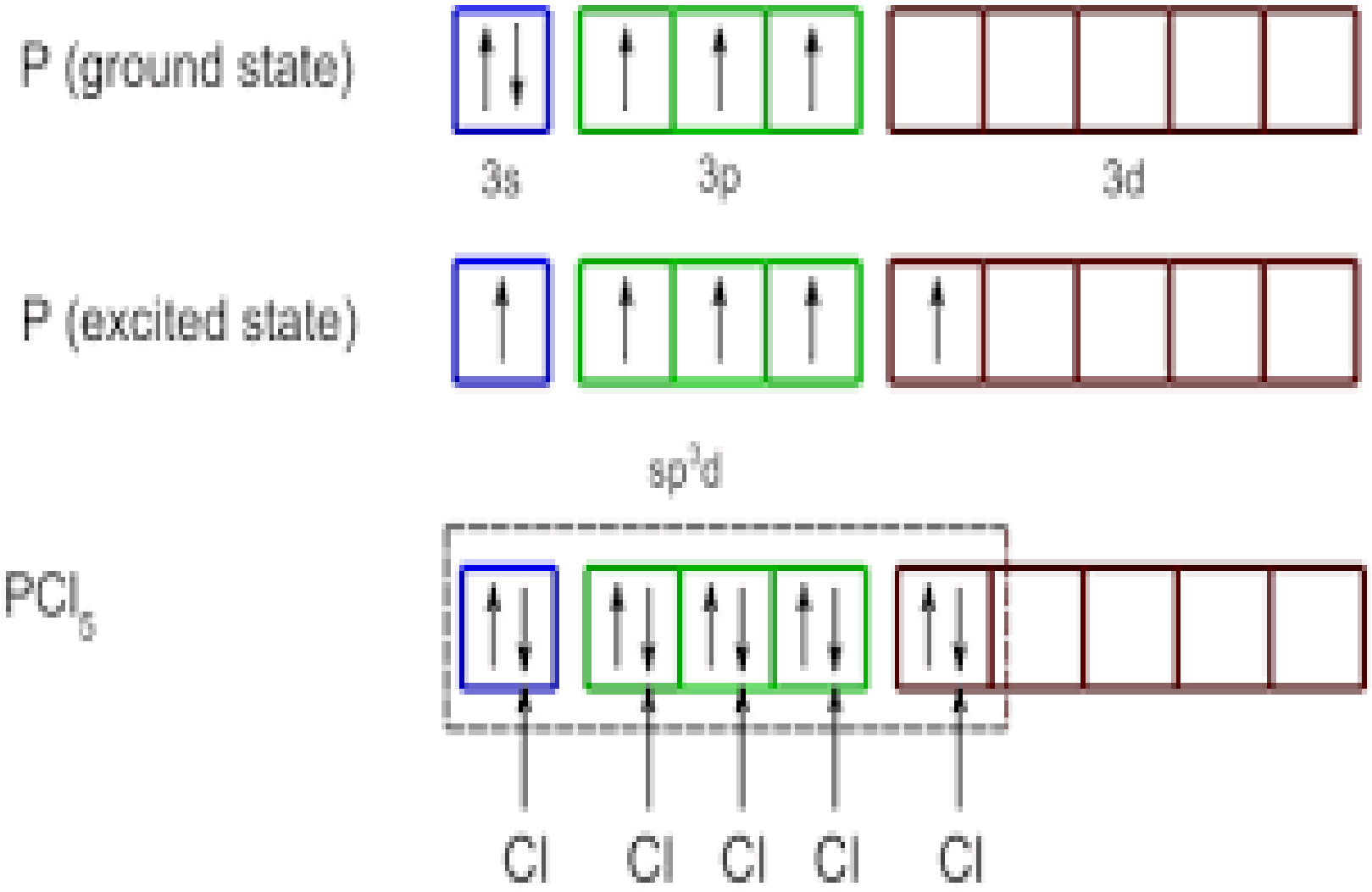
- The bonds formed by the overlap of these orbitals are called **axial bonds** .They are denoted by **'a'**.


3S
3P$_x$
x
3P$_y$
z
z
3P$_z$
z
y
x
3d^2_z
sp^{3}d hybrid orbitals
having trigonal
bipyramidal geometry

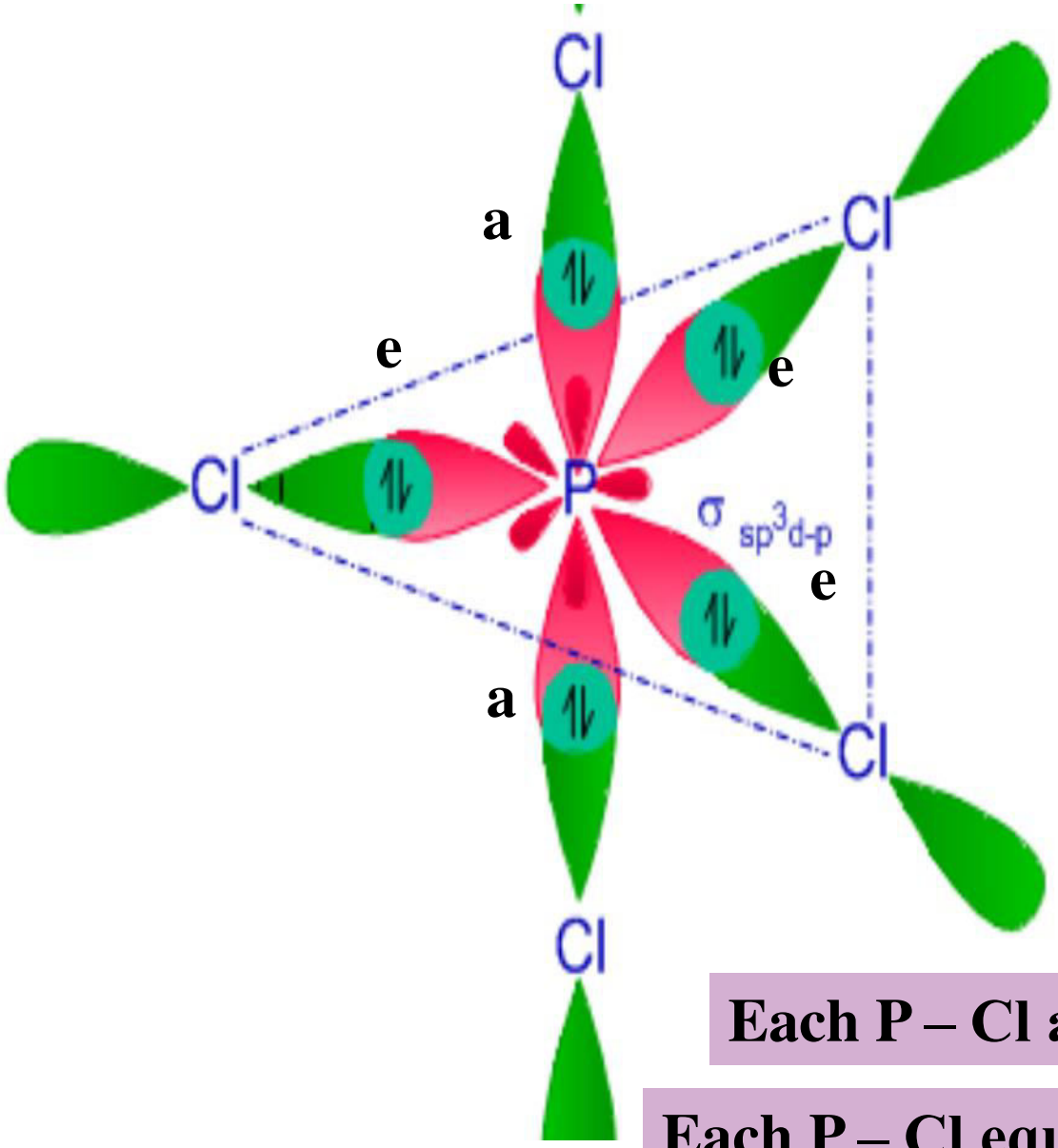
Regions of high electron density	Electronic geometry	Hybridization at central atom (angle)	Hybridized orbital orientation
5	Trigonal bipyramidal	sp^3d or dsp^3 (90°, 120°, 180°)	

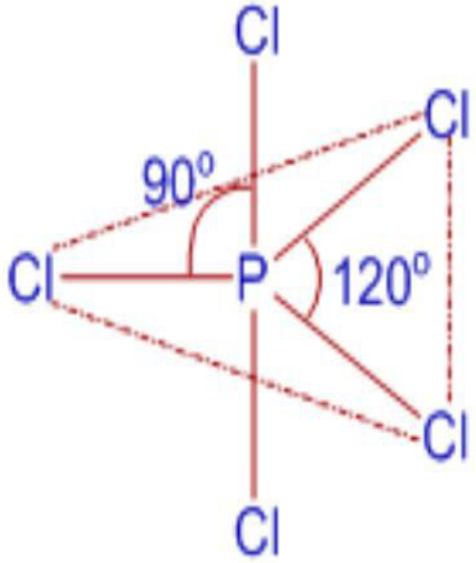


Phosphorus pentachloride molecule (PCl_5)



TRIGONAL BIPYRAMIDAL GEOMETRY



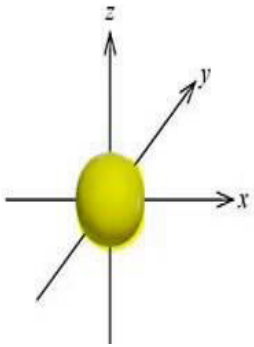


Each P – Cl axial bond = 2.19 Å

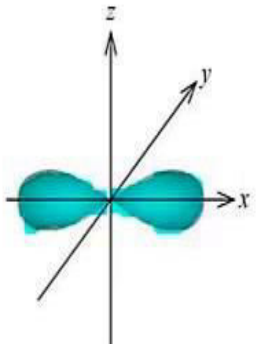
Each P – Cl equatorial bond = 2.04 Å

sp^3d^2 - hybridisation

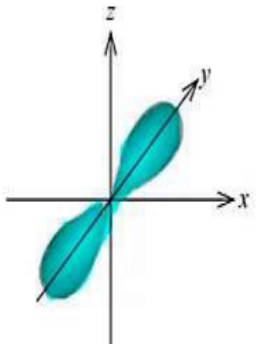
- **sp^3d^2** – hybridisation involves the inter – mixing of one s, three p and two d orbitals to give rise to **six** equivalent hybrid orbitals of same energy.
- These six hybrid orbitals are called **sp^3d^2** hybrid orbitals.
- These six hybridised orbitals in **sp^3d^2** hybridisation are equivalent.
- These six hybridised orbitals are directed towards the corners of a **regular octahedron**.
- The d orbitals used in **sp^3d^2** hybridisation are **$d_{x^2 - y^2}$** and **d_{z^2}**



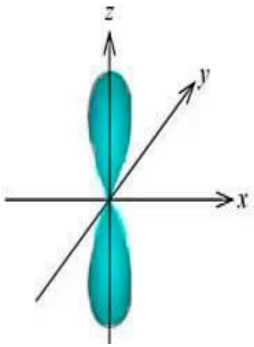
s



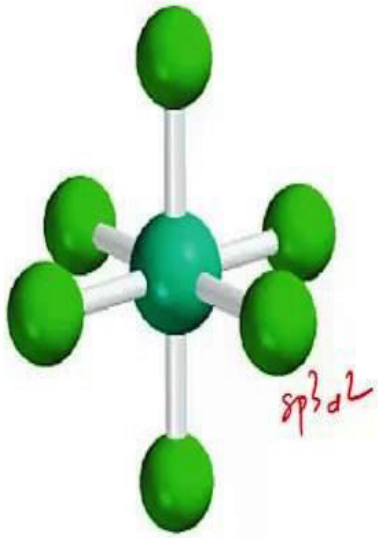
p_x

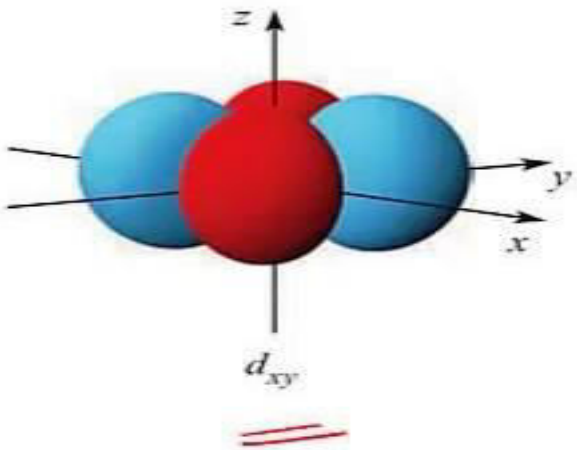


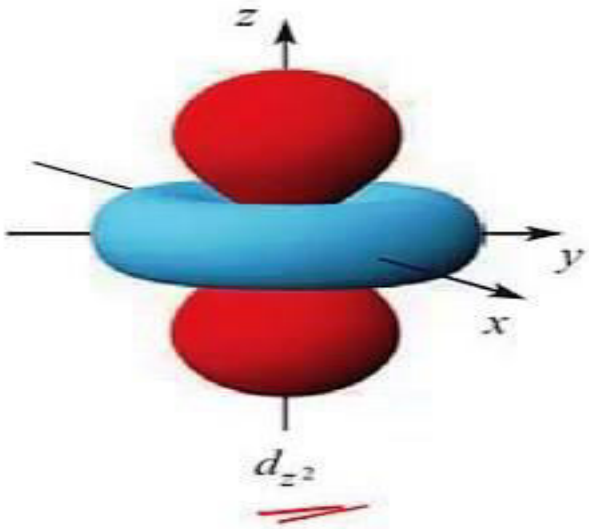
p_y

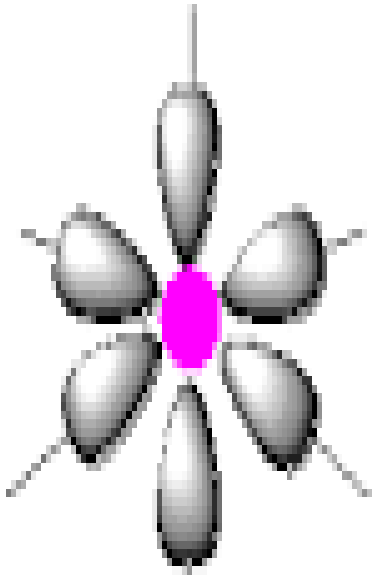


p_z

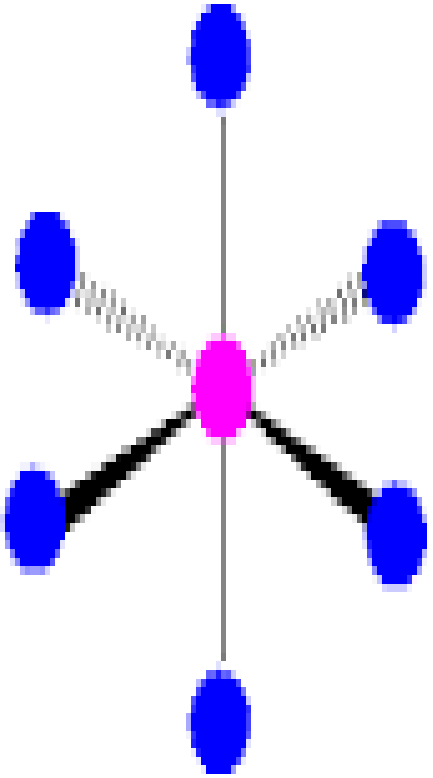




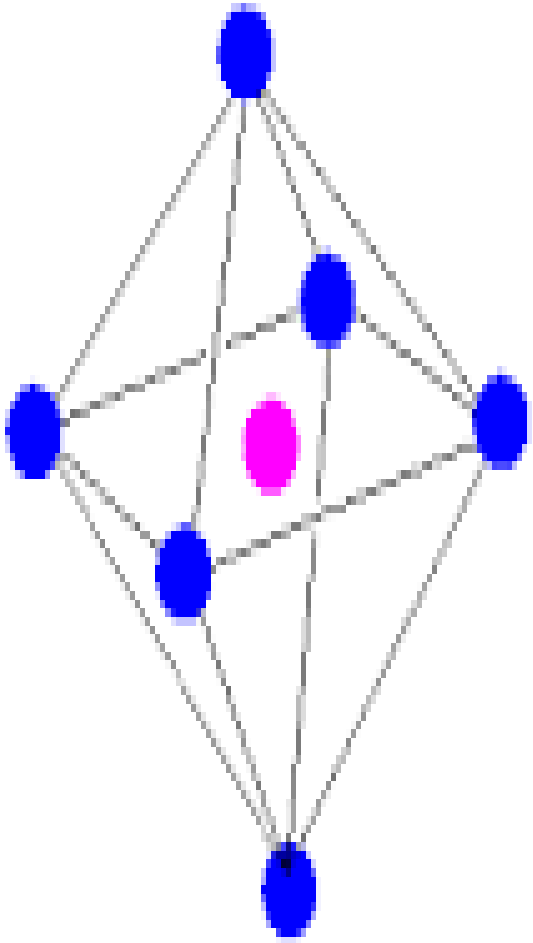




sp^3d^2 orbital picture

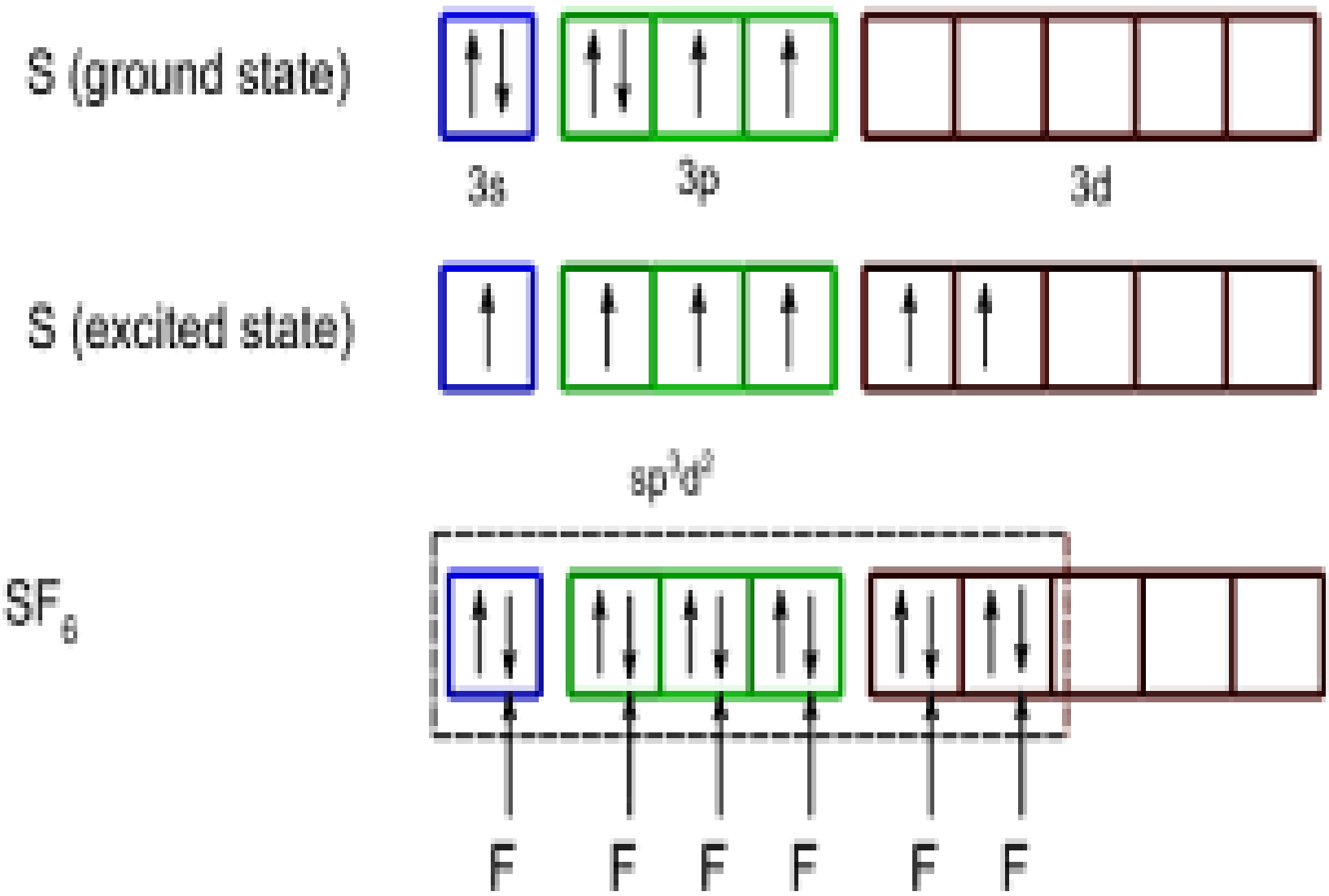


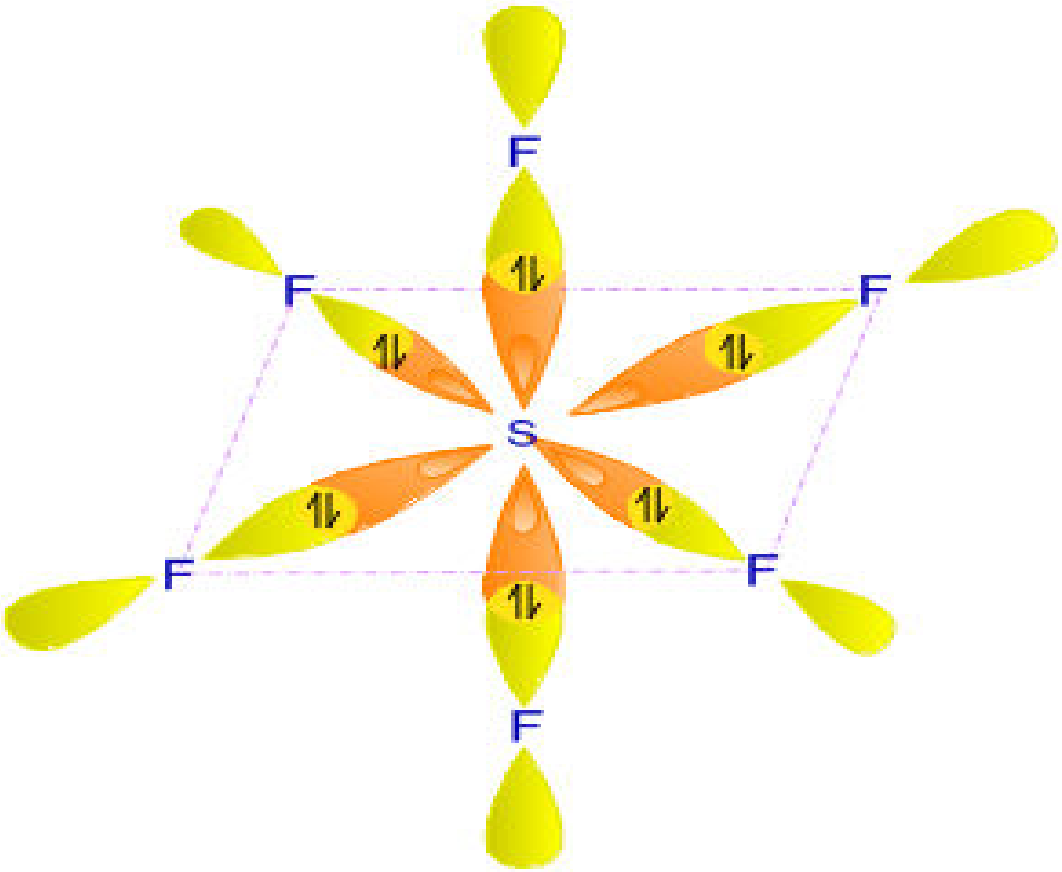
atomic arrangement of an octahedral structure

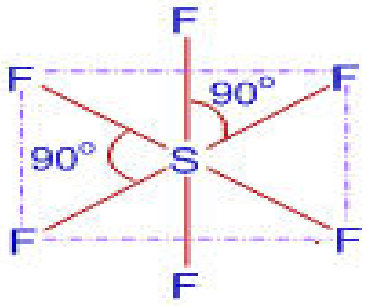


The central atom is centered within the octahedron.

Sulphur hexafluoride molecule (SF_6)







octahedral structure of sulfur hexafluoride

All the six bonds are equivalent and all the bond angles are equal to 90^{o}

sp^3d^3 - hybridisation

- **sp^3d^3** – hybridisation involves the inter – mixing of one s, three p and three d orbitals to give rise to **seven** equivalent hybrid orbitals of same energy.

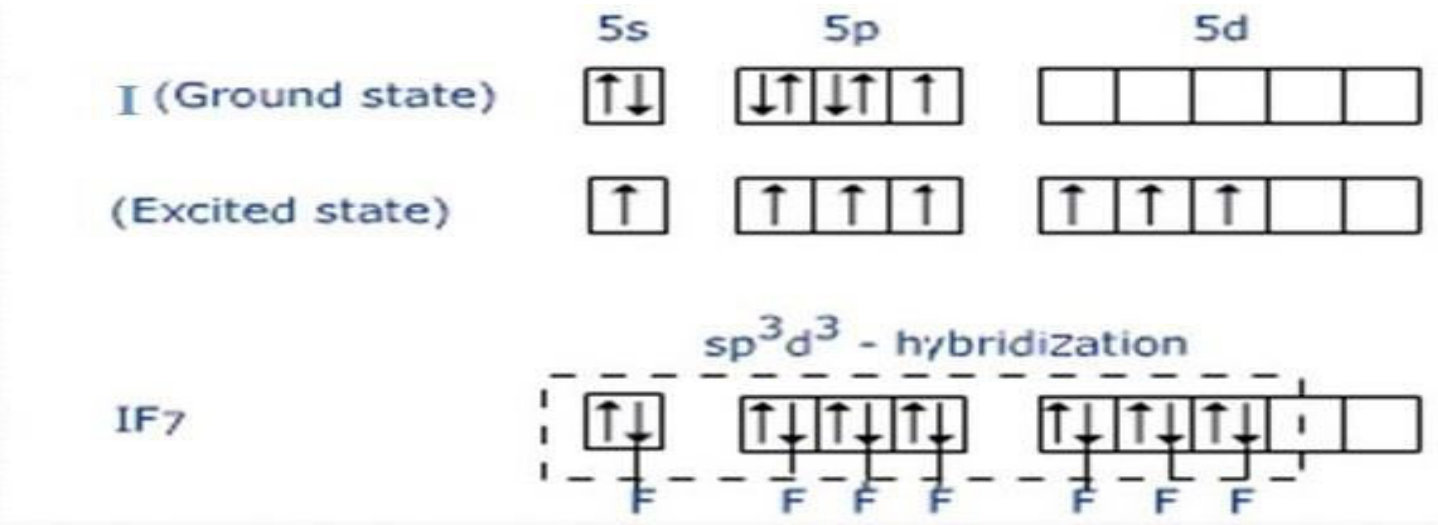
- These seven hybrid orbitals are called **sp^3d^3** hybrid orbitals.

- These seven hybridised orbitals in **sp^3d^3** hybridisation are **not equivalent**.

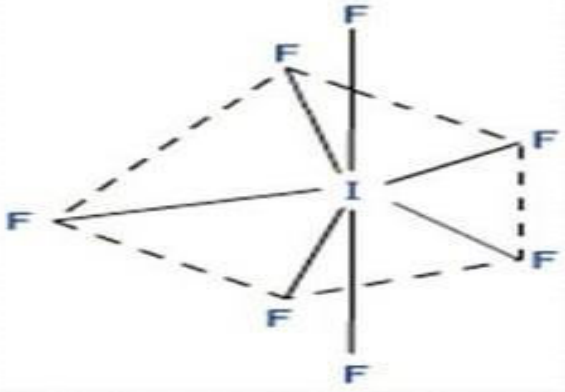
- The first set consists of five of these **sp^3d^3** hybridised orbitals which are directed towards the vertices of a regular pentagon making an angle of 72^o with one another.

- The remaining two **sp^3d^3** hybrid orbitals are at right angles to the plane of first set of five hybridised orbitals.
- The d orbitals used in **sp^3d^3** hybridisation are **d_{xy} , d_{yz}** and **d_{xz} .**
- The geometry in this case is **pentagonal bipyramidal.**
- In this geometry **all the bonds are not equivalent**.
- Due to different bond angles the axial and equitorial bonds are of **different bond lengths**.
- The axial bonds **are larger** than the equitorial bonds.

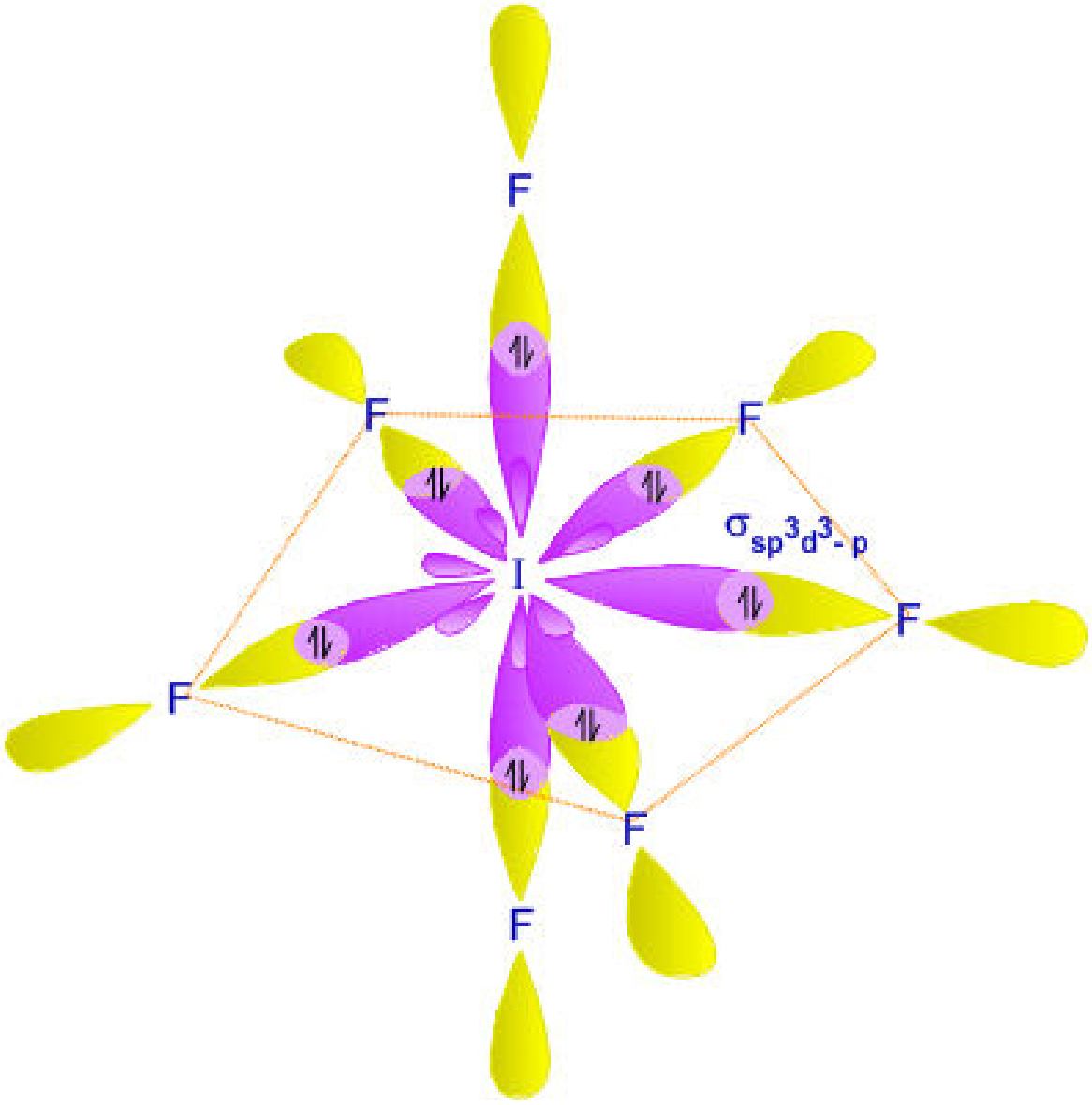
Iodine heptafluoride molecule (IF_7)

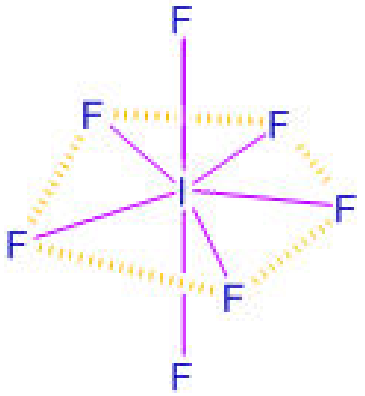


Formation of IF_7 molecule involving sp3d3 hybridization

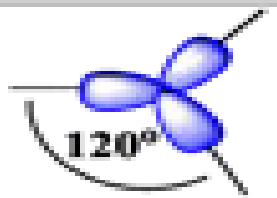
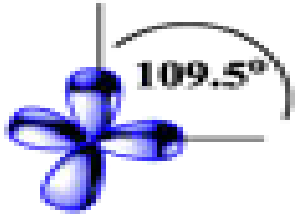
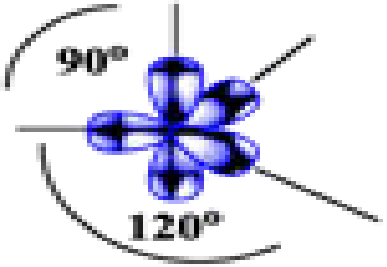
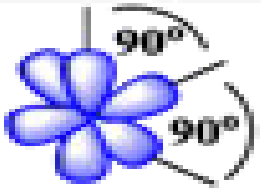


Pentagonal bipyramidal geometry of IF7 molecule





Pentagonal bipyramidal structure of IF_7

Hybrid Orbitals and Geometry			
Atomic Orbitals Used	Hybrid Orbitals Formed	Geometry	Example Compound
s,p	Two sp orbitals	Linear	CO_2
s,p,p	Three sp^2 orbitals	 Trigonal Planar	SO_3
s,p,p,p	Four sp^3 orbitals	 Tetrahedral	$GeCl_4$
s,p,p,p,d	Five dsp^3 orbitals	 Trigonal Bipyramidal	PCl_5
s,p,p,p,d,d	Six d^2sp^3 orbitals	 Octahedral	$Mo(CO)_6$

SHAPES OF MOLECULES HAVING LONE PAIRS AND BOND PAIRS

- In all the **previous discussed cases** of hybridisation, the central atom **did not have lone pair of electrons**. The geometry only depended on the bonded pair of electrons.

- In above cases, the molecules are said to have a **regular geometry.**

- The cases which **will be discussed under the above heading** involve the presence of both bonded as well as non bonded (lone pair) pair of electrons.

- Hybridisation in such cases will depend on the total electron pairs [both bonded as well as non bonded (lone pair)]in the valence shell of the central atom.

- Due to the presence of both bond pairs and lone pairs in the valence shell of the central atom, their geometry gets distorted.

- This occurs because the repulsive interactions between the bond pair and the lone pair of electrons are different.

- The bonded pair of electrons is under the influence of two nuclei and its electron cloud is oriented between the two nuclei.

- However, the lone pair of electrons is under the influence of one nucleus. Its electron cloud is more spread out.

- Due to greater spreading, it repels the electrons in the neighbouring orbitals more .

- The repulsive interactions between different pair of electrons follow the order

Lone pair – Lone pair > Lone pair – Bond pair > Bond pair – Bond pair

- Hybridisation will depend on the total number of electron pairs in the valence shell of central atom irrespective of the number of bonded and lone pairs.

- Due to involvement of lone pair of electrons in hybridisation, the bond angles change from their normal values and the regular geometry of the molecule gets distorted.

Stannous chloride molecule ($SnCl_2$)

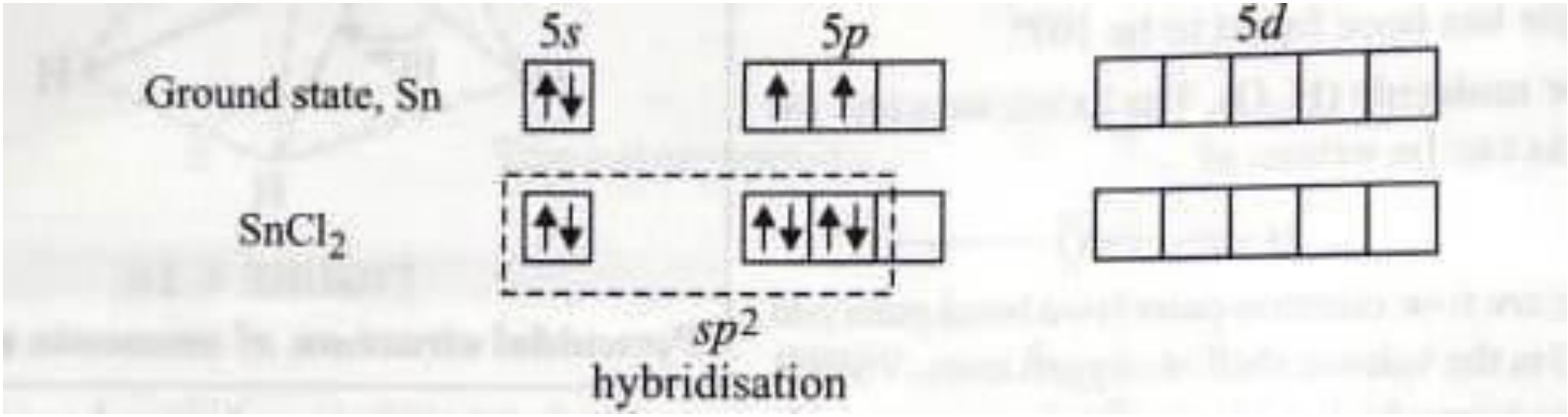
- The ground state electronic configuration of Tin (Z = 50) is $[Xe]4d^{10}\ 5s^2\ 5p_x^{\ 1}\ 5p_y^{\ 1}$.

- The electronic configuration of chlorine (Z = 17) is $[Ne]\ 3s^2\ 3p_x^{\ 2}\ 3p_y^{\ 2}\ 3p_z^{\ 1}$.

- Sn has two unpaired electrons required for forming bonds with two chlorine atoms. So, no promotion of electrons is required.

- However, all the valence electrons (lone pairs and bond pairs) will be involved in hybridisation.

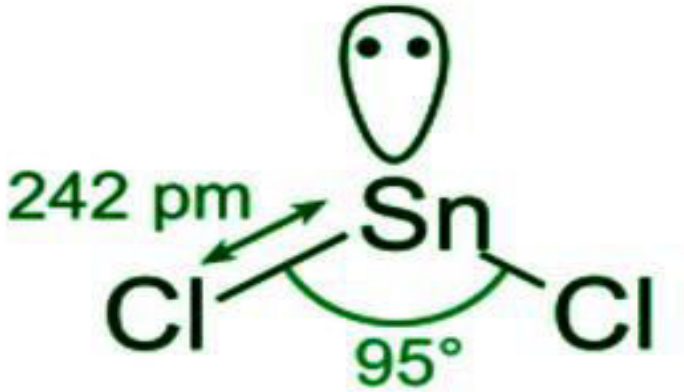
- The three orbitals (one 5s and two 5p) of tin hybridise to give rise to three sp^2 hybrid orbitals of equal energy.
- These three sp^2 hybrid orbitals adopt trigonal planar geometry.
- One sp^2 hybrid orbital has a lone pair of electrons whereas the two remaining sp^2 hybrid orbitals having unpaired electron overlap with 3p – orbital of chlorine to form two Sn – Cl bond.



- The geometry of the molecule should be trigonal planar with each bond angle equal to 120^o.

- But due to repulsive interactions between lone pair - bond pair being greater than bond pair – bond pair , distortion in the shape of molecule occurs.

- The bond angle is slightly less than 120^o and the molecule assumes **V - shaped geometry**.



Angular / V – shaped / Bent Geometry

Xenon tetrafluoride molecule (XeF_4)

- The ground state electronic configuration of Xenon (Z = 54) is [Kr] $4d^{10}\ 5s^2\ 5p_x^{\ 2}\ 5p_y^{\ 2}\ 5p_z^{\ 2}$.

- The electronic configuration of fluorine (Z = 9) is [He] $2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 2}\ 2p_z^{\ 1}$.

- Xenon has no unpaired electrons for forming bonds with the fluorine atoms in the ground state. So, promotion of electrons is required.

- Two of the 5p electrons are promoted to the 5d orbitals,

resulting in four unpaired electrons required for bond formation with four fluorine atoms.

- All the valence electrons (lone pairs and bond pairs) will be involved in hybridisation.

- The six orbitals (one 5s, three 5p and two 5d) of Xenon hybridise to give rise to **six sp^3d^2** hybrid orbitals of equal energy.

- These **six sp^3d^2** hybrid orbitals adopt **Octahedral geometry.**

- **Two sp^3d^2** hybrid orbital have a lone pair of electrons whereas the **four remaining sp^3d^2** hybrid orbitals having unpaired electron overlap with 2p – orbital of fluorine to form four Xe – F bond.

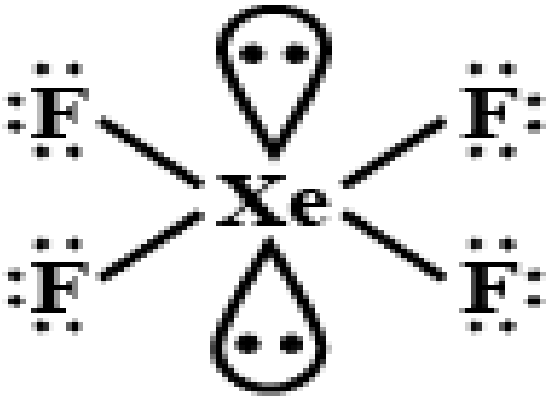
- The **six sp^3d^2 hybrid orbitals** are directed towards the corners of an octahedron.

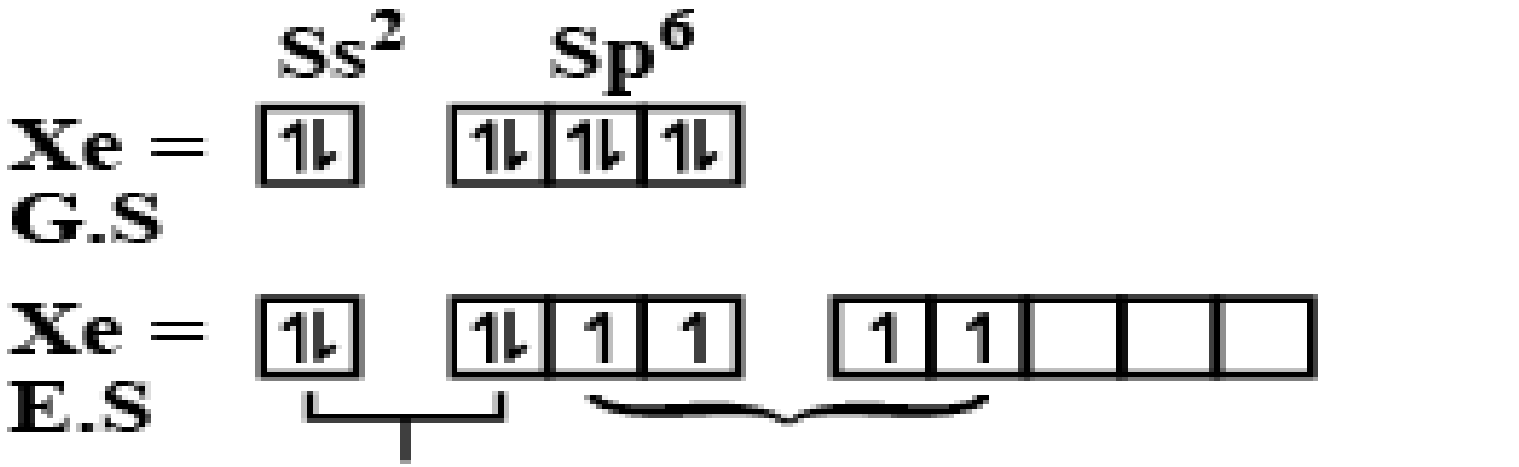
- The geometry of the molecule can be imagined as an octahedron with the two **axial** positions occupied by the lone pair of electrons.

- However the geometry of **XeF_4** can be regarded as **Square planar.**

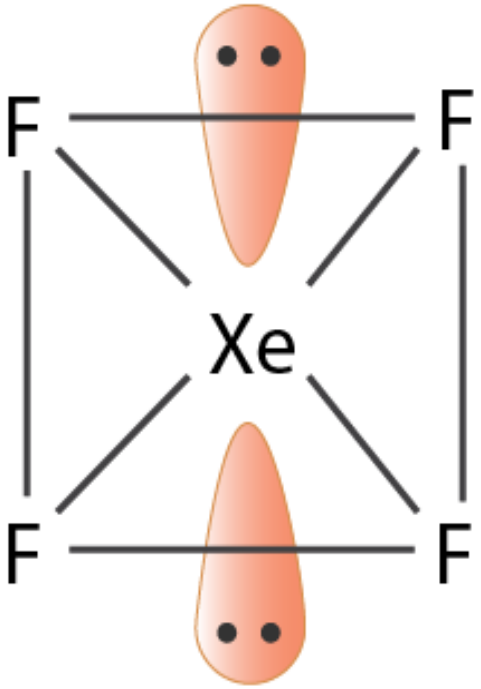
Hybrid orbitals in XeF_4 :-

$8 + 7(4) = 36$

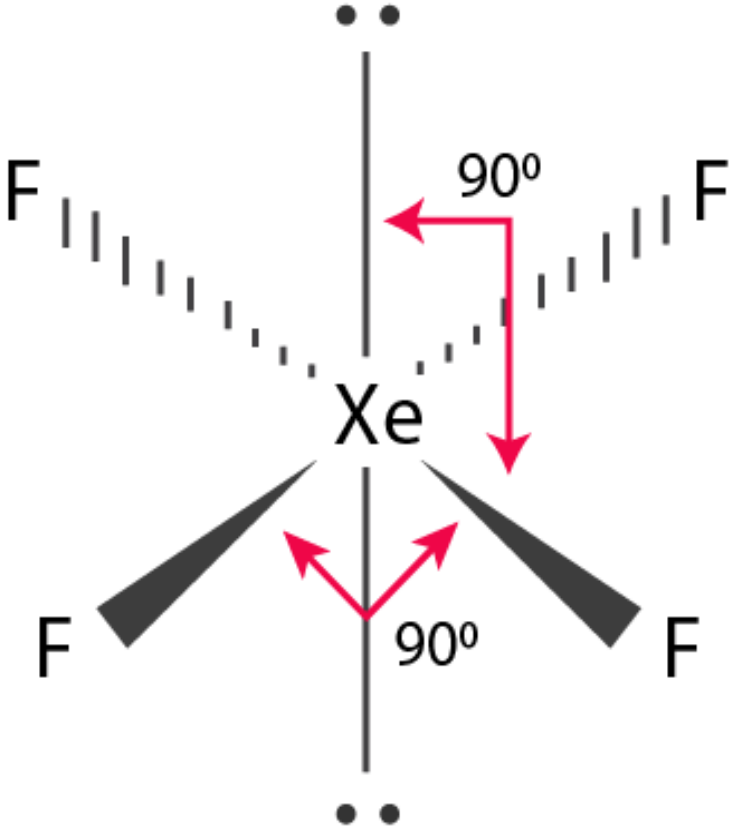




total 6 Hybrid orbitals

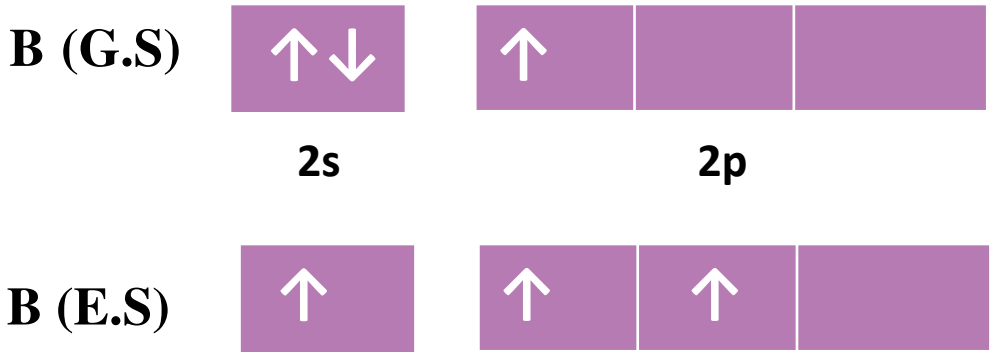


XeF_4



Boron tetrafluoride ion (BF_4^-)

- The ground state electronic configuration of Boron (Z = 5) is [He] $2s^2\ 2p_x^1\ 2p_y^0\ 2p_z^0$.



- The 2s electron is promoted to the vacant $2p_y$ orbital of the Boron atom .

- Boron forms four bonds with fluorine, so four hybrid orbitals of boron are needed.

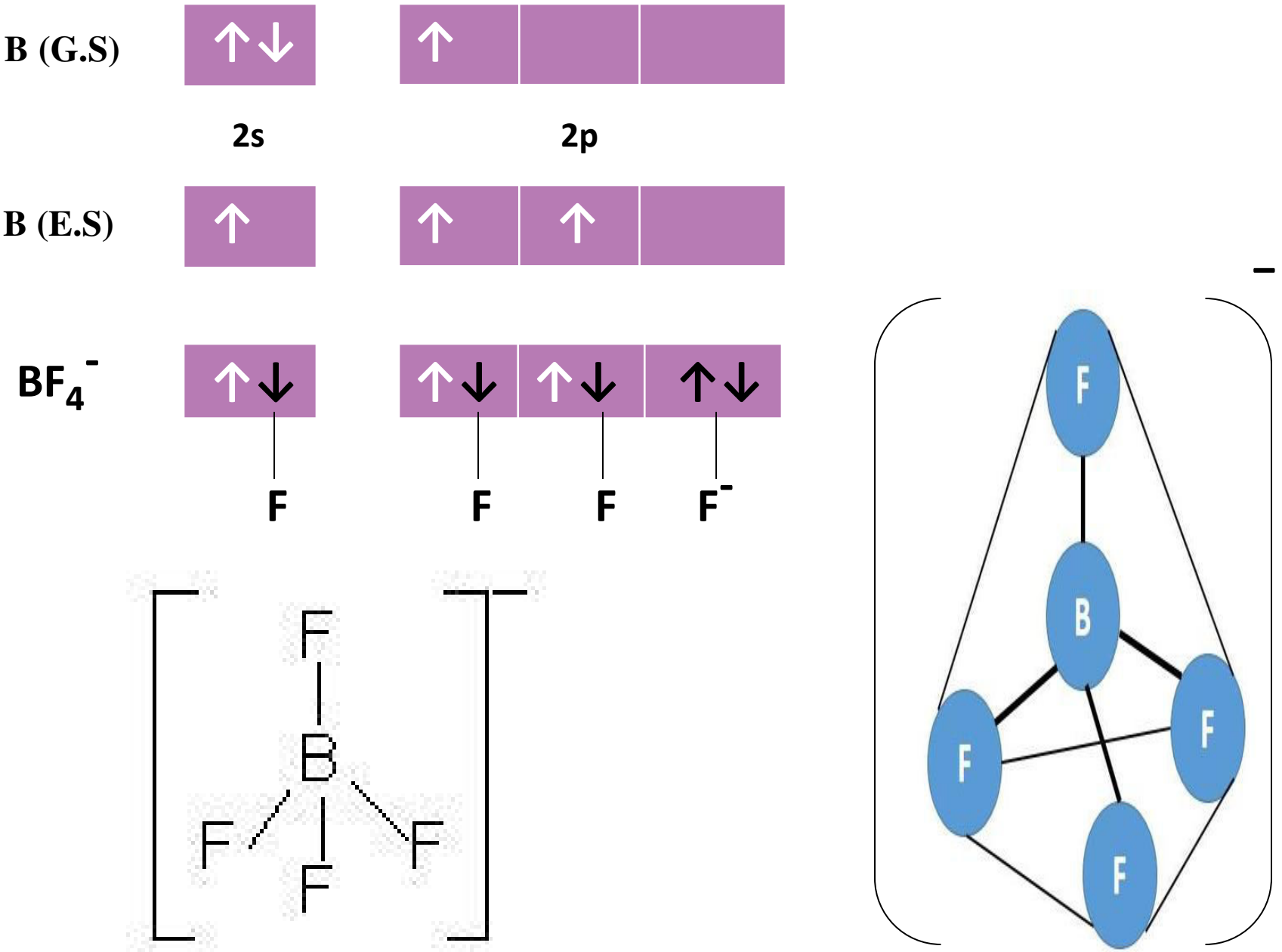
- One 2s and three 2p orbitals of Boron undergo hybridisation to give rise to four equivalent **sp^3** hybrid orbitals.
- These **four sp^3** hybrid orbitals are directed towards the corners of a tetrahedron.
- Three of these **sp^3** hybrid orbitals are half filled whereas the fourth is vacant.
- The electronic configuration of **three fluorine atoms** (Z = 9) is [He] $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$,

- whereas the **fourth fluorine exists as an anion F^-** having electronic configuration [He] $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$

- The **three half filled sp^3** hybrid orbitals of Boron overlap with the three $2p_z$ orbital of the three fluorine atom to form three B – F bonds.

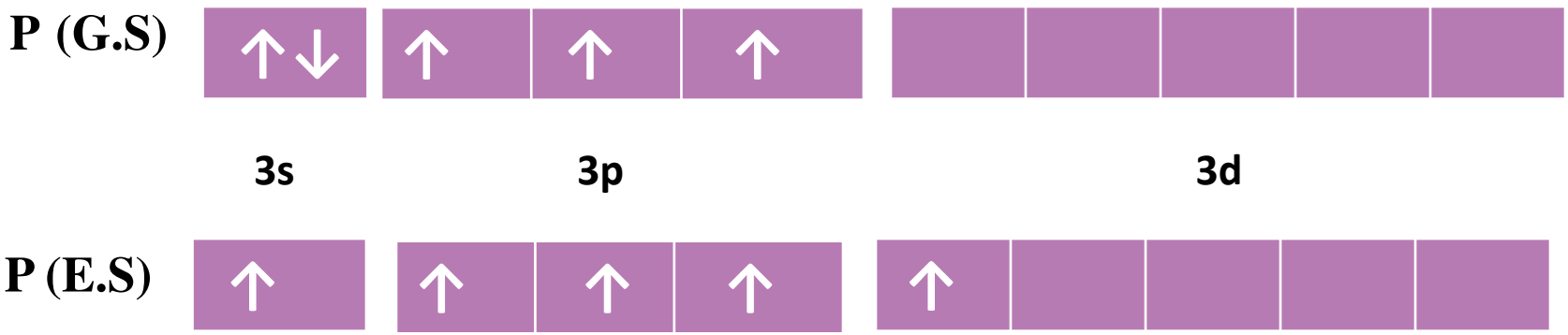
- The **vacant sp^3** hybrid orbital of Boron accepts a pair of electrons from the fluoride ion (F^-) and forms a **co-ordinate / dative bond**.

- In this way Boron atom in **BF_4^-** ion is able to complete its octet.


B (G.S)
2s
2p
B (E.S)
BF_4^-
F
F
F
F^-
F
B
F
F
F
F
F
F
−

Phosphorus hexafluoride ion (PF_6^-)

- The ground state electronic configuration of Phosphorus (Z = 15) is [Ne] $3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$.



- The 3s electron is promoted to the vacant 3d orbital of the Phosphorus atom .

- Phosphorus forms six bonds with fluorine, so six hybrid orbitals of Phosphorus are needed.

- One 3s, three 3p and two 3d orbitals of Phosphorus undergo hybridisation to give rise to six equivalent **sp^3d^2** hybrid orbitals.

- These **six sp^3d^2** hybrid orbitals are directed towards the corners of a regular octahedron.

- **Five** of these **sp^3d^2** hybrid orbitals are **half filled** whereas the **sixth is vacant**.

- The electronic configuration of **five fluorine atoms** (Z = 9) is [He] $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$,

- whereas the **sixth fluorine exists as an anion F^-** having electronic configuration [He] $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$

- The **five half filled sp^3d^2** hybrid orbitals overlap with the five $2p_z$ orbital of the five fluorine atom to form five P – F bonds.

- The **sixth vacant sp^3d^2** hybrid orbital accepts a pair of electrons from the fluoride ion (F^-) and forms a **co-ordinate / dative bond [$F^- \longrightarrow$ P]**.

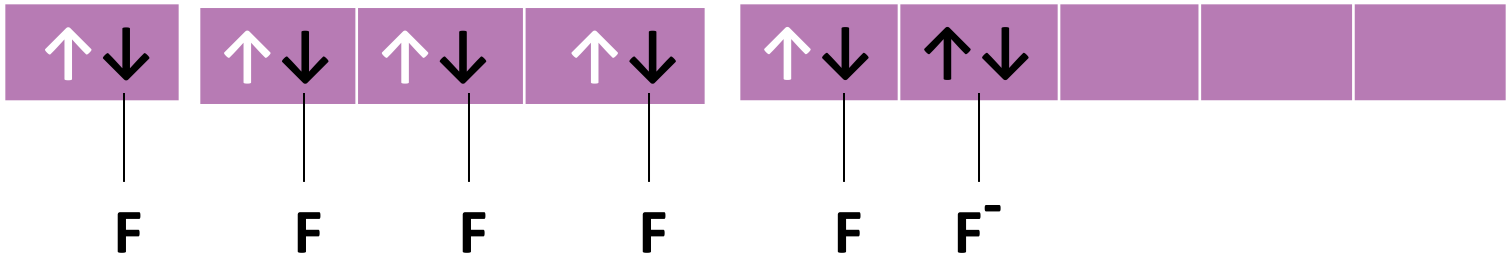
- However, the central Phosphorus atom has more than eight electrons in its valence shell and the geometry of the ion PF_6^- is octahedral.

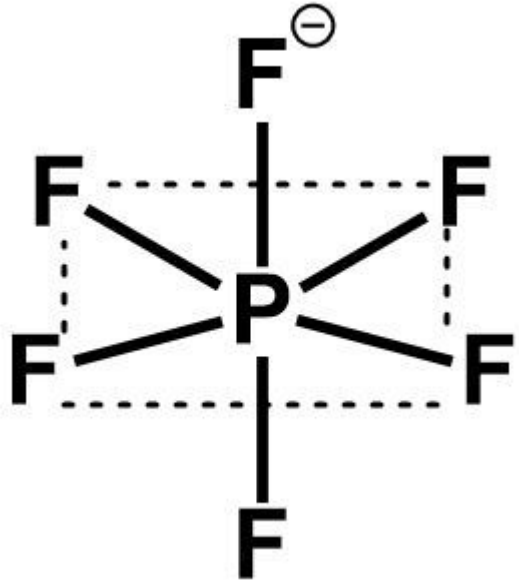
P (G.S)

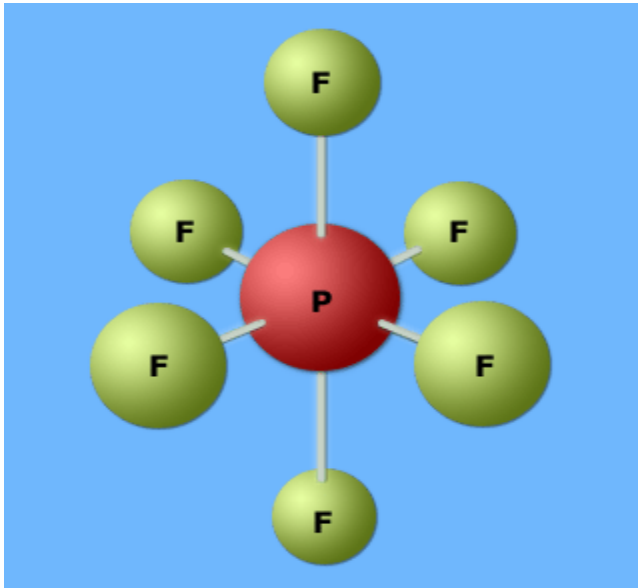
3s 3p 3d

P (E.S)

PF_6^-

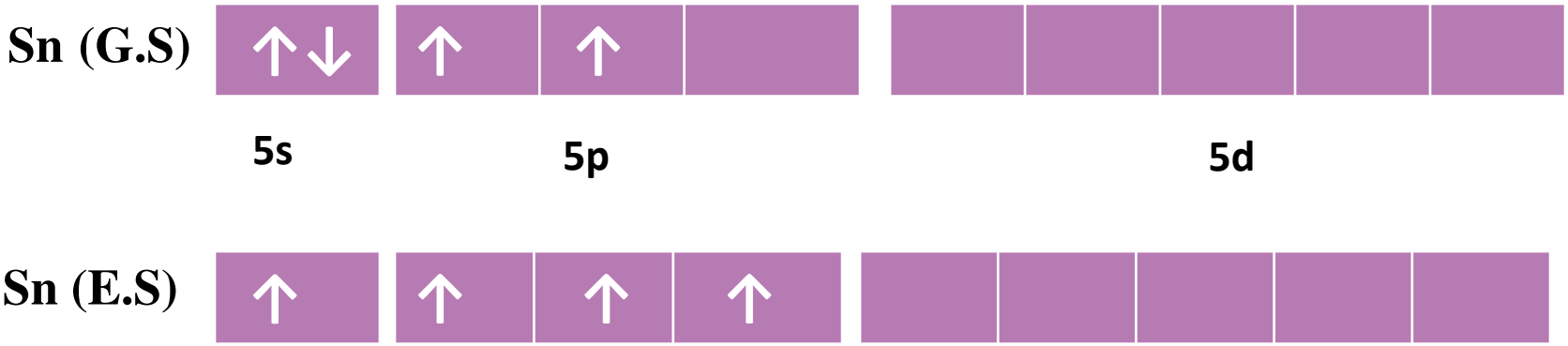






Tin hexachloride ion ($SnCl_6^{2-}$)

- The ground state electronic configuration of Tin (Z = 50) is [Kr] $5s^2\ 5p_x^1\ 5p_y^1\ 5p_z^0$.



- The 5s electron is promoted to the vacant 5p orbital of Tin atom .
- Tin forms six bonds with chlorine atoms, so six hybrid orbitals of Tin are needed.

- One 5s, three 5p and two 5d orbitals of Tin undergo hybridisation to give rise to six equivalent **sp^3d^2** hybrid orbitals.

- These **six sp^3d^2** hybrid orbitals are directed towards the corners of a regular octahedron.

- **Four** of these **sp^3d^2** hybrid orbitals are **half filled** whereas the fifth and the **sixth sp^3d^2** hybrid orbitals **are vacant**.

- The electronic configuration of **four chlorine atoms** (Z = 9) is [He] $3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$,

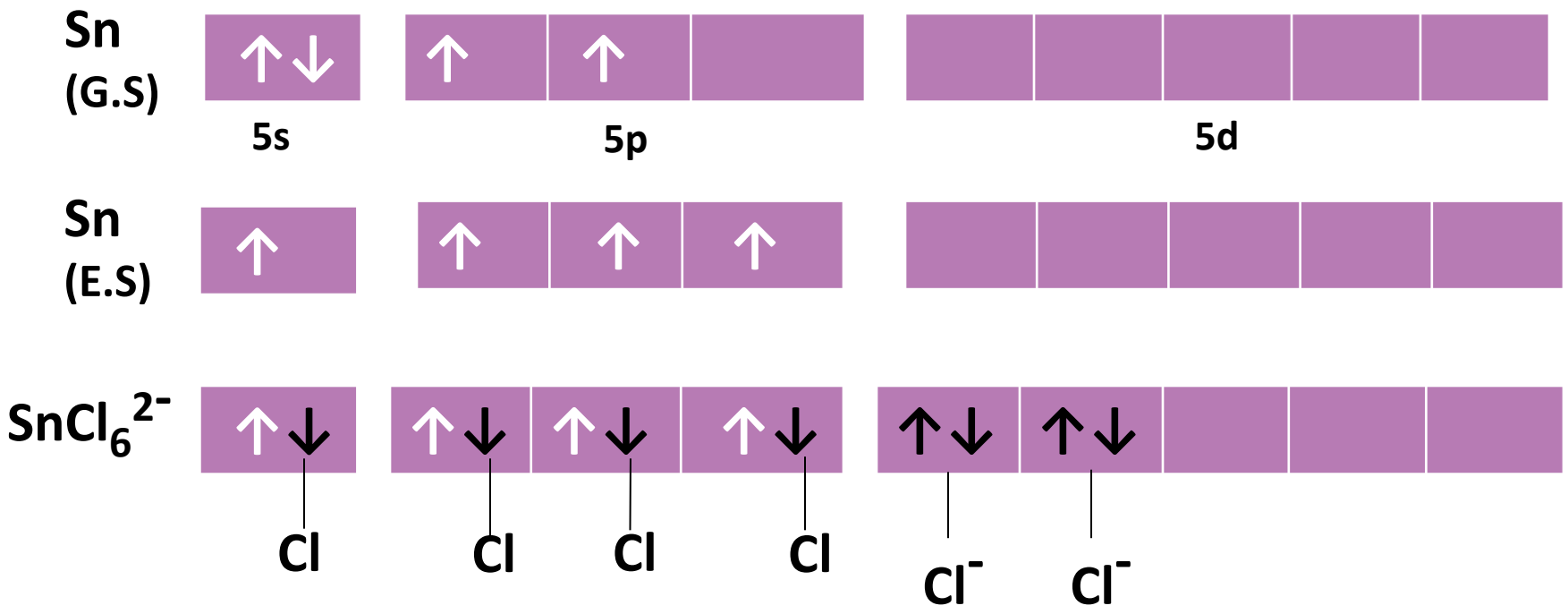
Cl

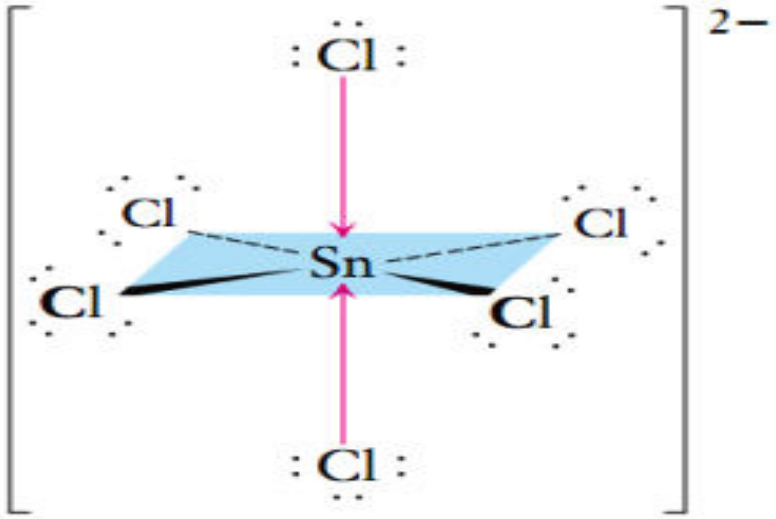
- whereas **the fifth and the sixth fluorine exists as chloride anions Cl^-** having electronic configuration $[He]3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$

- The **four half filled sp^3d^2** hybrid orbitals overlap with the four $2p_z$ orbital of the four chlorine atom to form four Sn – Cl bonds.

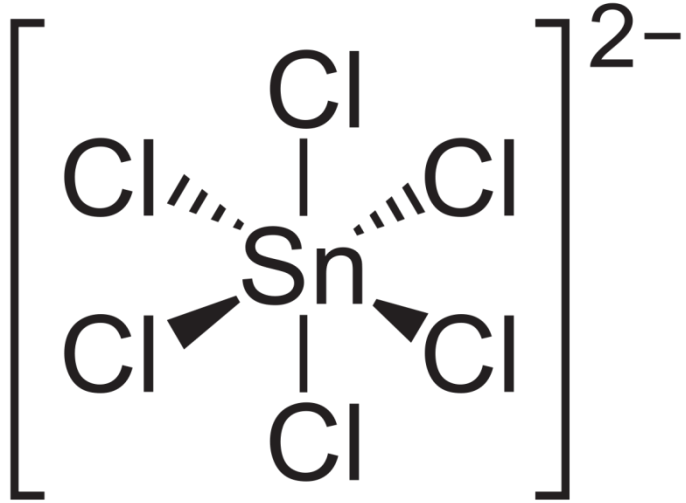
- The **two vacant sp^3d^2** hybrid orbital accept a pair of electrons each from the two chloride ion (**Cl^-**) and form **two co-ordinate / dative bond [$Cl^- \longrightarrow$ Sn]**.

- The ion **$SnCl_6^{2-}$** has a regular octahedral geometry.





hexachlorostannate(IV) ion



THANK

YOU