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MODULE ONE (A)

BOND THEORY

VSEPR THEORY

UNIT

ONE

What is a chemical bond?

A chemical bond is the force to attraction between atoms, ions or molecules that keeps them together to form molecules, crystals, solid or liquid states. Chemical bonds are formed by the transfer or sharing of electrons or being surrounded by an electron cloud.

- Molecules = formed from covalent bond between atoms.
- Crystal = formed from ionic bond between ions.
- Solid or liquid states = between atoms, or molecules.

TYPES OF BONDS

PRIMARY BONDS

- Ionic
- Covalent
- Coordinate covalent bond (dative bond)
- Metallic bond

SECONDARY BONDS

- Hydrogen bonding
- Dipole – dipole interactions
- Van der Waals forces

THE 3 THEORIES ON BONDING!

- Valence Shell Electron Pair Repulsion (VSEPR) Theory
- Valence Bond Theory (VBT)
- Molecular Orbital Theory (MOT)

UNIT TWO VSEPR THEORY

- In this theory the only the valence electrons i.e. the electrons in the outermost shell are involved in bonding.
- A stable compound is formed when the valence shell of the atoms involved in bonding have 8 electrons each. It is said to have a complete octet. This excludes H and He, these would only require 2 electrons in their valence shell to attain stability.
- The electrons in a bond as a unit (bond pair [bp]) would experience force of repulsion from any other bond pair or any electrons in the valence that is not involved in bonding (lone pair [lp]).
- Therefore they would arrangement themselves as far from each other as possible.
- The geometrical arrangement of these electrons around the central atom affect the shape of the molecule.
- In the order of increasing strength of repulsion $bp-bp < lp-bp < lp-lp$. This means that $lp-lp$ is the strongest and $bp-bp$ is the weakest.
- This in turns means that the bond angles caused by lone pairs would be greater and the bond angles by bond pairs would be least.

The valence shell electrons are the electrons in the outermost shell.

$C = 1s^2, 2s^2, 2p^2$ no of valence electrons – 4

$S = 1s^2, 2s^2, 2p^6, 3s^2, 3p^4$ no of valence electrons – 6

$K = 1s^2, 2s^2, 2p^4, 3s^2, 3p^4, 4s^1$ no of valence electrons – 1

$Ga = 1s^2, 2s^2, 2p^4, 3s^2, 3p^4, 3d^{10}, 4s^2, 4p^1$ no of valence electrons – 3

$Co = 1s^2, 2s^2, 2p^4, 3s^2, 3p^4, 3d^7, 4s^2$ no of valence electrons – 2

LEWIS STRUCTURE

This is a diagram that shows the bonding between atoms of a molecule as well as any lone pairs of electrons that may exist in the molecule.

By drawing Lewis structure you can predict the number of bond pairs and lone pairs present in a molecule.

(PS: O level Chemistry)

Ionic bond = complete transfer of electrons.

Covalent bond = sharing of electrons that each atoms brings.

Dative bond = one atom brings the electrons that both atoms would share.

Step 1: Determining the number of bond pair and lone pair from the Lewis structure.

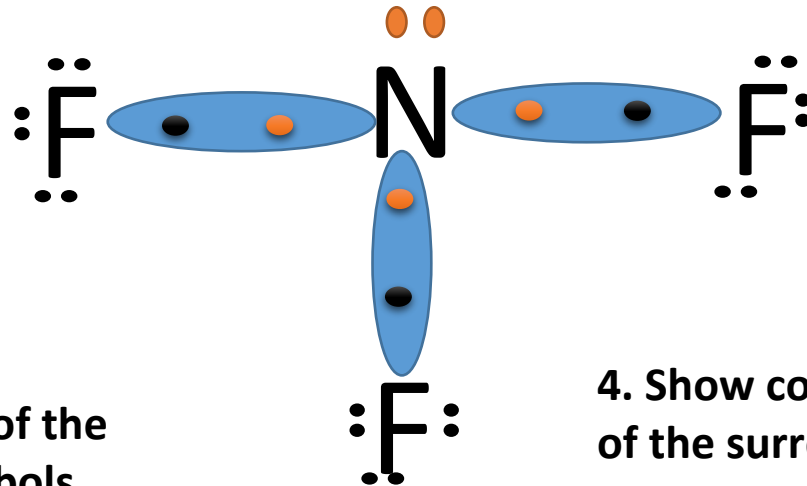


$$\text{N} = 5e$$

$$3\text{F} = 7e \times 3 = 21e$$

$$\text{Total} = 26e$$

2. Count the total number of valence electrons present.



1. Write the skeletal structure of the compound, using chemical symbols and placing bonding atoms next to one another.

4. Show complete octet of the surrounding atoms.

5. Add extra electrons to central atom as lone pair.

NF_3 has 3 bp and 1 lp

- Remember that these are covalent bonds – each atom donates an electron and they share, forming the bond
- N is contributing 5e but to complete its octet it is using 3e, one from each F atom.
- Similarly, each F atom has 7e and is using one electron from N to complete its octet.

3. Draw a single covalent bond between the central atom and each of the surrounding atoms.

Formal Charge

This is the charge assigned to an atom in a molecule, **assuming** that electrons in the bond are shared equally irrespective of the relative electronegativity differences or type of bonding.

To determine *FC*:

1. draw the Lewis structure
2. assign all nonbonding electrons of an atom to that atom
3. bonding electrons should be shared equally between sharing atoms.
4. For electrically neutral molecules has total formal charge of zero 0. For cations the sum of the formal charge must be equal to the positive charge and for anions it must be equal to the negative charge.

FC of a given atom is expressed as

$$FC = V - N - \frac{B}{2}$$

V = is the number of valence electrons of the particular isolated atom.

N = is the number of nonbonding electrons of that same atom when in a molecule.

B = is the number of bonding electrons of the same atom when in a molecule.



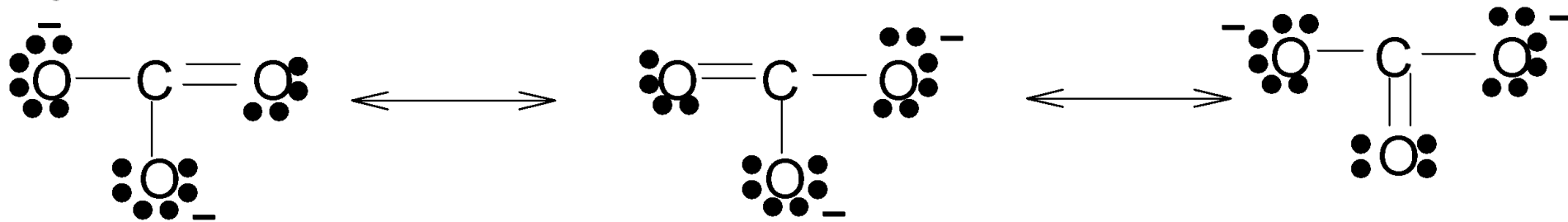
	C	O _a	O _b	O _c
V	4	6	6	6
N	0	4	6	6
B				
	0	0	-1	-1

Exception to Octet Rule

- Incomplete octet e.g. BeH_2 , BF_3
- Odd electron molecules e.g. NO and NO_2
- Expanded octet SF_6 , PCl_5

Resonance Structures

- Resonance structures are two or more Lewis structures for a single molecule that cannot be represented accurately by only one single Lewis structure. Similarly CO_3^{2-} has 3 resonance structures



In selecting the most preferred Lewis structure, the follow serve as guide lines

- A Lewis structure where there is no formal charge on each atom is the preferred.
- Lewis structures with smaller formal charges are more preferable (+1, -1, 0)
- For Lewis structures that have the same total formal charge, the more preferable one is the one which the -ve formal charge is place on the more electronegative atoms.
- For central elements that can expand their octet, the resonance structure where it obeys the octet rule is preferred even if the expanded octet has fewer formal charges.

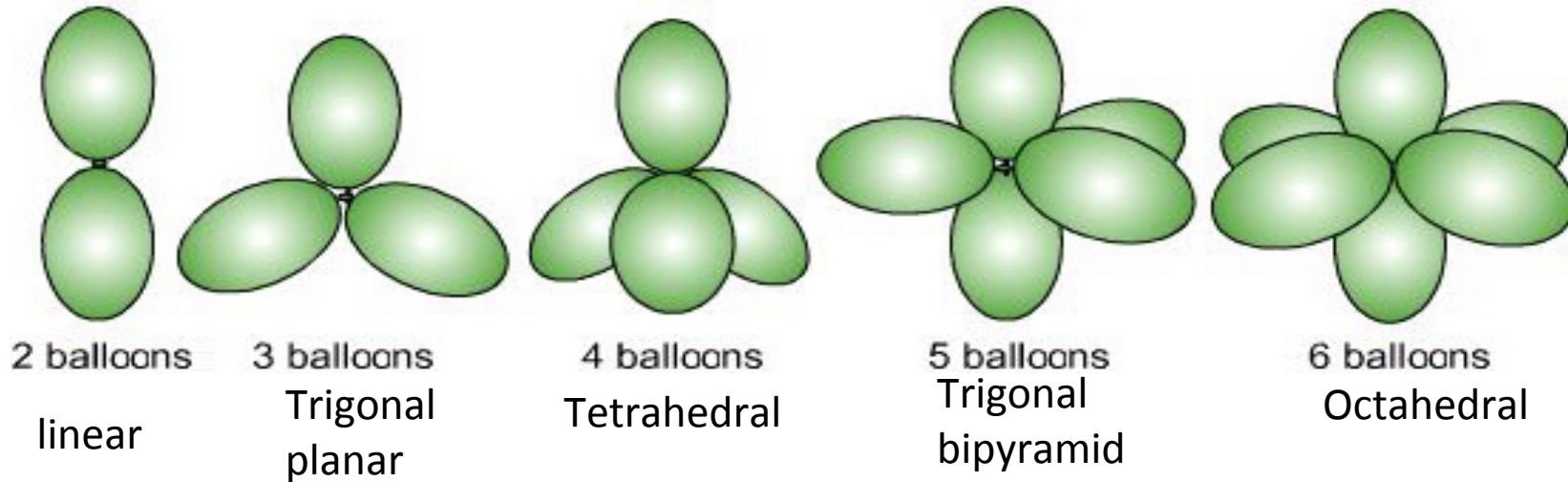
UNIT THREE

MOLECULAR GEOMETRY BASED ON VSEPR THEORY

- The molecular geometry of a molecule has an important influence on its physical and chemical properties such as melting point, boiling point as well as its reactivity.
- Molecular geometry is a 3-d arrangement of atoms in a molecule.
- In this theory we have 2 cases to consider:
 - ☐ **Case I:** Molecules in which the central atom has no lone pair.
 - ☐ **Case II:** In this case these molecules are those in which the central atoms have one or more lone pairs.

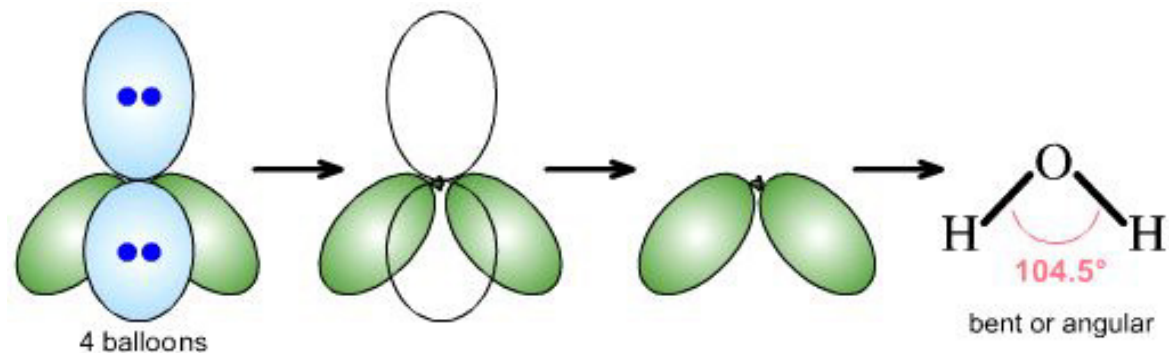
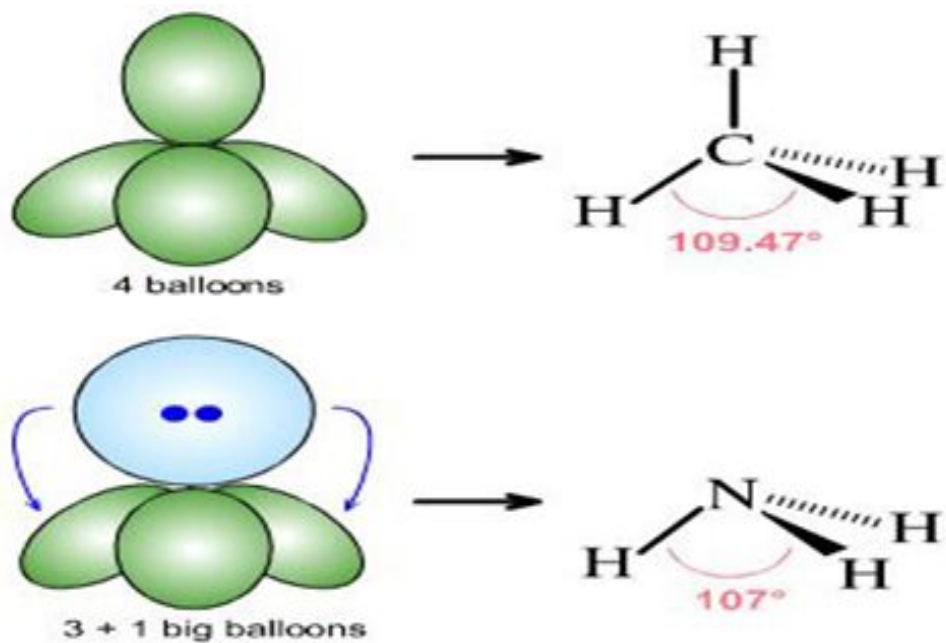
CASE I IN VSEPR THEORY

Taking into consideration a molecule made up of 2 types of atoms A and B, where A is the central atoms and B is the surrounding atoms so that the formula would be AB_x ($x = 1, 2, 3, \dots, 6$). The electrons only experience bond pair-bond pair repulsion.



CASE II

- The valence electrons in this molecule would experience 3 types of repulsion: - lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion. The formula in this case is AX_pE_q , where A = central atom, X = surrounding atoms and E = lone pair. p = no of bond pair, q = no of lone pair.



Step 2: Using the info from the Lewis structure and apply VSEPR theory

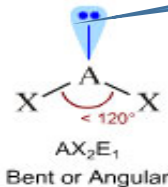
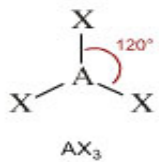
- Write the Lewis structure of the molecules considering the electron pair around the central atom of the molecule.
- Count the number of electron pairs around the central atom (bonding pairs and lone pairs). Treat double bonds and triple bonds as though they are single bonds.
- Study and apply the table below.

2 e
pairs



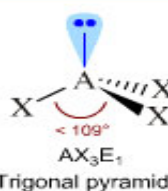
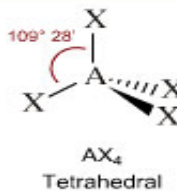
1lp, 2bp
Bent shape

3 e
pairs

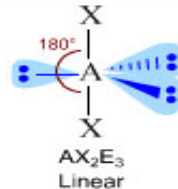
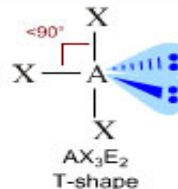
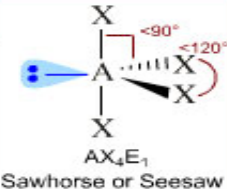
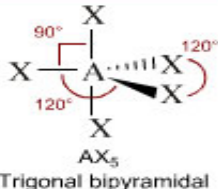


For example, after drawing the Lewis structure of a molecule that has 6 e pairs – **5 bp and 1 lp**, from the table below its shape will be square pyramidal.

4 e
pairs

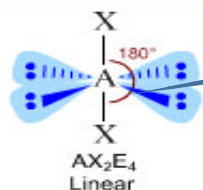
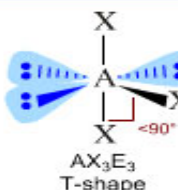
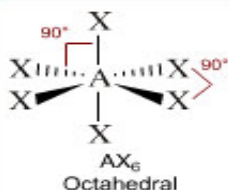


5 e
pairs

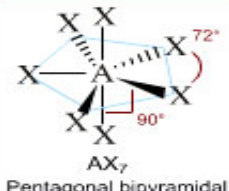


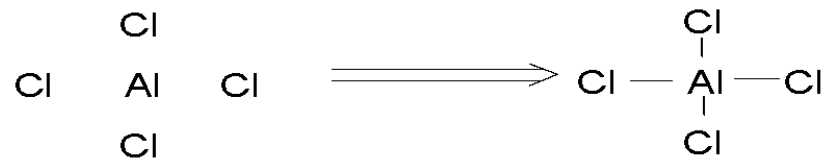
4lp, 2bp
Linear shape

6 e
pairs

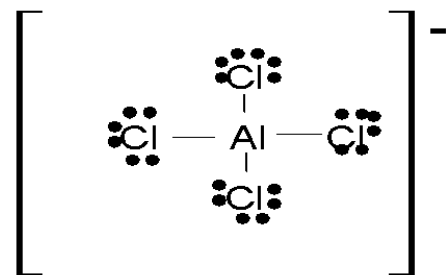


7 e
pairs



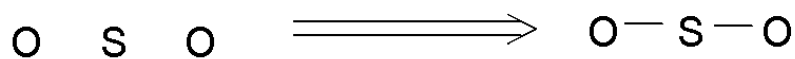
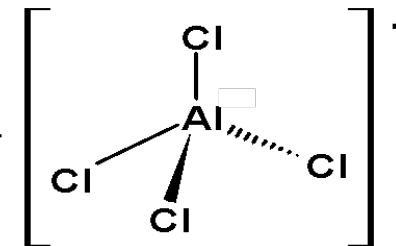


$$\begin{aligned} \text{Al} &= 3e \\ 4\text{Cl} &= 4 \times 7 = 28e \\ \text{charge} &= 1e \\ \text{Total} &= 32e \end{aligned}$$

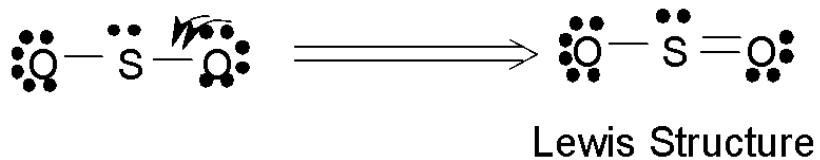


Lewis Structure

no of lone pair around Al = 0
no of bond pair around Al = 4
 $\therefore \text{AB}_4$ tetrahedral

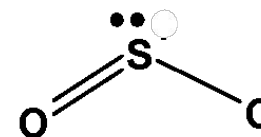


$$\begin{aligned} \text{S} &= 6e \\ 2\text{O} &= 2 \times 6 = 12e \\ \text{Total} &= 18 \end{aligned}$$



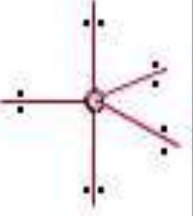
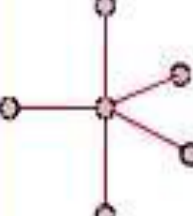
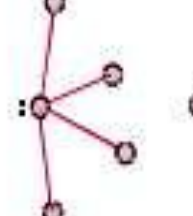
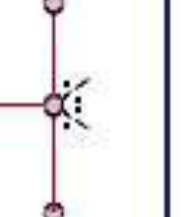
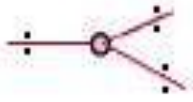
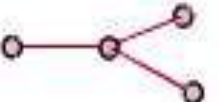

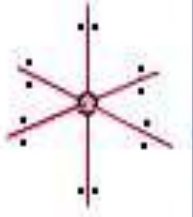
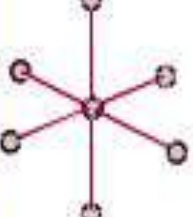
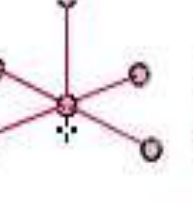
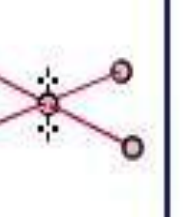


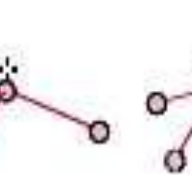
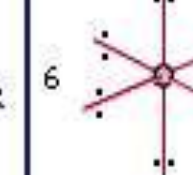
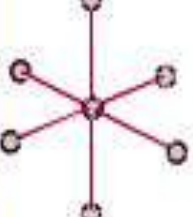
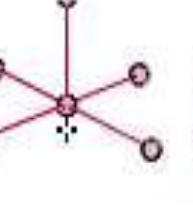
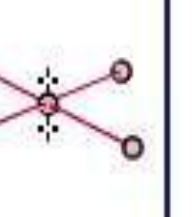


Lewis Structure

no of lone pair around S = 1
no of bond pair around S = 2
 $\therefore \text{AB}_2$ Bent



STEP 3: Draw the shape

VSEPR Electron-Pair Arrangements and Associated Molecular Shapes						
number and arrangement of electron pairs	molecular shapes	number and arrangement of electron pairs	molecular shapes			
2  linear	 linear	5  trigonal bipyramidal	 trigonal bipyramidal	 seesaw	 T-shaped	
3  trigonal planar	 trigonal planar	 angular	6  octahedral	 octahedral	 square pyramidal	 square planar
4  tetrahedral	 tetrahedral	 trigonal pyramidal	 angular	6  octahedral	 square pyramidal	 square planar

Dots are electrons (lp or bp) and circles are atoms

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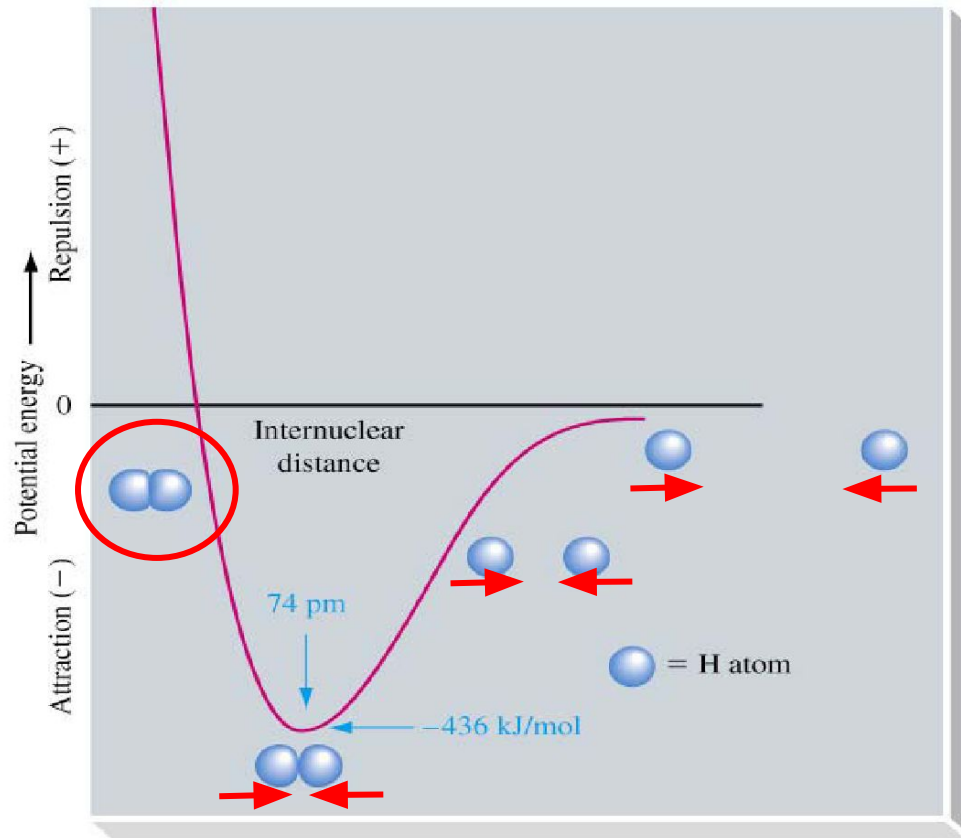
MODULE ONE (B)

BOND THEORY

VB THEORY

UNIT

FOUR Valence Bond Theory (VBT)



- The theory assumes that electrons occupy atomic orbitals of individual atoms within a molecule, and that the electrons of one atom are attracted to the nucleus of another atom.
- This attraction increases as the atoms approach one another until the atoms reach a minimum distance where the electron density begins to cause repulsion between the two atoms.
- This electron density at the minimum distance between the two atoms is where the lowest potential energy is acquired, and it can be considered to be what holds the two atoms together in a chemical bond

QUANTUM MECHANICS

- A mathematician called Schrodinger derived a wave function φ (an equation) that describes the simplest atom, the H-atom (1 electron and 1 proton) based on the dual nature of electron (particle and a wave).
- The square of this wave function gives the atomic orbital. For H-atom $\varphi_H^2 = 1s \text{ orbital}$.
- An atomic orbital is therefore a region or space where there is a probability of finding an electron.
- The solution to the Schrodinger Equation provides the wave functions for the following atomic orbitals: $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f$, etc.
- An atomic orbital is really the energy state of an electron bound to an atomic nucleus.
- This energy state changes when one atom is bonded to another atom.
- Quantum mechanical approaches by combining the wave functions to give new wave functions are called hybridization of atomic orbitals.

BONDING IN VBT

- In this theory bonds are formed as a result of hybridization of two or more atomic orbitals. Hybridization is an imaginary mixing process that converts a set of atomic orbitals to a new set of hybrid orbitals.
- The two atomic orbitals (wave functions) are in phase and so amplitude increases hence the probability of finding an electron is also increased.
- Strong bonds are as a result of greater overlapping.
- A set of overlapping orbitals can only contain a maximum 2 electrons of opposite spin.

VBT vs VSEPR

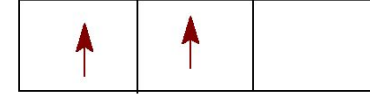
VSEPR theory	VB theory
Based on Lewis structures	Based on quantum mechanics
Covalent bond are formed by sharing electrons	Covalent bonds are formed by overlapping of atomic orbitals
The atomic orbitals are the same in the molecules. Pure orbitals	The valence atomic orbitals in a molecule are <i>different</i> from those in isolated atoms. Hybrid orbitals
Cannot explain differences in bond length (BL) and bond energy (BE) between in different molecules.	Can explain differences in bond length and bond energy can be explained. H-H BE 436.4kJ/mol, BL 74 pm; F-F BE 150 kJ/mol, BL 142 pm.
Assumes that bonds in all molecules are the same as it does not distinguish between sigma bonds and pi bonds	Can distinguish between sigma bonds and pi bonds.

SAMPLE OF LIMITATION OF VSEPR THEORY

Ground State (GS)
electron configuration
of the valence orbital
of carbon



$2s^2$

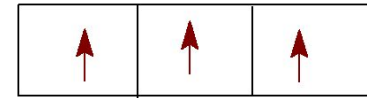


$2p^2$

Excited State (ES)
electron configuration
of the valence orbital
of carbon



$2s^1$



$2p^3$

To apply VSEPR theory in Methane: Here if one of the 2s electron is promoted to the empty 2p orbital (energetically excited as illustrated above) there would four unpaired electrons for bonding however this does not solve the problem as the 3-2p orbitals would be 90° to each other (p-orbitals are 90° to each other) but bond angles in CH_4 are 109.5° . VB bond theory is able to explain this phenomena using hybrid orbitals.

UNIT

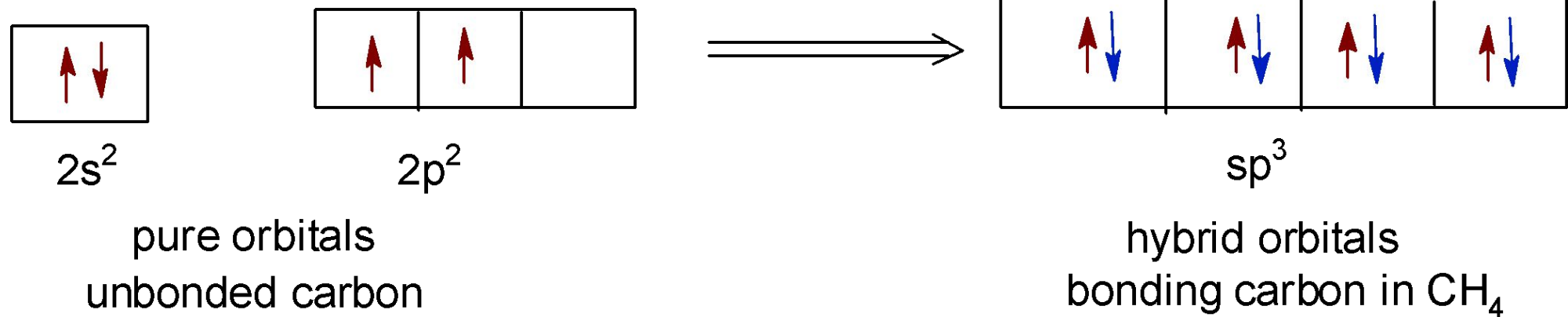
FIVE

HYBRIDIZATION

- Hybrid orbitals as atomic orbitals obtained when two or more non-equivalent orbitals of the same atom combine in preparation for covalent bond formation.
- Hybridization is the mixing of atomic orbitals in an atom (usually the central atom) to generate a set of hybrid atomic orbitals.
- Hybridization is favourable because the energy lost during bond formation (exothermic) compensates for the energy required (absorbed) for hybridization (endothermic).
- **The number of hybrid orbitals is equal to the number of pure atomic orbitals involved in the hybridization.**

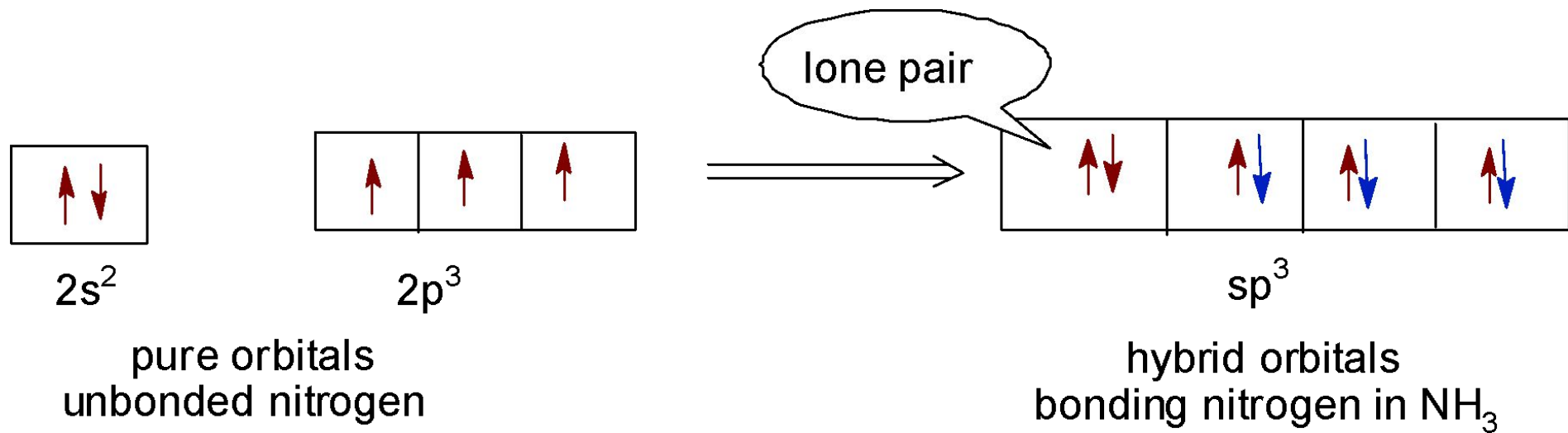
sp^3 HYBRIDIZATION

- In the case of CH_4 in order for carbon to bond with 4-H atoms to form the stable compound, the 2s and 3-2p orbitals of carbon would mix to form a hybrid called sp^3 orbitals. They are four in number ($1-s + 3-p = 4 sp^3$), are form regular **tetrahedral shape** (no lone pair) as described in VSEPR model.

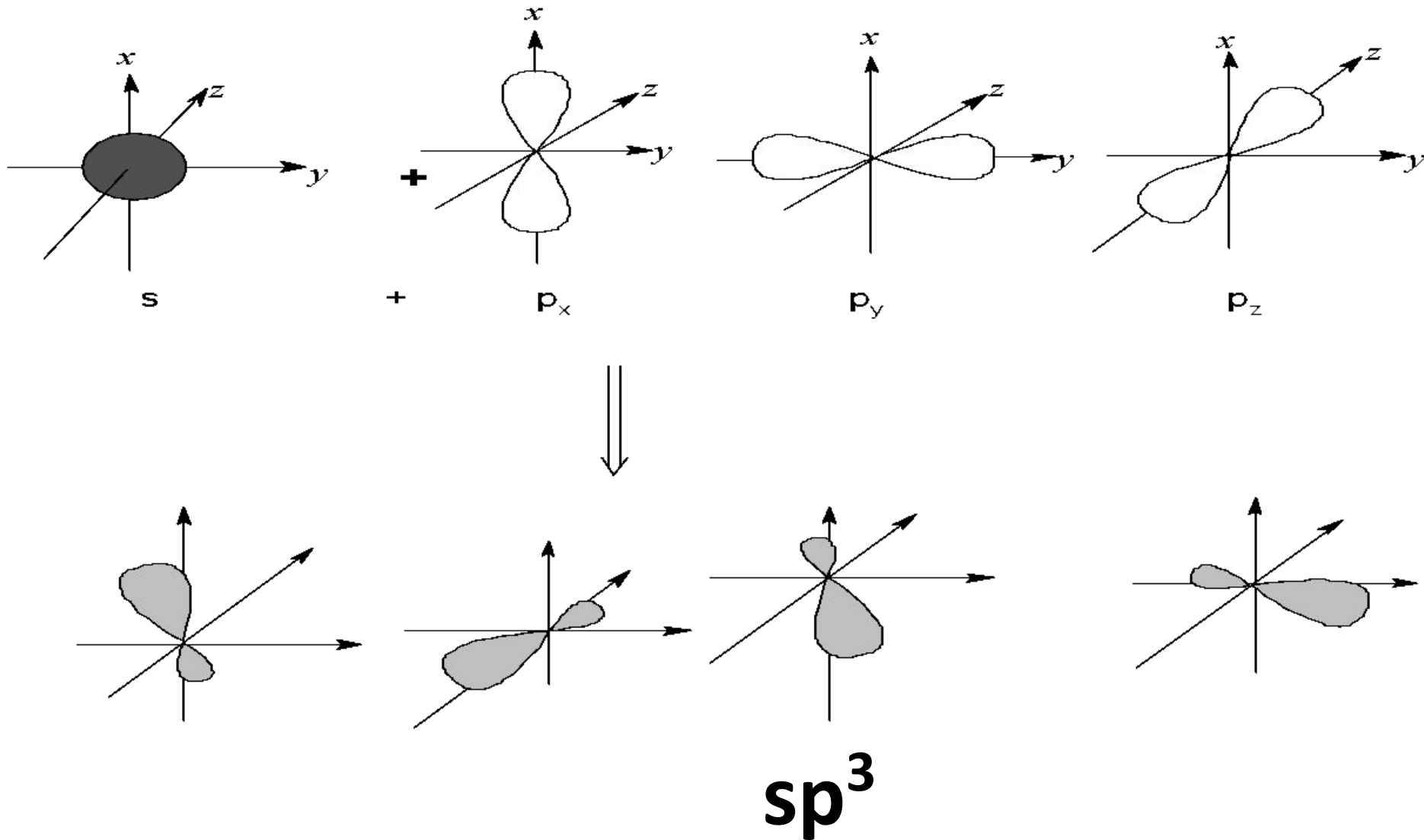


Blue arrows are electrons from H-atoms

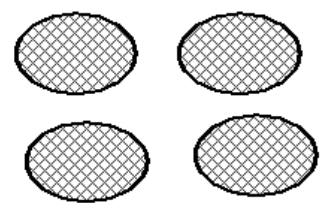
- For NH_3 , the valence orbital of N is sp^3 hybridized but its bond angle is 107.3° because of the lone pair-bond pair repulsion effect therefore **trigonal pyramidal** in shape.



Blue arrows are electrons from H-atoms

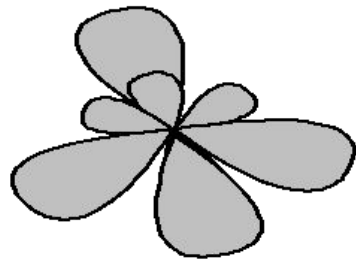


Hybrid orbitals exhibit feature of parent atomic orbitals

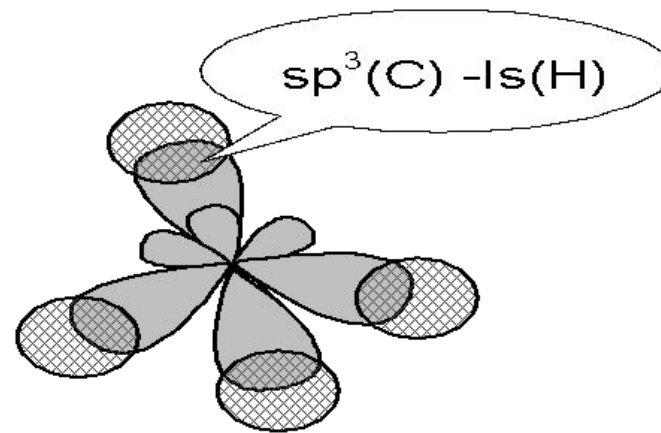
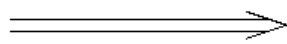


4 $1s(\text{H})$

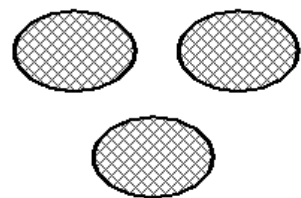
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4 $sp^3(\text{C})$

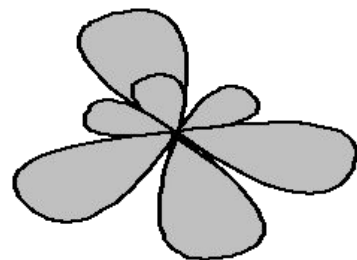


CH_4

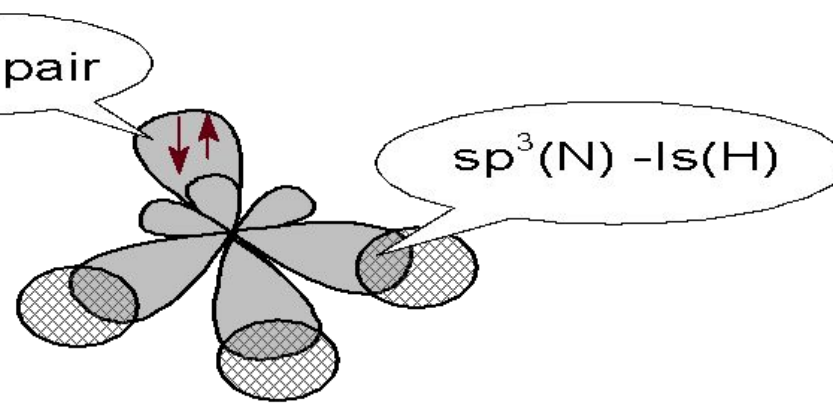
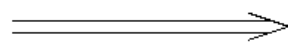


3 $1s(\text{H})$

+



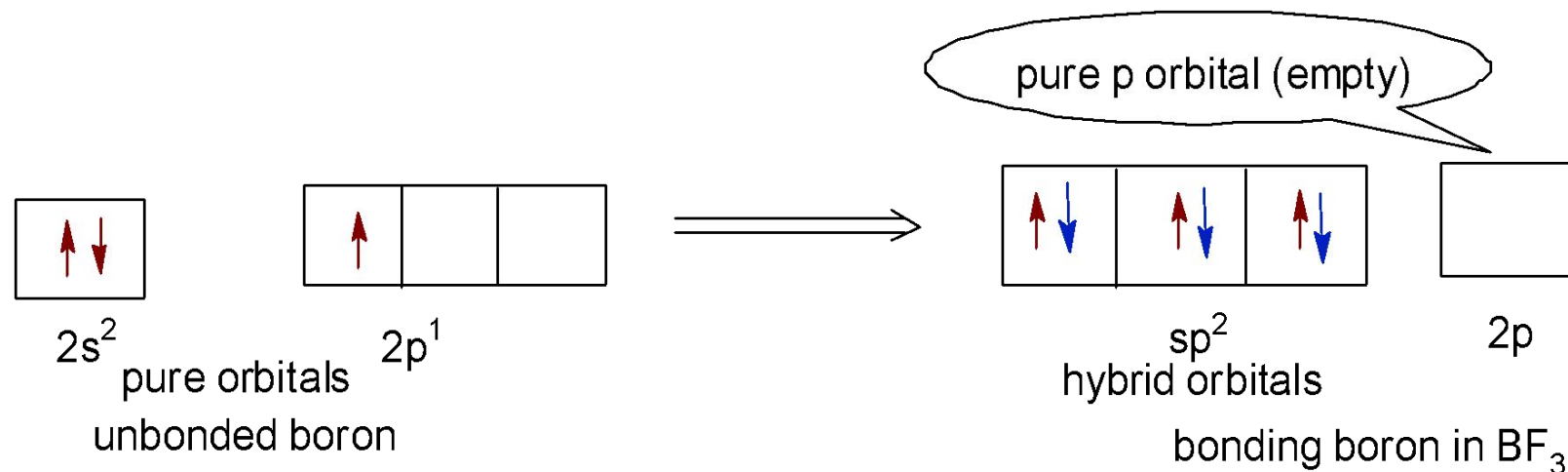
4 $sp^3(\text{N})$



NH_3

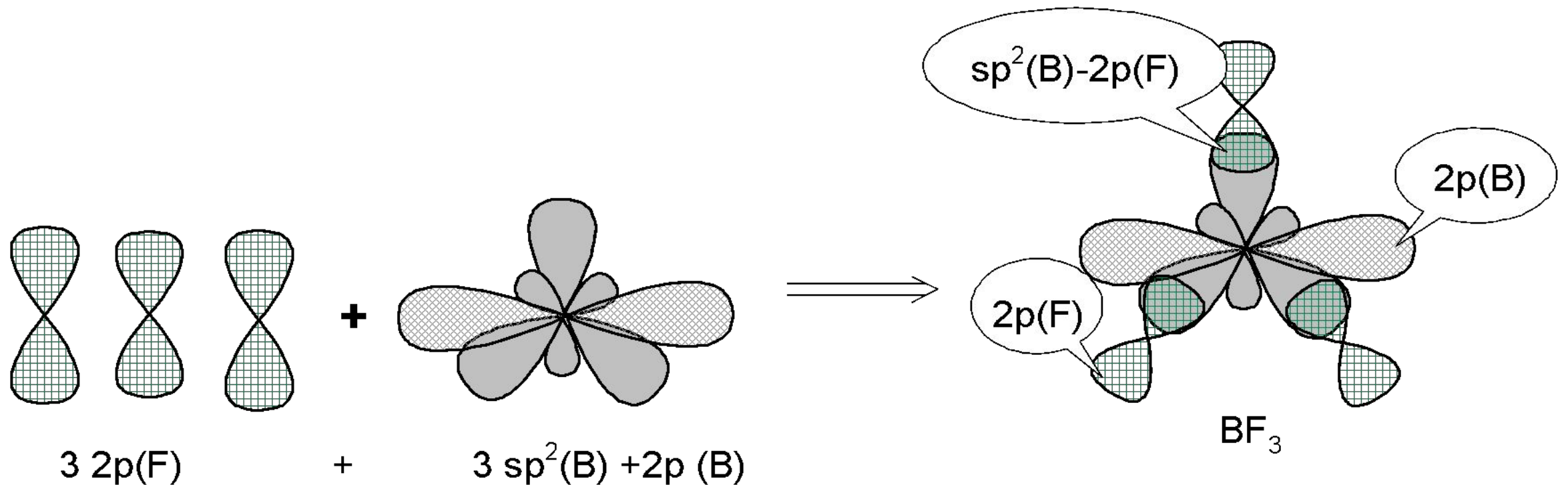
sp^2 HYBRIDIZATION

- This is the mixing of a 1-s orbital with 2-p orbitals to form the hybrid sp^2 which are three orbitals in number ($1-s + 2-p = 3-sp^2$).



Blue arrows are electrons from Fluoride-ions

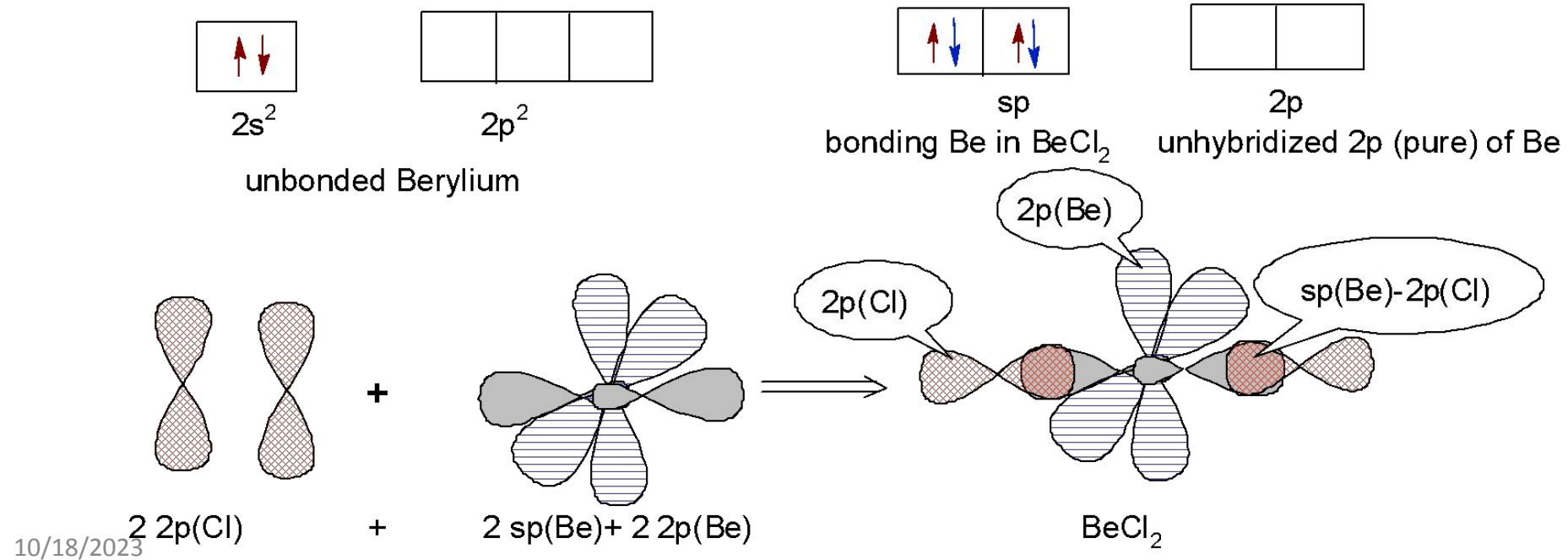
In the absence of lone pair the molecular geometry of such a molecule would be trigonal planar as in the case of BF_3 as each of sp^2 orbitals of Boron overlap with one $2p$ orbital of F. The unhybridized empty $2p$ orbital of B is therefore available to accept lone pair (coordinate bonding).



sp HYBRIDIZATION

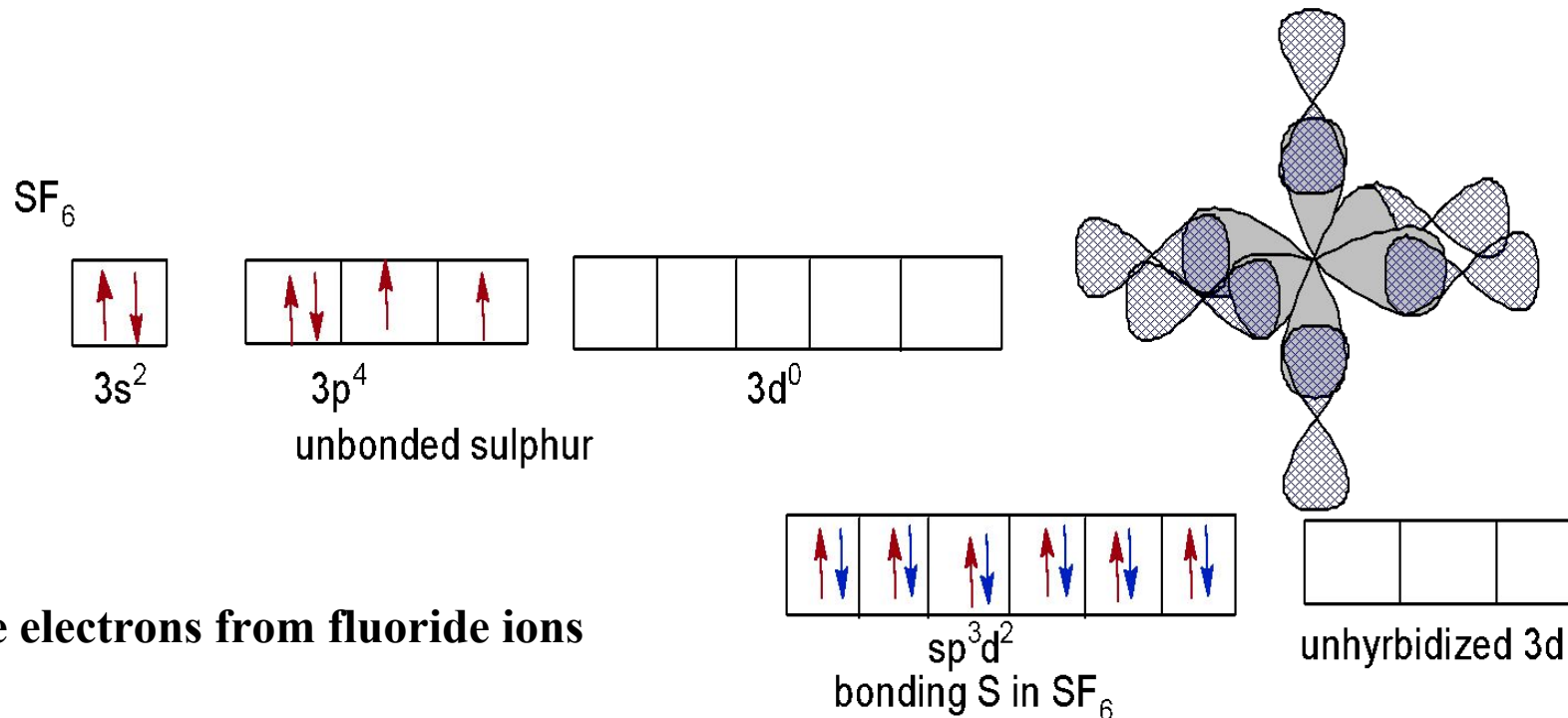
- This involves the mixing of 1-s orbital with 1-p orbital, such that the total number of hybrid orbital is 2 with 2 empty pure p orbital ($1-s + 1-p = 2-sp$). The shape of such hybridization in the absence of lone pair of electrons is linear as in the case of BeCl_2 .

Blue arrows are electrons from chloride-ions

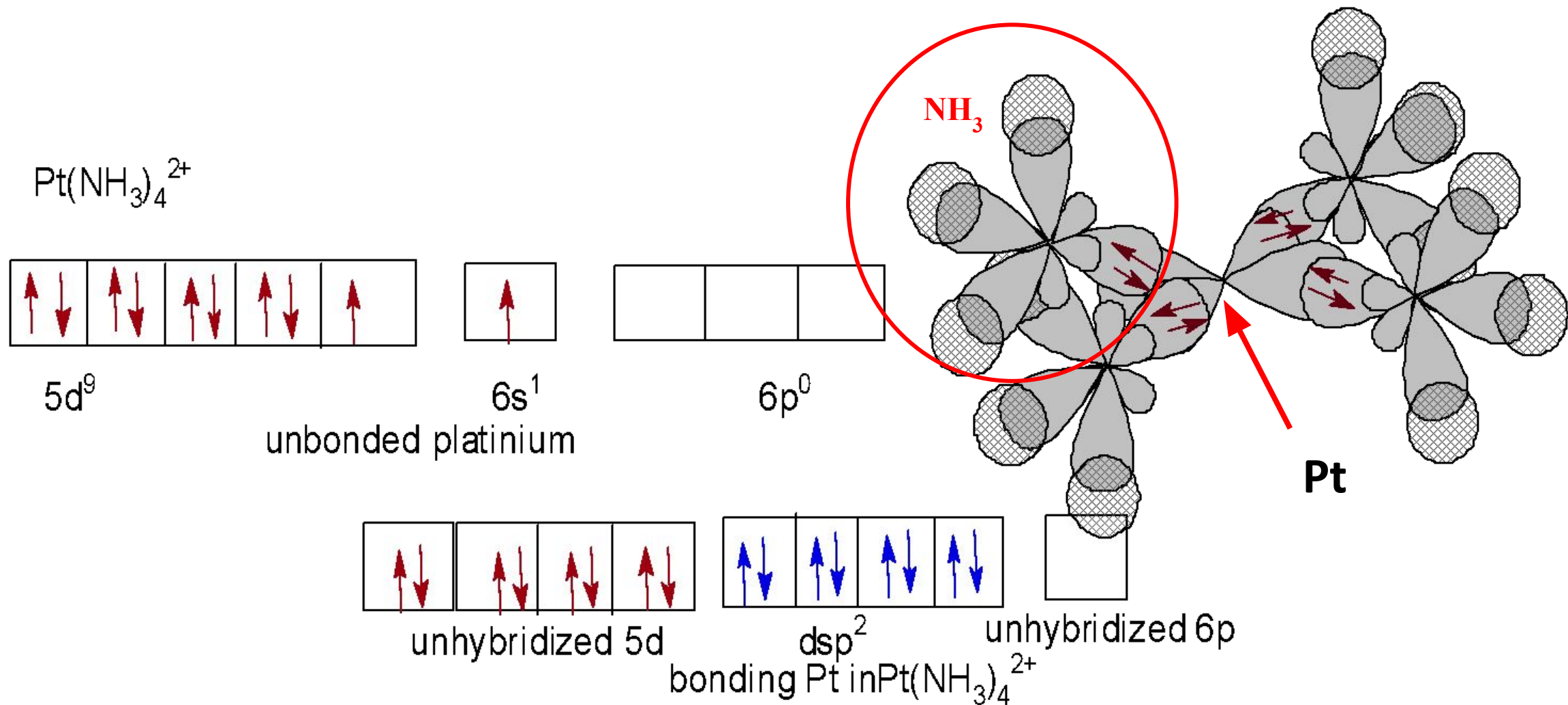


Hybridization involving s, p, and d orbitals

- This type of hybrid orbitals account for the expand octet as in the case PCl_5 and SF_6 and in formation of complexes between a transition metal and ligands.



Blue arrows are electrons from fluoride ions

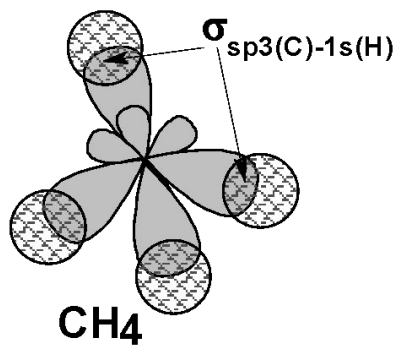


Blue arrows are electrons from the lone pair on ammonia.

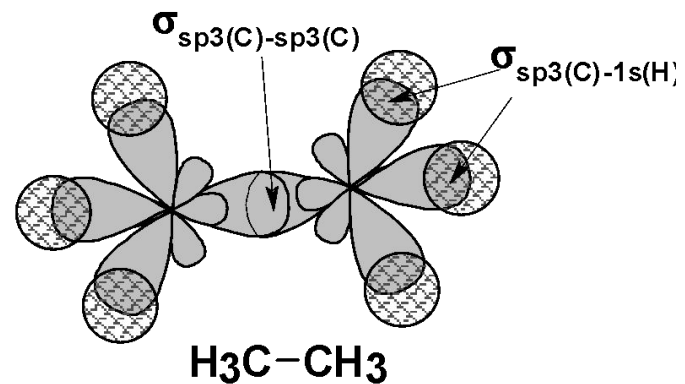
UNIT

SIX SIGMA AND PI BONDS

- When atomic orbitals (hybridized or not) overlap horizontally they form sigma covalent bond (simply sigma bond, σ bond). This is described as end-to-end overlapping. All the bond described above are sigma bonds.
- When the atomic orbitals overlap vertically i.e. side-to-side they form pi covalent bonds (simply pi bonds π bond)

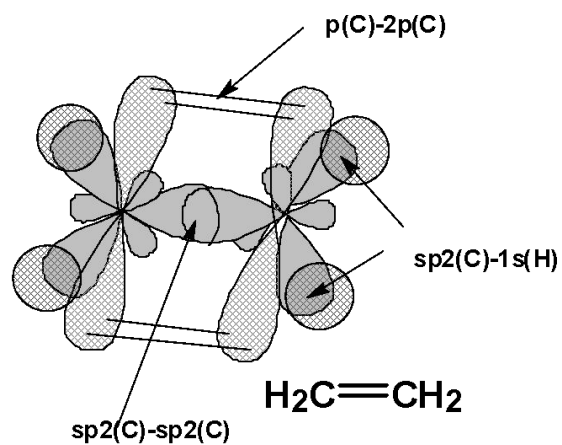


Four $\sigma_{sp^3(C)-1s(H)}$ bonds



Six $\sigma_{sp^3(C)-1s(H)}$ bonds

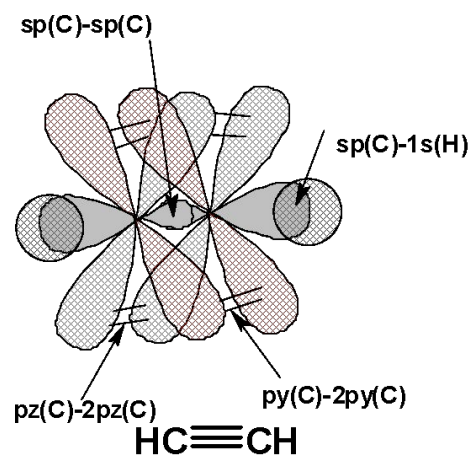
One $\sigma_{sp^3(C)-sp^3(C)}$ bond



Four $\sigma_{sp^2(C)-1s(H)}$ bonds

One $\sigma_{sp^2(C)-sp^2(C)}$ bonds

One $\pi_{2p(C)-2p(C)}$ bond



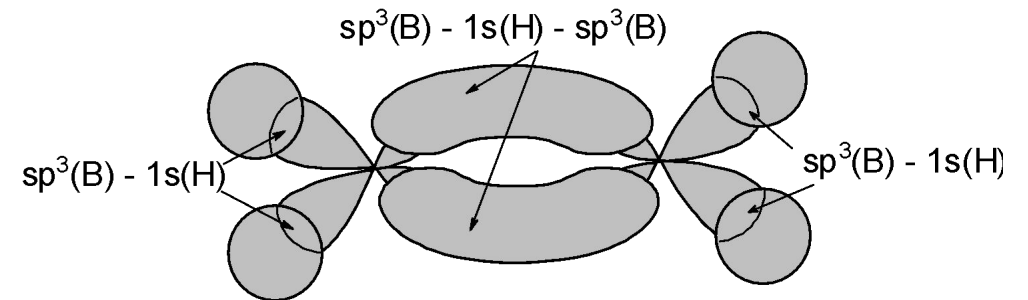
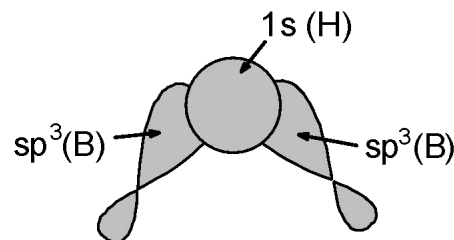
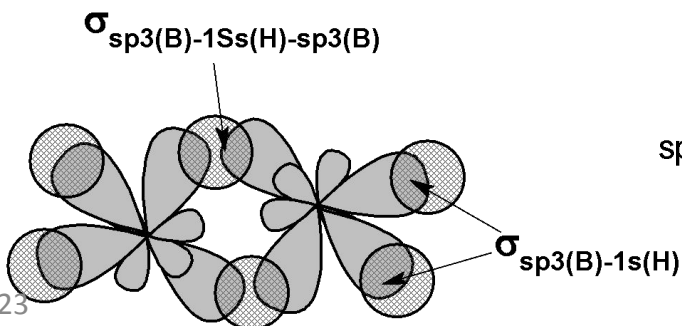
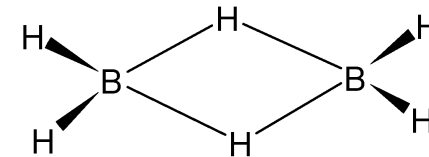
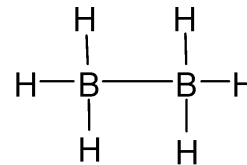
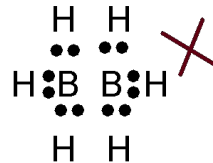
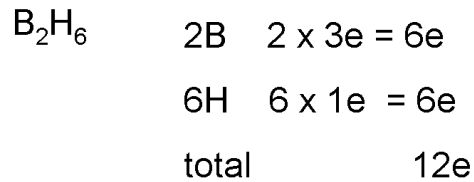
Two $\sigma_{sp(C)-1s(H)}$ bonds

One $\sigma_{sp(C)-sp(C)}$ bonds

Two $\pi_{2p(C)-2p(C)}$ bonds

2-Electron, 3-Center Bonds

- In this type of bonding, three atoms are bound by a single molecular orbital containing two electrons. This phenomenon occurs with molecules that have incomplete octet or are electron deficient. An example is diborane (B_2H_6).



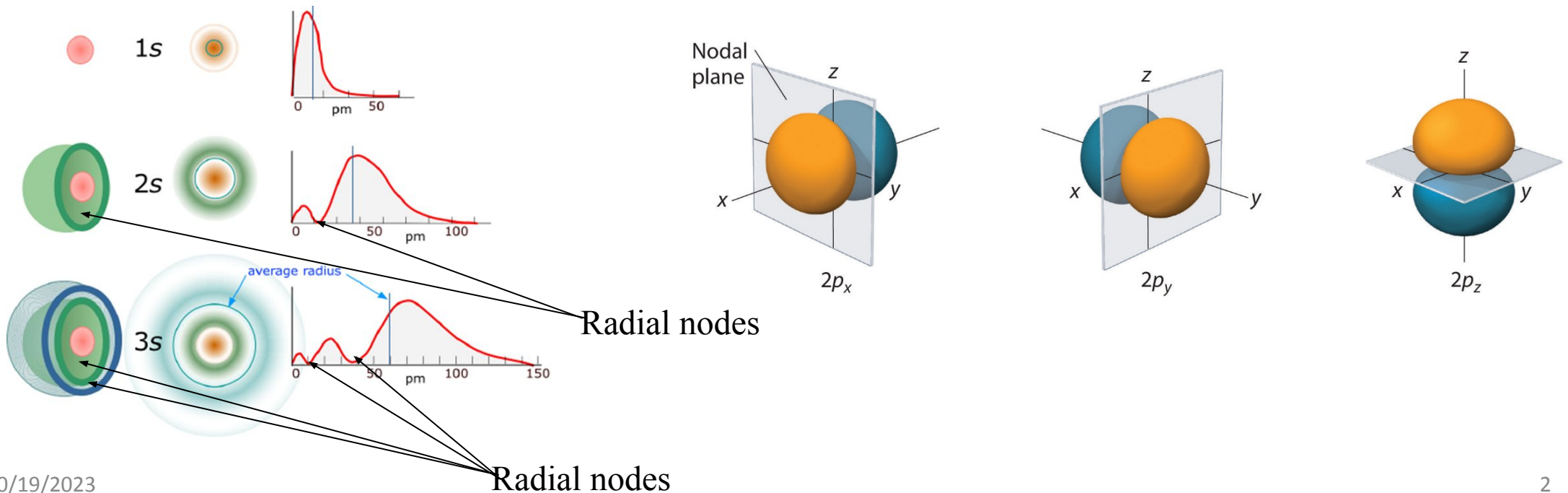
MODULE ONE (C)

MO THEORY

UNIT SEVEN

Atomic orbitals

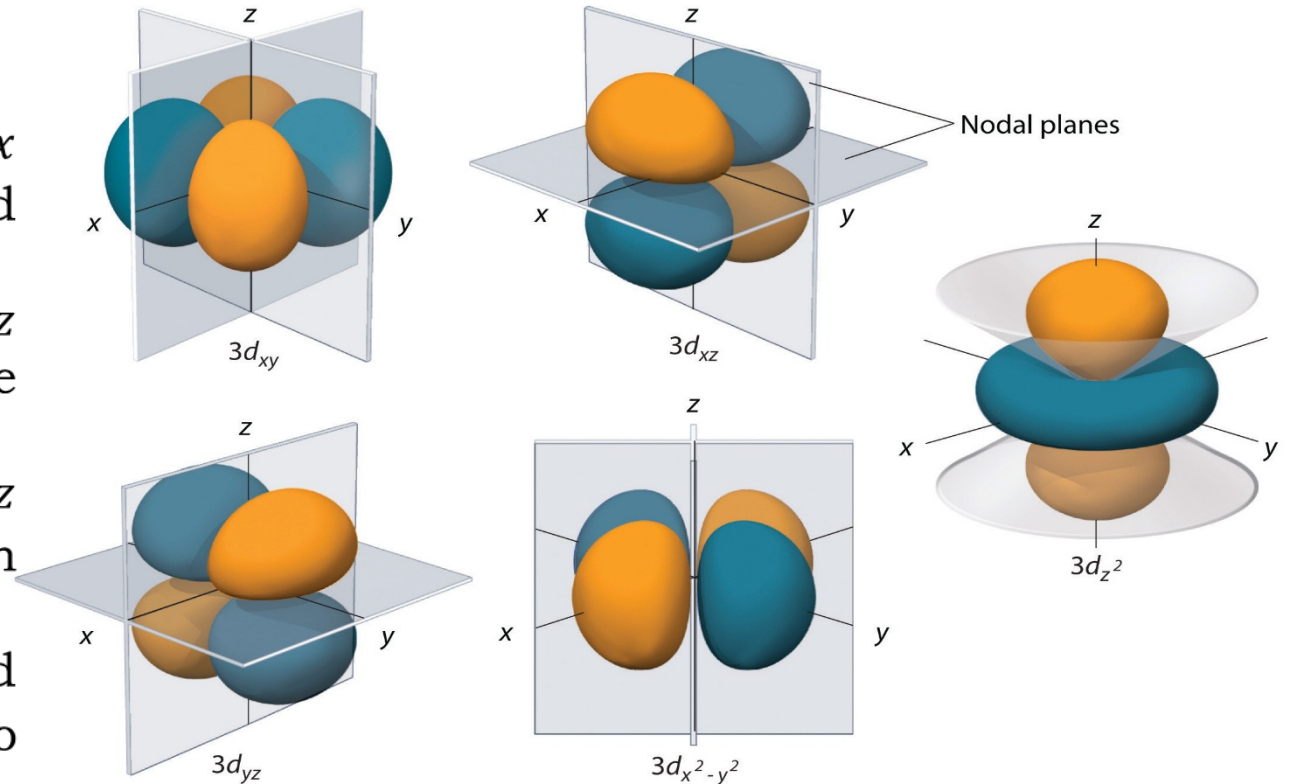
- The region with an orbital where an electron cannot be found is the node. It could be radial or a plane.
- The s orbitals are spherical. The 1s orbital has no nodes but 2s and above have radial nodes. 2s has 1, and 3s has 2, ... 5s will have 4.
- The p-orbitals have dumbbell shapes and so have nodal planes.



What about d-orbitals?

Use the 3d orbitals

- The d_{xy} has its lobes in between the x and y axes and 2 nodal planes (xz and yz planes in line with the z -axis).
- d_{xz} has its lobes between the x and z axes and has 2 nodal planes (yz (in line with the z -axis) and xy planes).
- The d_{yz} has its lobes between y and z axes with 2 nodal planes (xz (in line with the z -axis) and xy planes).
- The $d_{x^2-y^2}$ orbital has its lobes on x and y axes and has 2 nodal planes (at 45° to the these axis and in line with the z axis).
- d_{z^2} has no nodal plane because it is symmetrical around the z -axis.



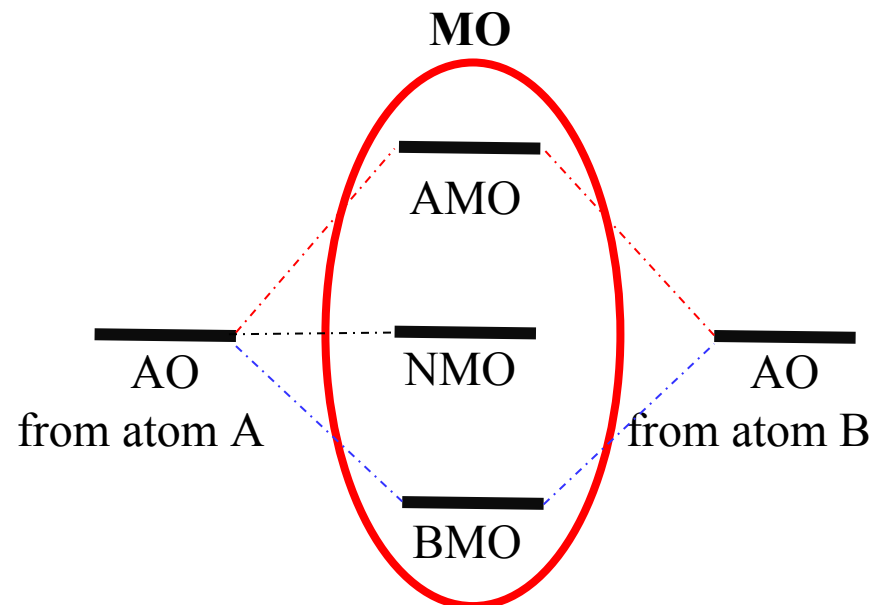
MOLECULAR ORBITAL THEORY (MOT)

- Just like VOT, it is based on quantum mechanics.
- **It is computer simulated.**
- Instead of hybridization, the interactions of atomic orbitals (AO) result in molecular orbitals (MO).
- In VBT, the overlapping atomic orbitals (AO) are associated with only the valence electrons of individual atom. In MOT, the interactions involve electrons in all of the atomic orbitals (AO) are associated with the entire molecule.
- For there to be overlapping the orbitals must be close in energy and have similar symmetry.

- When 1 AO overlaps with another 1 AO it creates two MO - one which is a bonding MO (BMO) and the other is an anti-bonding (AMO).

$$1 \text{ AO} + 1 \text{ AO} = 2 \text{ MO} \text{ (1 BMO and 1 AMO)}$$

- Similarly $3 \text{ AO} + 3 \text{ AO} = 6 \text{ MO}$ (3 BMO and 3 AMO).
- BMOs have lower energy and therefore greater stability than its initial AOs from which it was formed while AMOs have higher energy and lower stability than its initial AOs from which it was formed.
- Non-bonding molecular orbitals (NMO) have the same energy as the AOs. Therefore an electron occupying an NMO does not affect the stability of the molecule.



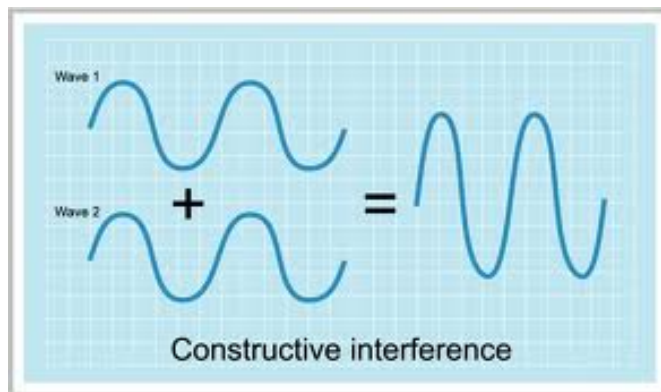
WAVE FUNCTION

In terms of the formation of BMO, it corresponds to constructive interaction of the wave function of each AO. This results in a new wave function of lower energy than those of the AOs and increased probability of finding an electron in the molecular orbital.

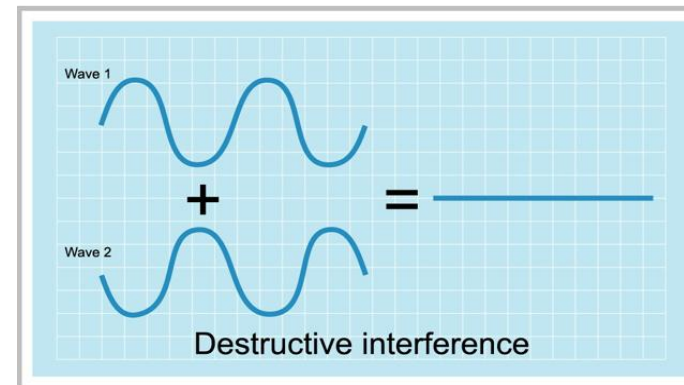
$$\begin{aligned}\varphi_{AO} + \varphi_{AO} &= \varphi_{MO} \\ \varphi_{AO} &> \varphi_{MO}\end{aligned}$$

While AMO is produced from destructive interaction of the wave function of each AO. This results in new wave function of higher energy than those of the AOs. with a decreased probability of finding an electrons in the molecular orbital.

$$\begin{aligned}\varphi_{AO} + \varphi_{AO} &= \varphi_{MO}^* \\ \varphi_{AO} &< \varphi_{MO}^*\end{aligned}$$



In-phase resulting in increase amplitude



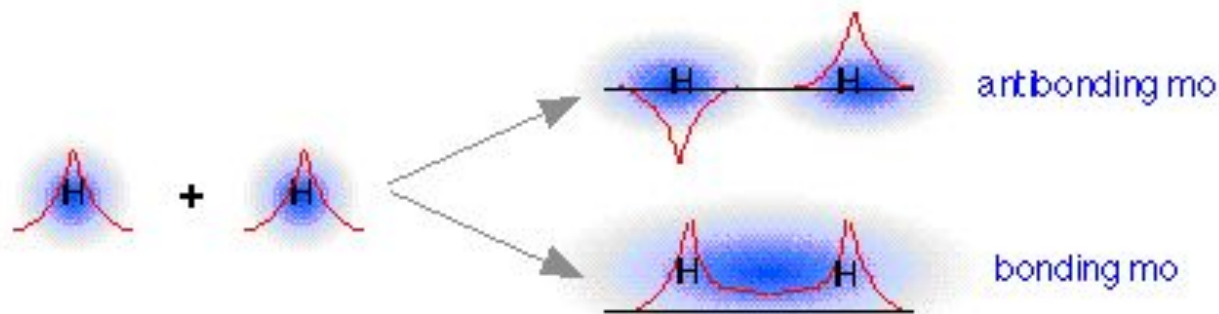
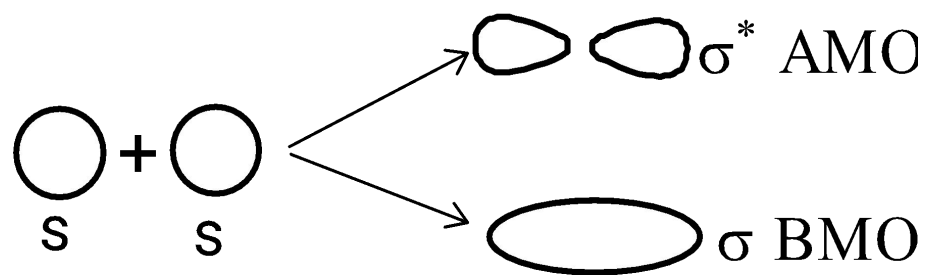
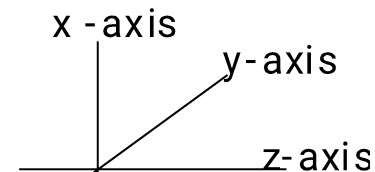
Out-of-phase resulting in decrease amplitude

UNIT EIGHT

OVERLAPPING OF TWO

s-ORBITALS

- These orbitals have spherical symmetry around the inter-nuclear axis (taken as the z-axis).
- And approach each other end-to-end.
- This interaction between any two s-orbitals produces σ MOs – sigma bonding (σ) and sigma antibonding molecular orbitals (σ^*).
- The BMO is symmetrical around the inter-nuclear axis.



Inter-nuclear axis is an imaginary line that joins the nuclei of two atomic orbitals.

OVERLAPPING OF TWO p-ORBITALS

The p-orbitals because of their dumbbell shape can overlap in two ways: horizontally or vertically. There 3-p orbital, the p_x orbital lies on the x-axis, the p_y on the y-axis and the p_z on the z-axis. The p_x and the p_y overlap vertically (side-to-side) resulting in **π -molecular orbital**. While the overlapping of the p_z is end-to-end resulting in **σ -molecular orbitals**.

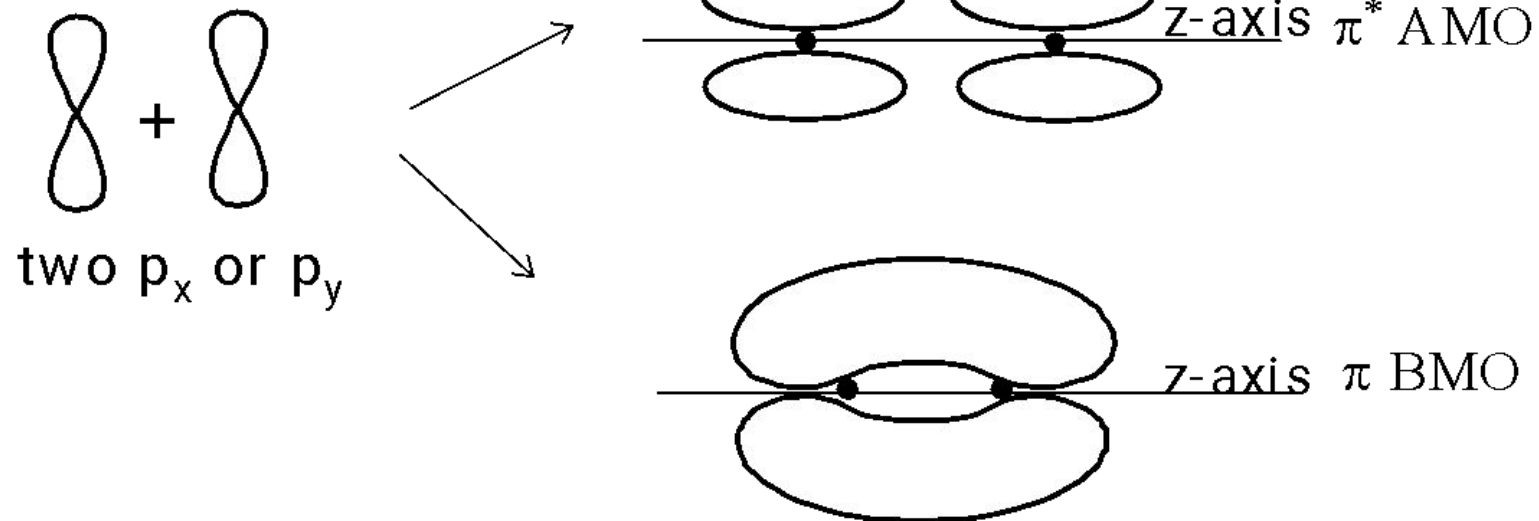
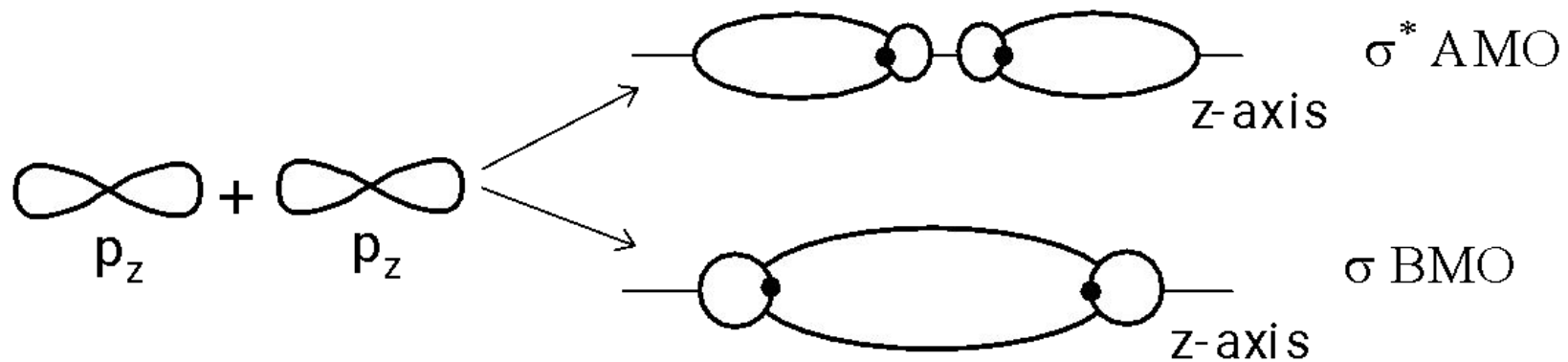
Note:

p_z will overlap with only p_z

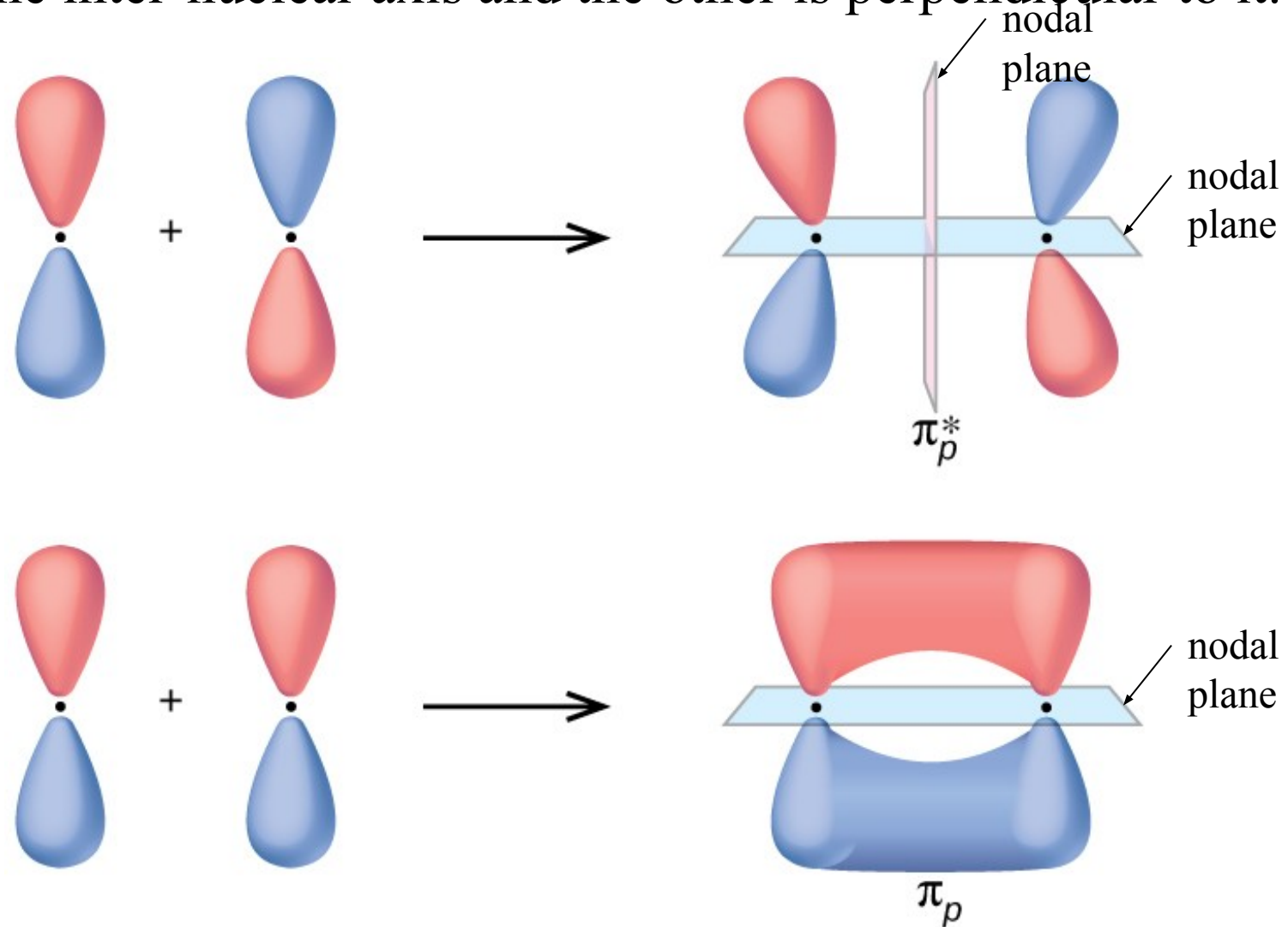
p_x will overlap with p_x and p_y

p_y will overlap with p_x and p_y

} The lie on the same plane



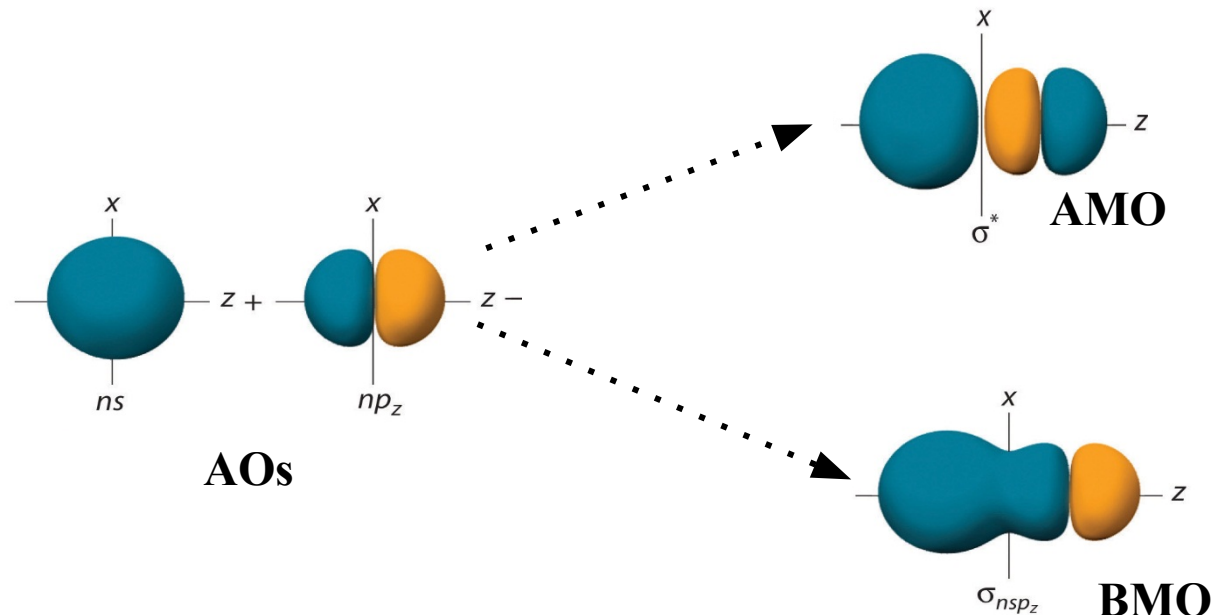
p_x and p_y -orbitals have only 1 node (nodal plane) in their BMO which is in-line with the inter-nuclear axis (z-axis). In their AMO there are 2 nodal planes, one is in-line with the inter-nuclear axis and the other is perpendicular to it.



OVERLAPPING OF AN s-ORBITAL TO A p-ORBITAL

This is possible provided:

- The p-orbital is lying on the z-axis just as the s-orbital is. This way they would overlap end-to-end resulting in a sigma MO (bonding and antibonding). Therefore only the p_z -orbital will overlap with an s-orbital.
- They must be close in energy. 1s cannot overlap with 3s but may overlap with 2s or $2p_z$ if they are close in energy.



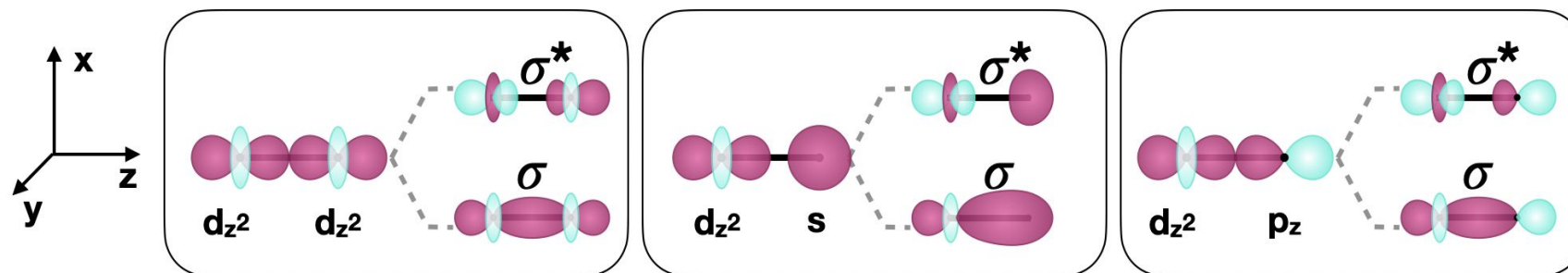
UNIT NINE

OVERLAPPING OF d-ORBITAL

The d orbitals are d_{xy} , d_{yz} , d_{xz} , d_{z^2} and $d_{x^2-y^2}$

SIGMA BONDS in d-ORBITALS

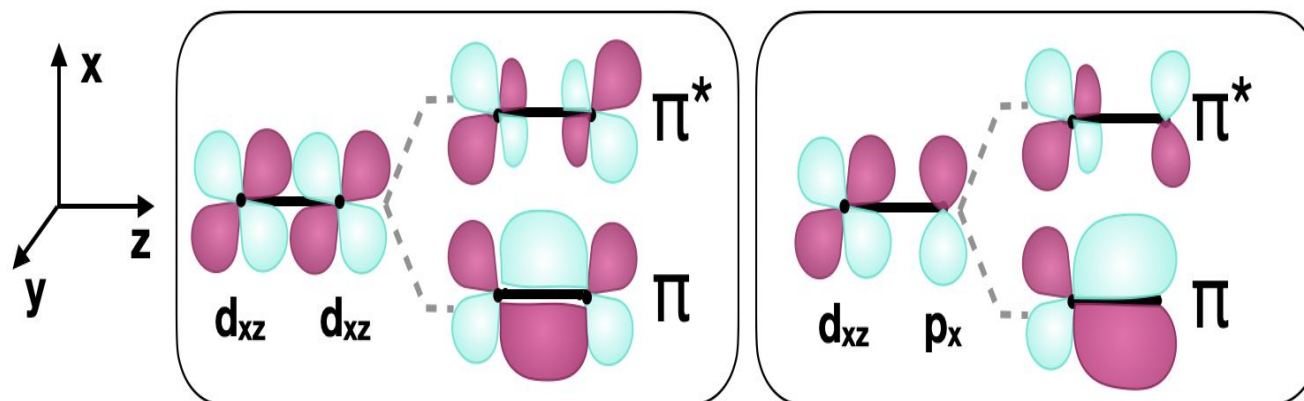
- The d_{z^2} orbitals can form d-d sigma bonds since it has cylindrical symmetry w.r.t. the inter-nuclear axis (z-axis). It can also overlap with s and p_z -orbitals.



- Two $d_{x^2-y^2}$ can also form sigma bond. This is because their lobes lie on x and y axes therefore, these sigma bonds will be formed along these axes.

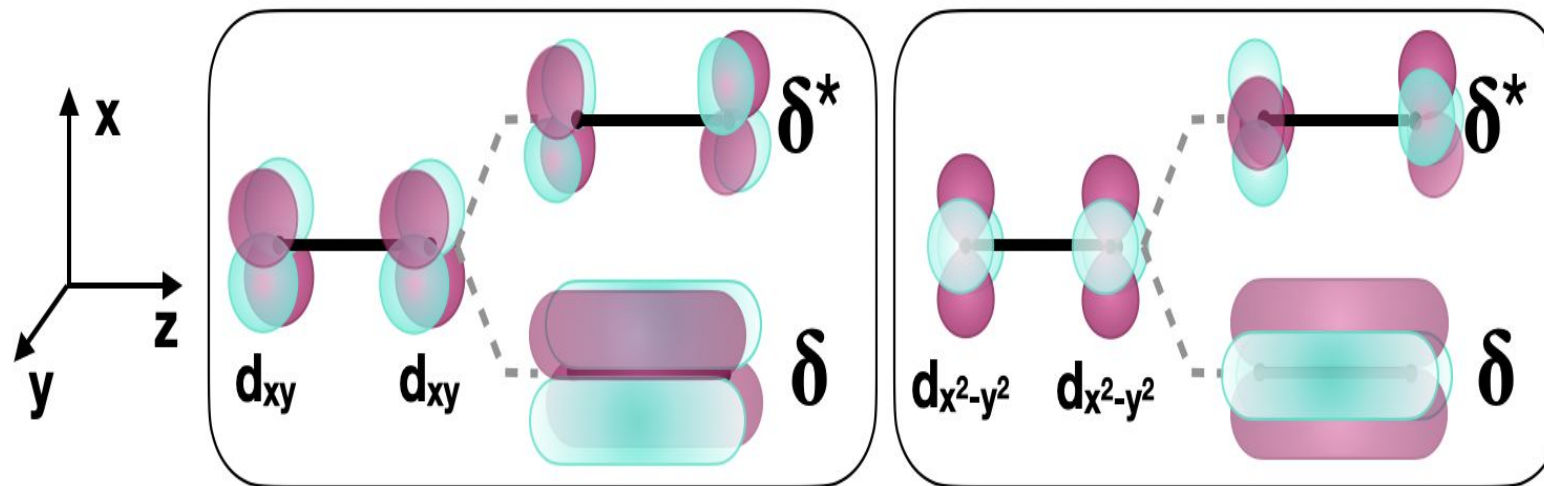
PI BONDS IN d-ORBITALS

- π bonds are those bonds with one nodal plane is in line with the inter-nuclear axis.
- The d-orbitals that would exhibit this are the overlapping of the d_{xz} and d_{yz} .
- They can also form pi bonds with p_x and p_y orbitals because they lie in the same plane. (Have the same symmetry).



DELTA BONDS IN d-ORBITALS (δ -BONDS)

- δ bonds are those bonds with two nodal planes is in line with the inter-nuclear axis.
- The d-orbitals that would exhibit this are the overlapping of the d_{xy} and $d_{x^2-y^2}$.



UNIT TEN

MOLECULAR ORBITAL ELECTRONIC CONFIGURATION

Just as we have atomic orbital electronic configuration and we have rules guiding this, we have molecular orbital electronic configurations and there are also rules guiding this.

Rules

- The number of MO formed is equal to the sum of number of all the atomic orbitals involved.
- The filling of MO proceeds from the low energy orbitals to the high energy orbitals (from bonding to anti bonding).
- It obeys Pauli's Exclusion Principle – electrons fill in pair i.e. a maximum of 2 electrons per MO.
- It obeys Hund's rule - electron will fill in MO of the same energy singly before pairing.
- The number of electrons in the MO is equal to the sum of all the electrons in the bonding atoms.

HOMONUCLEAR DIATOMIC MOLECULES OF THE FIRST PERIOD (H_2 and He_2)

- Homonuclear mean exactly the same type atoms
- Diatomic means 2 atoms
- H and He belong to the first period in the periodic table having only 1s orbitals.

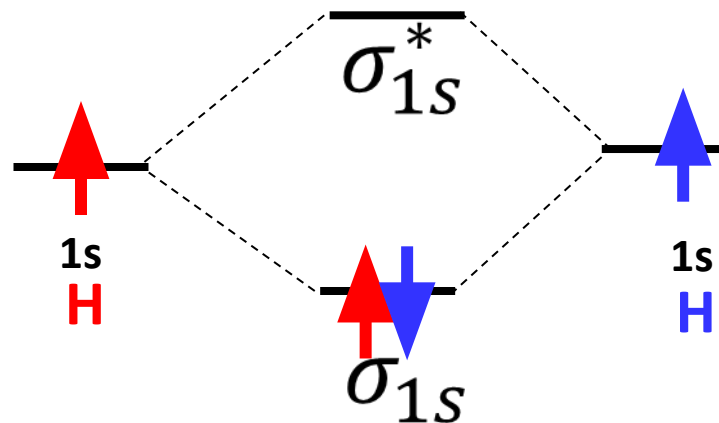
Dihydrogen molecule (H_2)

H – $1s^1$

H – $1s^1$

Total number of electrons = $2e$

Total number of MO = 2



BOND ORDER, STABILITY, MAGNETIC PROPERTIES

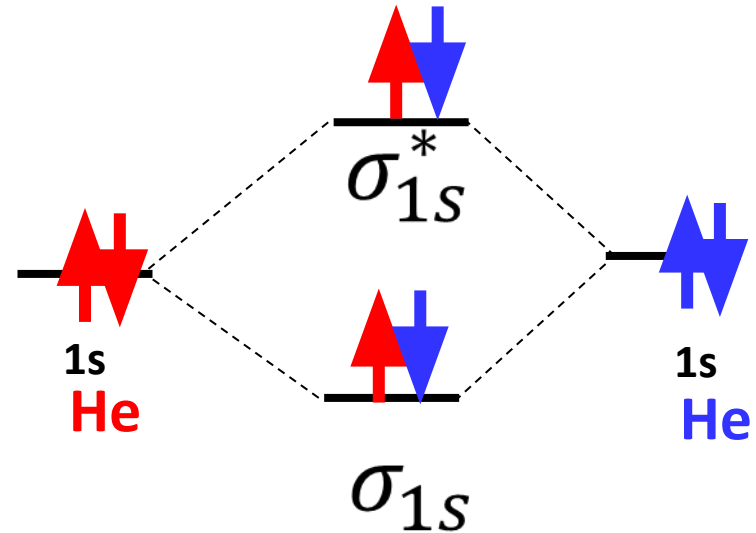
- Overlapping of the two 1s orbital atomic orbitals = $\sigma_{1s}, \sigma_{1s}^*$ 2 molecular orbitals
- Filling of these orbital = $\sigma_{1s}^2, \sigma_{1s}^*$. This is the molecular orbital electronic configuration of H_2
- We can determine the stability of the molecule can be from the bond order using
- *bond order* = $\frac{1}{2}(\text{no of electrons in BMO} - \text{no of electrons in AMO})$
$$\frac{1}{2}(2 - 0) = 1$$
- The bond order is 1 and therefore this molecule is stable and its a single bond.
- There are no unpaired electrons so it is diamagnetic.

Dihelium molecule (He_2)

He – $1s^2$

He – $1s^2$

Total number of electrons = $4e$



Overlapping of the two $1s$ atomic orbital = $\sigma_{1s}, \sigma_{1s}^*$ 2 molecular orbitals

Filling of these orbital = $\sigma_{1s}^2, \sigma_{1s}^{*2}$

We can determine the stability of the molecule can be from the bond order using

$$\text{bond order} = \frac{1}{2} (\text{no of electrons in BMO} - \text{no of electrons in AMO})$$

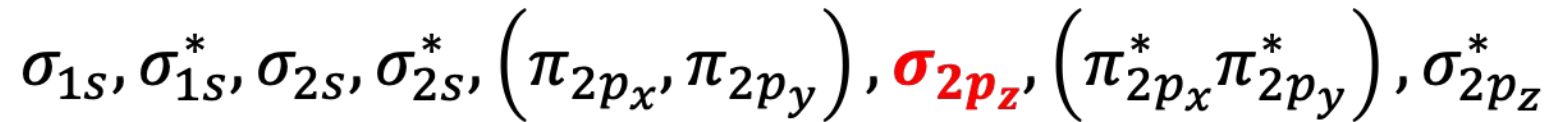
$$\frac{1}{2} (2 - 2) = 0$$

The bond order is 0 and therefore this molecule is not stable and does not exist.

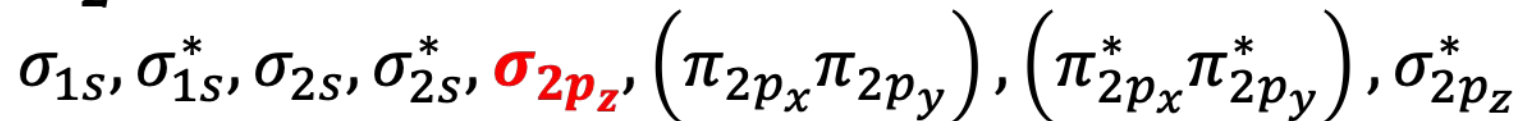
UNIT ELEVEN HOMONUCLEAR DIATOMIC MOLECULES OF THE SECOND PERIOD (Li₂, Be₂, B₂, C₂, N₂, O₂, F₂, Ne₂)

- In this group the general atomic orbitals are 1s, 2s, 2p_x, 2p_y, 2p_z (at most 5 atomic orbitals from each atom) such that when two of atoms form a diatomic molecule, the interaction of the atomic orbitals would produce at most 10 molecular orbitals.

Below is the molecular orbital electronic configuration for **Li₂, Be₂, B₂, C₂, N₂**



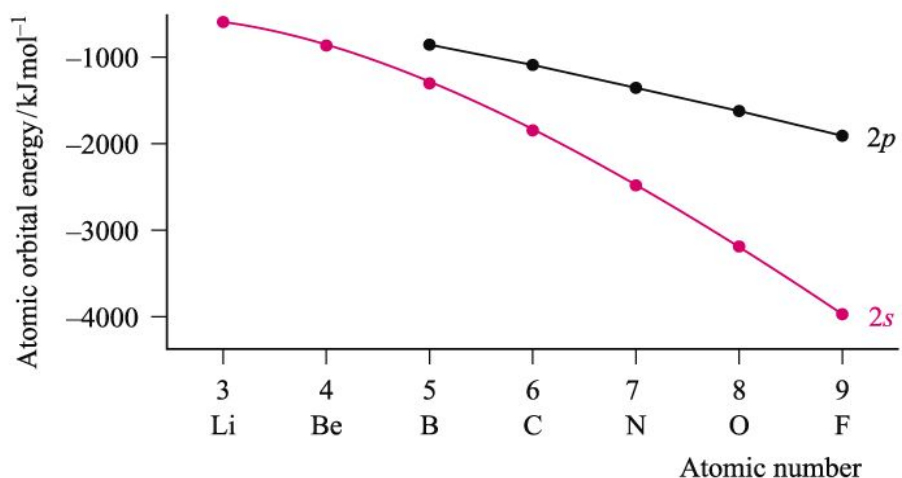
For **O₂, F₂, Ne₂**



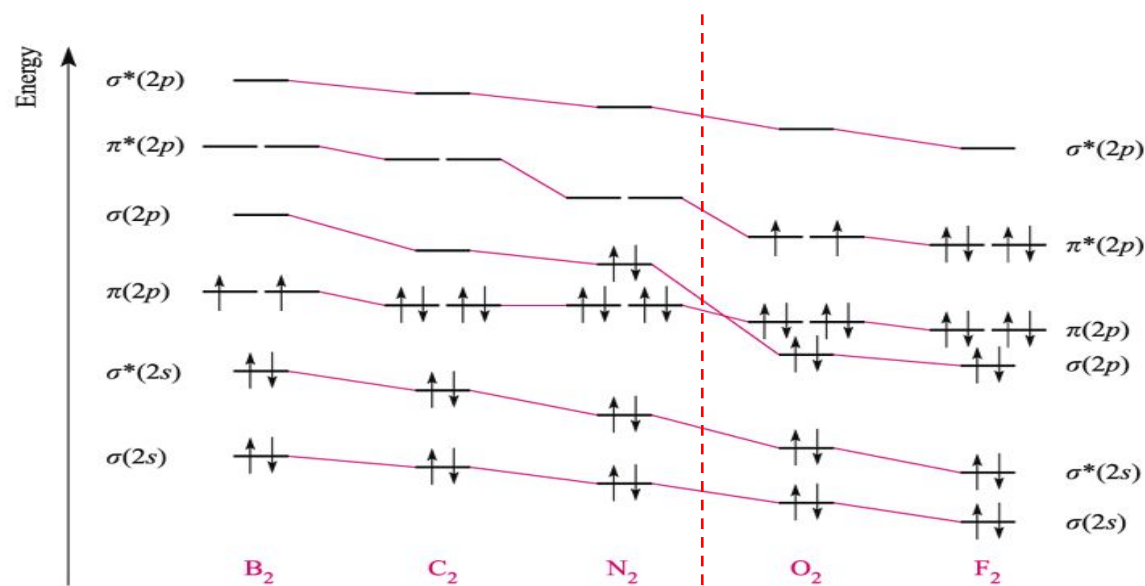
The pi orbitals in the brackets are degenerate i.e. they are equal in energy ($\pi_{2p_x} = \pi_{2p_y}$) and ($\pi_{2p_x}^* = \pi_{2p_y}^*$) therefore electrons would fill in singly before pairing.

THE REASON WHY!

The position of the σ_{2p_z} orbital is different and this is due to sharp decrease in the energy of the 2s orbital as you move across the period which is most prominent from O to Ne (see diagram below).



Energy level of the 2nd row of homonuclear diatomic molecules



Molecules Li_2 , Be_2 , B_2 , C_2 and N_2 have $\pi(2p)$ lower in energy than $\sigma(2p)$

Molecules O_2 , F_2 and Ne_2 have $\pi(2p)$ higher in energy than $\sigma(2p)$

Diboron molecule B₂

B – 1s², 2s², 2p_x¹, 2p_y⁰, 2p_z⁰

B – 1s², 2s², 2p_x¹, 2p_y⁰, 2p_z⁰

Total number of electrons = 10e

Overlapping of the two of 1s, 2s and 2p_x atomic orbital (total of 6 atomic orbital) = 6

molecular orbitals = σ_{1s}, σ_{1s}^{*}, σ_{2s}, σ_{2s}^{*}, (π_{2p_x}, π_{2p_y})

Filling of these orbital = σ_{1s}², σ_{1s}^{*2}, σ_{2s}², σ_{2s}^{*2}, (π_{2p_x}¹, π_{2p_y}¹)

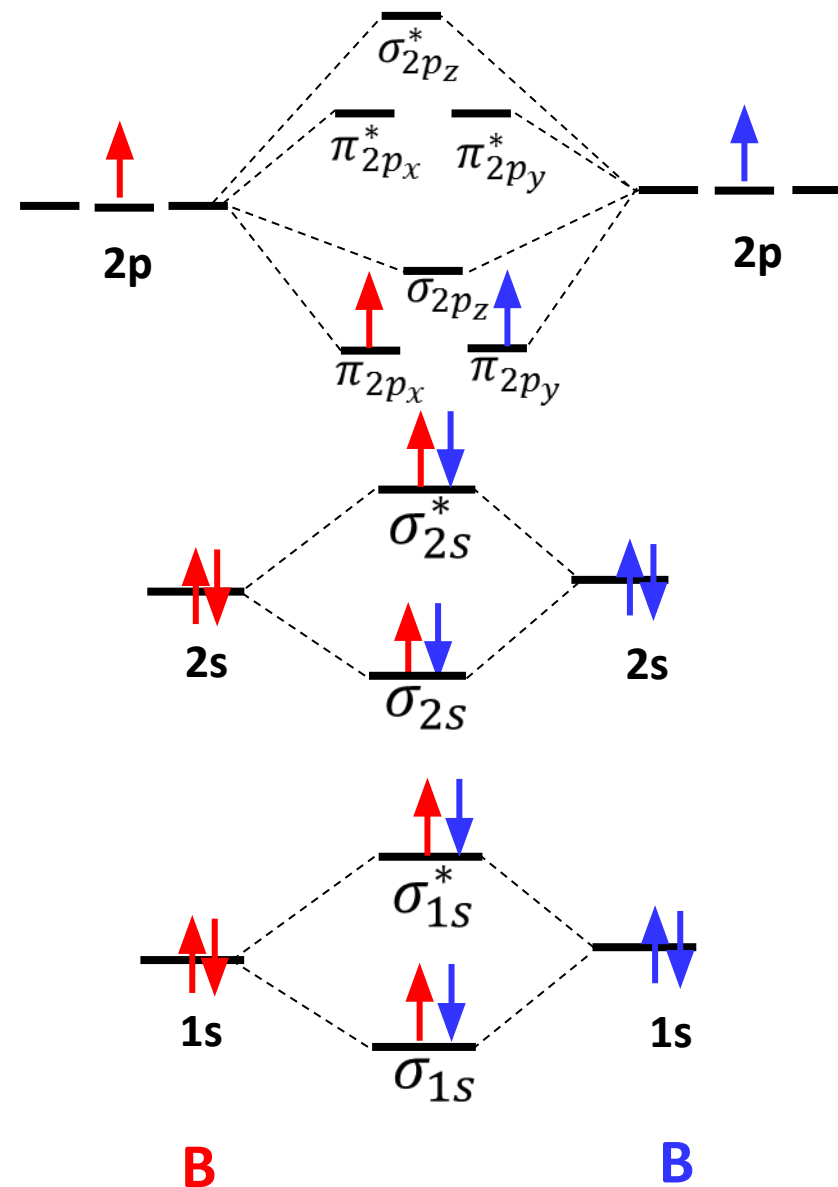
We can determine the stability of the molecule can be from the bond order using

bond order

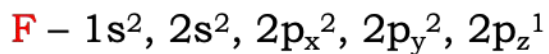
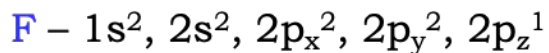
$$= \frac{1}{2} (\text{no of electrons in BMO} - \text{no of electrons in AMO})$$

$$\frac{1}{2} (6 - 4) = 1$$

The bond order is 1 and therefore this molecule is stable and does exist. It has 2 unpaired electrons and therefore paramagnetic.

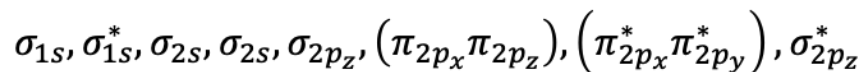


Diflourine molecule F₂



Total number of electrons = 18e

Overlapping of the two of 1s², 2s², 2p_x², 2p_y², 2p_z¹ (total of 10 atomic orbitals) = 10 molecular orbital



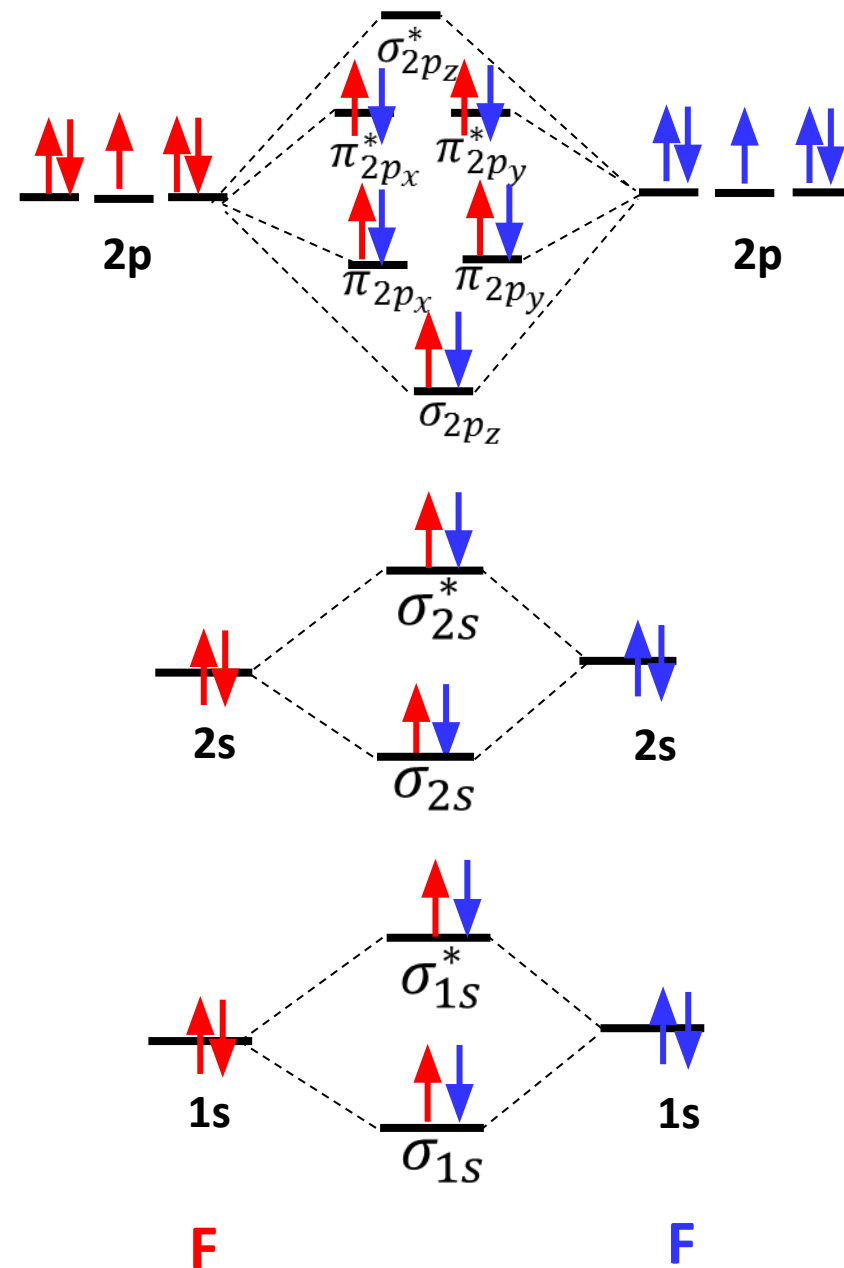
Filling of these orbital = $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_z}^2, (\pi_{2p_x}^2 \pi_{2p_y}^2), (\pi_{2p_x}^{*2} \pi_{2p_y}^{*2})$

We can determine the stability of the molecule can be from the bond order using

$$\text{bond order} = \frac{1}{2} (\text{no of electrons in BMO} - \text{no of electrons in AMO})$$

$$\frac{1}{2} (10 - 8) = 1$$

The bond order is 1 and therefore this molecule is stable and exists. It is diamagnetic.



FRONTIER ORBITALS

- Highest Occupied Molecular Orbital (HOMO)
- Lowest Unoccupied Molecular Orbital (LUMO)
- The HOMO and the LUMO are known as FRONTIER ORBITALS and these orbital are used to explain a lot of reaction mechanism, kinetic, structural and spectroscopic studies.

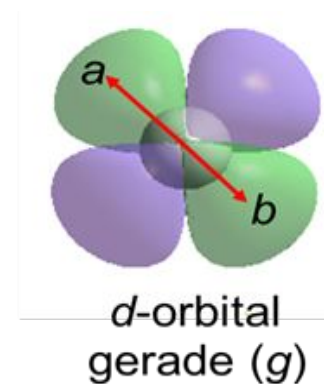
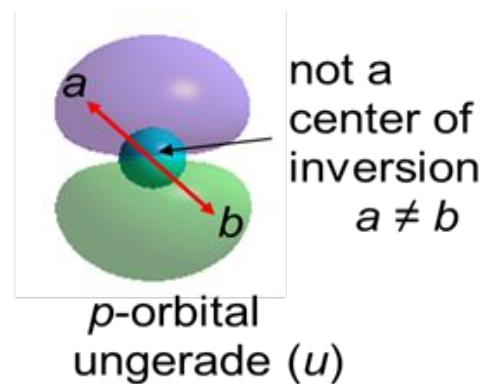
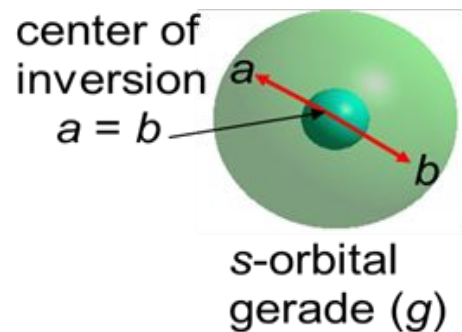
The HOMO for B_2 is $\pi_{2p_x}\pi_{2p_y}$ and its LUMO is σ_{2p_z}

The HOMO for F_2 is $\pi_{2p_x}^*\pi_{2p_y}^*$, and its LUMO is $\sigma_{2p_z}^*$

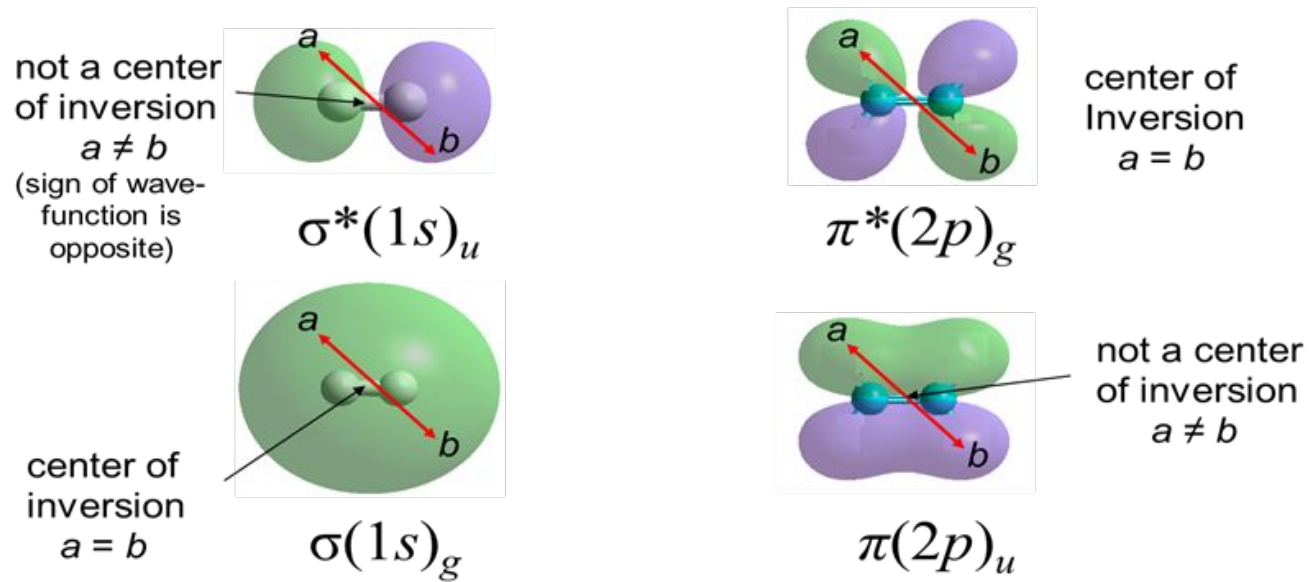
UNIT TWELVE

GERADE AND UNGERADE ORBITALS

- An orbital with a centre of symmetry (inversion) is called to gerade (g) and one that does not have one is called ungerade (u).
- A centre of inversion is a symmetry operation that involves starting at an arbitrary point in the molecule, travelling in a straight line to the centre of the molecule and then continuing an equal distance out on the other side of the centre.



According to the Laporte selection rules, electron will moving from $g \rightarrow u$ and $u \rightarrow g$ are allowed, but $g \rightarrow g$ and $u \rightarrow u$ are forbidden. An orbital is g if it has a center of inversion, and u if it does not.

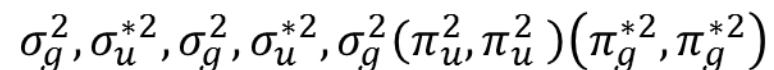


The following little table will help you to label molecular orbitals as g or u . For σ -overlap, the bonding orbitals are g , while the antibonding orbitals are u , while for π -overlap the opposite is true:

	bonding MO	anti-bonding MO
σ-bonding	g	u
π-bonding	u	g

Below is the molecular electronic configuration of F_2 , $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_z}^2, (\pi_{2p_x}^2, \pi_{2p_y}^2), (\pi_{2p_x}^{*2}, \pi_{2p_y}^{*2})$

To **rewrite this based on symmetry** would become



UNIT

THIRTEEN

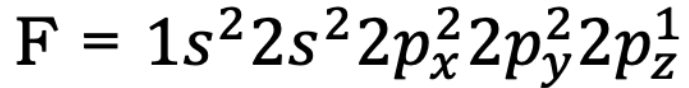
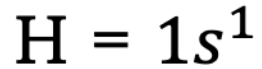
HETERONUCLEAR DIATOMIC MOLECULE (HF, LiF, CO, NO etc)

- These molecules are made of 2 atoms of different elements and because of these differences, their contribution to the formation of the molecular orbital would not be the same.
- This is unlike the case of homonuclear diatomic molecule whose contribution to the molecular orbital is the same.
- The differences arise as a result of the difference in electronegativity.

Drawing the molecular orbital diagram of heteronuclear diatomic molecules

- Place the more electronegative atom on a lower level, while the less electronegative atom is placed on a higher level. The larger the electronegativity difference the wider this gap between the combining species.
- In drawing the MO diagram, the more electronegative atom has the BMO closer to it while the less electronegative atom has the AMO closer to it.
- Only orbitals of similar energy and symmetry would overlap to produce MO.
- Because this time when an s atomic orbital would overlap with a p_z orbital to produce a sigma MO the labeling of the MO of heteronuclear diatomic molecules is 1σ , 2σ , 3σ etc or 1π , 2π etc

HF



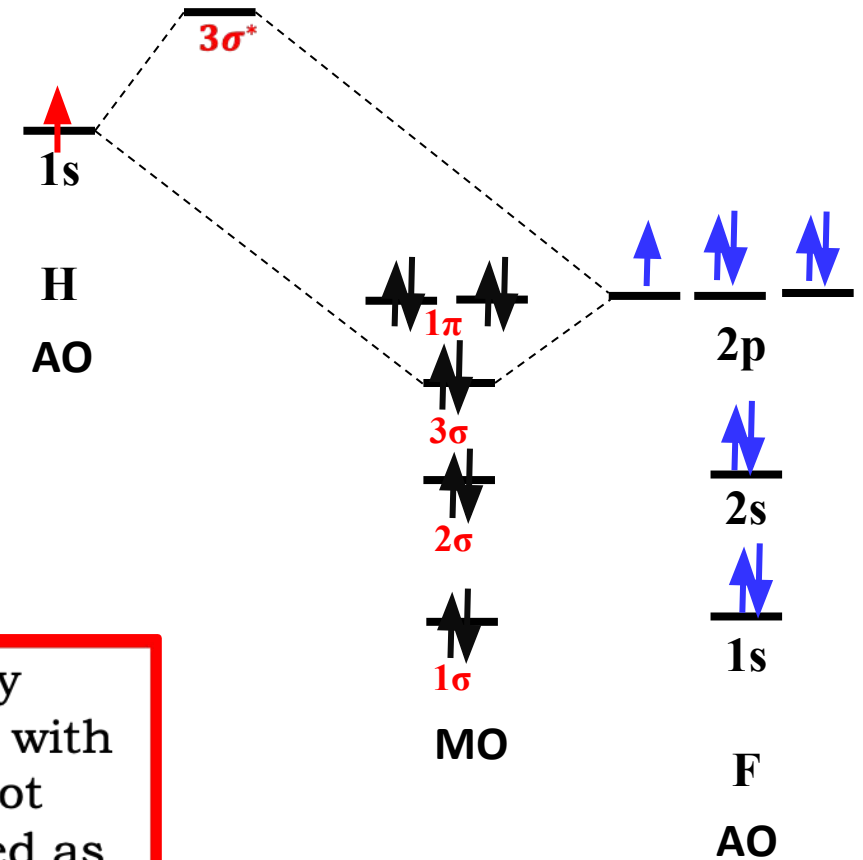
Total number of electrons $1+9 = 10$

Total number of atomic orbitals involved = 6

Therefore, total number of molecular orbitals = 6

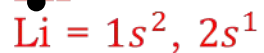
Because of wide energy difference between the $1s(\text{F})$ and $2s(\text{F})$ they cannot overlap with $1s(\text{H})$ and are therefore NMOs. $1s(\text{H})$ overlaps with $2p_z(\text{F})$ to yield the 3σ (BMO) and $3\sigma^*$ (AMO). The $2p_x$ and $2p_y$ did not overlap with any orbital and because of their symmetry are labelled as 1π , these are also NMO.

NOTE: The number 1, 2, 3 is just serial labelling of the MO as they occurred.



The Molecular electronic configuration of HF is $1\sigma^2, 2\sigma^2, 3\sigma^2, 1\pi^4$

LiF



Total number of valence electron $3+9 = 12$

Total number of atomic orbitals involved = 7

Therefore, total number of molecular orbitals = 7

Because the difference in energy between the 1s of Li and 1s of F is very large, they do not overlap and therefore ignored.

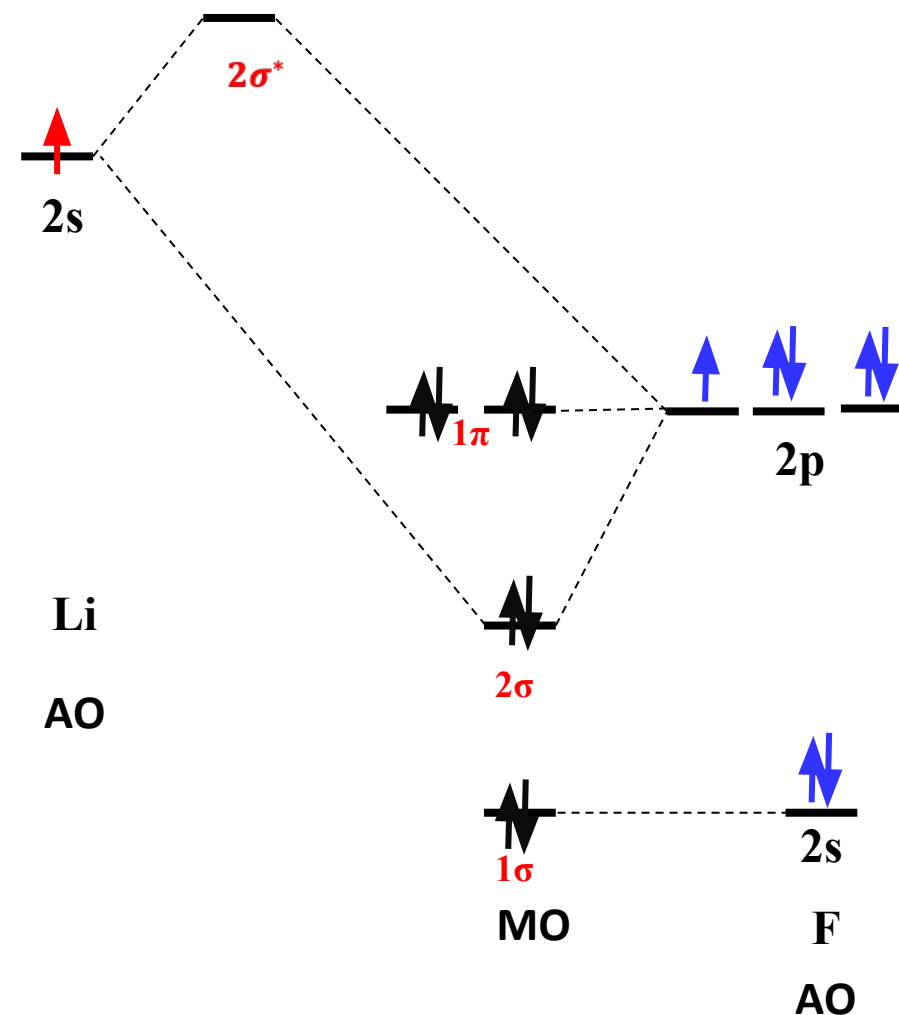
Total number of valence electron $1+7 = 8$

Total number of atomic orbitals involved = 5

Therefore, total number of molecular orbitals = 5

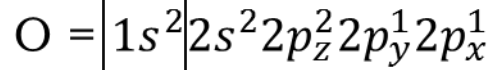
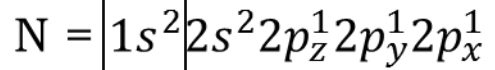
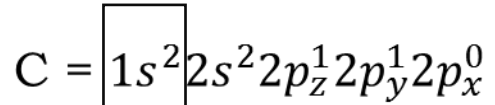
It is for the same reason the 2s orbitals do not overlap. For $2s(\text{Li}) = -5.5$ eV and for $2s(\text{F}) = -48.5$ eV. However the $2s(\text{Li})$ overlaps with the $2p(\text{F})$ because it is relatively closer in energy ($2p(\text{F}) = -21.6$ eV). The wide difference in energy accounts for the ionic nature of the LiF bond.

(Energy of $1s(\text{H}) = 13.6$ eV is much closer to that of the $2p(\text{F}) = 21.6$ eV).



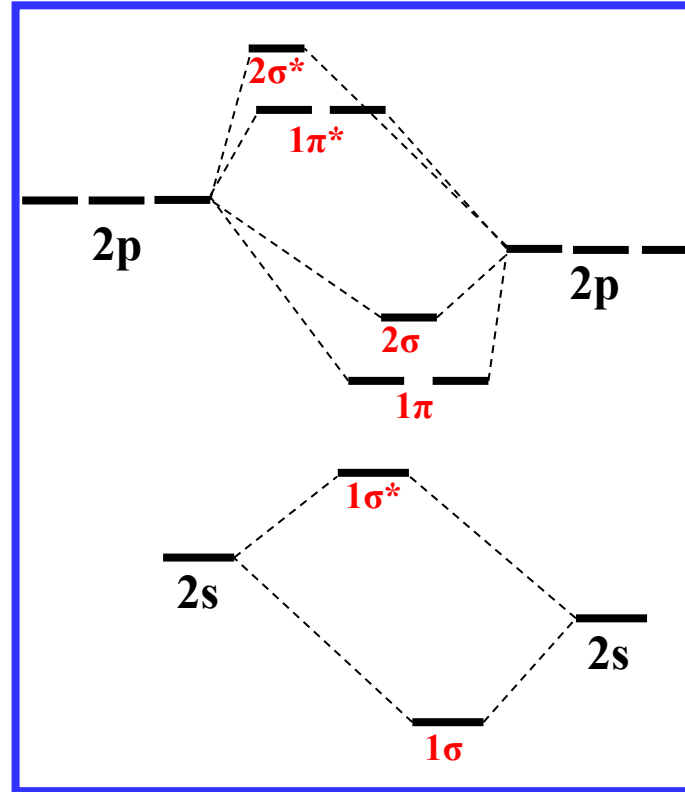
The Molecular electronic configuration of LiF is $1\sigma^2, 2\sigma^2, 1\pi^4$

NO, CN⁻, CO

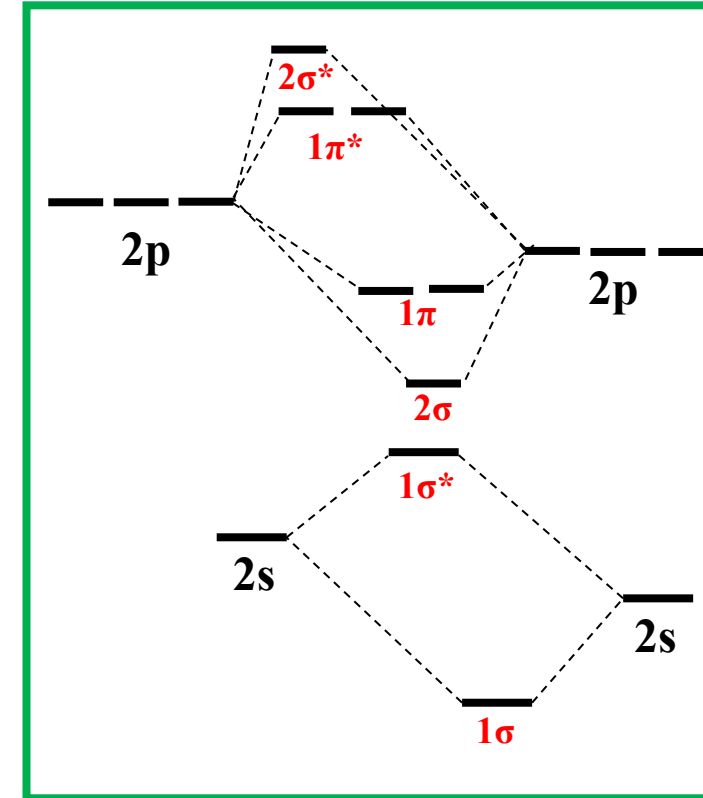


Just as with LiF we are going to ignore the 1s orbitals cos their energies are very low and not really involved directly in bonding.

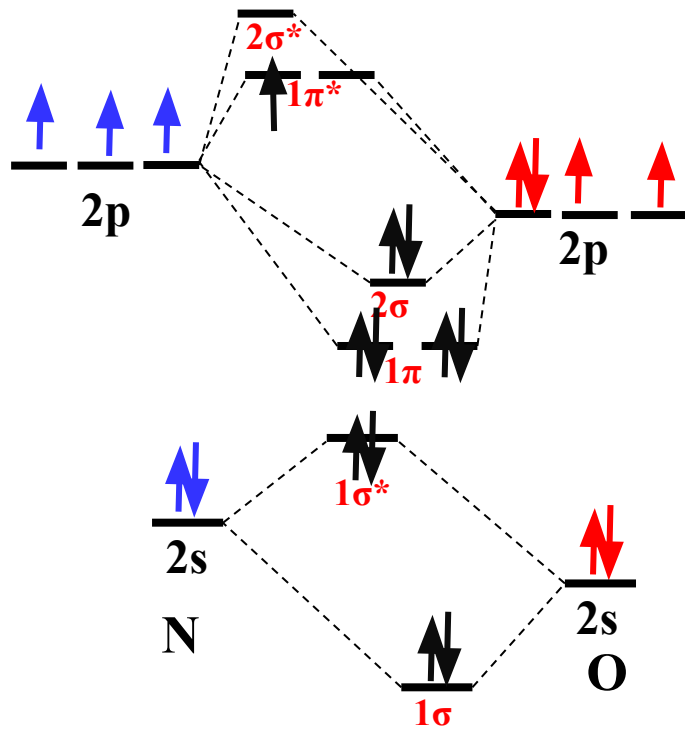
There are two possible order of arrangement of the molecular orbitals of the species, A or B.



A

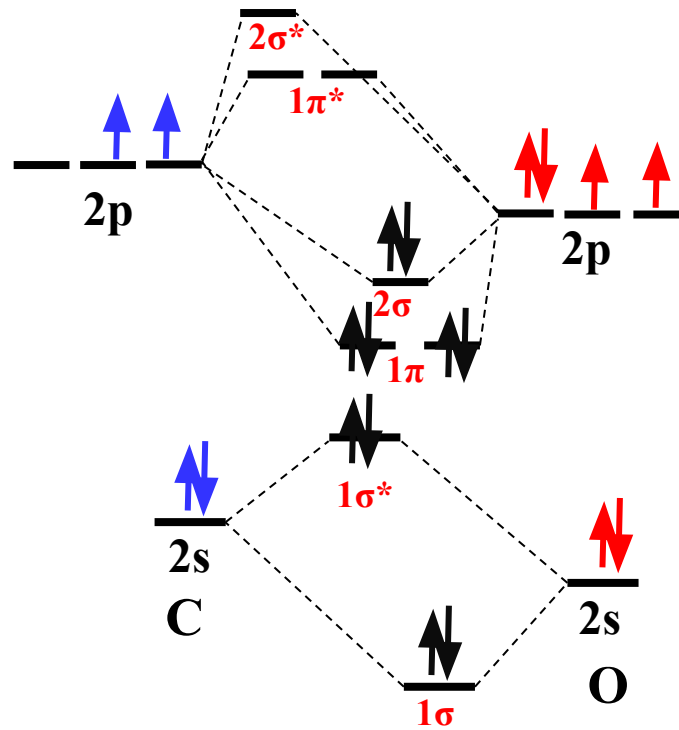


B



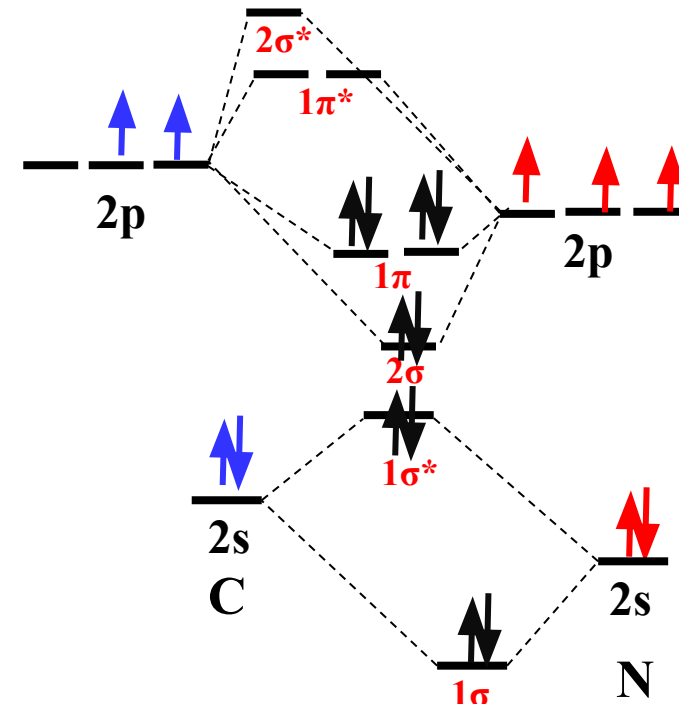
NO

Total number of electrons (excluding the 1s electrons) = 11



CO

Total number of electrons (excluding the 1s electrons) = 10



CN⁻

Total number of electrons (excluding the 1s electrons) = 10

The pattern observed is due to the 2s (O) and 2p(O) are wide apart in energy compared to those of N and C, causing energy of the π -MOs to be lowered and the 2σ -MO raised.

MODULE ONE

BOND THEORY

UNIT ONE - INTRODUCTION

A chemical bond is the force of attraction between atoms, ions or molecules that keeps them together to form molecules, crystals, solid or liquid states. Chemical bonds are formed by the transfer or sharing of electrons or being surrounded by an electron cloud.

- Molecules are formed from covalent bond between atoms (H_2O , BF_3).
- Crystals are formed from ionic bond between ions (salts like NaCl , KNO_3).
- Solid or liquid states are formed by bonds between ions (salts), atoms (metal atoms), or molecules (water).

Types of Bonds

PRIMARY BONDS

- Ionic
- Covalent
- Coordinate covalent bond (dative bond)
- Metallic bond

SECONDARY BONDS

- Hydrogen bond
- Dipole –dipole interactions
- Van der Waals forces

There are 3 theories used to explain bonding

- Valence Shell Electron Pair Repulsion (VSEPR) Theory
- Valence Bond Theory (VBT)
- Molecular Orbital Theory (MOT)

UNIT TWO - VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) MODEL (INTRO)

This model is based on the fact the valence shell holds the electrons that are usually involved in bonding. A stable compound is formed when the valence shell of the atoms involved in bonding have 8 electrons each. It is said to have a complete octet. This excludes H and He, as these would only require 2 electrons in their valence shell to attain stability. These electron pairs experience electrostatic repulsion thus would stay far away from each other as possible, resulting a definite geometric arrangement of these electrons around the central atom, which in turn causes the molecule to adopt a specific shape.

The valence electrons in a molecule would experience 3 types of repulsion: - lone pair-lone pair repulsion, lone pair-bond pair repulsion, bond pair-bond pair repulsion. Lone pair (lp) are 2 electrons that are not involved in bonding and bond pair (bp) are those involved in bonding. In the order of increasing strength of repulsion $bp-bp < lp-bp < lp-lp$. This means that $lp-lp$ is the strongest and $bp-bp$ is the weakest.

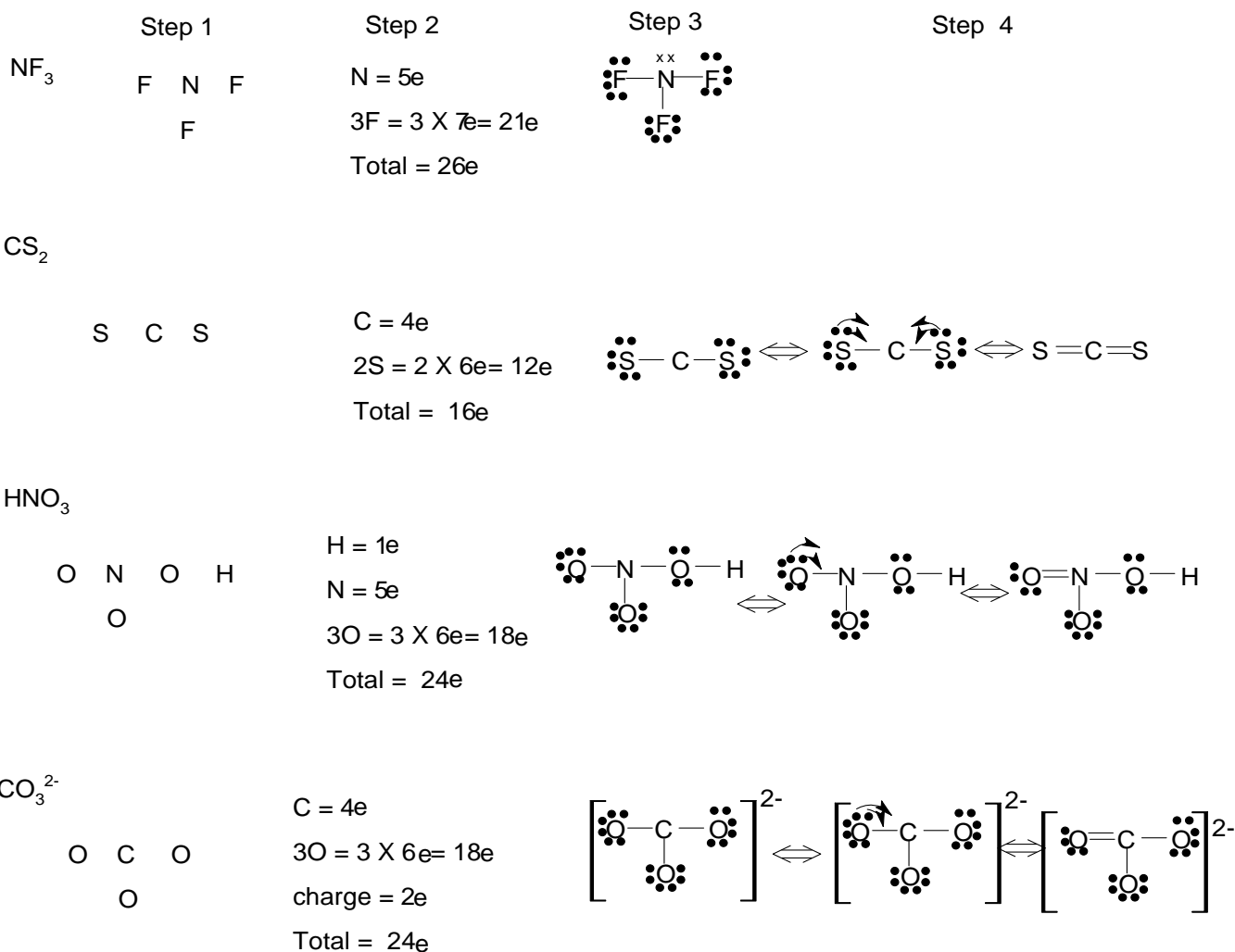
LEWIS STRUCTURE

This is a diagram that shows the bonding between atoms of a molecule as well as any lone pairs of electrons that may exist in the molecule. Single covalent bond has 2 electrons, double bond has 4 electrons, triple bond has 6 electrons.

By drawing Lewis structure, you can predict the number of bond pairs and lone pairs present in a molecule.

Writing Lewis Structure

1. Write the skeletal structure of the compound, using chemical symbols and placing bonding atoms next to one another.
2. Count the total number of valence electrons present
 - a) For polyatomic anions e.g. CO_3^{2-} add the additional number electrons responsible for the charges
 - b) For polyatomic cations e.g. NH_4^+ remove the number of electrons responsible positively charge.
3. Draw a single covalent bond between the central atom and each of the surrounding atoms, show complete octet of the surrounding atoms, and add extra electrons to central atom as lone pair.
4. If after steps 1-3 the central atom has less than 8e, then add double bonds or triple bonds between the central atom and the surrounding atoms using lone pairs from the surrounding atoms to complete the octet of the central atom.



Formal Charge (*FC*):

This is the charge assigned to an atom in a molecule, assuming that electrons in the bond are shared equally irrespective of the relative electronegativity differences or type of bonding. By determining *FC* on each atom we can determine the distribution of electrons in the molecules or ions and then draw the most plausible Lewis structure.

Formal charge of an atom is the electrical charge difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in the Lewis Structure. To determine *FC*:

- (i) draw the Lewis structure
- (ii) assign all nonbonding electrons of an atom to that atom
- (iii) bonding electrons should be shared equally between sharing atoms.

For electrically neutral molecules has total formal charge of zero 0. For cations the sum of the formal charge must be equal to the positive charge and for anions it must be equal to the negative charge.

FC of a given atom is expressed as

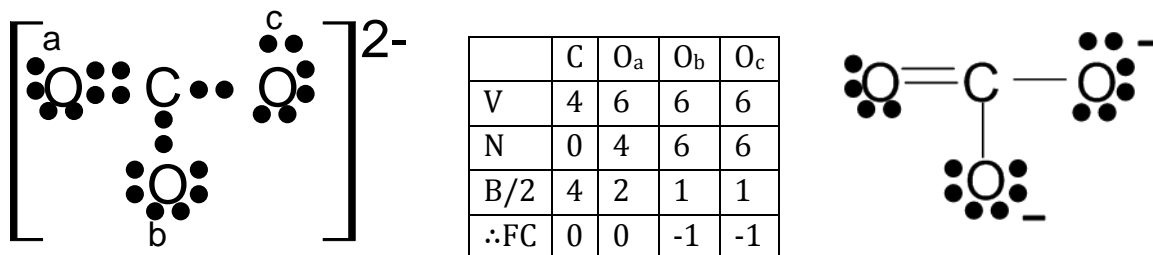
$$FC = V - N - \frac{B}{2}$$

V = is the number of valence electrons of the particular isolated atom.

N = is the number of nonbonding electrons of that same atom when in a molecule.

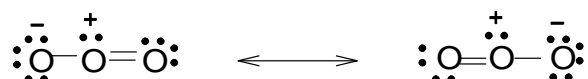
B = is the number of bonding electrons of the same atom when in a molecule.

Therefore for CO_3^{2-} its Lewis structure is



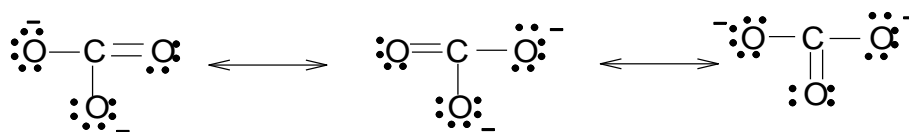
Resonance

The Lewis structure of O_3 can be represented in 2 ways which are equivalent



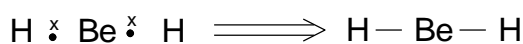
If any of these are the true structure of O_3 then the bond length of the double bond would be shorter than the bond length of the single bond. However experimental results have shown that these oxygen-to-oxygen bond lengths are equal. The structures above are not absolutely true and are called Resonance structures.

Resonance structures are two or more Lewis structures for a single molecule that cannot be represented accurately by only one single Lewis structure. Similarly CO_3^{2-} has 3 resonance structures.

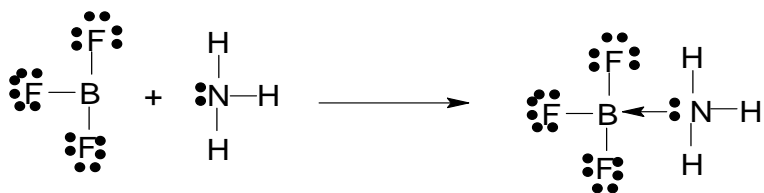


Exception to the Octet Rule

1. Incomplete octet: This occurs when the central atom of a stable compound has less than 8 electrons. Examples are Beryllium, Boron and Aluminium.

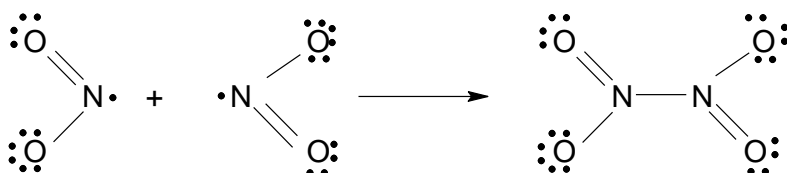


Because of the incomplete octet these class of compound can react with other compound that have lone pair via coordinate bonding.

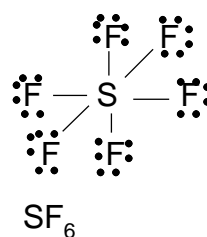
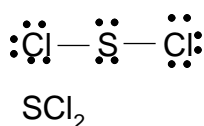


2. Odd Electron molecules: These molecules contain an odd number of electrons and therefore do not obey the octet rule e.g. NO (nitrogen(II) oxide) and NO₂ (nitrogen(IV) oxide).

Odd electron molecules are often called radicals, they are very reactive and have the tendency to form covalent bond with other unpaired electron on another molecule e.g. N₂O₄ dinitrogen tetraoxide.



3. The Expanded Octet: This occurs when the central atom of the molecule can take more than 8 electrons in its valence shell. Atoms in the second period cannot do this, only those in the 3rd and above periods of the periodic table. This is because they can make use of the d, f, ... orbitals as the case may be to form an expanded octet.



In selecting the most preferred Lewis structure, the follow serves as guide lines

- A Lewis structure where there is no formal charge on each atom is the preferred more than those with formal charges.
- Lewis structures with smaller formal charges on each atom are more preferable
- For Lewis structures that have the same total formal charge, the more preferable one is the one which the -ve formal charge is place on the more electronegative atoms.
- For central elements that can undergo expanded octet, the resonance structure where it obeys the octet rule is preferred even if the expanded octet has fewer formal charges.

Home work

1. Draw the Lewis structure of XeF_4
2. Write the Lewis structure of the following molecules and ions
 - (a) OF_2
 - (b) Si_2H_6
 - (c) CH_2ClOO^-
 - (d) CH_3NH_3^+
3. Write the Lewis structure and show formal charges of the following
 - (a) O_2^{2-}
 - (b) C_2^{2-}
 - (c) NO^+
4. Draw 3 resonance structures of the chlorate ions ClO_3^-
5. Draw the Lewis structure(s) of H_2SO_4 , which would be the preferred structure?

UNIT THREE – MOLECULAR GEOMETRY BASED ON VSPER THEORY

The molecular geometry of a molecule has an important influence on its physical and chemical properties such as melting point, boiling point as well as its reactivity. Molecular geometry is a 3-d arrangement of atoms in a molecule.

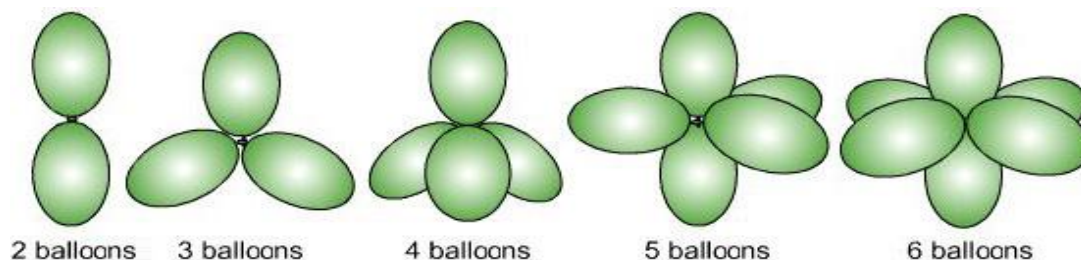
We shall consider 2 cases:

Case I: Molecules in which the central atom has no lone pair

Case II: Molecules in which the central atom has lone pair(s)

CASE I

Taking into consideration a molecule made up of 2 types of atoms A and B, where A is the central atom and B is the surrounding atoms so that the formula would be AB_x ($x = 1, 2, 3, \dots, 6$). The electrons only experience bond pair-bond pair repulsion. The balloons represent the shape the molecule would have when $x = 2, 3, 4, 5$ and 6.



2 Balloons give a **linear** geometry

3 Balloons give a **trigonal planar** geometry

4 Balloons give a **tetrahedral** geometry

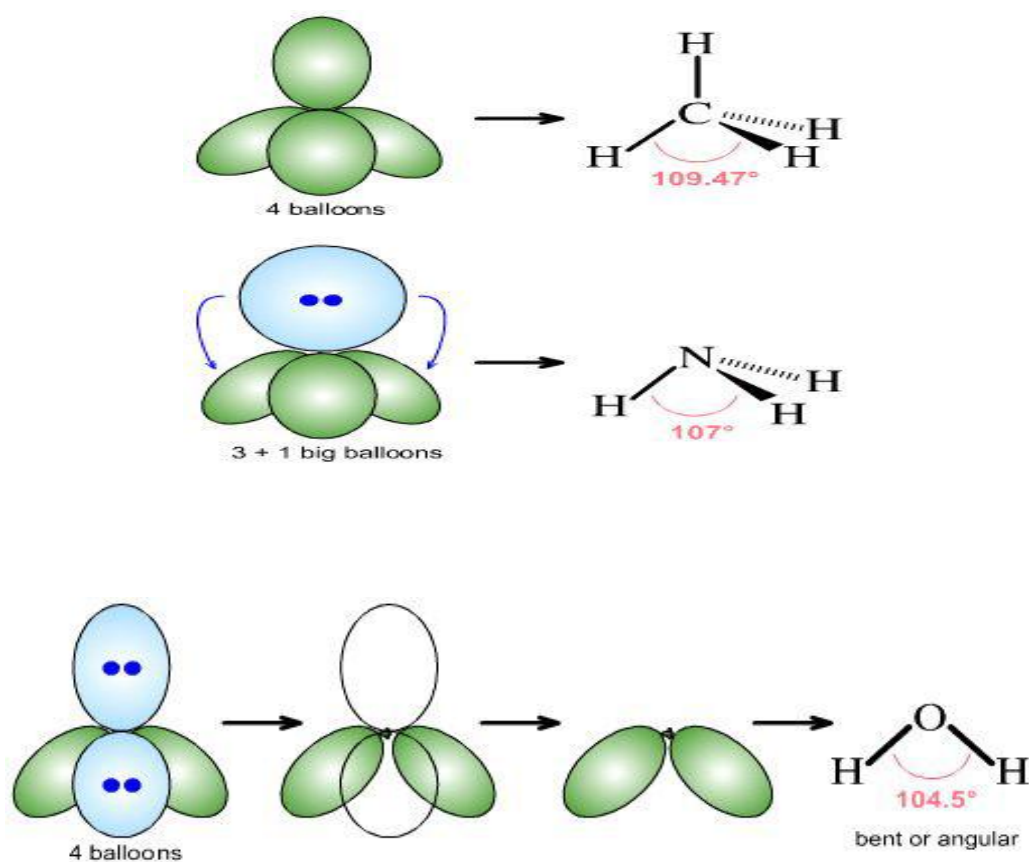
5 Balloons give a **trigonal bipyramid** geometry

6 Balloons give an **octahedral** geometry

X	No of Electron Pair	Formula	Bond Angles	Molecular Geometry	Examples
2	2	AB ₂	180°	Linear	BeCl ₂ , HgCl ₂
3	3	AB ₃	120°	Trigonal Planar	BF ₃
4	4	AB ₄	109.5°	Tetrahedral	CH ₄ , NH ₄ ⁺
5	5	AB ₅	a = 120° b = 90°	Trigonal bipyramid	PCl ₅
6	6	AB ₆	a = 90° b = 90°	Octahedral	SF ₆

CASE II

The valence electrons in this molecule would experience 3 types of repulsion: - lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion. The formula in this case is **AX_pE_q**. A = central atom, X = surrounding atoms and E = lone pair. **p** = no of bond pair, **q** = no of lone pair.



p	q	TEP	AE	Formula	Molecular Geometry	Examples
2	1	3	Trigonal planar	$\ddot{A}B_2$	Bent or Angular	SO ₂
3	1	4	Tetrahedral	$\ddot{A}B_3$	Trigonal pyramidal	NH ₃
2	2	4	Tetrahedral	$\ddot{A}B_2$	Bent or Angular	H ₂ O
4	1	5	Trigonal bipyramid	$\ddot{A}B_4$	Sawhorse or Seesaw	SF ₄
3	2	5	Trigonal bipyramid	$\ddot{A}B_3$	T-shape	ClF ₃
2	3	5	Trigonal bipyramid	$\ddot{A}B_2$	Linear	I ₃ ⁻
5	1	6	Octahedral	$\ddot{A}B_5$	Square pyramidal	BrF ₅
4	2	6	Octahedral	$\ddot{A}B_4$	Square planar	XeF ₄
3	3	6	Octahedral	$\ddot{A}B_3$	T-shape	
2	4	6	Octahedral	$\ddot{A}B_2$	Linear	

TEP = Total no of electron pairs

AE = Arrangement of electrons (Electronic geometry)

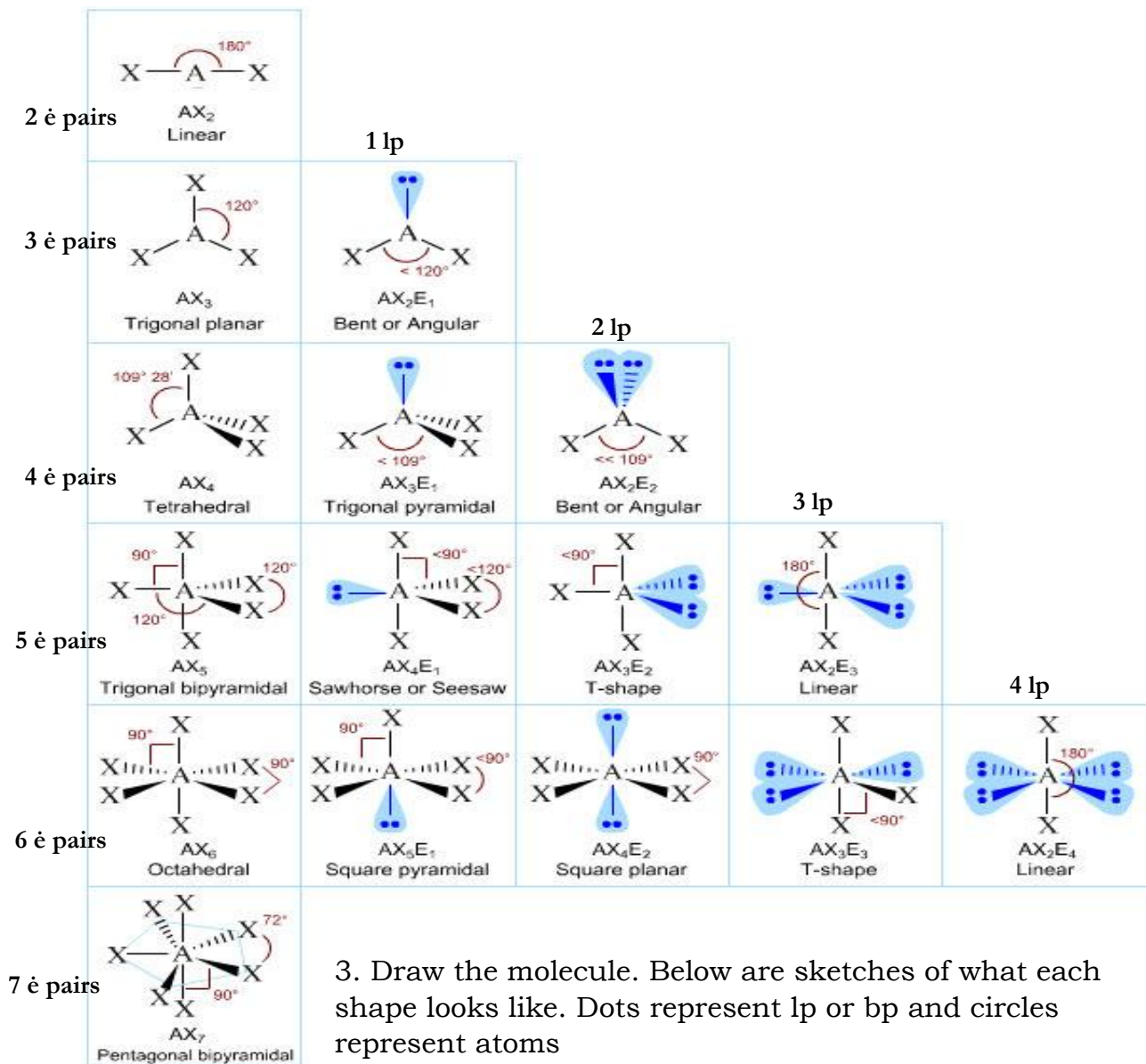
PREDICTING SHAPE

Guide lines for applying VSEPR model

1. Write the Lewis structure of the molecules considering the electron pair around the central atom of the molecule.
2. Count the number of electron pairs around the central atom (bonding pairs and lone pairs). Treat double bonds and triple bonds as though they are single bonds

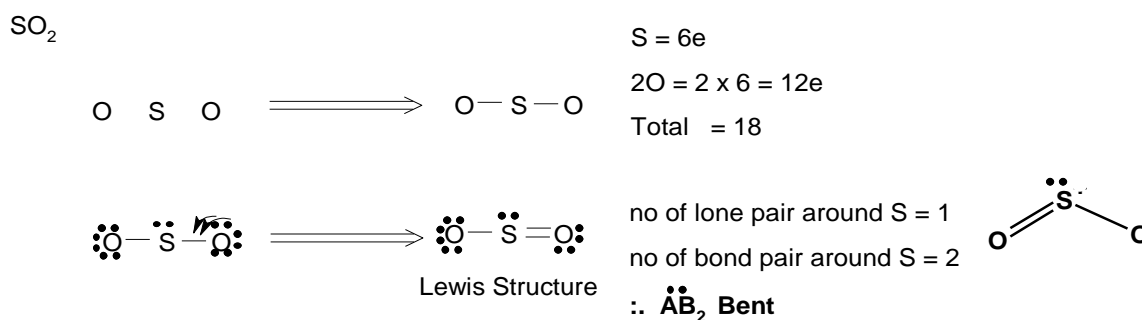
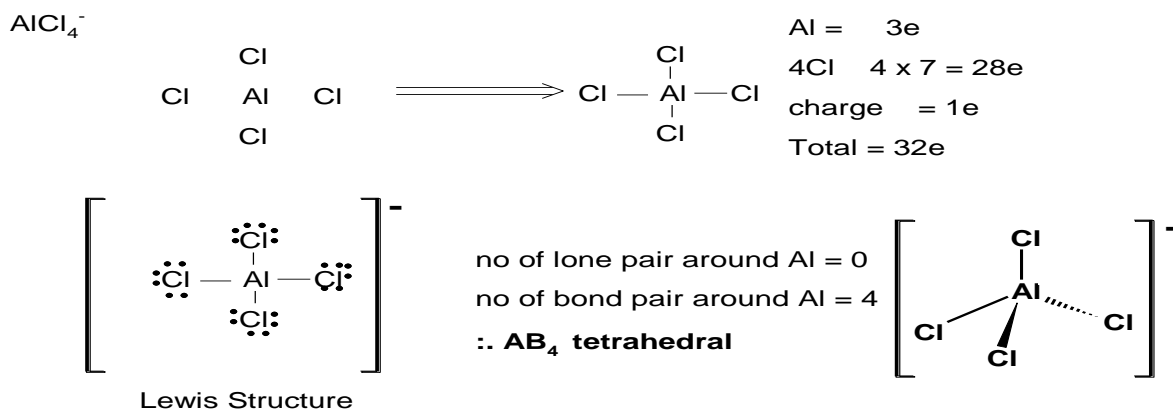
Below is a summary of all of possible molecular geometries and their corresponding names, use it to predict the geometry noting where there might be lone pairs or not

No lone pairs (lp)



3. Draw the molecule. Below are sketches of what each shape looks like. Dots represent lp or bp and circles represent atoms

number and arrangement of electron pairs	molecular shapes	number and arrangement of electron pairs	molecular shapes
2 linear	linear	5 trigonal bipyramidal	trigonal bipyramidal, seesaw, T-shaped
3 trigonal planar	trigonal planar, angular	6 octahedral	octahedral, square pyramidal, square planar
4 tetrahedral	tetrahedral, trigonal pyramidal, angular		



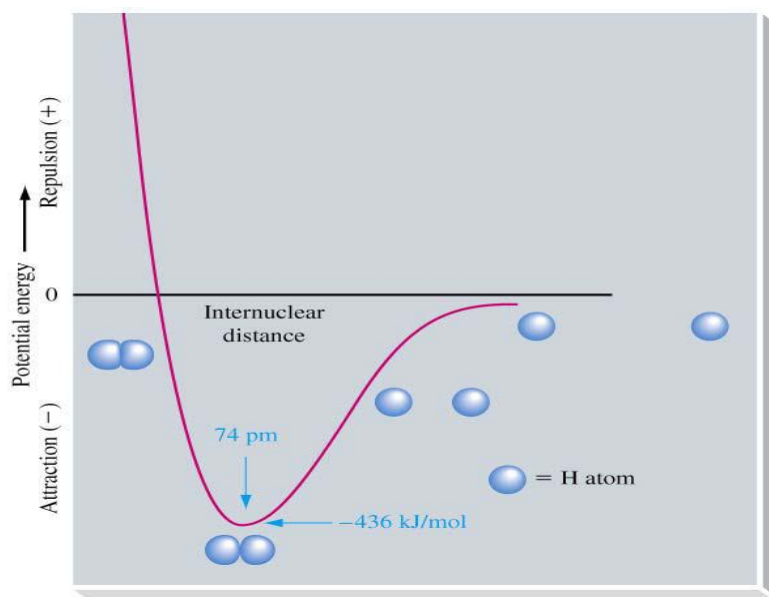
Home Work

Sketch the shape of the following compounds

- | | |
|------------------|-------------------------|
| a. BF_3 | e. XeF_4 |
| b. CH_4 | f. XeF_5 |
| c. SF_6 | g. XeF_2 |
| d. SF_4 | h. H_2O |

UNIT FOUR - VALENCE BOND (VB) THEORY (INTRO)

This theory is based on quantum mechanics; it describes the electronic structure of molecules as well as covalent bond formation. The theory assumes that electrons occupy atomic orbitals of individual atoms within a molecule, and that the electrons of one atom are attracted to the nucleus of another atom. This attraction increases as the atoms approach one another until the atoms reach a minimum distance where the electron density begins to cause repulsion between the two atoms. This electron density at the minimum distance between the two atoms is where the lowest potential energy is acquired, and it can be considered to be what holds the two atoms together in a chemical bond (see picture below).



Potential energy diagram of the bonding of 2 H-atoms.

BONDING

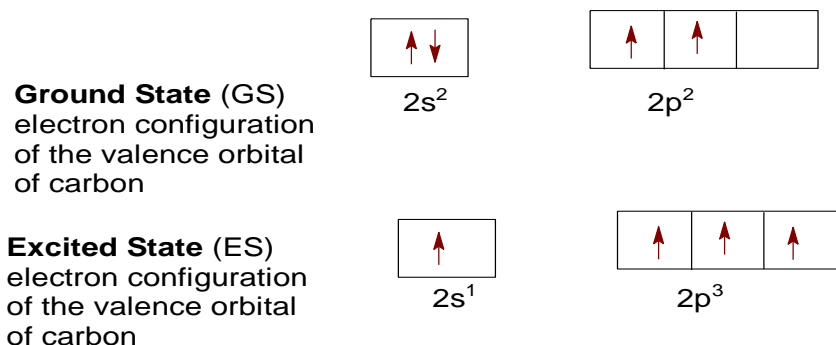
Before bonds are formed the atomic orbitals would undergo hybridization. Hybridization is an imaginary mixing of process that converts a set of atomic orbital to a new set of hybrid orbitals.

The atomic orbital involved are in phase and so amplitude increase hence the probability of finding an electron also increases. It is the overlapping of the orbitals that result in bonding. Strong bonds are due to greater overlapping. As set of overlapping orbitals can only contain a maximum of 2 electrons of opposite spin.

VSEPR theory	VB theory
Based on Lewis structures	Based on quantum mechanics
Covalent bond are formed by sharing electrons	Covalent bonds are formed by overlapping of atomic orbitals
The atomic orbitals are the same in the molecules. Pure orbitals	The valence atomic orbitals in a molecule are <i>different</i> from those in isolated atoms. Hybrid orbitals
Cannot explain differences in bond length (BL) and bond energy (BE) between in different molecules.	Can explain differences in bond length and bond energy can be explained. H-H BE 436.4kJ/mol, BL 74 pm; F-F BE 150 kJ/mol, BL 142 pm.
Assumes that bonds in all molecules are the same as it does not distinguish between sigma bonds and pi bonds	Can distinguish between sigma bonds and pi bonds.

Limitations of VSEPR Theory

Using methane (CH_4) as an example



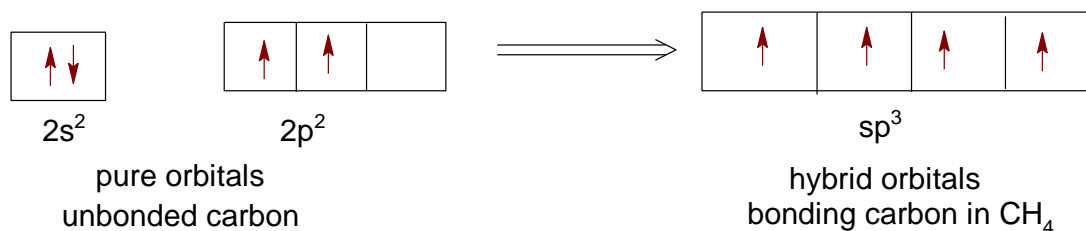
If one of the 2s electron is promoted to the empty 2p orbital (energetically excited as illustrated above) there would four unpaired electrons for bonding however this does not solve the problem as the 3-2p orbitals would be 90° to each other (p-orbitals are 90° to each other) but the bond angles in CH_4 are 109.5° VB theory is able to explain this phenomena using hybrid orbitals.

UNIT FIVE - HYBRIDIZATION

We can define hybrid orbitals as atomic orbitals obtained when two or more non-equivalent orbitals of the same atom combine in preparation for covalent bond formation. Hybridization is the mixing of atomic orbitals in an atom (usually the central atom) to generate a set of hybrid atomic orbitals. Hybridization is favourable because the energy lost during bond formation (exothermic) compensates for the energy required (absorbed) for hybridization (endothermic). The number of hybrid orbitals is equal to the number of pure atomic orbitals involved in the hybridization.

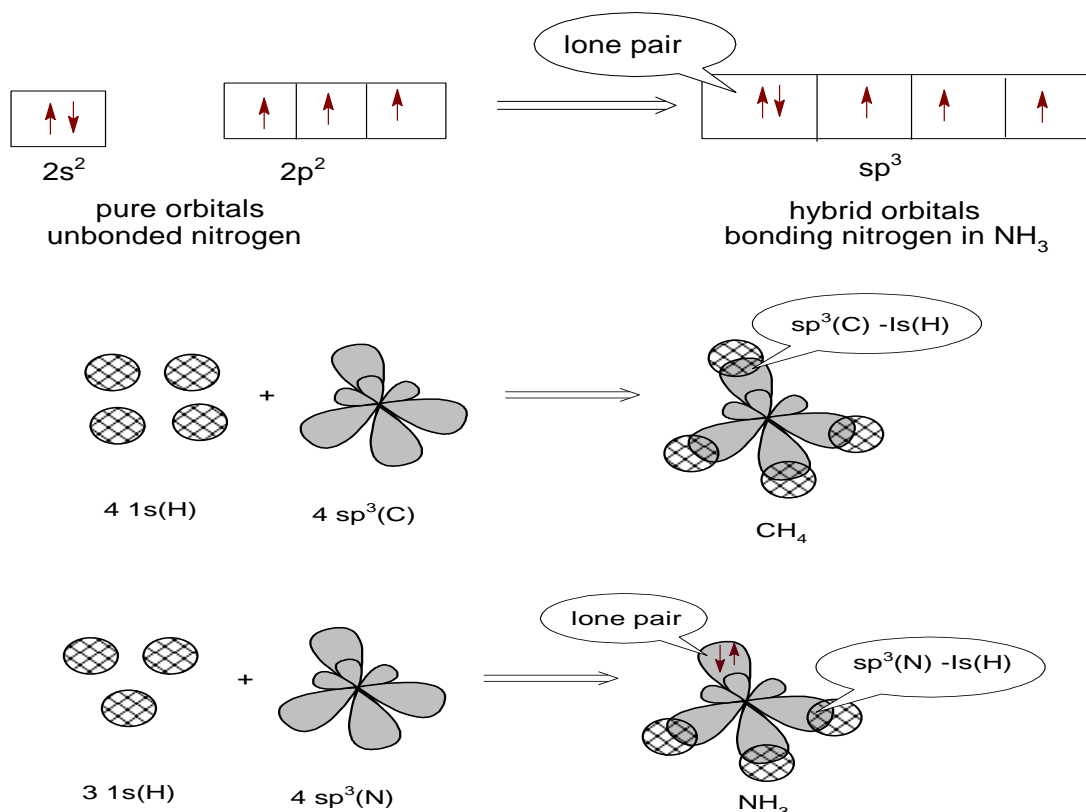
sp^3 Hybridization

In the case of CH_4 in order to for carbon to bond with 4-H atoms to form the stable compound, the 2s and 3-2p orbitals of carbon would mix to form a hybrid called sp^3 orbitals. They are four in number ($1-s + 3-p = 4 sp^3$), are form regular tetrahedral shape (no lone pair) as described in VSEPR model.



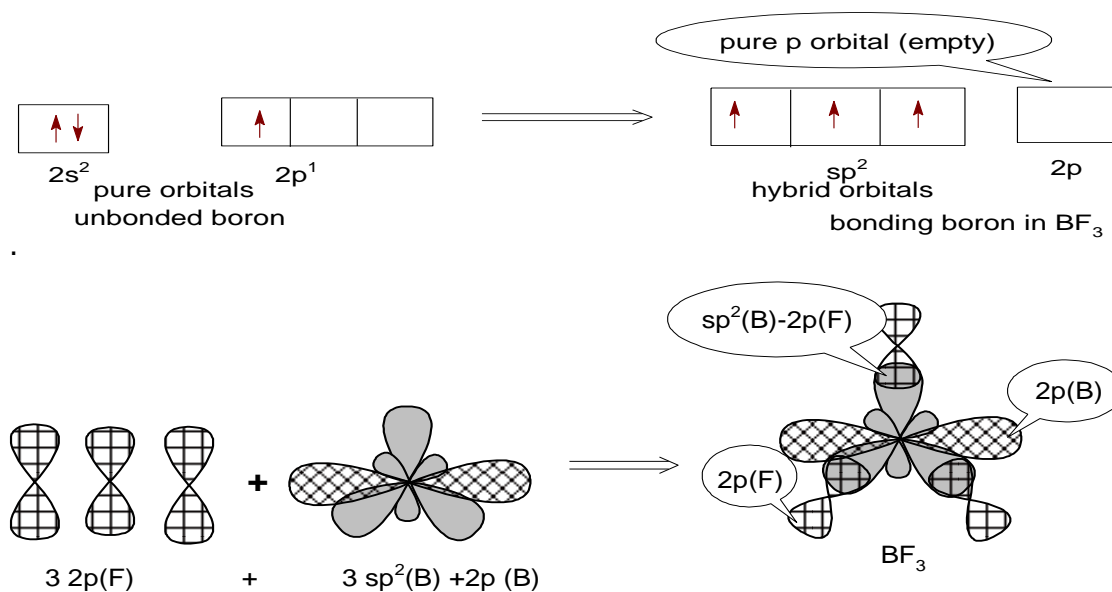
Use a blue pen to add the electrons from the surrounding atoms into the hybridized orbital for all the examples.

For NH_3 , the valence orbital of N is sp^3 hybridized but its bond angle is 107.3° because of the lone pair-bond pair repulsion effect therefore trigonal pyramidal in shape.



sp^2 Hybridization

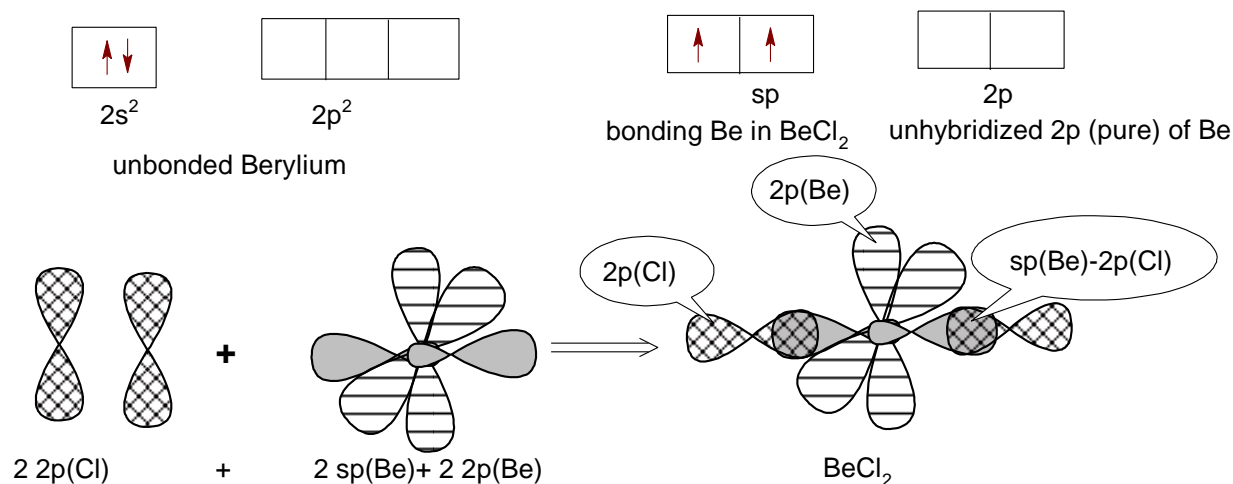
This is the mixing of a 1-s orbital with 2-p orbitals to form the hybrid sp^2 which are three orbitals in number ($1-s + 2-p = 3-\text{sp}^2$). In the absence of lone pair, the molecular geometry of such a molecule would be trigonal planar as in the case of BF_3 as each of sp^2 orbitals of Boron overlap with one 2p orbital of F.



The unhybridized empty 2p orbital of B is therefore available to accept lone pair (coordinate bonding).

sp hybridization

From the previous examples we can say that it involves the mixing of 1-s orbital with 1-p orbital, such that the total number of hybrid orbital is 2 with 2 empty pure p orbital ($1-s + 1-p = 2-sp$). The shape of such hybridization in the absence of lone pair of electrons is linear as in the case of BeCl_2 .



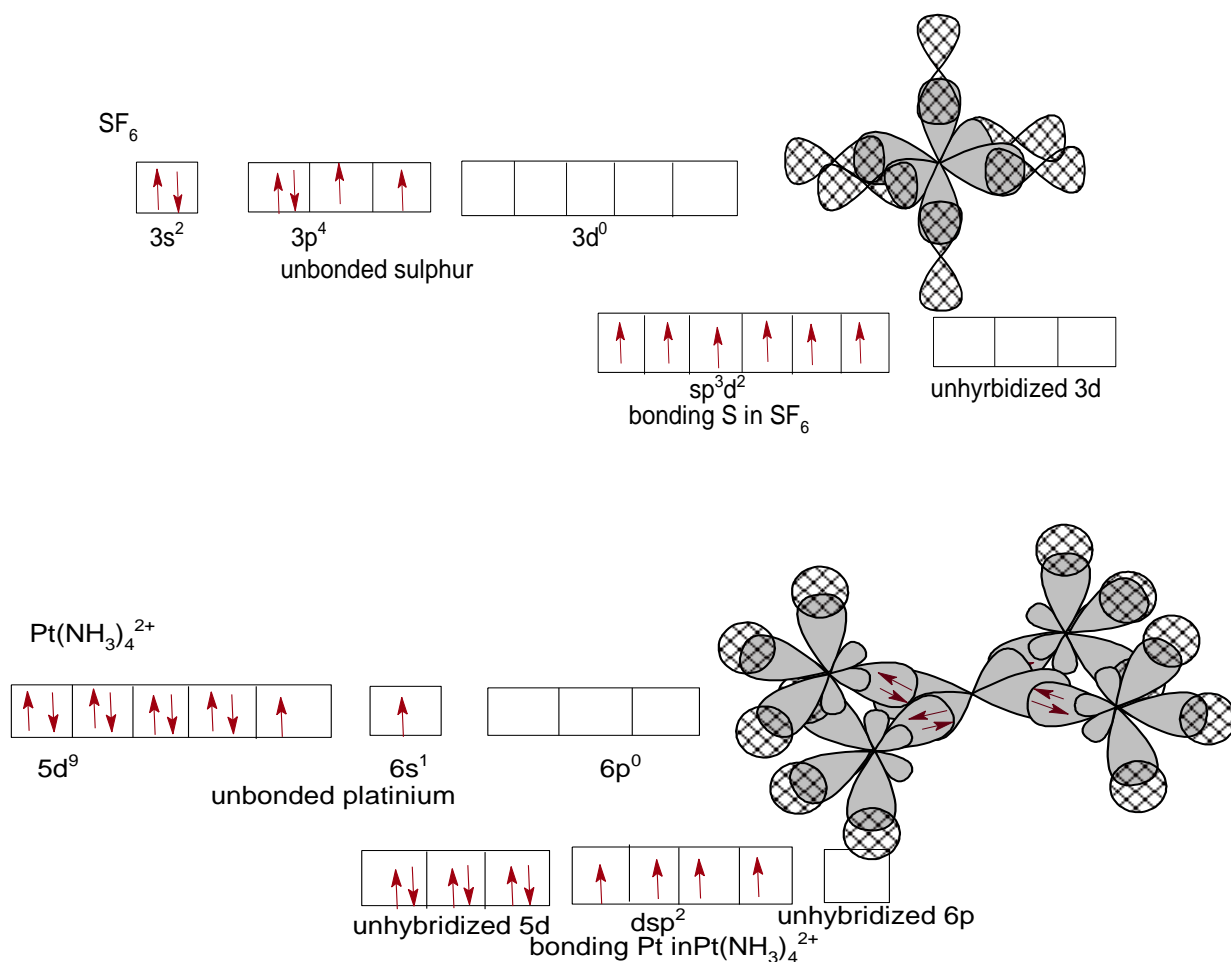
Hybridization involving s, p, and d orbitals

This type of hybrid orbitals account for the expand octet as in the case PCl_5 and SF_6 and in formation of complexes between a transition metal and ligands.

Below are some examples (in the absence of lone pairs) Note that if there are lone pairs then the shape would change.

Hybrid orbital	No of electron pairs	Shape	Not involved in hybridization	Examples
dsp^2	4	Square planar	4-d, 1-p	$\text{Pt}(\text{NH}_3)_4^{2+}$
d^2sp^3	6	Octahedral	3-d	$[\text{PtCl}_6]^{2-}$
sp^2d	4	Square planar	4-d, 1-p	-
sp^3d	5	Trigonal bipyramid	4-d	PCl_5
sp^3d^2	6	octahedral	3-d	SF_6
spd^3	5	Trigonal bipyramid	2-d, 2-p	-
sp^3d^3	7	Pentagonal bipyramid	2-d	IF_7

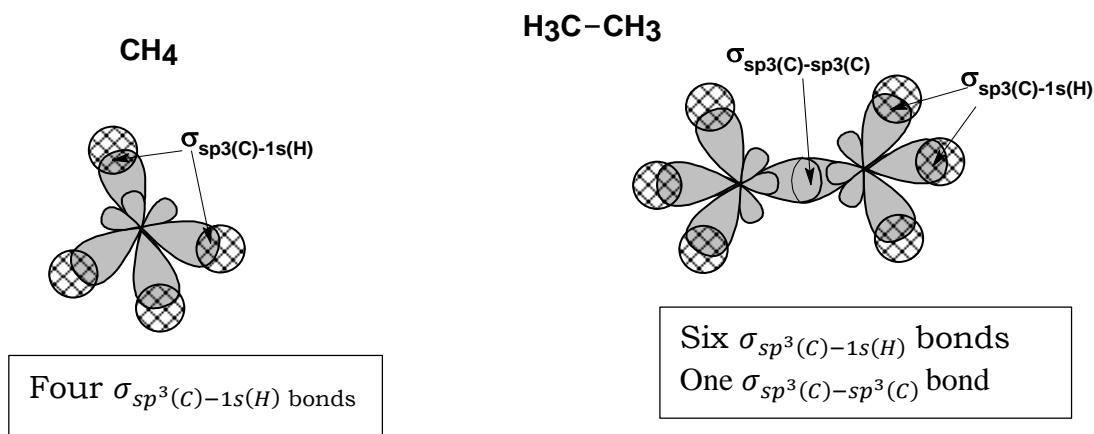
Transition metals make use of inner d orbital because they have low energy and are not completely filled (for this reason they form complexes) while main group element make use of outer d orbitals.

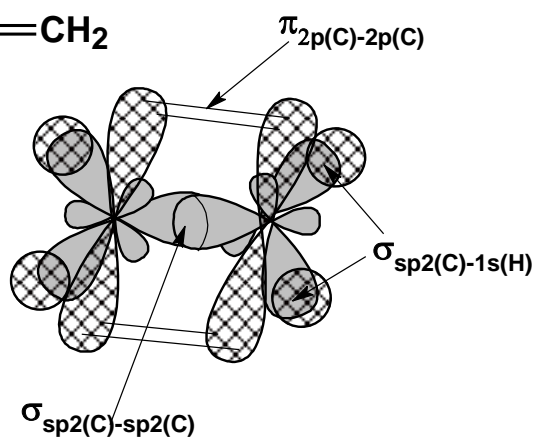
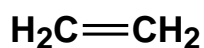


UNIT SIX –SIGMA AND PI BONDS

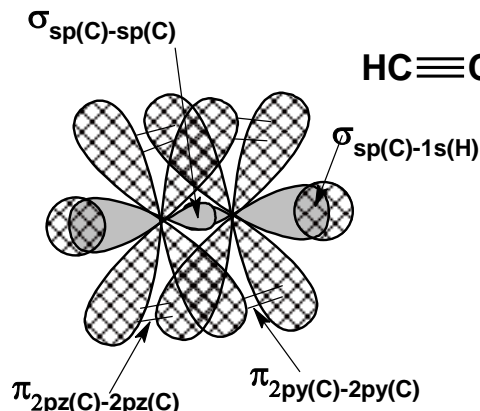
Under this theory there are two types of covalent bonds- sigma bond (σ bond) and pi bond (π bond).

- When atomic orbitals (hybridized or not) overlap horizontally they form sigma covalent bond (simply sigma bond, σ bond). This is described as end-to-end overlapping. All the bond described above are sigma bonds.
- When the atomic orbitals overlap vertically i.e. side-to-side they form pi covalent bonds (simply pi bonds π bond)





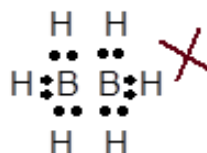
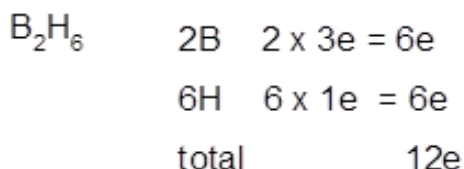
Four $\sigma_{sp^3(C)-1s(H)}$ bonds
 One $\sigma_{sp^3(C)-sp^3(C)}$ bonds
 One $\pi_{2p(C)-2p(C)}$ bond



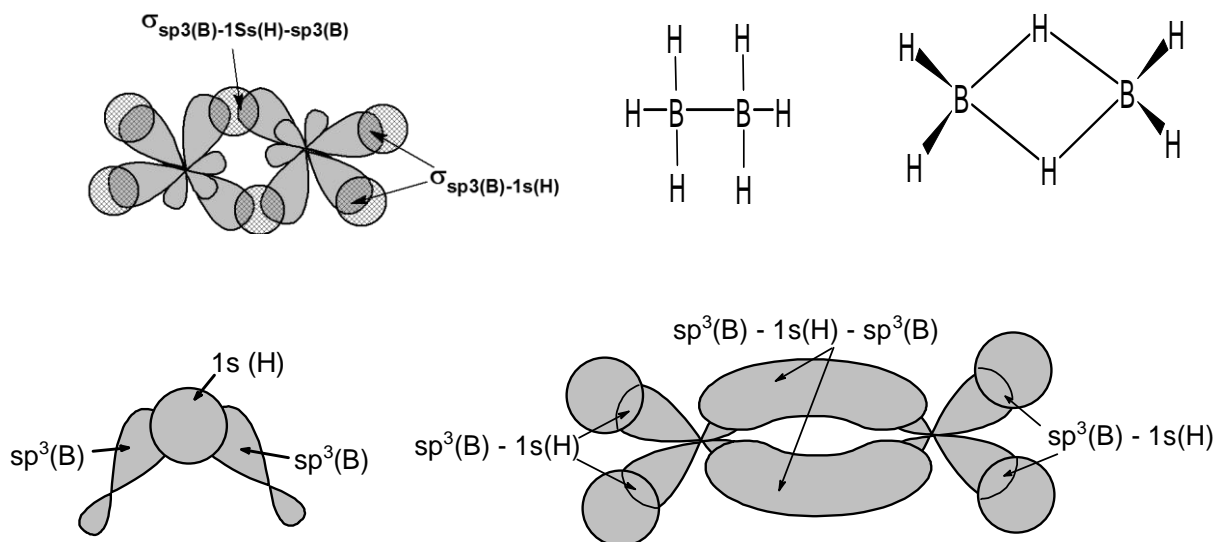
Two $\sigma_{sp^3(C)-1s(H)}$ bonds
 One $\sigma_{sp^3(C)-sp^3(C)}$ bonds
 Two $\pi_{2p(C)-2p(C)}$ bonds

Two-Electron, Three-Center Bonds

In this type of bonding, three atoms are bound by a single molecular orbital containing two electrons. This phenomenon occurs with molecules that have incomplete octet or are electron deficient. An example is diborane (B_2H_6), boron has 3 valence electrons and each hydrogen atom has one. Each boron atom therefore can form bonds with 3 hydrogen atoms. But after these bonds are formed there is no additional electrons to bond the two BH_3 together.

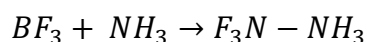
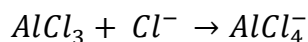


Experimental studies have shown that the formula of diborane is B_2H_6 and this structure has a total of 12 electrons. $2(\text{BH}_3)$ would need 14 electrons. In order to form this molecule, B is sp^3 hybridized and each B atom forms 2 regular sigma covalent bonds (B-H) with 1s orbitals of 2 H-atoms, resulting in $4\sigma_{sp^3(B)-1s(H)}$ bonds. The remaining 2 sp^3 orbital of each B share the remaining 2 H-atom, in such a way that 1 sp^3 orbital of one boron atom overlap with 1 hydrogen atom while another sp^3 orbital of the other boron overlaps the same hydrogen atom resulting a sigma bond B-H-B $\sigma_{sp^3(B)-1s(H)-sp^3(B)}$. Two sets of these are formed and each set accommodates a pair of electrons and forms a two-electron, three-center B-H-B Bridge between the two boron atoms.



Home Work.

1. What is the geometry of the following ions or molecules SnCl_5 , SeF_4 , CdCl_4^{2-} , SnI_2 ?
2. Draw and label the types of bonds formed in the molecule $\text{CH}_3\text{CCCH}_2\text{OH}$.
3. Describe the change in hybridization if any of Al atom and B atom in the following reactions.

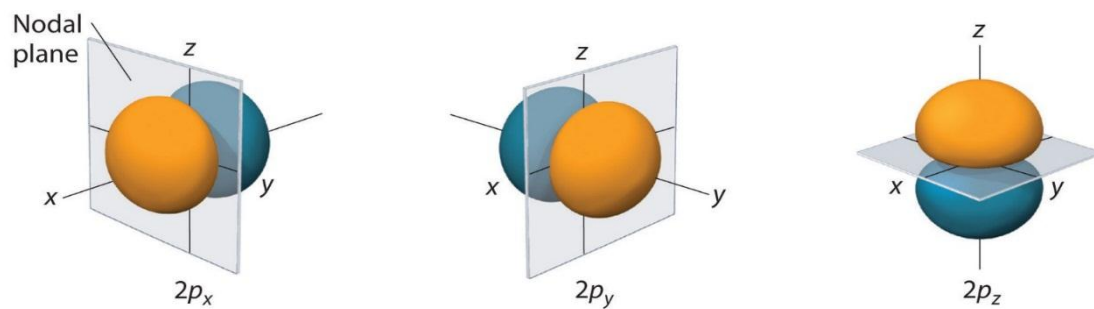
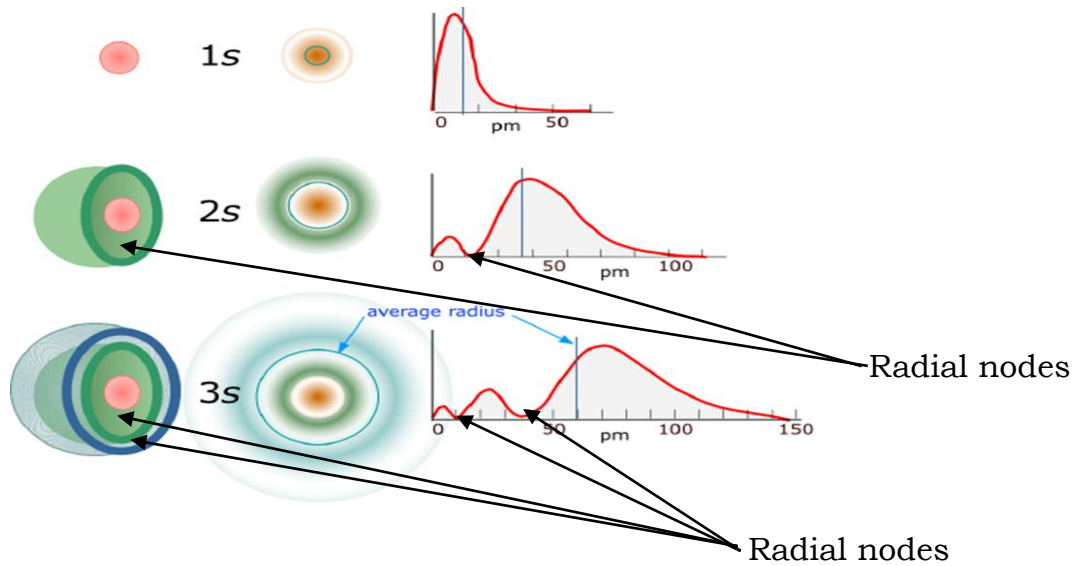


4. Determine the type of shape and hybridization that exist in the following
(a) XeF_2 (b) XeF_4 (c) XeF_6

UNIT SEVEN – MOLECULAR ORBITAL THEORY (INTRO)

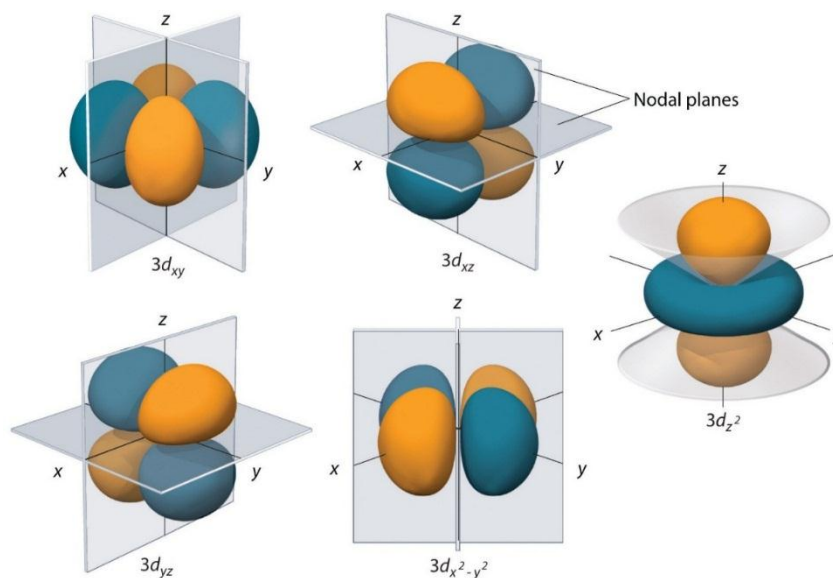
ATOMIC ORBITALS

This is the region of space where there is the probability of finding an electron. Depending on the shape of the orbital, the lobes are where the electrons reside. The region with an orbital where an electron cannot be found is the node. It could be radial or a plane. The s orbitals are spherical. The 1s orbital has no nodes but 2s and above have radial nodes. 2s has 1, and 3s has 2, ... 5s will have 4. The p-orbitals have dumbbell shapes and so have nodal planes.



Use the 3d orbitals

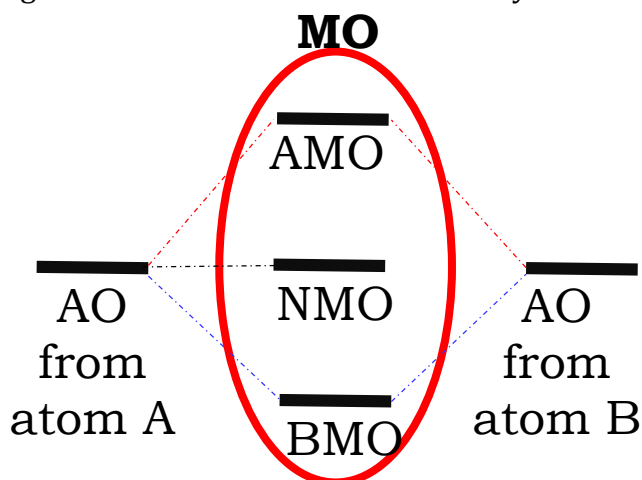
- The d_{xy} has its lobes in between the x and y axes and 2 nodal planes (xz and yz planes in line with the z -axis).
- d_{xz} has its lobes between the x and z axes and has 2 nodal planes (yz (in line with the z -axis) and xy planes).
- The d_{yz} has its lobes between y and z axes with 2 nodal planes (xz (in line with the z -axis) and xy planes).
- The $d_{x^2-y^2}$ orbital has its lobes on x and y axes and has 2 nodal planes (at 45° to these axes and in line with the z axis).
- d_{z^2} has no nodal plane because it is symmetrical around the z -axis. Its nodal region is cone shaped.



MOLECULAR ORBITAL THEORY

This theory is based on quantum mechanics and the images you see above are computer simulated, based on certain mathematical models. Instead of hybridization as in VBT, the interactions of atomic orbitals (AO) result in the formation of molecular orbitals (MO). In VBT, the overlapping of AOs are associated only with valence orbitals of the individual atoms, where as in MOT the interactions involves all the atomic orbitals. For there to be overlapping the atomic orbitals must have the same symmetry, align on same axis and be close in energy.

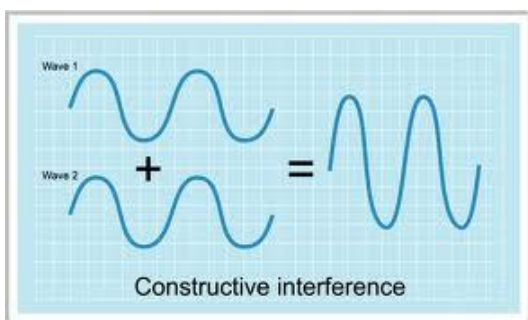
According to MO theory, when 1 AO overlaps with another 1 AO it creates two MO, one which is a bonding MO (BMO) and the other is an anti-bonding (AMO). Similarly, 3 AO + 3 AO = 6 MO (3 BMO and 3 AMO). BMOs have lower energy and therefore greater stability than its initial AOs from which it was formed while AMOs have higher energy and lower stability that its initial AOs from which it was formed. Non-bonding molecular orbitals (NMO) have the same energy as the AOs. These are orbitals that are present but did not overlap because one or more of the conditions listed above are not present. Therefore, an electron occupying an NMO does not affect the stability of the molecule.



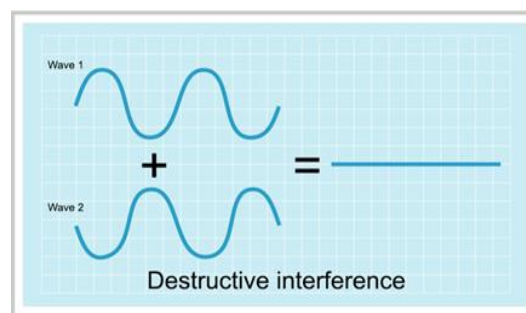
WAVE FUNCTION

In terms of wave function, the formation of BMO corresponds to constructive interferences of the wave function of each AO. This results in a new wave function of lower energy than those of the parent AOs and an increased probability of finding an electron in the MO.

$\begin{aligned}\psi_{AO} + \psi_{AO} &= \psi_{MO} \\ \psi_{AO} &> \psi_{MO}\end{aligned}$	$\begin{aligned}\psi_{AO} + \psi_{AO} &= \psi_{MO}^* \\ \psi_{AO} &< \psi_{MO}^*\end{aligned}$
--	--



In-phase resulting in increase amplitude



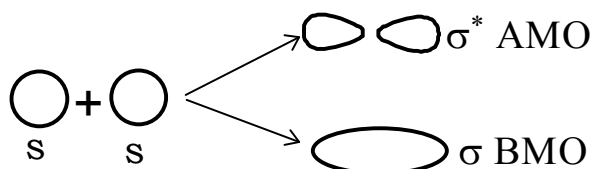
Out-of-phase resulting in decrease amplitude

While AMO is produced from destructive interaction of the wave function of each AO. This results in new wave function of higher energy than those of the AOs. with a decreased probability of finding an electron in the molecular orbital.

UNIT EIGHT – TYPES OF OVERLAPPINGS

OVERLAPPING OF TWO s-ORBITALS

These orbitals have spherical around the inter-nuclear axis and approach each other end-to-end. This interaction between any two s-orbitals produces σ MOs – sigma bonding (σ) and sigma antibonding molecular orbitals (σ^*). The BMO is symmetrical around the inter-nuclear axis. The inter-nuclear axis is an imaginary line joining the nucleus of the bonding atoms and it is take as the z-axis.



OVERLAPPING OF TWO p-ORBITALS

The p-orbitals, because of their dumbbell shape can overlap in two ways: horizontally or vertically. There 3-p orbitals, the p_x orbital lies on the x-axis, the p_y on the y-axis and the p_z on the z-axis. The p_x and the p_y overlap vertically (side-to-side) resulting in π -molecular orbital. While the overlapping of the p_z is end-to-end resulting in σ -molecular orbitals.

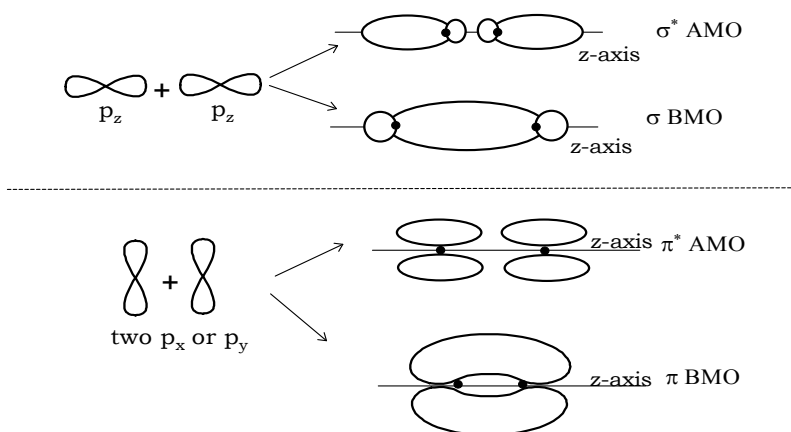
Note:

p_z will overlap with only p_z

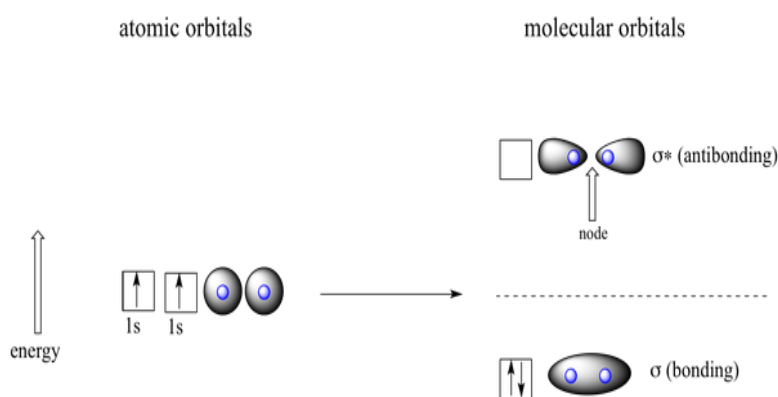
p_x will overlap with p_x and p_y

p_y will overlap with p_x and p_y

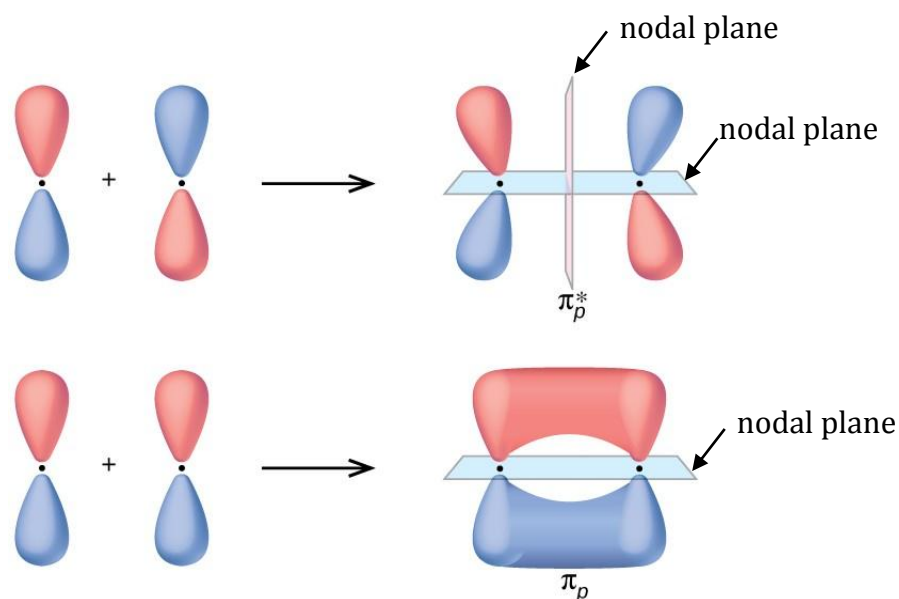
} They lie on the same



s-orbitals or p_z -orbitals overlapping have only 1 node (nodal plane) in the AMO. A node is a region where no electrons would be found.



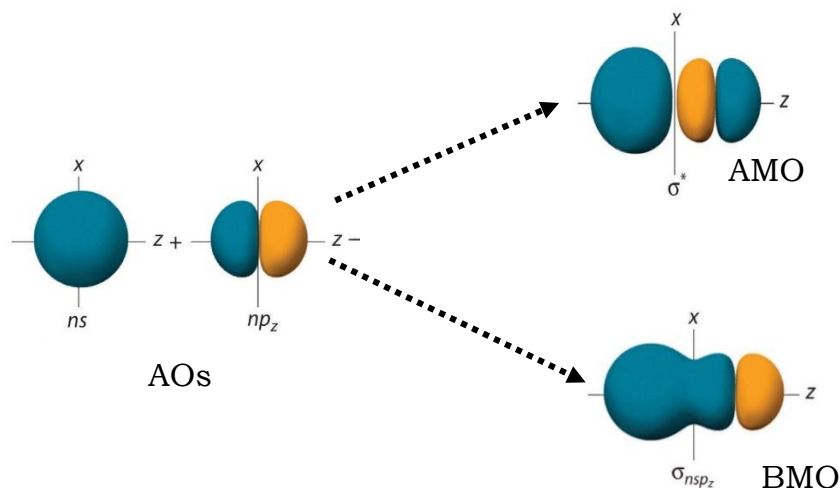
p_x and p_y -orbitals have only 1 node (nodal plane) in their BMO which is in-line with the inter-nuclear axis (z-axis). In their AMO there are 2 nodal planes, one is in-line with the inter-nuclear axis and the other is perpendicular to it.



OVERLAPPING OF s- AND p- orbitals

This is possible provided:

- The p-orbital is lying on the z-axis just as the s-orbital is. This way they would overlap end-to-end resulting in a sigma MO (bonding and antibonding). Therefore, only the p_z -orbital will overlap with an s-orbital.
- They must be close in energy. 1s cannot overlap with 3s but may overlap with 2s.

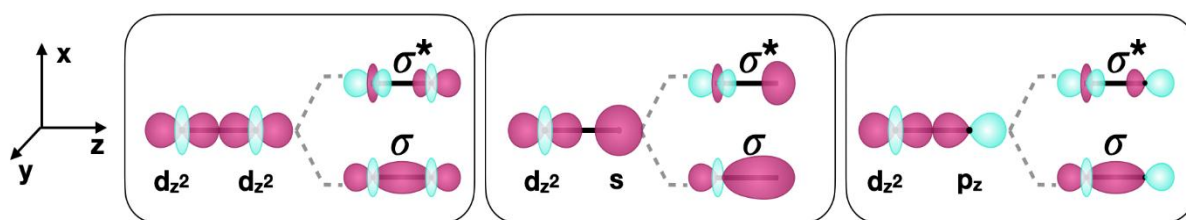


UNIT NINE - OVERLAPPING OF d-ORBITALS

The d orbitals are d_{xy} , d_{yz} , d_{xz} , d_{z^2} and $d_{x^2-y^2}$

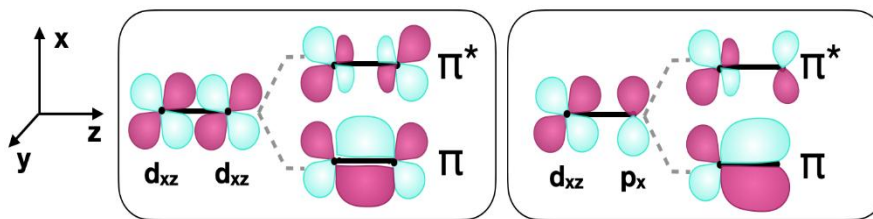
SIGMA BONDS IN d-ORBITALS

- The d_{z^2} orbitals can form d-d sigma bonds since it has cylindrical symmetry w.r.t. the inter-nuclear axis (z-axis). It can also overlap with s and p_z -orbitals.
- Two $d_{x^2-y^2}$ can also form sigma bond. This is because their lobes lie on the x and y axes therefore, these sigma bonds will be formed along these axes.



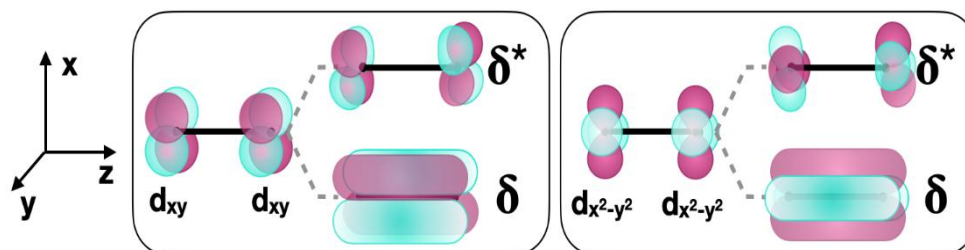
PI BONDS IN d-ORBITALS

- π bonds are those bonds with one nodal plane is in line with the inter-nuclear axis.
- The d-orbitals that would exhibit this are the overlapping of the d_{xz} and d_{yz} .
- They can also form pi bonds with p_x and p_y orbitals because they lie in the same plane. (Have the same symmetry).



DELTA BONDS IN d-ORBITALS (δ -BONDS)

- δ bonds are those bonds with two nodal planes is in line with the inter-nuclear axis.
- The d-orbitals that would exhibit this are the overlapping of the d_{xy} and $d_{x^2-y^2}$.



UNIT TEN – MOLEUCLAR ORBITAL ELECTRONIC CONFIGURATION

Just as we have atomic orbital electronic configuration and we have rules guiding this, we have molecular orbital electronic configurations and there are also rules guiding this.

Rules

1. The number of MO formed is equal to the sum of number of all the atomic orbitals involved.
2. The filling of MO proceeds from the low energy orbitals to the high energy orbitals (from bonding to anti bonding).
3. It obeys Pauli's Exclusion Principle – electrons fill in pair i.e. a maximum of 2 electrons per MO.
4. It obeys Hund's rule - electron will fill in MO of the same energy singly before pairing.
5. The number of electrons in the MO is equal to the sum of all the electrons in the bonding atoms.

HOMONUCLEAR DIATOMIC MOLECULES OF THE FIRST PERIOD (H_2 AND He_2)

Homonuclear means exactly the same type of atoms and diatomic means 2 atoms. H and He below to the first period in the periodic table having only 1s orbital. Since it two atomic orbital overlapping (1s) and overlapping of s-orbitals produces sigma molecular orbitals, we then have 2 molecular orbitals σ_{1s} , σ_{1s}^* to be filled by the electrons of this group.

Dihydrogen molecule (H₂)

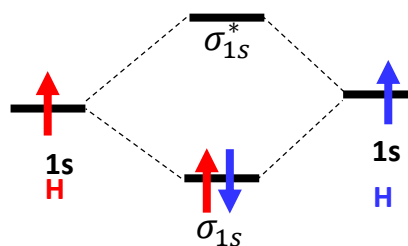
H - 1s¹

H - 1s¹

Total number of electrons = 2e

Overlapping of the two 1s orbital atomic orbitals = $\sigma_{1s}, \sigma_{1s}^*$ 2 molecular orbitals

Filling of these orbital = $\sigma_{1s}^2, \sigma_{1s}^*$



Dihelium molecule (He₂)

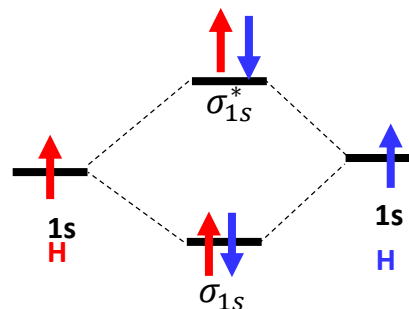
He - 1s²

He - 1s²

Total number of electrons = 4e

Overlapping of the two 1s orbital atomic orbitals = $\sigma_{1s}, \sigma_{1s}^*$ 2 molecular orbitals

Filling of these orbital = $\sigma_{1s}^2, \sigma_{1s}^{2*}$



BOND ORDER, STABILITY, MAGNETIC PROPERTY

We can determine the stability of the molecule can be from the bond order using

$$\text{bond order} = \frac{1}{2}(\text{no of electrons in BMO} - \text{no of electrons in AMO})$$

For H₂ the bond order is 1 and therefore this molecule is stable and is a single bond. There are no unpaired electrons so it is diamagnetic.

$$\frac{1}{2}(2 - 0) = 1$$

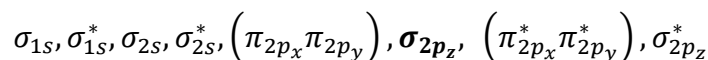
For He₂, the bond order is 0 and therefore this molecule does not exist.

$$\frac{1}{2}(2 - 2) = 0$$

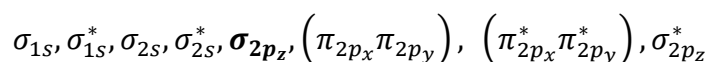
UNIT ELEVEN - HOMONUCLEAR DIATOMIC MOLECULES OF THE SECOND PERIOD (Li₂, Be₂, B₂, C₂, N₂, O₂, F₂, Ne₂)

In this group the general atomic are is 1s, 2s, 2p_x, 2p_y, 2p_z (at most 5 atomic orbitals from each atom) such that when two of atoms form a diatomic molecule, the interaction of the atomic orbital would produce at most 10 molecular orbitals.

Below is the molecular orbital electronic configuration for Li₂, Be₂, B₂, C₂, N₂

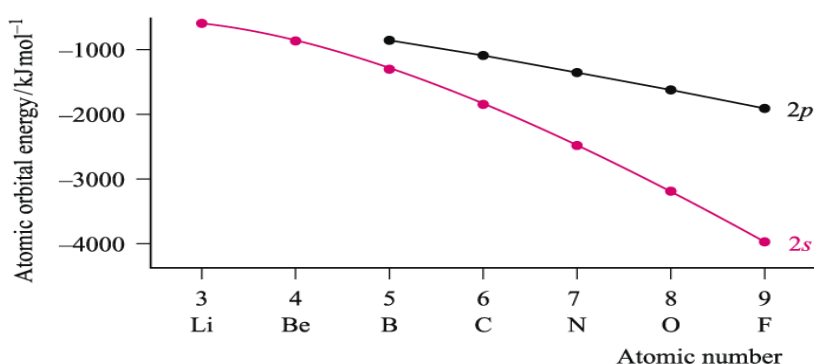


For O₂, F₂, Ne₂

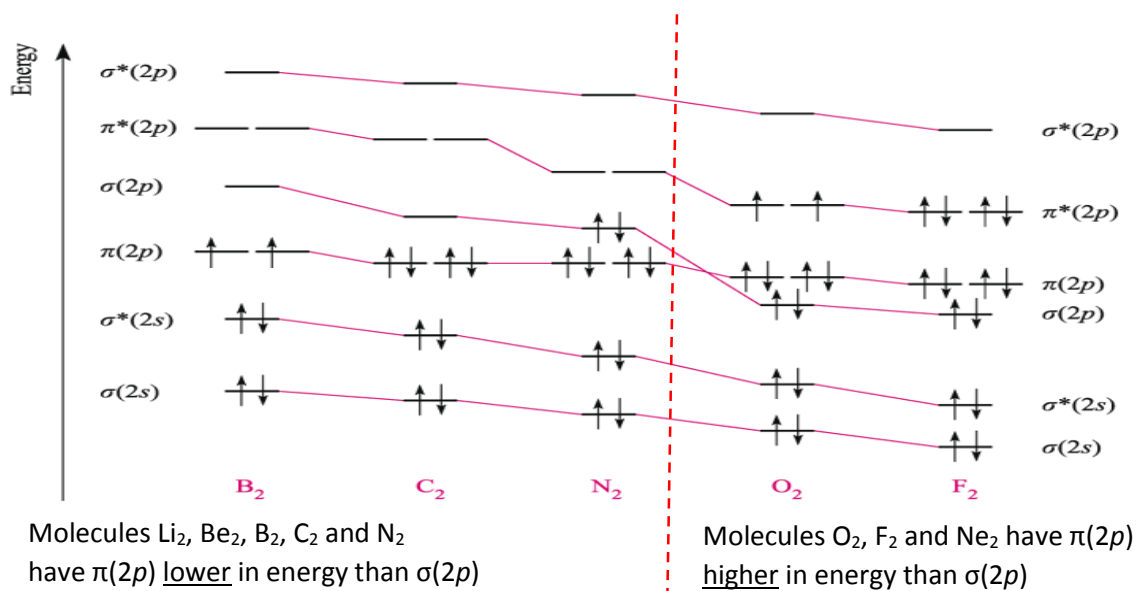


The pi orbital in the bracket are degenerate i.e. they are equal in energy ($\pi_{2p_x} = \pi_{2p_y}$) and ($\pi_{2p_x}^* = \pi_{2p_y}^*$) therefore electrons would fill in singly before pairing.

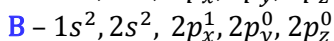
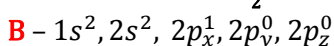
Notice that the position of the σ_{2p_z} orbital is different. This is due to sharp decrease in the energy of the 2s orbital as you move across the period which is most prominent from O to Ne (see diagram below).



Energy level of the 2nd row of homonuclear diatomic molecules



Diboron molecule B₂



Total number of electrons = 10e

Overlapping of the two of 1s, 2s and 2p_x atomic orbital

(total of 6 atomic orbital) = 6

molecular orbitals = $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, (\pi_{2p_x}, \pi_{2p_y})$

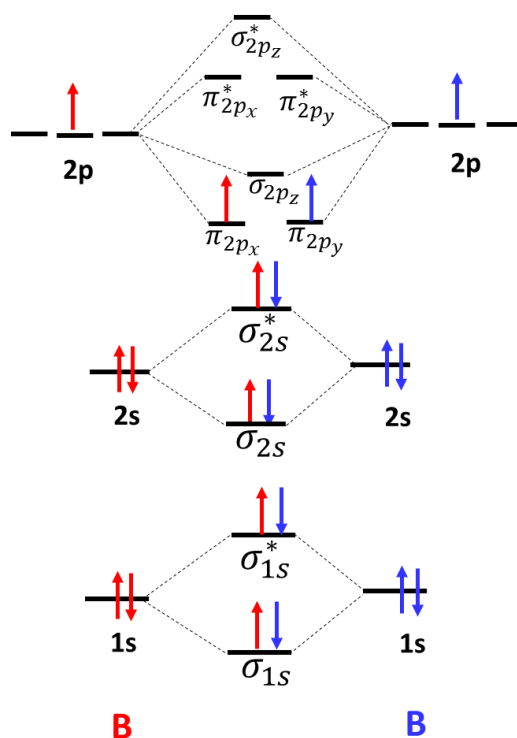
Filling of these orbital = $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, (\pi_{2p_x}^1, \pi_{2p_y}^1)$

We can determine the stability of the molecule can be from the bond order using

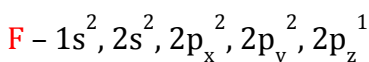
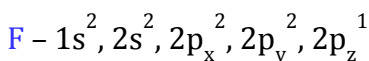
$$\text{bond order} = \frac{1}{2}(\text{no of electrons in BMO} - \text{no of electrons in AMO})$$

$$\frac{1}{2}(6 - 4) = 1$$

The bond order is 1 and therefore this molecule is stable, it a single bond and does exist. It has 2 unpaired electrons and therefore paramagnetic.



Difluorine molecule F₂



Total number of electrons = 18e

Overlapping of the two of 1s², 2s², 2p_x², 2p_y², 2p_z¹

(total of 10 atomic orbitals) = 10 molecular orbitals

$\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_{2p_z}, (\pi_{2p_x}, \pi_{2p_y}), (\pi_{2p_x}^*, \pi_{2p_y}^*), \sigma_{2p_z}^*$

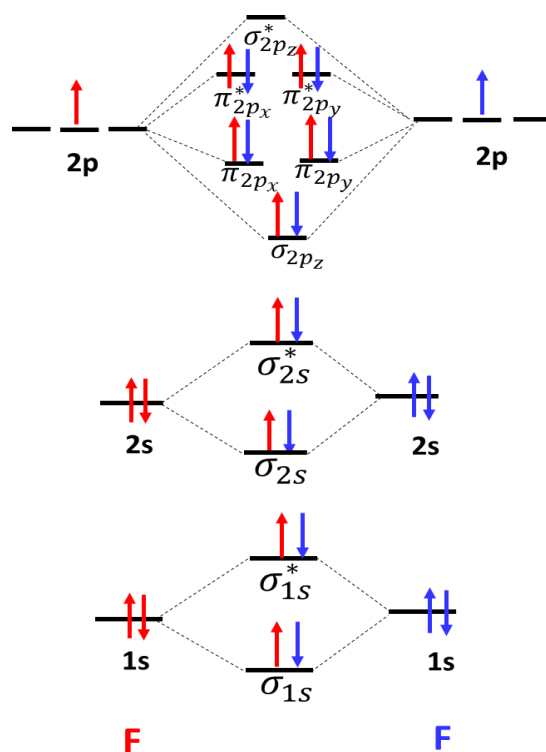
Filling of these orbital =

$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_z}^2, (\pi_{2p_x}^2, \pi_{2p_y}^2), (\pi_{2p_x}^{*2}, \pi_{2p_y}^{*2})$

We determine the stability of the molecule

$$\frac{1}{2}(10 - 8) = 1$$

The bond order is 1 and therefore this molecule is stable and exists. It is diamagnetic.



Highest Occupied Molecular Orbital (HOMO)

Lowest Unoccupied Molecular Orbital (LUMO)

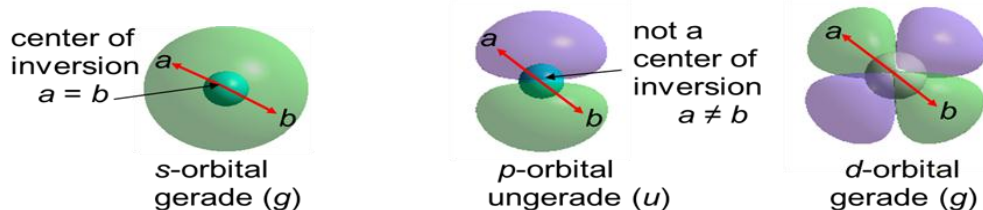
The HOMO and the LUMO are known as FRONTIER ORBITALS and these orbitals are used to explain a lot of reaction mechanism, kinetic, structural and spectroscopic studies.

The HOMO for B_2 is $\pi_{2p_x}\pi_{2p_y}$ and its LUMO is σ_{2p_z}

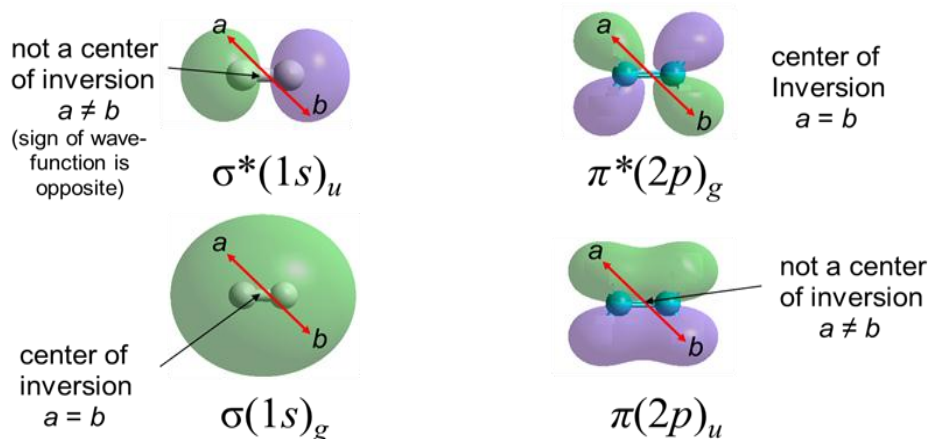
The HOMO for F_2 is $\pi_{2p_x}^*\pi_{2p_y}^*$, and its LUMO is $\sigma_{2p_z}^*$

UNIT TWELVE – GERADE AND UNGERADE ORBITALS

An orbital with a center of symmetry (inversion) is called gerade (*g*) and one that does not have one is called ungerade (*u*). A center of inversion is a symmetry operation that involves starting at an arbitrary point in the molecule, travelling in a straight line to the center of the molecule and then continuing an equal distance out on the other side of the center.



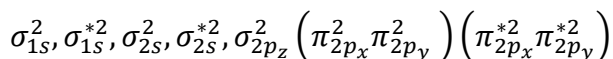
According to the Laporte selection rules, electron will move from $g \rightarrow u$ and $u \rightarrow g$ are allowed, but $g \rightarrow g$ and $u \rightarrow u$ are forbidden.



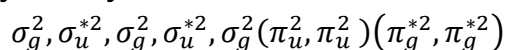
The following little table will help you to label molecular orbitals as *g* or *u*. For σ -overlap, the bonding orbitals are *g*, while the antibonding orbitals are *u*, while for π -overlap the opposite is true:

	bonding MO	anti-bonding MO
σ -bonding	g	u
π -bonding	u	g

Below is the molecular electronic configuration of F_2 ,



To rewrite this based on symmetry would become



Home Work

- N_2^+ was formed by bombarding N_2 with a fast moving electron. Confirm the existence of N_2^+ and its magnetic properties. Draw the molecular orbital energy diagram of N_2 and determine how many bonds it has.
- Write the electron configuration of O_2, O_2^-, O_2^{2-} in terms of symmetry and determine their stability and magnetic properties.

UNIT THIRTEEN - HETERONUCLEAR DIATOMIC MOLECULE (HF, LiF, CO, NO etc)

These molecules are made of 2 atoms of different elements and because of these differences their contribution to the formation of the molecular orbital would not be the same. This is unlike the case of homonuclear diatomic molecule whose contribution to the molecular orbital is the same. The differences arise as a result of the difference in electronegativity

In drawing the molecular orbital diagram of heteronuclear diatomic molecules we follow the procedure below

- Place the more electronegative atom on a lower level, while the less electronegative atom is placed on a higher level. The larger the electronegativity difference the wider this gap between the combining species

atom	F	Li	H	C	N	O
χ	3.98	0.98	2.20	2.55	3.04	3.44

- In drawing the MO diagram, the more electronegative atom has the BMO closer to it while the less electronegative atom has the AMO closer to it.
- Only orbitals of similar energy and symmetry would overlap to produce MO.
- Because this time when an s atomic orbital would overlap with a p_z orbital to produce a sigma MO the labelling of the MO of heteronuclear diatomic molecules is $1\sigma, 2\sigma, 3\sigma, 4\sigma, 1\pi, 2\pi, 3\pi, 4\pi$ etc. Another style of labelling would be $1\sigma, 1\sigma^*, 2\sigma, 2\sigma^*, 1\pi, 1\pi^*, 2\pi, 2\pi^*$. These two are the same.

HF

H $1s^1$

F $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$

Total number of electron $1+7 = 10$

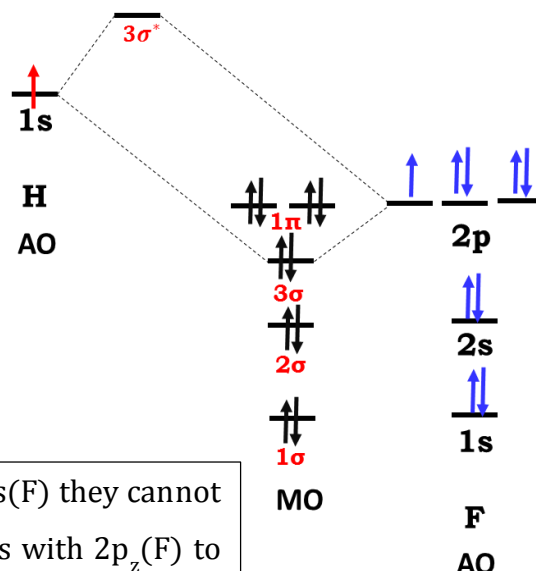
Total number of atomic orbitals involved = 6

Therefore, total number of molecular orbitals = 6

MO electronic configuration of HF = $1\sigma^2, 2\sigma^2, 3\sigma^2, 1\pi^4$

Because of wide energy difference between the $1s(F)$ and $2s(F)$ they cannot overlap with $1s(H)$ and are therefore NMOs. $1s(H)$ overlaps with $2p_z(F)$ to yield the 3σ (BMO) and $3\sigma^*$ (AMO). The $2p_x$ and $2p_y$ did not overlap with any orbital and because of their symmetry are labelled as 1π , these are also NMO.

NOTE: The number 1, 2, 3 is just serial labelling of the MO as they occurred.



H-F the bond pair of electron are not shared equally rather due to high electronegativity of F the bond pair have more F character and due to this polarization the bond has partial ionic character (polar bond) hence is illustrated in the MO energy diagram to be more towards F than central.

Bond order = $\frac{1}{2} (2-0) = 1$, the compound has a single polar covalent bond. It is stable and is diamagnetic.

LiF

Because the difference in energy between the $1s$ of Li and $1s$ of F is very large, they do not overlap and therefore ignored.

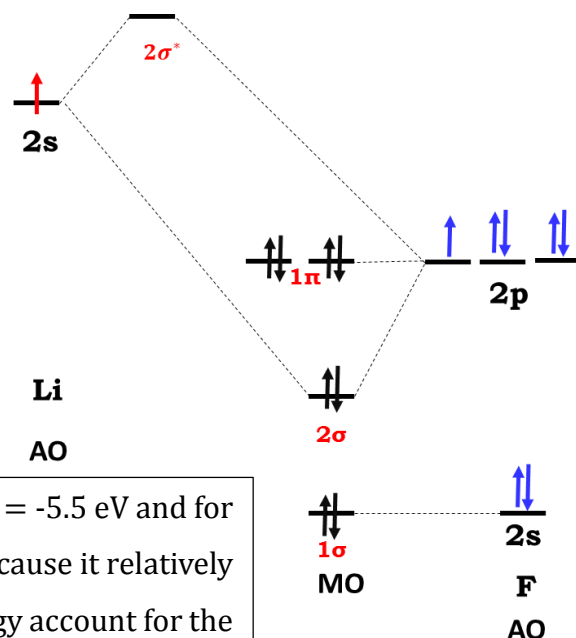
Total number of valence electron $1+7 = 8$

Total number of atomic orbitals involved = 5

Therefore, total number of molecular orbitals = 5

It is for the same reason the $2s$ orbitals do not overlap. For $2s(Li) = -5.5$ eV and for $2s(F) = -48.5$ eV. However, the $2s(Li)$ overlaps with the $2p(F)$ because it is relatively closer in energy ($2p(F) = -21.6$ eV). The wide difference in energy accounts for the ionic nature of LiF bond.

(Energy of $1s(H) = 13.6$ eV is much closer to that of the $2p(F) = 21.6$ eV).



Molecular orbital electronic configuration of LiF = $1\sigma^2, 2\sigma^2, 1\pi^4$

We can also ignore the 1s(F) orbital in HF therefore its electronic configuration = $1\sigma^2, 2\sigma^2, 1\pi^4$

NO, CO, CN⁻

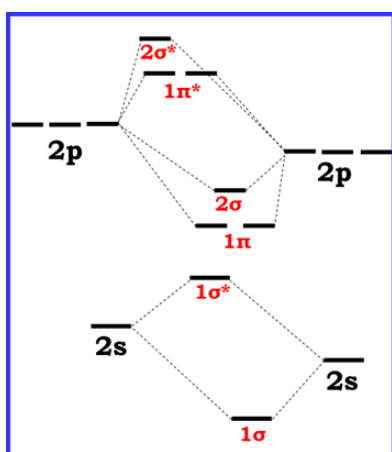
C $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z$

N $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

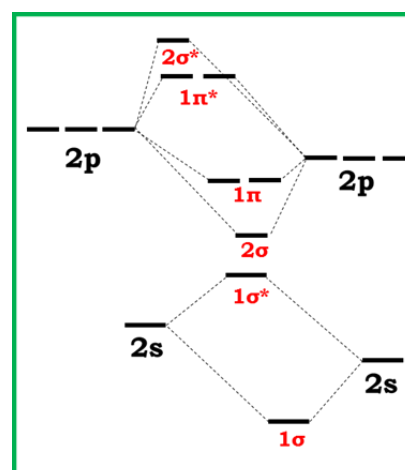
O $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$

Just as with LiF we are going to ignore the 1s orbitals cos their energies are very low and not really involved directly in bonding. There are two possible order of arrangement of the molecular orbitals of the species, A or B.

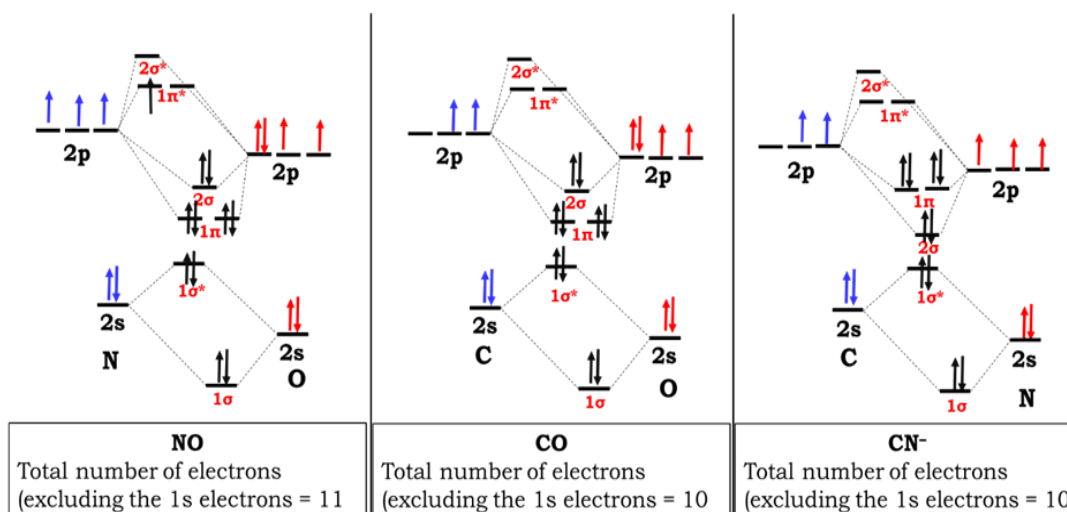
The pattern observed is due to the 2s (O) and 2p(O) are wide apart in energy compared to those of N and C, causing energy of the π -MOs to be lowered and the 2σ -MO raised.



A



B



	MO electronic configurations
HF	$1\sigma^2, 2\sigma^2, 3\sigma^2, 1\pi^4, 3\sigma^{*0}$
LiF	$1\sigma^2, 2\sigma^2, 1\pi^4, 2\sigma^{*0}$
NO	$1\sigma^2, 2\sigma^2, 1\pi^4, 3\sigma^2, 1\pi^{*1}, 3\sigma^{*0}$
CO	$1\sigma^2, 2\sigma^2, 1\pi^4, 3\sigma^2, 1\pi^{*0}, 3\sigma^{*0}$
CN ⁻	$1\sigma^2, 2\sigma^2, 3\sigma^2, 1\pi^4, 1\pi^{*0}, 3\sigma^{*0}$

	Bond order	Stability	No of bonds	Magnetic property
HF	$\frac{1}{2}(2 - 1) = 1$	stable	Single bond	diamagnetic
NO	$\frac{1}{2}(8 - 3) = 2.5$	stable	It has a double bond and a radical	paramagnetic
CO	$\frac{1}{2}(8 - 2) = 3$	stable	It has a triple bond	diamagnetic
CN ⁻	$\frac{1}{2}(8 - 2) = 3$	stable	It has a triple bond	diamagnetic

Home work

- Sketch the MO energy diagram of the following compounds
 - ICl
 - NO⁻
 - NO⁺
- Write their molecular electronic configuration not showing the specific AO and showing the specific AO.
- Discuss the properties of this compound.

ASSIGNMENT TO MODULE ONE

1. Write the Lewis structure of the following molecules and ions and show formal charges

(a) OF_2

(b) CH_2ClOO^-

2. Draw 3 resonance structures of the chlorate ions ClO_3^-

3. Sketch the shape of the following compounds and the name of the shape

a. CH_4

b. SF_4

c. XeF_4

4. Draw and label the types of bonds formed in the molecule $\text{CH}_3\text{CCCH}_2\text{OH}$.

5. Sketch the MO energy diagram of the following compounds

i. ICl

ii. NO^-

iii. NO^+

a. Write their molecular electronic configuration not showing the specific AO and showing the specific AO.

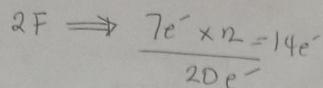
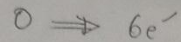
b. Discuss the properties of this compound.

Solution to Assignment 1

Dr George

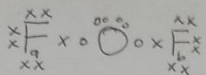
1a
OF₂

Valence electrons



1

Distribution



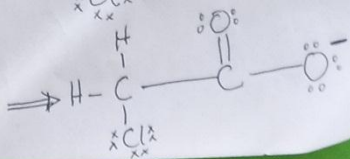
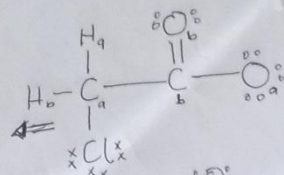
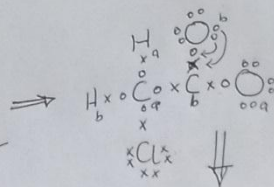
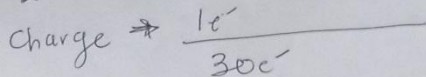
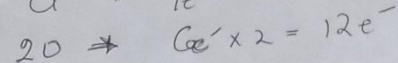
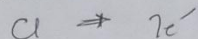
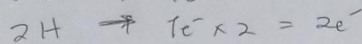
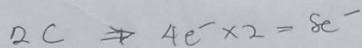
Lewis structure

Determining formal charge

	O	F _a	F _b
V	6	7	7
N	4	6	6
$\frac{B}{2}$	2	1	1
FC	0	0	0

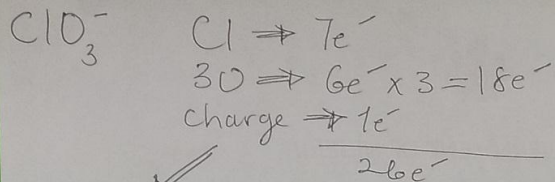
No formal charge

1b The question is wrong. It should be CH₂ClCOO⁻

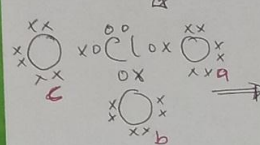


Calculate formal charge

	C _a	C _b	H _a	H _b	O _a	O _b	Cl
V	4	4	1	1	6	6	7
N	0	0	0	0	6	4	6
$\frac{B}{2}$	4	4	1	1	2	2	1
FC	0	0	0	0	-1	0	0

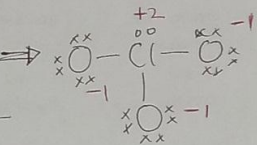


2

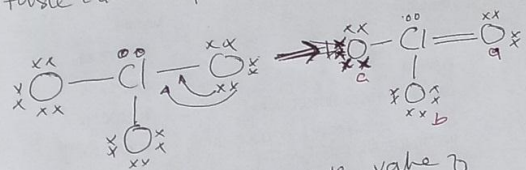


Find the formal charge

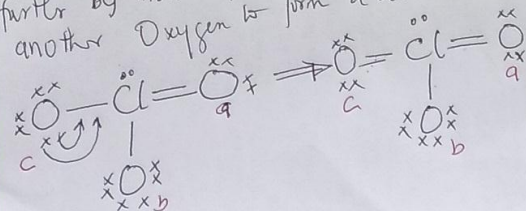
	Cl	O _a	O _b	O _c
V	7	6	6	6
N	2	6	6	6
B _{1/2}	3	1	1	1
FC	+2	-1	-1	-1



The formal charge on Cl is +2 which is high and el. We shall redraw the structure to reduce the formal charge on Cl, by moving a lone pair of electron from any of the oxygen(s). This would form a double bond between them. This is possible because chlorine being on the 2 row in the periodic table can expand its octet.



We can still reduce the value of the formal charge on Cl even further by moving another pair from another oxygen to form a double bond.



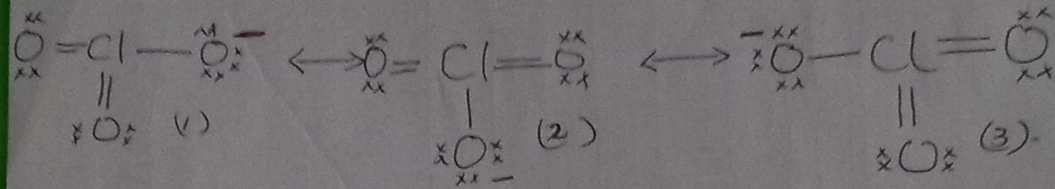
Formal charge

	Cl	O _a	O _b	O _c
V	7	6	6	6
N	2	4	6	6
B _{1/2}	4	2	1	1
FC	+1	0	-1	-1

Formal charge

	Cl	O _a	O _b	O _c
V	7	6	6	6
N	2	4	6	4
B _{1/2}	5	2	1	2
FC	0	0	-1	0

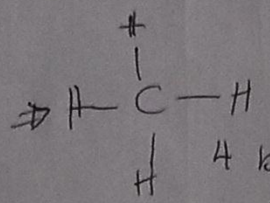
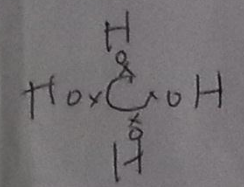
All the Oxygen atoms in the molecule are equivalent so the formal charge can be on any one of them. This means there will be 3 resonance structures



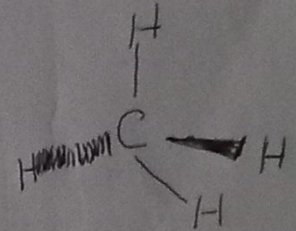
3 CH₄

$$\begin{aligned}
 C &= 4e^- \\
 4H &= 1e^- \times 4 = 4e^- \\
 \hline
 &= 8e^-
 \end{aligned}$$

3

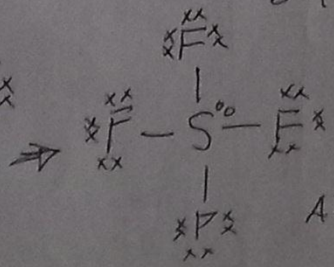
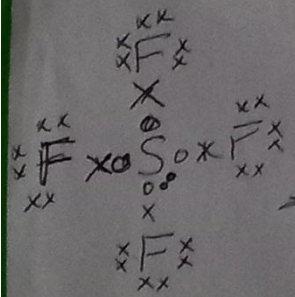


4 bp no lp
Shape is tetrahedral

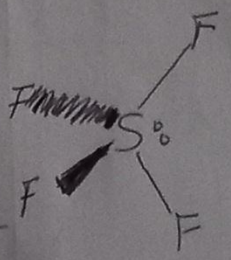


SF₄

$$\begin{aligned}
 S &= 6e^- \\
 4F &= 7e^- \times 4 = 28e^- \\
 \hline
 &= 34e^-
 \end{aligned}$$

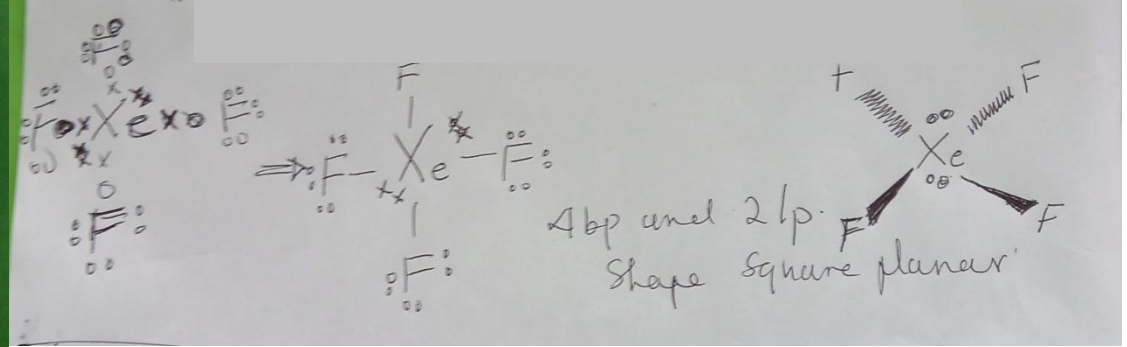


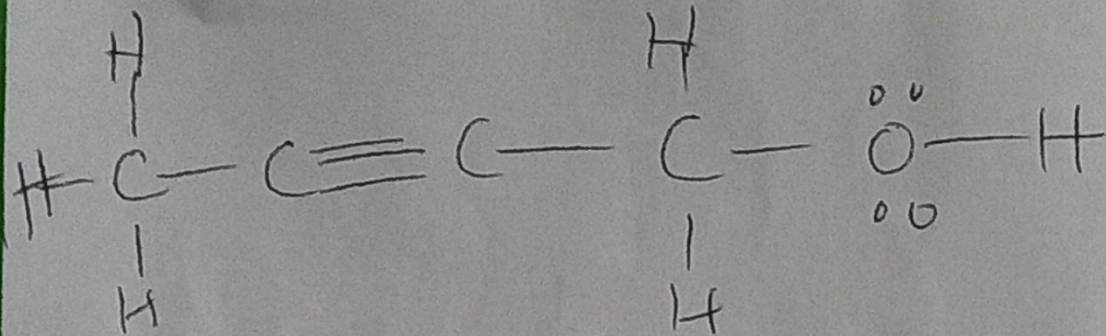
4bp 1 lone pair
Shape is SeeSaw



XeF₄

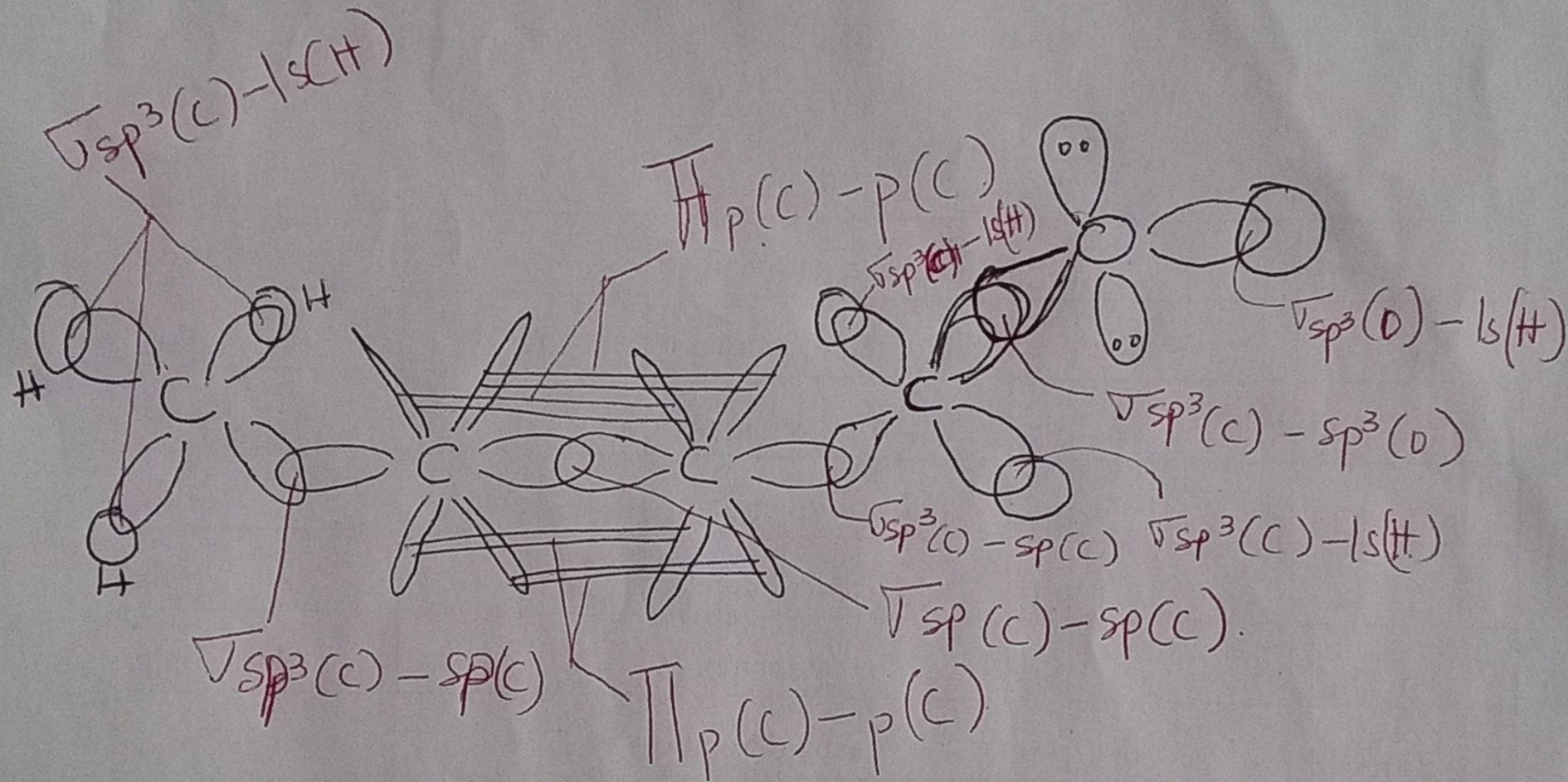
$$\begin{aligned}
 Xe &= 8e^- \\
 4F &= 7e^- \times 4 = 28e^- \\
 \hline
 &= 36e^-
 \end{aligned}$$





4

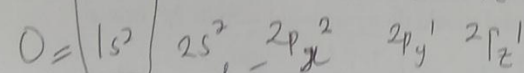
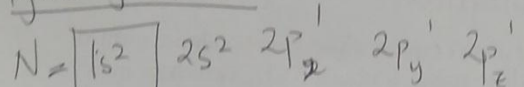
4



Ignore Question 5a, elements are in the 3rd & 4th period.

NO⁻

Ignoring the 1s

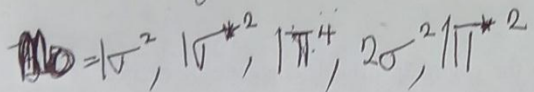


charge = +1e⁻

Total no of AO = 8AO

Total no of MO = 8MO

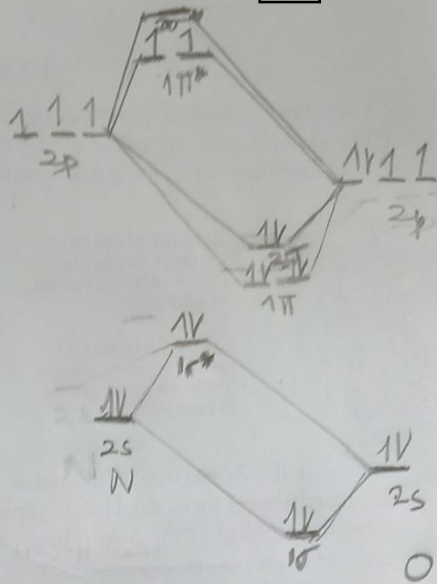
Total no of electrons = 12e⁻



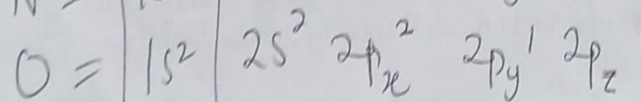
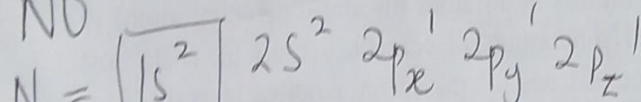
$$BO = \frac{1}{2}(8-4) = \frac{4}{2} = 2$$

The compd is stable and has a double bond
it has 2 unpaired electrons, hence paramagnetic.

5



NO⁺

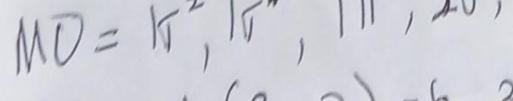


charge = +1e⁻

Total no of AO = 8AO

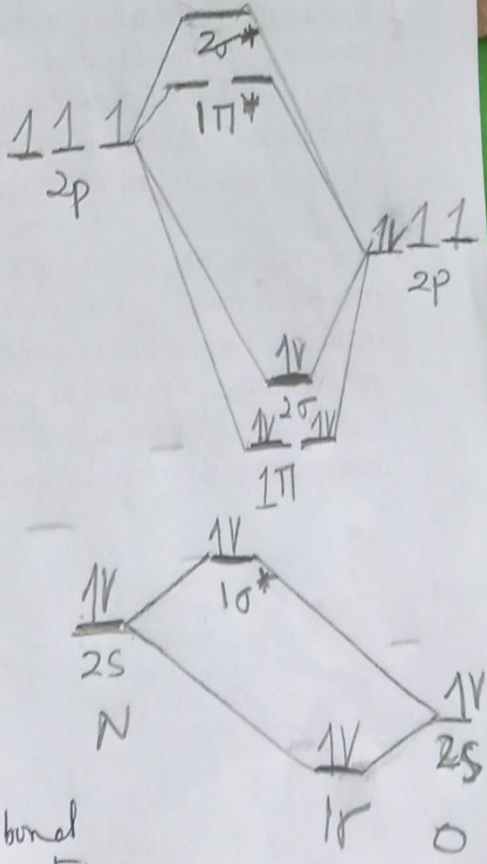
Total no of MO = 8MO

Total no of electrons = 10e⁻



$$BO = \frac{1}{2}(8-2) = \frac{6}{2} = 3$$

This compd is stable, having a triple bond
with no unpaired electrons it is diamagnetic.



MODULE TWO

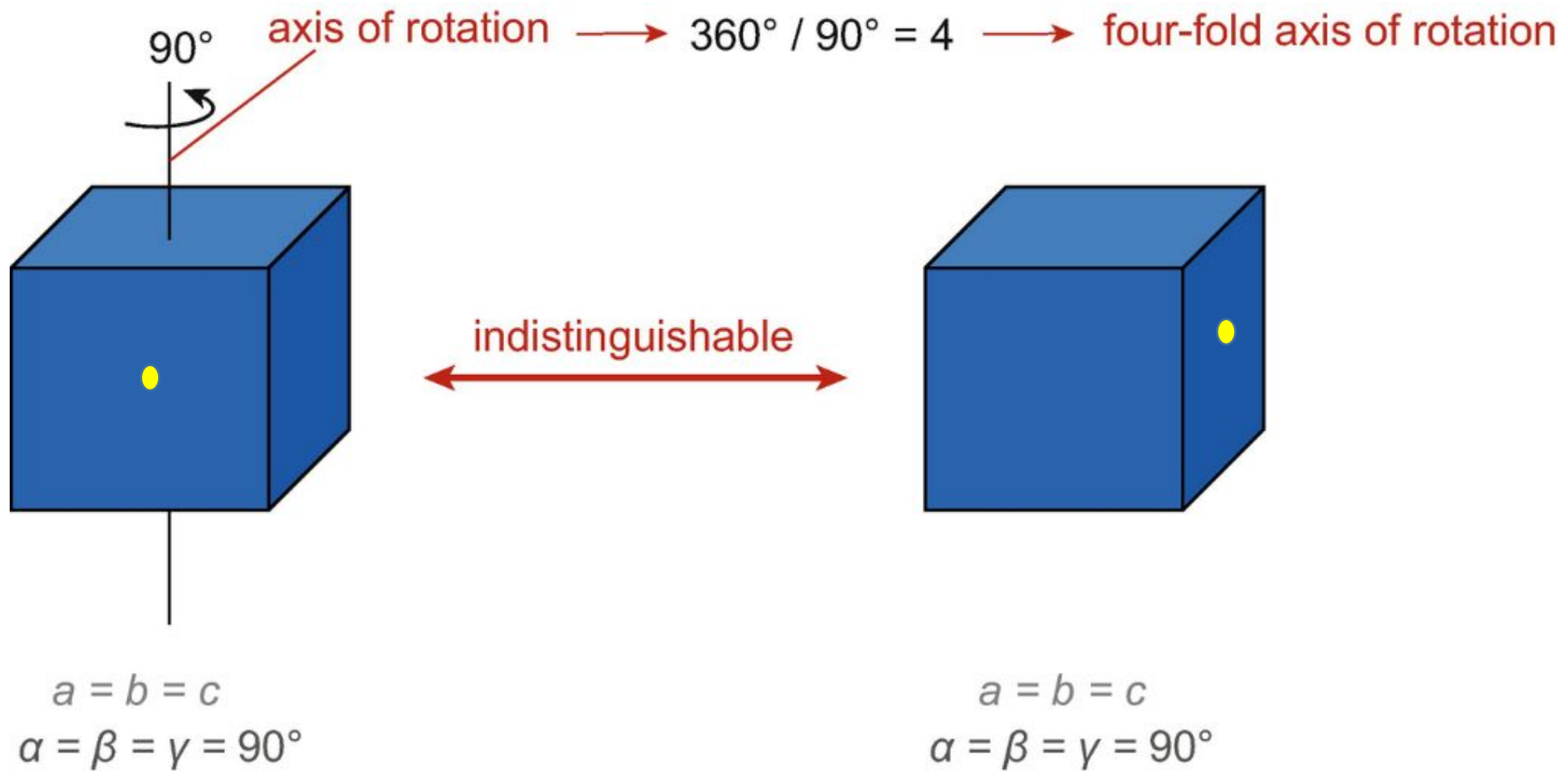
Symmetry Operations

- ◆ Unit One – Identity and n-fold Rotation
- ◆ Unit Two – Reflection and inversion
- ◆ Unit Three – Improper rotation
- ◆ Unit Four – Point group

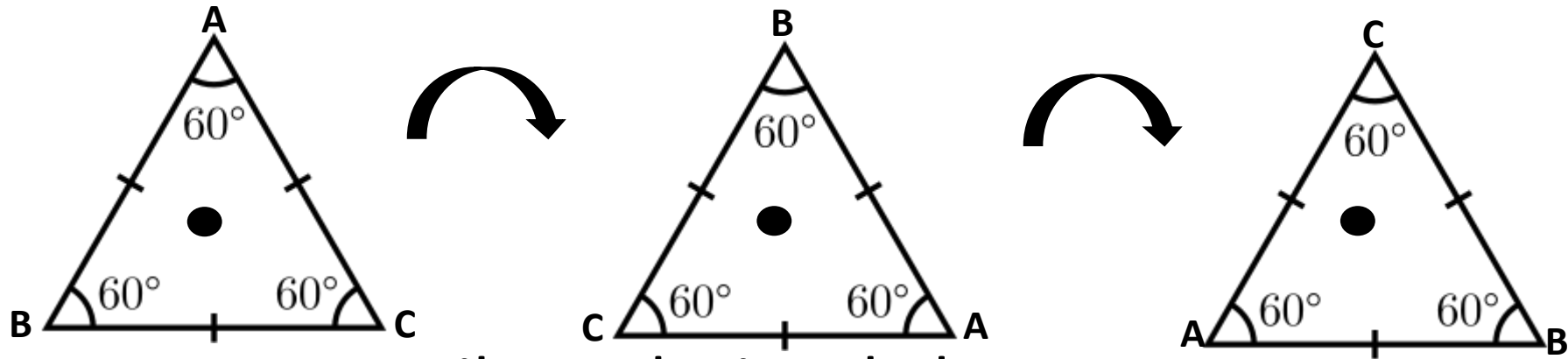
UNIT
ONE

Identity and n-fold Rotation

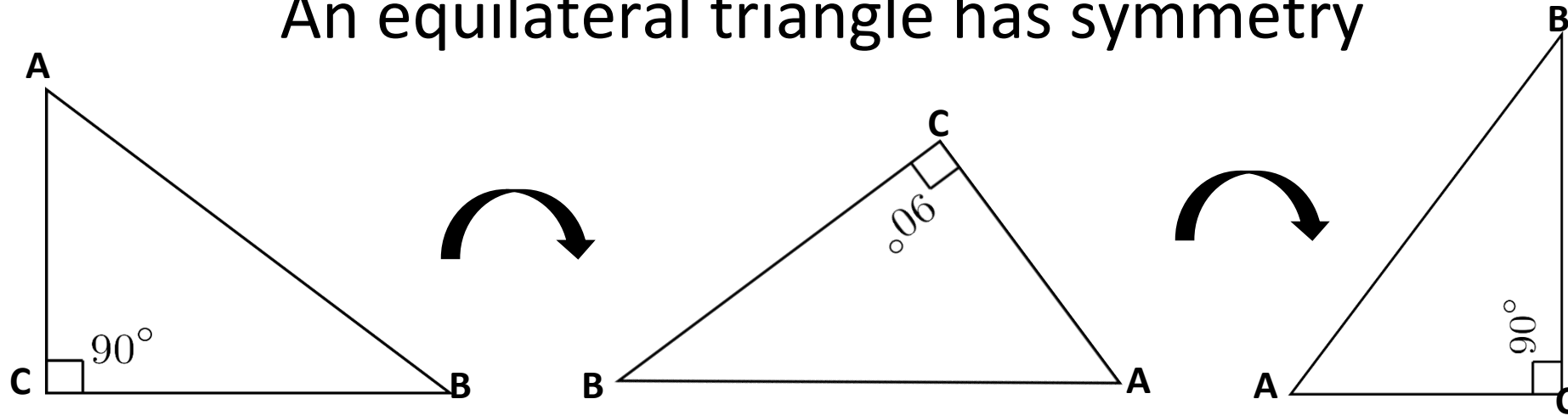
- A molecule is said to have **symmetry** if when it is 'turned' there is no change in the placement of the atoms of the molecules.
- **A symmetry element** is a line, a plane, a point in or through an object (a molecule), about which the 'turnings' are made and the object has an orientation that cannot be differentiated from the original.
- **A symmetry operation** is the movement of the object (molecule) about a line, plane or point.



'Turning'



An equilateral triangle has symmetry



A right-angle triangle has no symmetry

Types of Operations

- There are 5 kinds of operations
- 1. Identity
- 2. n-Fold Rotations
- 3. Reflection
- 4. Inversion
- 5. Improper n-Fold Rotation

Identity E: For this operation no 'turning' is done to the molecule. The molecule does not move and all the atoms of the molecule stay at the same place. **EVERY MOLECULE HAS E**

n-fold Rotation (C_n)



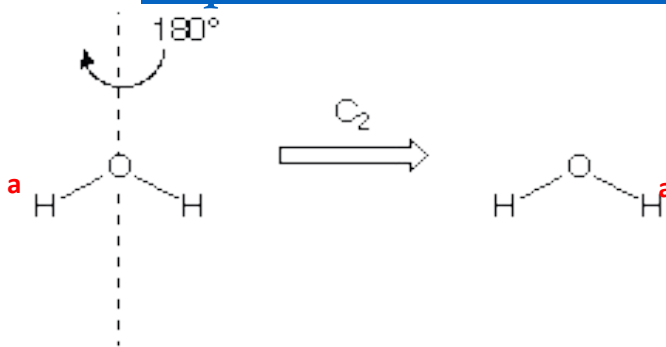
This is a rotation by $\frac{360^\circ}{n}$ about a particular axis called the **n-fold rotation axis** which is symmetry element (a line).

No of Rotating atom	n	Degree of rotation	Symmetry operation	Example
2	2		C_2	H_2O
3	3		C_3	BF_3
4	4		C_4	XeF_4

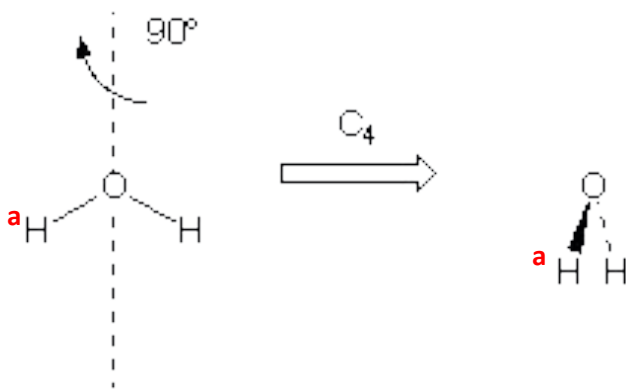
Water has bent shape. The n-fold rotating axis of H_2O is a line passing through **O** and bisecting the **H–O–H** bond angle.

This will be a 180° rotation to give the same molecule back.

Therefore, H_2O possesses the C_2 symmetry element. (the letter **a** is used to distinguish the hydrogen atoms). To see this operation in 3D visit <https://www.chemtube3d.com/sym-waterc2v/>

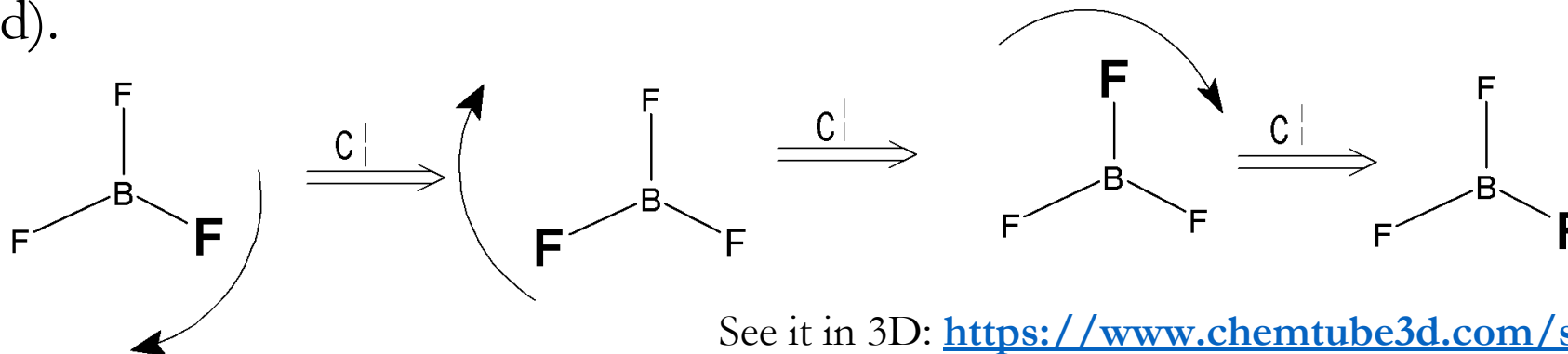


However, rotation by 90° about the same axis does not give back the identical molecule. Here H_a is in front of the other H instead of beside it. Therefore, H_2O does NOT possess a C_4 symmetry axis.



H_2O has E and C_2 – operations (but these are not all)

BF_3 is trigonal planar in shape. It possesses a C_3 rotation axis of symmetry. This is a line passing through **B** coming out of the paper. (Both directions of rotation must be considered).



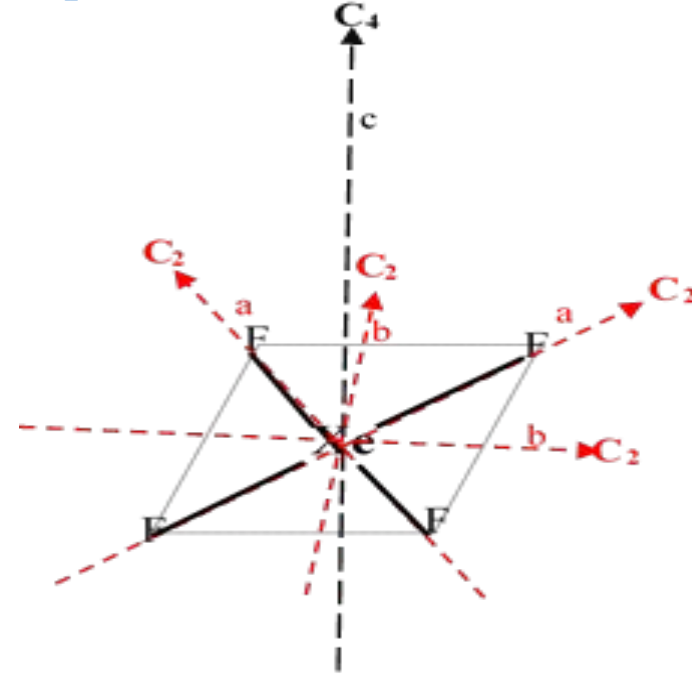
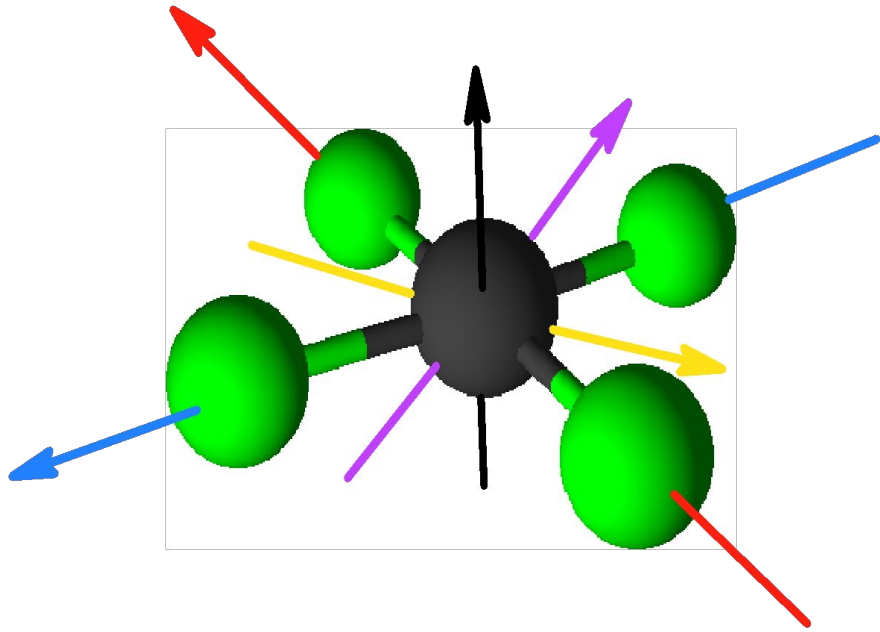
See it in 3D: <https://www.chemtube3d.com/sym-d3hbf3new/>

- C_2 means one 180° rotation
- C_3 means a 120°
- C_6^2 means two 60° rotations in the same direction
- C_6^5 means five 60° rotations in the same direction
- C_4^2 means two 90° rotations in the same direction
- $C_n^n = E$

Note: The axis with the greatest value of n is the PRINCIPLE AXIS

This means that BF_3 has $E, C_3, C_3^2, C_3^3 (= E)$ – operations (but these are not all).

See it in 3D <https://www.chemtube3d.com/xeF4-symmetry-d4h/>



XeF₄ is square planar in shape.

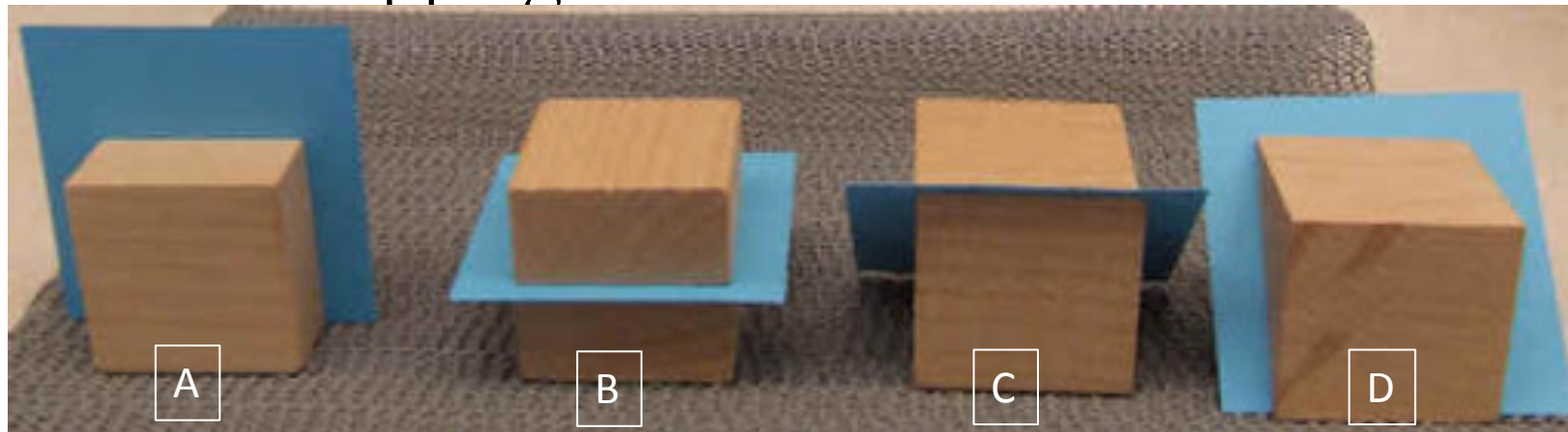
- It has four C₂ axes;
- 2 are *in line* with the F–Xe–F bonds (a) (blue and red)
- 2 are bisecting the F–Xe–F bond angle (b) (yellow and purple)
- It also has a C₄ axis coming out of the page through Xe (c) (black) and it is the principle axis because it has the largest n.

XeF₄ – has E, 4C₂, C₄, symmetry operations.

END OF UNIT ONE

Reflections (s or σ)

The symmetry element is called a mirror plane (or plane) of symmetry. The operation is 'flipping the molecule' to obtain its reflection.



In the image above the blue cardboard represent the mirror plane.

- A. The mirror is vertical.
- B. It is horizontal.
- C. It is diagonal (cutting across a set of angles)
- D. It is also diagonal (cutting across the other set of angles)

If you were to move the cube to the opposite side of the mirror, the cube would be exactly the same.

Image was got from the link below.

tcdsbstaff.ednet.ns.ca

[Cube Planes of Symmetry](#)

Terms and Conditions

If reflection about a mirror plane gives the same molecule/object back than there is a plane of symmetry (s/σ).

If plane lies on the principle rotation axis (i.e. parallel), it is a vertical plane (s_v or σ_v)

If plane is perpendicular to the principle rotation axis, it is a horizontal plane (s_h or σ_h)

If plane is parallel to the principle rotation axis, but bisects angle between 2 C_2 axes, it is a diagonal plane (s_d or σ_d)

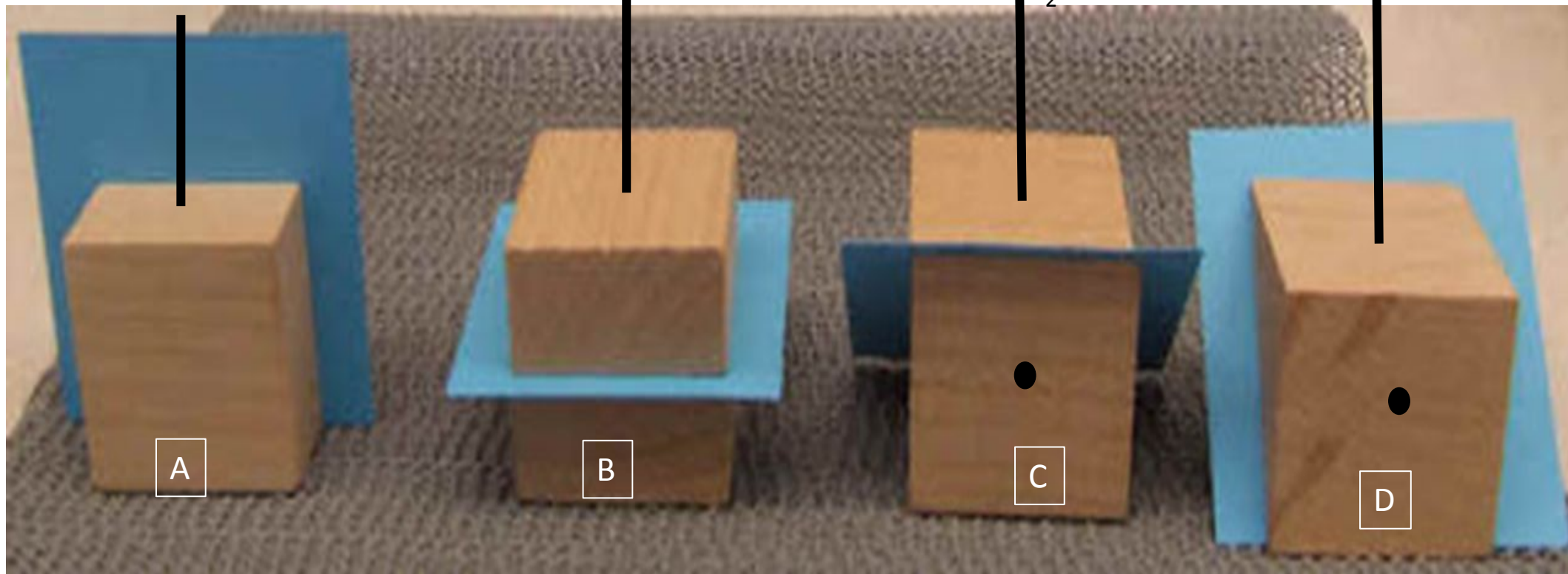
*If the shape of the molecule is linear, bent or planar (i.e. trigonal planar, square planar) they would always have a plane that cuts across ALL its atoms. This also occurs in octahedral and trigonal bipyramid molecules

Assuming the black line is the principle axis of rotation of these cubes (C_4)

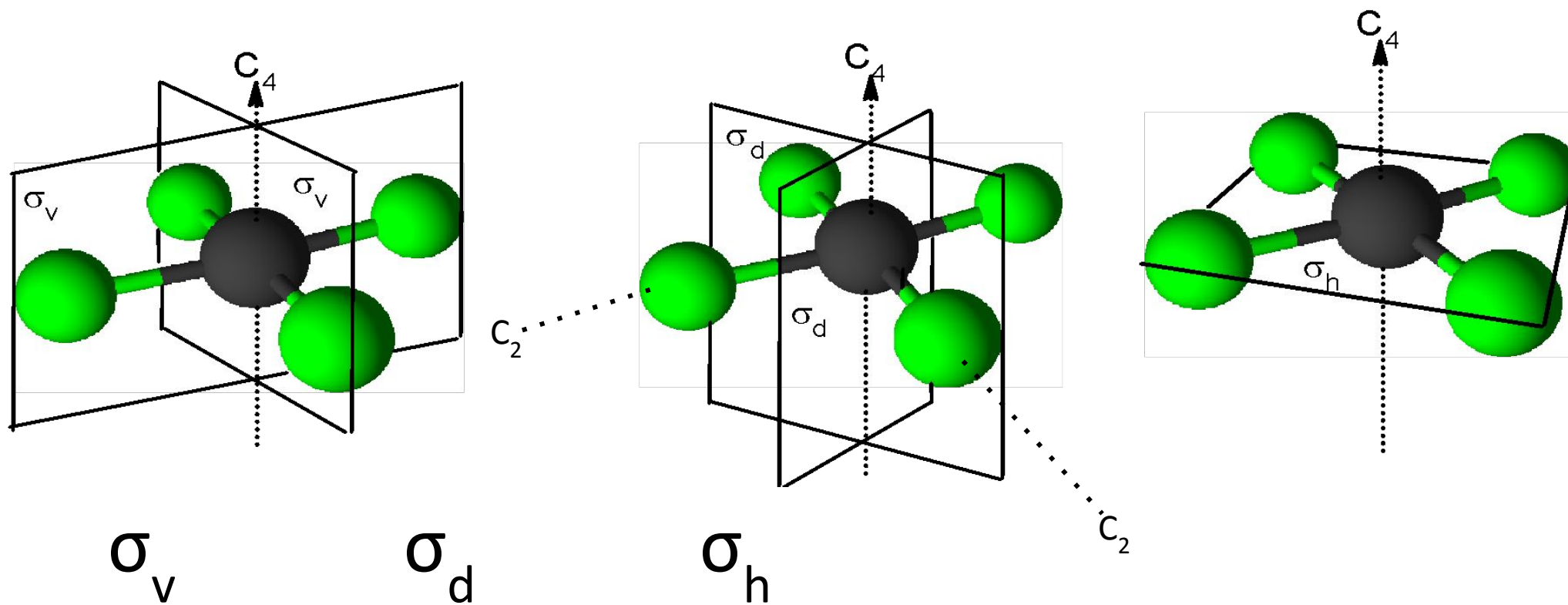
The box has a σ_v .
Notice that the black line is in line/parallel to the blue cardboard

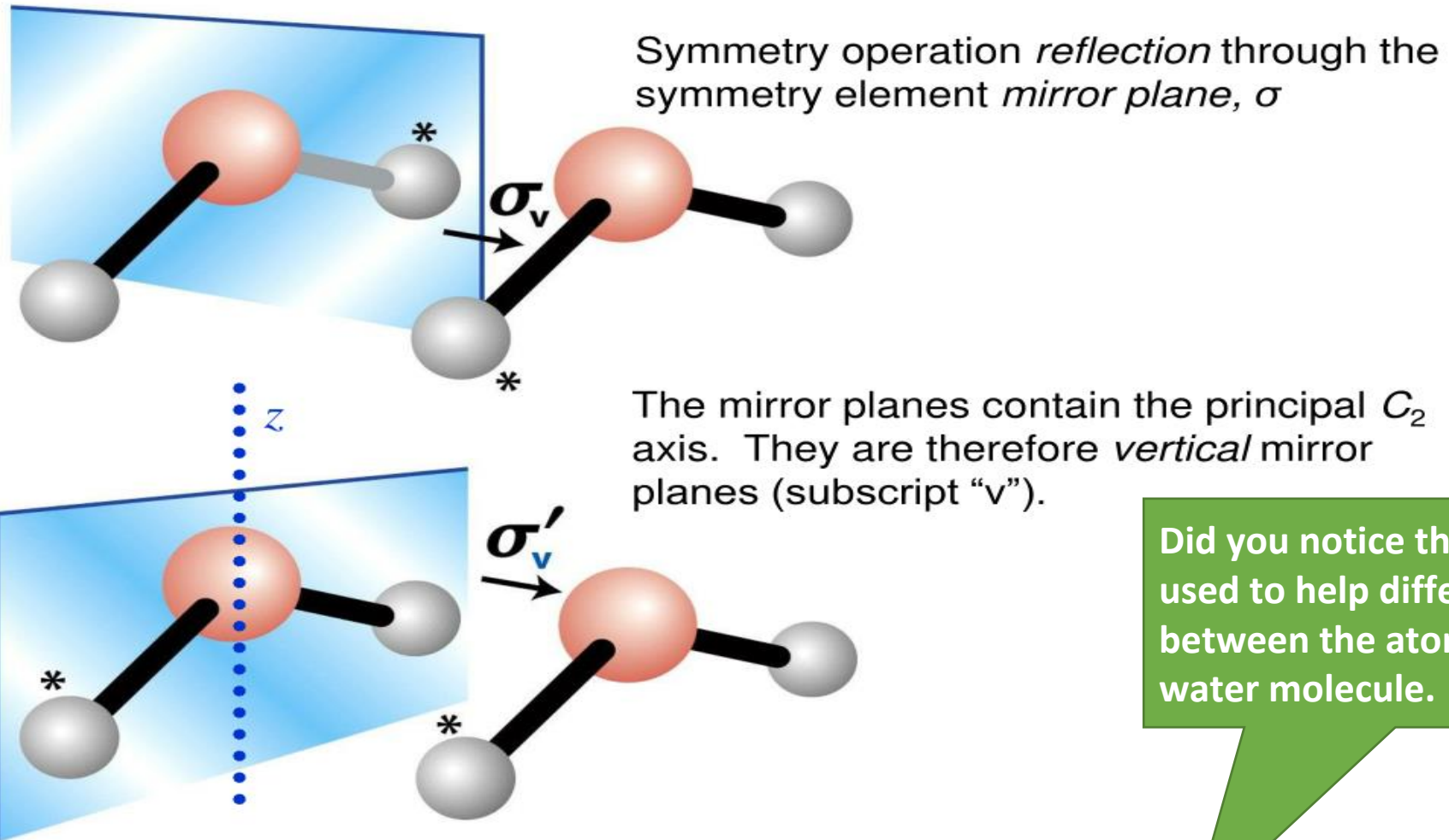
The box has a σ_h .
The black line is in perpendicular to the blue cardboard

The box has a σ_d . The black line is also a C_2 and the black dot is another C_2 axis of rotation. The blue cardboard is bisecting the angle the form by the two C_2 (s).



Green ball is fluorine
Black ball is xenon

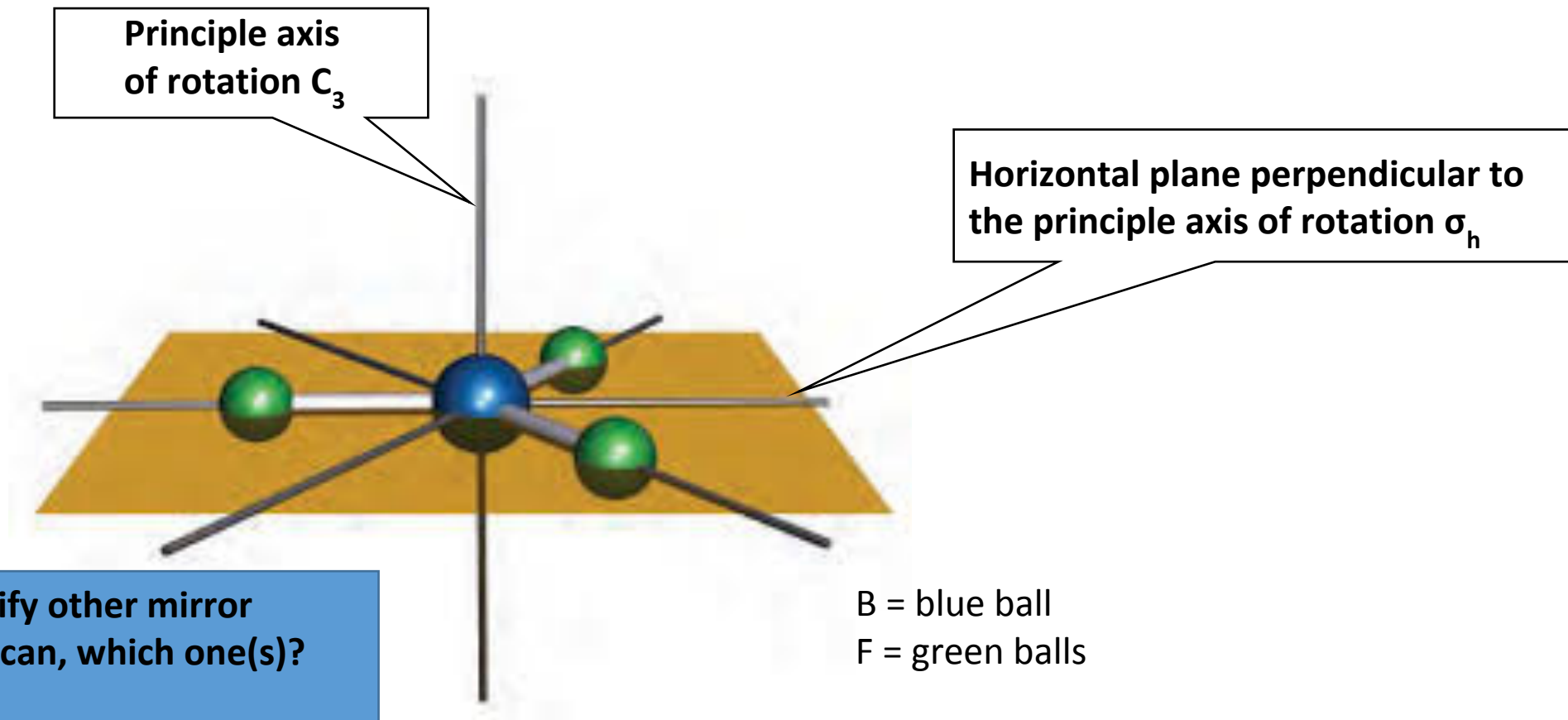




Did you notice the asterix. It was used to help differentiate between the atoms. (This is water molecule.)

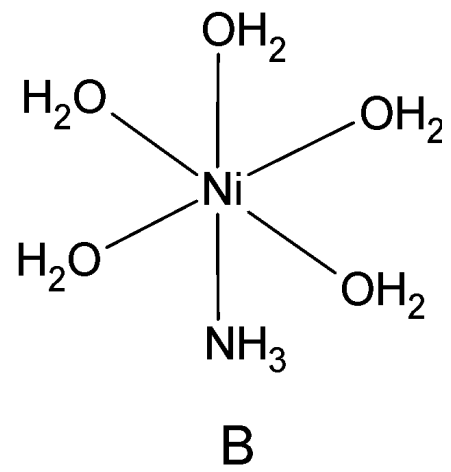
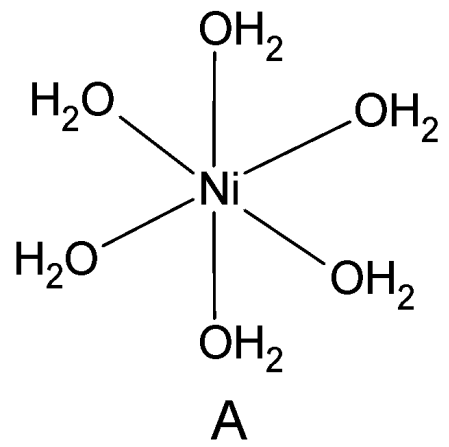
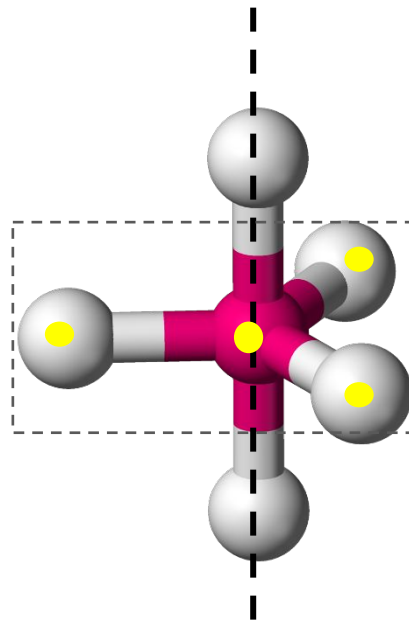
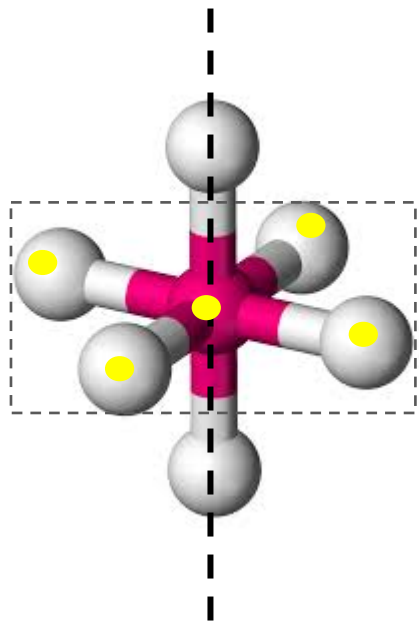


Figure 7-4
 Shriver & Atkins *Inorganic Chemistry, Fourth Edition*
 © 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong



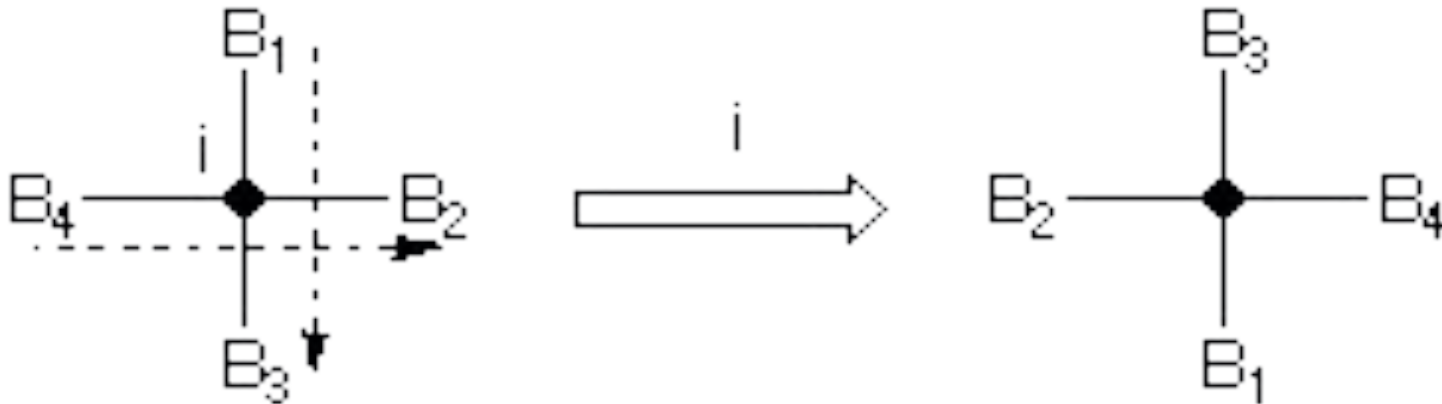
Can you identify other mirror planes. If you can, which one(s)?
See it in 3D.
<https://www.chemtube3d.com/sym-d3hbf3new/>

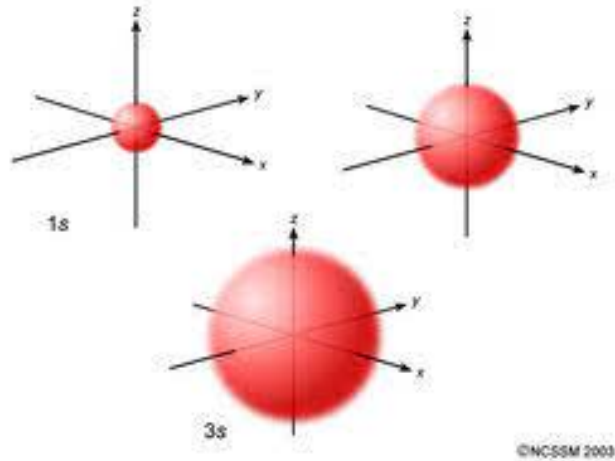




Inversion (i)

The element of this operation is a **point** found at the centre of the molecule and it's called the inversion center or center of symmetry. The operation is to move every atom in the molecule in a straight line through the inversion center to the opposite side of the molecule.





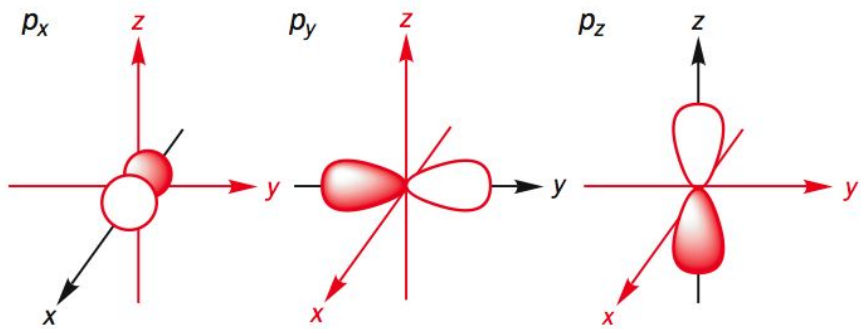
Orbitals *have a center of symmetry* can undergo an inversion operation and are said to be gerade (g).

Orbitals *don't have a centre of symmetry* are ungerade (u) and cannot undergo an inversion operation.

s-orbitals are gerade.

p-orbitals are ungerade

d-orbitals are gerade

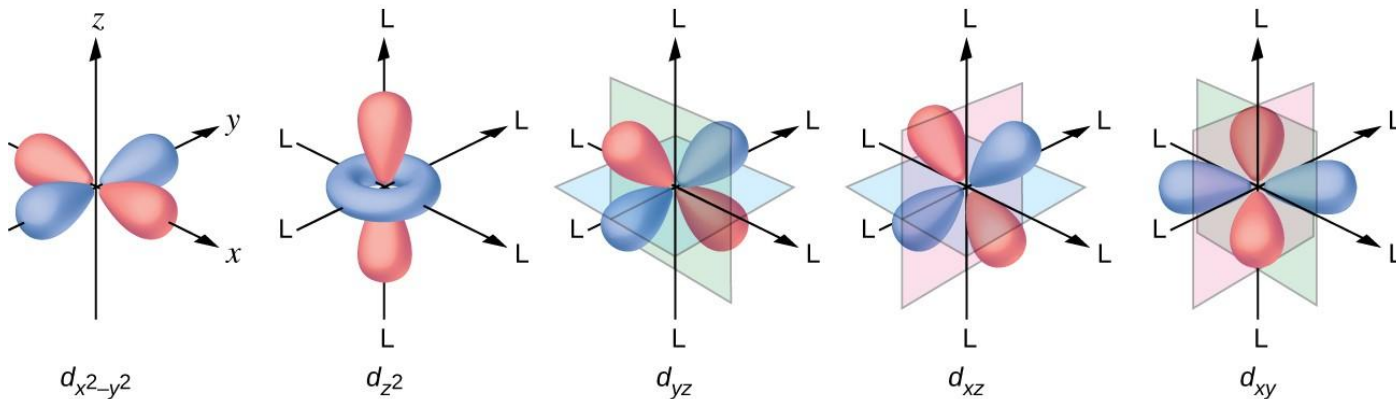


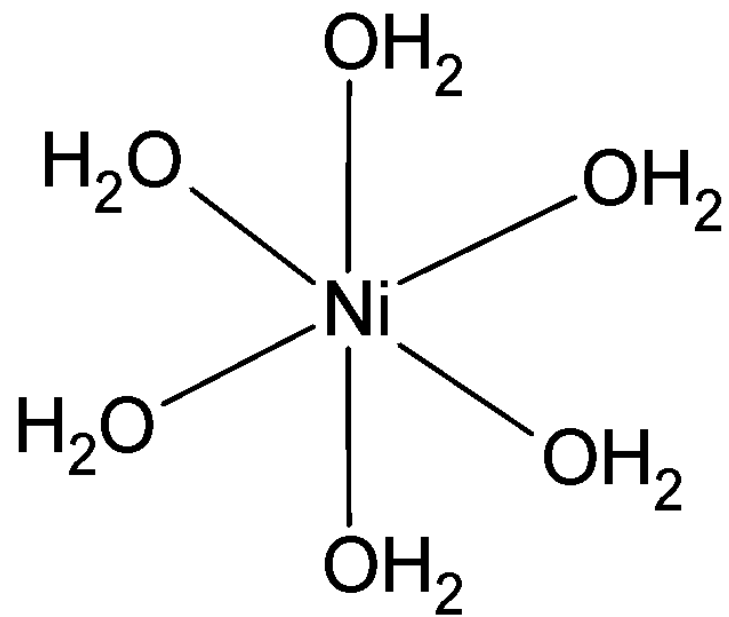
Remember the wave property of the electron.

In an s-orbital are in one phase (+ or -).

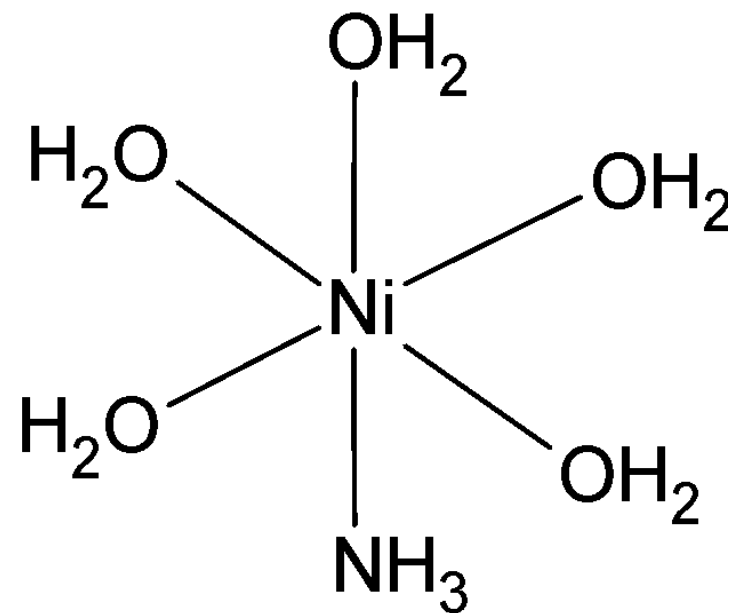
While for the p-orbitals each lobe exist in two phases at the same time (+ and -). One lobe is in a +ve phase (let say the red portion) while the second lobe in a -ve phase (white portion) at the same.

In d-orbitals each lobe exist in one phase, which is the opposite of the other lobe.





A



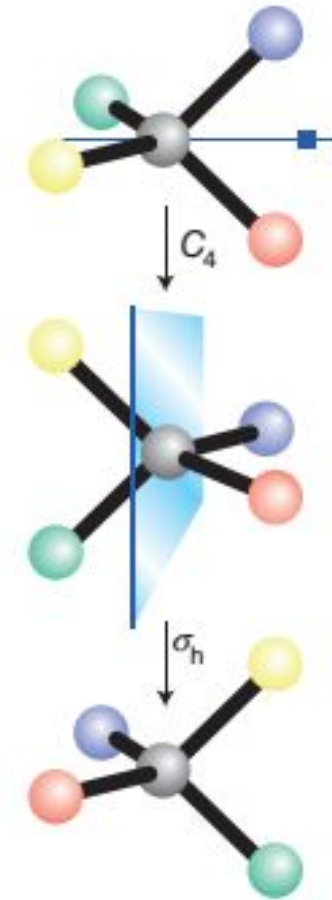
B

END OF UNIT TWO

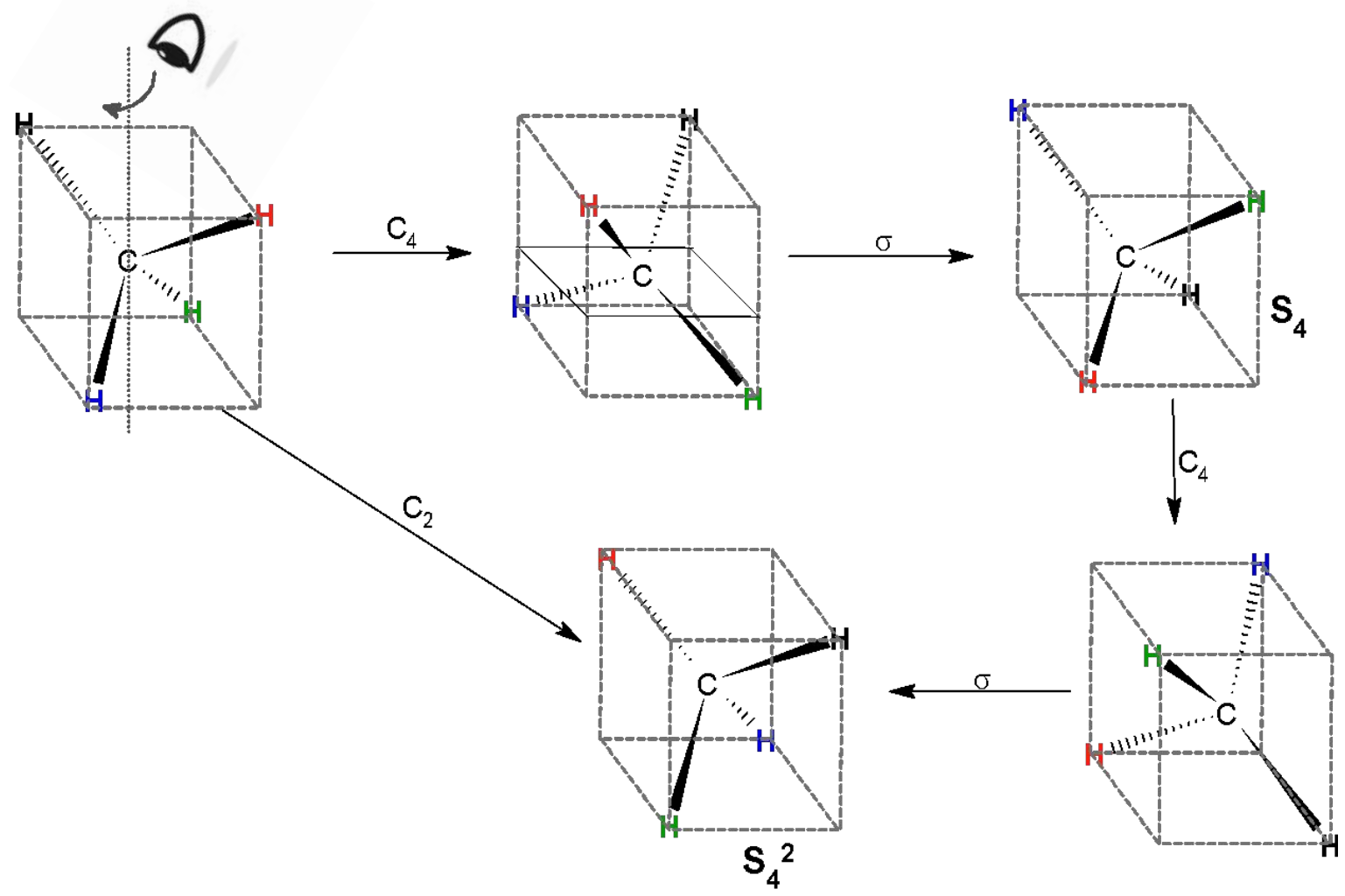
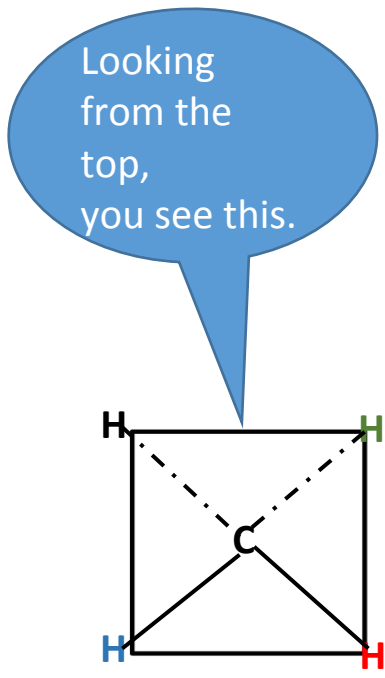
UNIT THREE

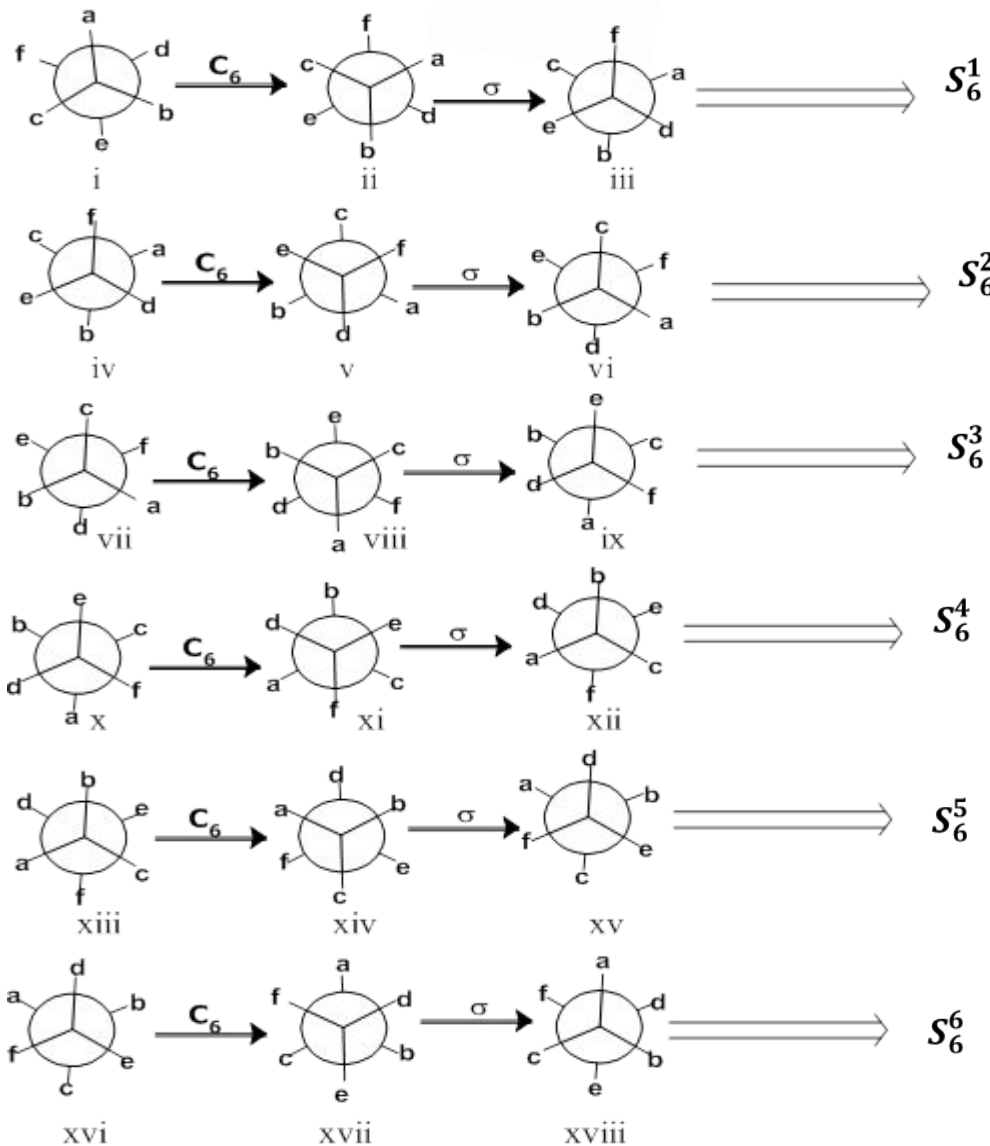
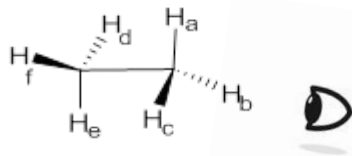
Improper rotation (S_n)

This is an n-fold rotation followed by reflection through mirror plane perpendicular to the axis of rotation. It can also be done in the reverse, first a reflection through the mirror plane then followed by the n-fold rotation. Whichever route is taken be consistent.



<http://openchemistryhelp.blogspot.com/2013/03/guide-to-symmetry.html>

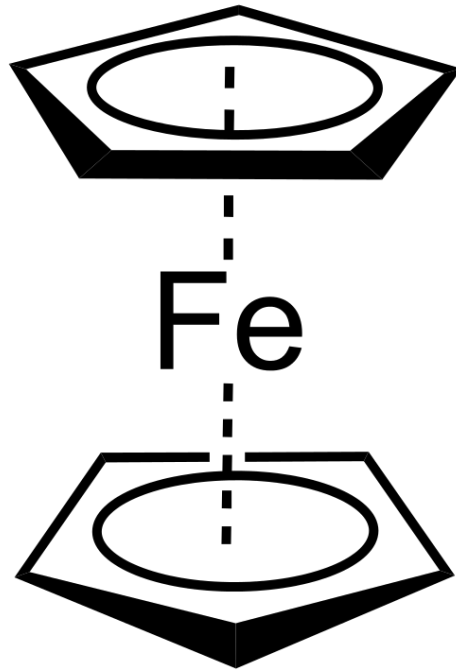




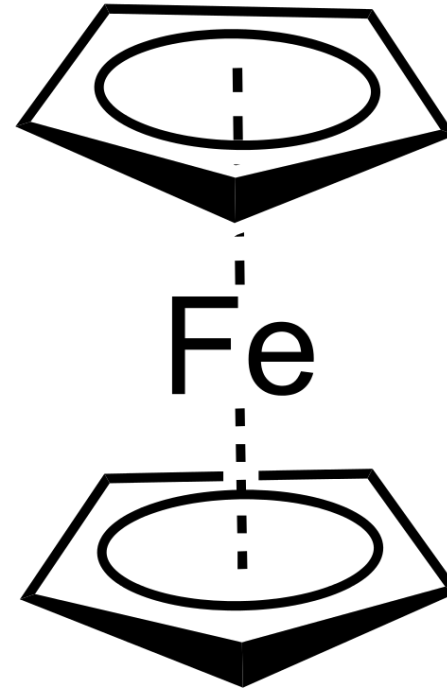
Doing a series of operation will lead to and equivalent operation. An S_6 axis will generate the following operations.

Operation	Symbol
H_3C-CH_3	

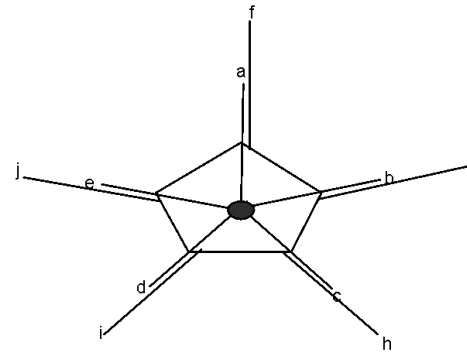
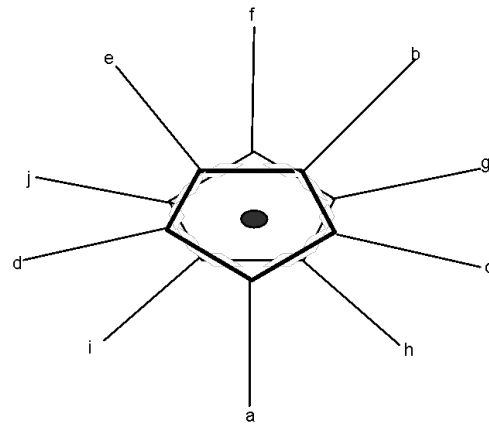
- σC_6 means the reflection is done followed by rotation by 60°
- S_2 means a C_2 (180° rotation) then the reflection
- σC_6^5 means a reflection followed by means five 60° rotations
- S_6^5 means a C_6 (60° rotation) then the reflection done five times



Staggered ferrocene



Eclipsed ferrocene



END OF UNIT THREE

Point Group

- The collection of symmetry elements present in a molecule forms a group and is technically called a **Point Group**. It called point group because all the symmetry elements (points, lines and planes) will intersect at a single point.
- Let's take water for example water has the following symmetry element E , C_2 , $2\sigma_v$ and it belongs to C_{2v} point group. Another molecule that belongs to the C_{2v} group is the boat conformation of cyclohexane.
- Even though they have different shapes they belong to the same point group. Therefore, molecules can be classified according to their symmetry.

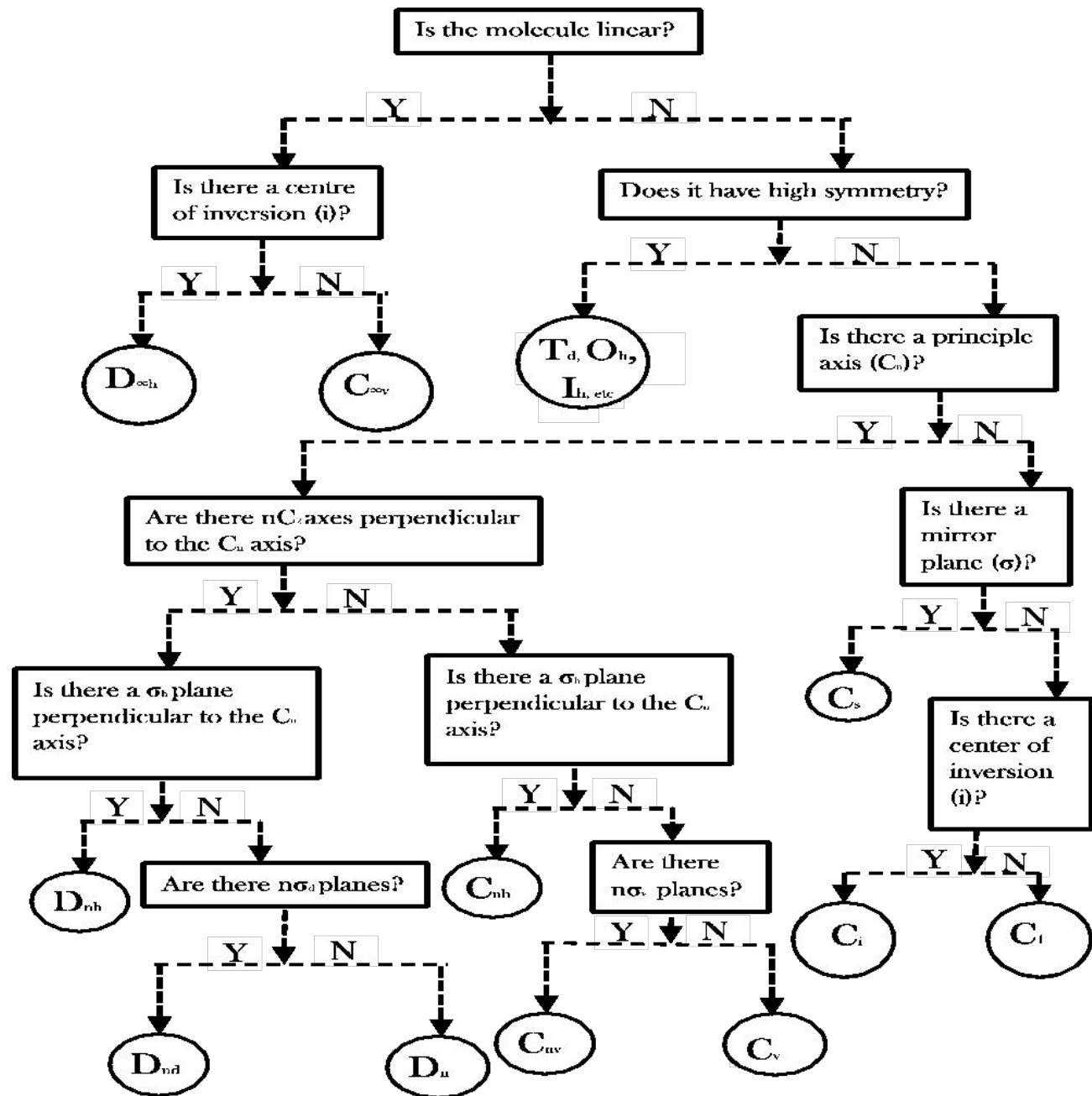
Point Group	Elements
$C_{\infty v}$	C_{∞}, E, σ_v
$D_{\infty h}$	$C_{\infty}, E, \sigma_v, \sigma_h$
C_1	E
C_i	E, i
C_s	E, σ
C_n	E, C_n
C_{nv}	E, C_n, σ_v
C_{nh}	E, C_n, σ_h
D_n	
D_{nh}	
D_{nd}	
S_n	E, S_n axis
T_d	$4C_3, 3C_2, 6\sigma_d$
T	$4C_3, 3C_2$
T_h	$4C_3, 3C_2, i$
O_h	E, $8C_3, 6C_2, 6C_4, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$
O	E, $8C_3, 6C_2, 6C_4, i, 6S_4, 8S_6$

That is the symbol for perpendicular

It is possible to determine the point group by finding the entire symmetry elements and then look up in set of tables called the character table until a match is found.

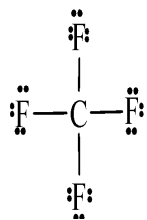
There are however molecules that have many symmetry elements an example is methane which has 24 symmetry elements.

So chemists have developed various flow charts that make the process simpler. See sample of chart below.

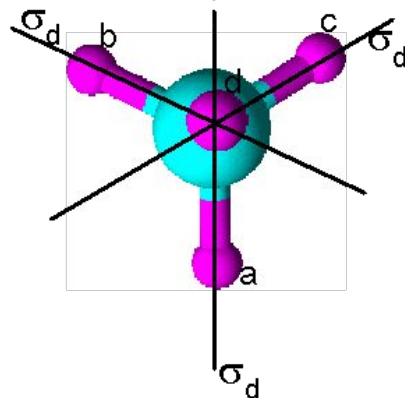
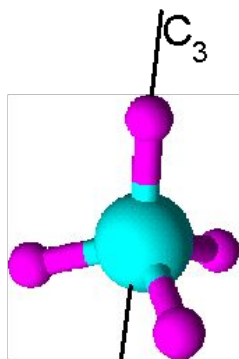
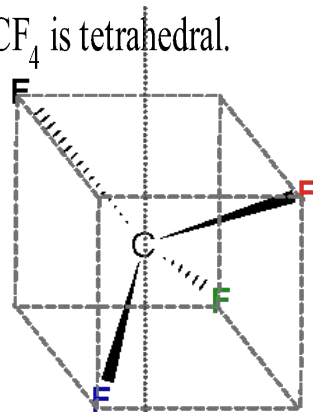


Determine the point group of CF₄

C 4e
 4F 4x7e = 28e
 Total 32e



Around C there are 4bp and no lp.
 The shape of CF₄ is tetrahedral.



Assuming that the tetrahedral molecule is in cube and 4 of its atoms are at various vertices of the cube. This molecule has 6 principle axis passing each passing through the centre of the a face of the cube. That is why it is a high symmetry molecule.

With each principle axis it can perform a S₄ operation. = 6S₄

recall that 2S₄ = C₂. This means that there will be a total of 3C₂,

Passing a rotational axis through the vertex of the cube where there is an atom would yeild 4C₃

There are also 6σ_d and are listed below (each fluorine atom is labelled as a,b,c,d to distinguish them)

a plane is bisecting the F_a-C-F_b

a plane is bisecting the F_a-C-F_c

a plane is bisecting the F_a-C-F_d

a plane is bisecting the F_b-C-F_c

a plane is bisecting the F_b-C-F_d

a plane is bisecting the F_c-C-F_d

Therefore this tetrahedral molecule CF₄ has E, 3C₂, 6S₄, 4C₃, 6σ_d

Following the chart

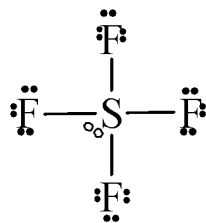
Is this molecule linear – No

Does it have a high symmetry – Yes, it can be with T_d, O_h, I_h.

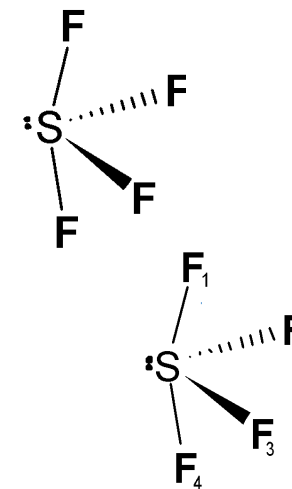
It is a tetrahedral molecule it would belong to the **T_d point group** since it has σ_d.

Determine the point group of SF₄

S		6e
4F	4x7e =	28e
Total		34e



Around S there are 4bp and 1lp.
The shape of SF₄ is see-saw.



Following the point group chart

Is the molecule linear? – **No**

Does it have high symmetry? – **No**

Is there a principle axis? – **Yes (C₂)**

SF₄ has a C₂ that passes through the F₂-S-F₃ angle as well as the F₁-S-F₄ angle

Are there nC₂ axes perpendicular to the C_n? – **No**

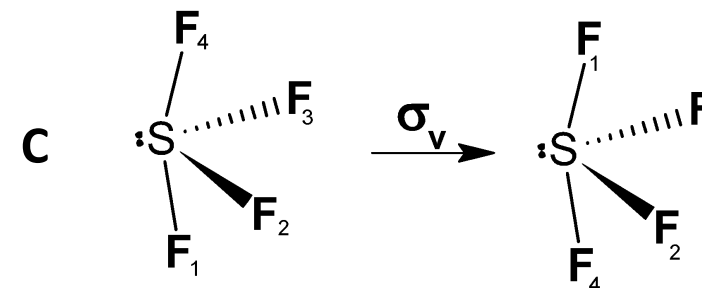
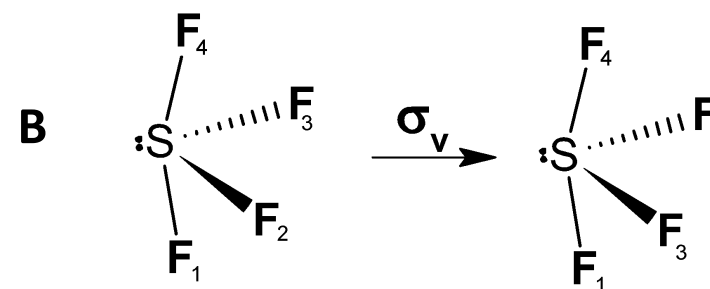
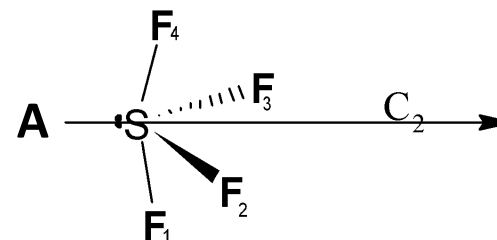
Is there σ_h a perpendicular to the C_n? – **No**

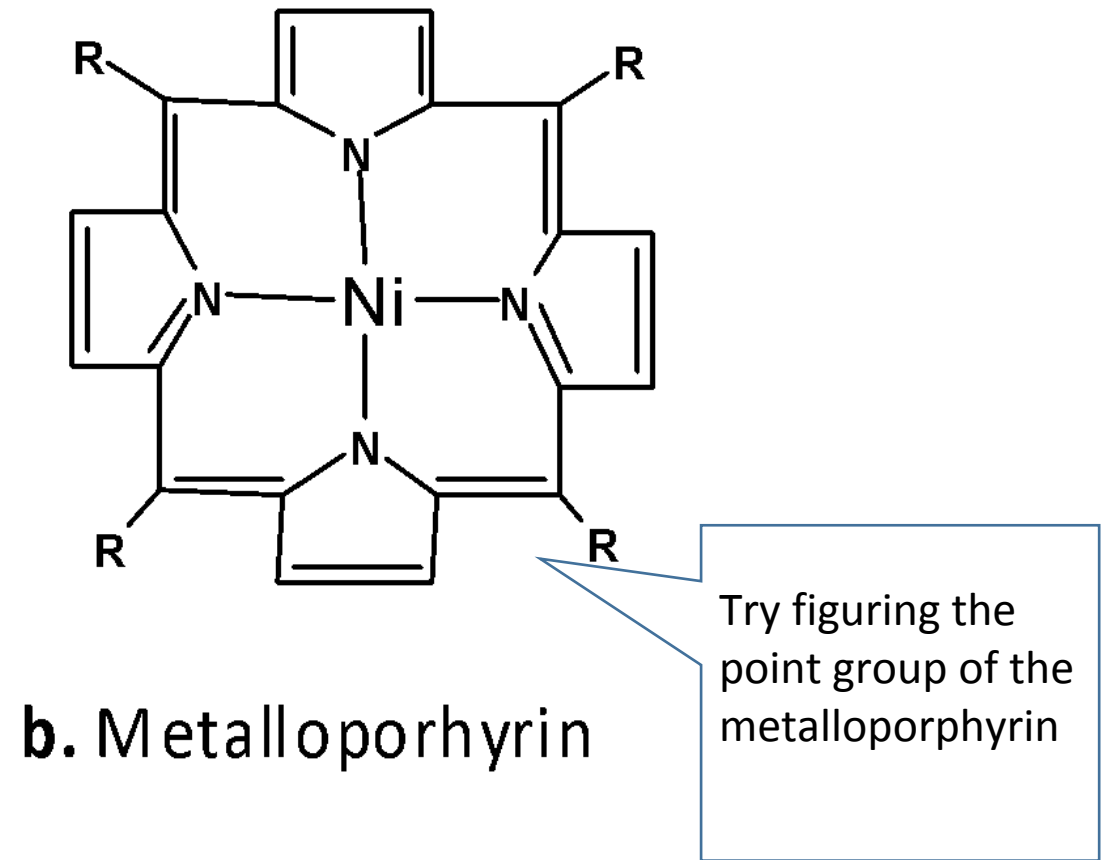
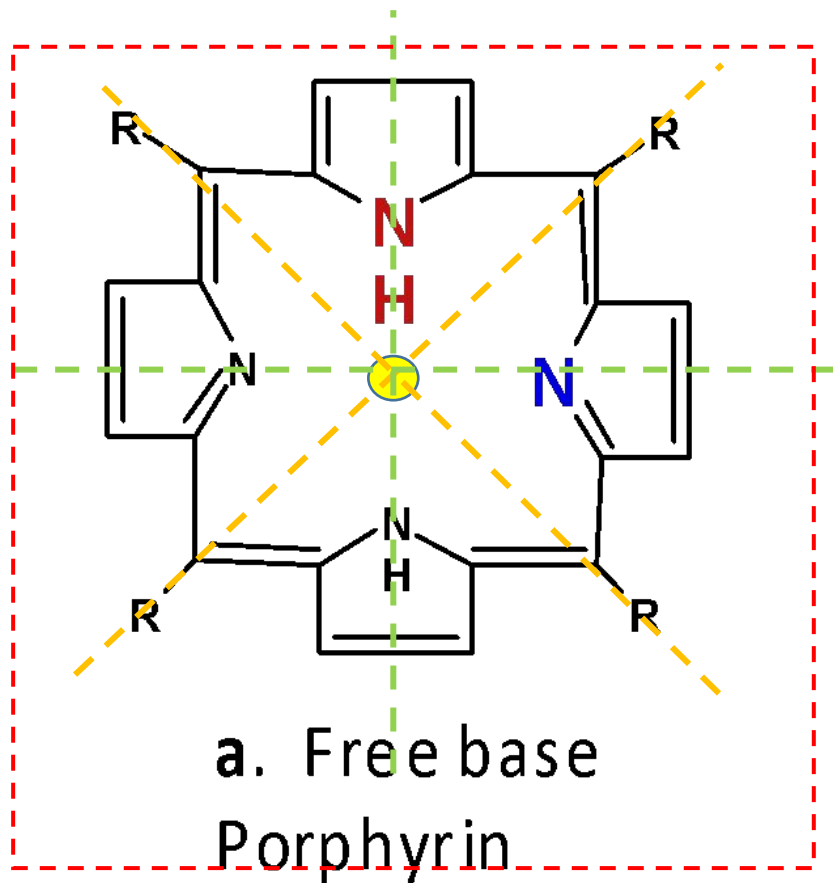
Are there nσ_v planes – **Yes**

It has a mirror plane parallel to the C₂, bisecting the F₂-S-F₃ angle and lie along F₁-S-F₄ (σ_v)

It has another mirror plane lie along F₂-S-F₃ angle but bisects the F₁-S-F₄ angle (σ_v)

The point group is C_{2v}, since the principle axis is C₂ then SF₄ belongs to C_{2v} point group





Following the point group chart

Is the molecule linear? – No

Does it have high symmetry? – No

Is there a principle axis? – Yes (C_2)

Are there nC_2 axes perpendicular to the C_n ? – Yes

Is there σ_h a perpendicular to the C_n ? – Yes

The point group is D_{nh} , since the principle axis is C_2 then free base porphyrin belongs to D_{2h} point group

MODULE TWO

SYMMETRY OPERATIONS

- **Unit One** – Identity and n-fold Rotation
- **Unit Two** – Reflection and inversion
- **Unit Three** – Improper rotation
- **Unit Four** – Point group

UNIT ONE – Identity and n-fold Rotation

A molecule is said to have symmetry if when it is 'turned' there is no change in the placement of the atoms of the molecules. The symmetry of a molecule is determined by the existence of **symmetry operations** performed with respect to **symmetry elements**.

A symmetry element is a line, a plane or a point in or through an object (a molecule), about which the 'turnings' are made and the object has an orientation that indistinguishable from the original.

A symmetry operation is the movement of the object (molecule) about a line, plane or point.

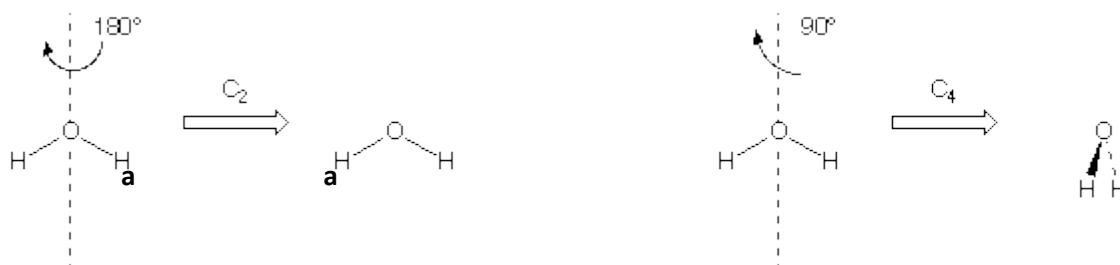
There are 5 kinds of operations

1. Identity
2. n-Fold Rotations
3. Reflection
4. Inversion
5. Improper n-Fold Rotation

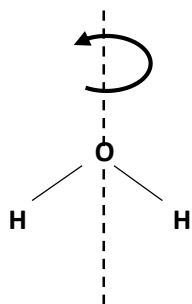
1. **Identity E:** For this operation there is no 'turning' is done to the molecule. The molecule does not move and all the atoms of the molecule stay at the same place. All molecules have the identity operation. Identity operation can also be a combination of different operations resulting in the molecule returning to its original position after these operations are performed.

2. **n-Fold Rotations C_n** , (where n is an integer). This is a rotation by $\frac{360^\circ}{n}$ about a particular axis defined as the **n-fold rotation axis**. The symmetry element is a line and the operation is a rotation along this line. $C_2 = 180^\circ$ rotation, $C_3 = 120^\circ$ rotation, $C_4 = 90^\circ$ rotation, $C_5 = 72^\circ$ rotation, $C_6 = 60^\circ$ rotation, etc. Clockwise and anticlockwise rotations must yield the same result for it to count.

Rotation of H_2O about the axis shown by 180° (C_2) gives the same molecule back. Therefore, H_2O possesses the C_2 symmetry element.

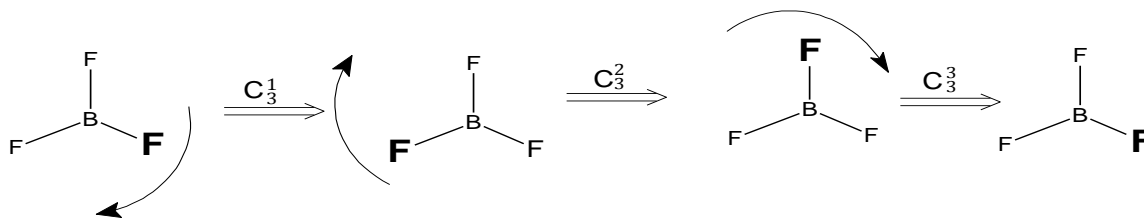


However, rotation by 90° about the same axis does not give back the identical molecule. Therefore, H_2O does NOT possess a C_4 symmetry axis.



Water has 1 C_2 ; one line passing through oxygen and bisecting the H-O-H bond angle.

BF_3 possesses a C_3 rotation axis of symmetry. This is a line passing through B coming out of the paper. (Both directions of rotation must be considered).

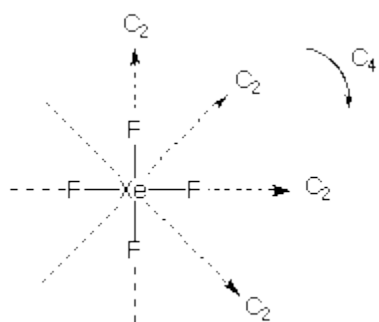


- C_2 means one 180° rotation
- C_3 means a 120°
- C_6^2 means two 60° rotations
- C_6^5 means five 60° rotations
- C_4^2 means two 90° rotations

Note:

The axis with the greatest value of n is the **PRINCIPLE AXIS**

$$C_n^n = E$$



XeF_4 is square planar. It has four DIFFERENT C_2 axes;

- 2 are in line with the F-Xe-F bonds
- 2 are bisecting the F-Xe-F bond angle.
- It also has a C_4 axis coming out of the page through Xe and it is the principle axis because it has the largest n.

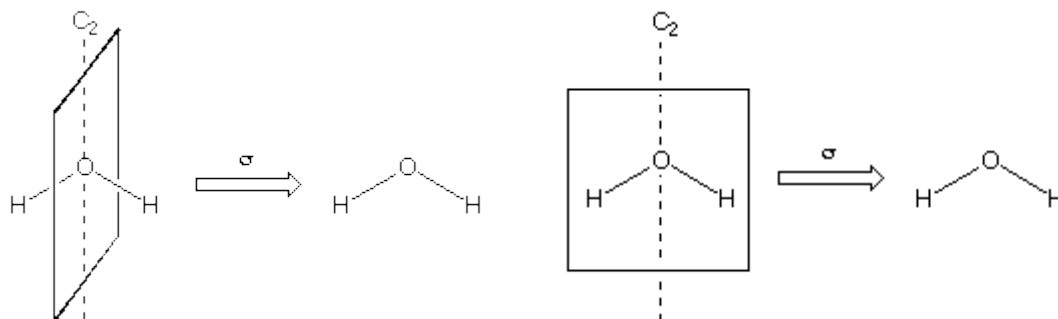
UNIT TWO – Reflection and Inversion

3. **Reflection:** s or σ the symmetry element is called a mirror plane (or plane) of symmetry.

- If reflection about a mirror plane gives the same molecule/object back than there is a plane of symmetry (s/σ).
- If plane lies on the principle rotation axis (i.e., parallel), it is a vertical plane (s_v or σ_v)
- If plane is perpendicular to the principle rotation axis, it is a horizontal plane (s_h or σ_h)
- If plane is parallel to the principle rotation axis, but bisects angle between 2 C_2 axes, it is a diagonal plane (s_d or σ_d)
- If the shape of the molecule is **linear, bent or planar** (i.e. trigonal planar, square planar) they would always appear to be “lying” on a plane and can only be labelled as σ_h if and only if this plane “they are lying on” is perpendicular to the principle rotation axis.

When mirror plane is operated n times, we have $\sigma^n = \begin{matrix} E & (\text{when } n \text{ is even}) \\ \sigma & (\text{when } n \text{ is odd}) \end{matrix}$

H_2O possess 2 σ_v mirror planes of symmetry because they are both parallel to the principle rotation axis (C_2).

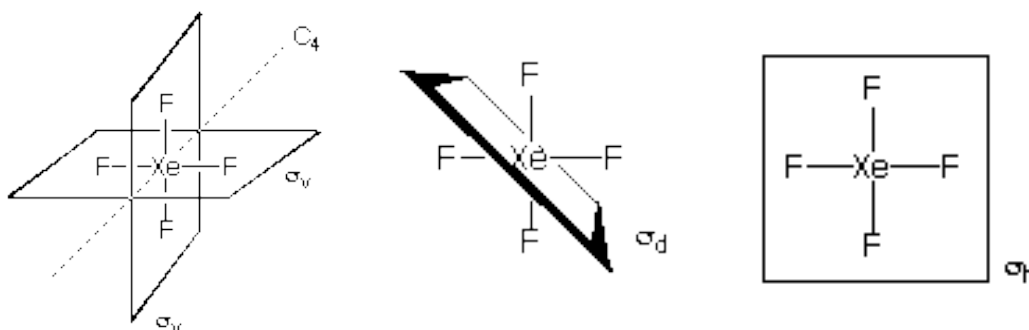


H_2O possesses 2 vertical mirror planes of symmetry because they are both parallel to the principle rotation axis (C_2). The first plane is bisecting the molecule through oxygen such that there is a hydrogen atom on either side of the plane such what is seen on the left side of the plane is seen at the right side as well.

The second plane is also bisecting the molecule but it is doing so through all the 3 atoms such that what is seen in front of the plane is the same as what is seen behind the plane.

Symmetry of operation of H₂O are: E, C₂, 2σ_v

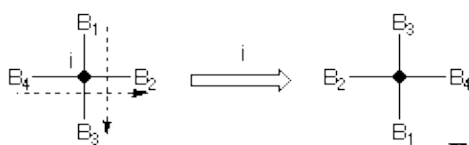
- XeF₄ has two planes of symmetry parallel to the principle rotation axis i.e. along the 2 F-Xe-F bonds: σ_v
- XeF₄ has two planes of symmetry parallel to the principle rotation axis and bisecting the angle between 2 C₂ axes i.e. bisecting the F-Xe-F bond angles: σ_d
- XeF₄ has one plane of symmetry perpendicular to the principle rotation axis. The whole molecule is sort of “lying” on this plane: σ_h



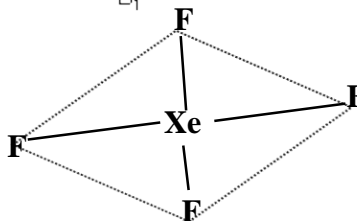
XeF₄ – has E, 4C₂, C₄, 2σ_v, 2σ_d and σ_h symmetry operations.

4. Inversion i:

The element of this operation is a point found at the centre of the molecule and it's called the inversion center or center of symmetry. The operation is to move every atom in the molecule in a straight line through the inversion center to the opposite side of the molecule.



XeF₄ possesses an inversion centre at the Xe atom.



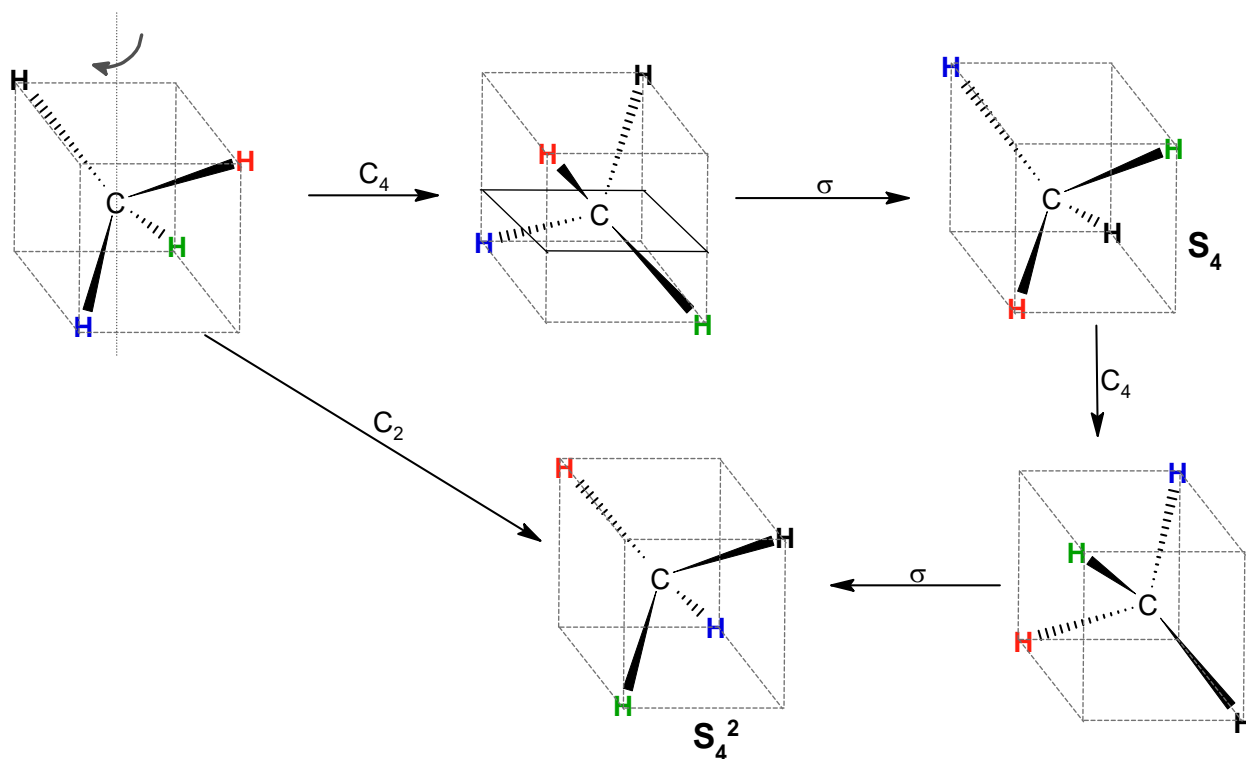
When inversion is operated n times, we have $i^n = \begin{matrix} E & (\text{when } n \text{ is even}) \\ i & (\text{when } n \text{ is odd}) \end{matrix}$

UNIT THREE – Improper Rotation

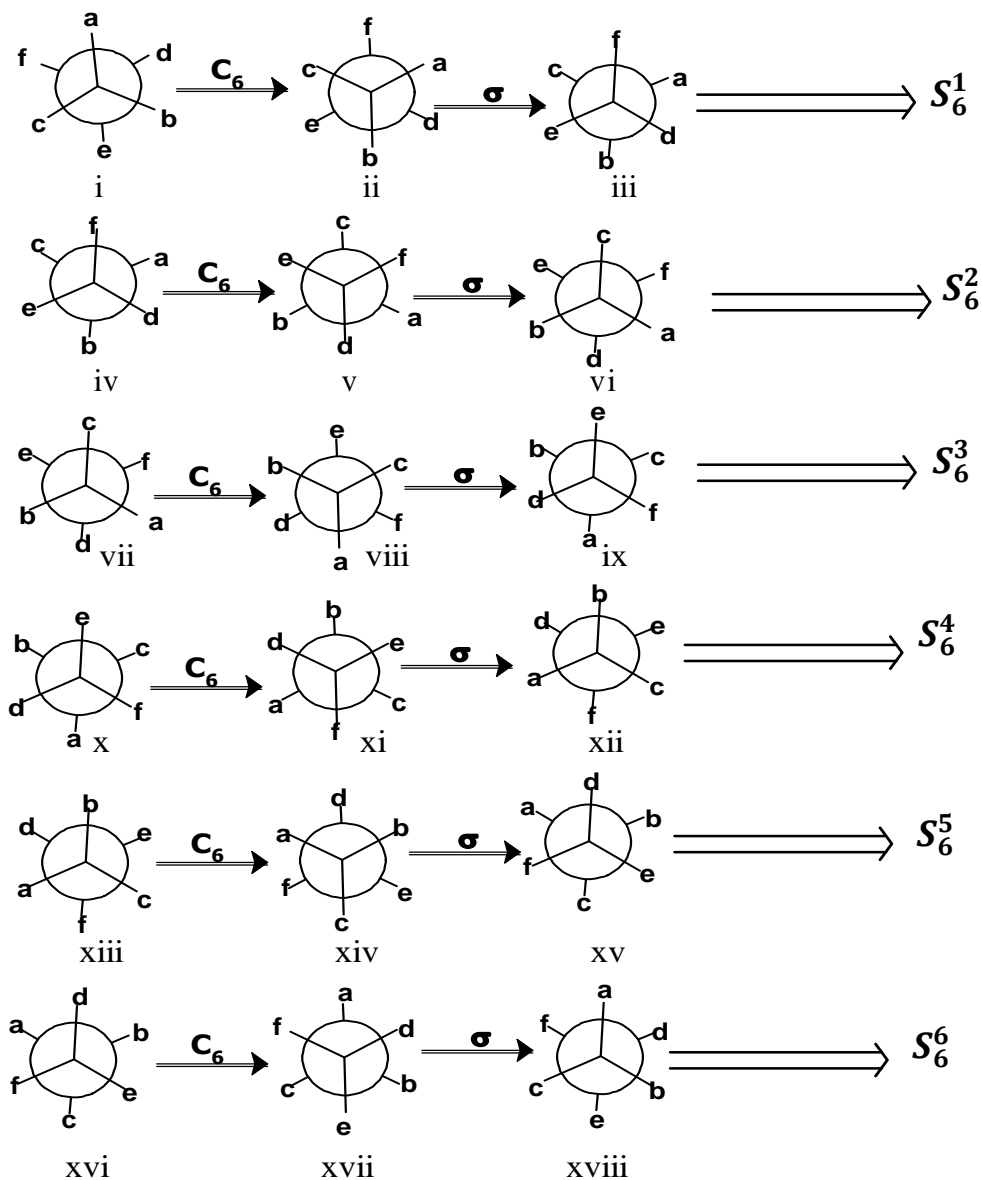
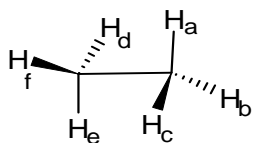
This is an n -fold rotation followed by reflection through mirror plane perpendicular to the axis of rotation. It can also be done in the reverse, first a reflection through the mirror plane then followed by the n -fold rotation. Whichever route is taken be consistent.

This is the improper rotation of tetrahedral molecule e.g. CH_4 , each hydrogen is distinguished from the other with different colours so as to be able to track the movement.

Notice that by just doing a C_2 you to methane you end up with S_4^2



Below is the **staggered conformation** of ethane (CH_3CH_3), several improper rotations were carried out on it.

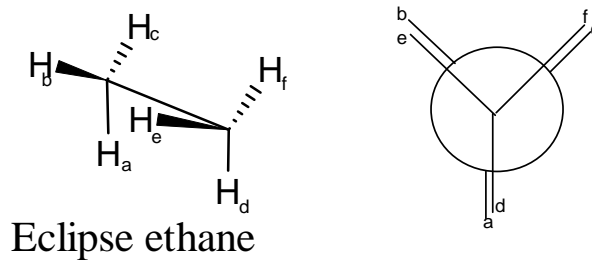


Doing a series of operation will lead to an equivalent operation. An S_6 axis will generate the following operations.

Operation	Symbol
$S_6 = \sigma C_6$	S_6
$S_6^2 = C_6^2 = C_3$	C_3
$S_6^3 = S_2 = (\sigma C_6^3 = \sigma C_2) = i$	i
$S_6^4 = C_6^4 = C_3^2$	C_3^2
$S_6^5 = \sigma C_6^5$	S_6^5
$S_6^6 = E$	E

- σC_6 means the reflection is done followed by rotation by 60°
 - S_2 means a C_2 (180° rotation) then the reflection
 - σC_6^5 means a reflection followed by means five 60° rotations
- S_6^5 means a C_6 (60° rotation) then the reflection done five times

For the **eclipse ethane**, it does not undergo C_6 operation but a C_3 .



An S_5 axis will generate the following operations.

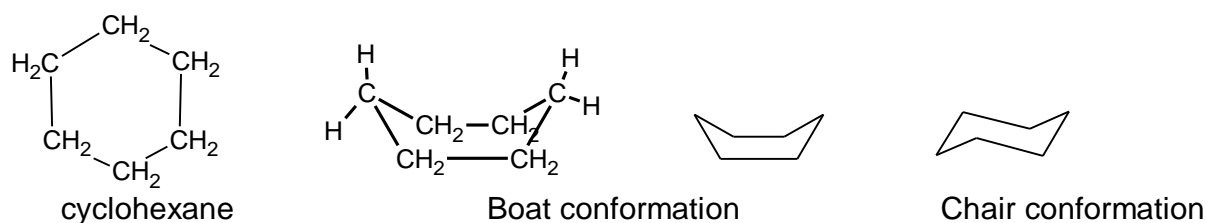
Operation	Symbol
$S_5 = \sigma C_5$	S_5
$S_5^2 = C_5^2$	C_5^2
$S_5^3 = \sigma C_5^3$	S_5^3
$S_5^4 = C_5^4$	C_5^4
$S_5^5 = \sigma$	σ
$S_5^6 = C_5$	C_5
$S_5^7 = \sigma C_5^2$	S_5^7
$S_5^8 = C_5^3$	C_5^3
$S_5^9 = \sigma C_5^4$	S_5^9
$S_5^{10} = E$	E

Generally for improper rotations S_n when n is EVEN, there are n operations $\{S_n^1, S_n^2, \dots, S_n^n\}$, while when n is ODD, there are $2n$ operations $\{S_n^1, S_n^2, \dots, S_n^{2n}\}$.

For an improper rotation S_n^m when m is even an alternative route of operation can be found e.g. $S_6^2 = C_3^2$ but when m is odd it the regular improper operation occurs $S_6^5 = \sigma C_6^5$.

UNIT FOUR – Point group

A selected collection of symmetry elements present in a molecule forms a group and is technically called a **Point Group**. It called point group because all the symmetry elements (points, lines and planes) will intersect at a single point. Let's take water for example water has the following symmetry element E , C_2 , $2\sigma_v$ and it belongs to C_{2v} point group. Another molecule that belongs to the C_{2v} group is the boat conformation of cyclohexane. Even though they have different shapes they belong to the same point group. Therefore, molecules can be classified according to their point group.

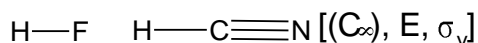


Molecular Point Groups

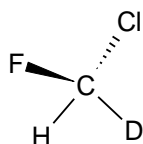
1. $C_{\infty v}$: Signifies the presence of an ∞ -fold axis of rotation which is possessed by a **linear molecule**. For molecules that belong to this group
 - will have an infinite number of σ_v planes
 - no σ_h planes or inversion centre.

The molecules that satisfy these conditions are

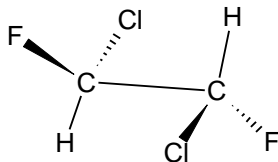
- (a) asymmetrical diatomic molecules HF , CO , CN^- and
- (b) linear polyatomic molecules (having 3 or more atoms) that do not and do not have a centre of symmetry OCS , HCN



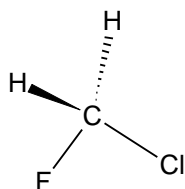
2. $D_{\infty h}$: These are symmetrical diatomics (e.g. H_2 , $[O_2]^{2-}$) and linear polyatomics (that contain a centre of symmetry (e.g. $[N_3]^-$, CO_2 , C_2H_2))
 - They have a σ_h plane
 - in addition to a C_{∞} axis and
 - an infinite number of σ_v planes.
3. C_1 : this contain only identity E (i.e. a C_1 rotation is a 360° rotation and it is the same as identity operation E e.g. $CDFHCl$)



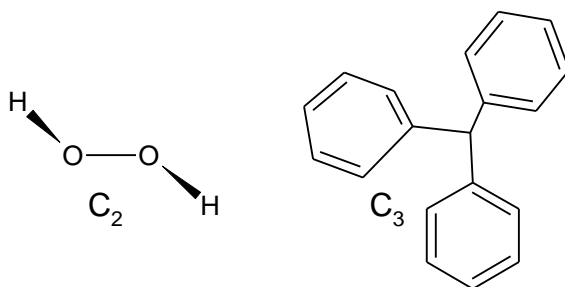
4. C_i : This group has only identity E and a centre of inversion i



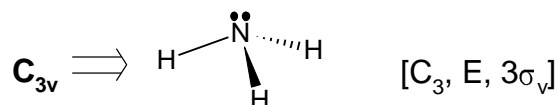
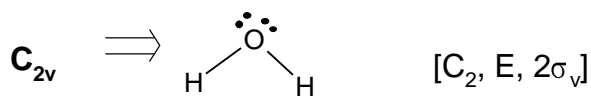
5. C_s : This has identity E and a plane of reflection σ



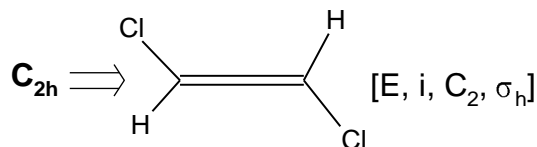
6. C_n : In this is identity E and an n-fold axis of rotation C_n



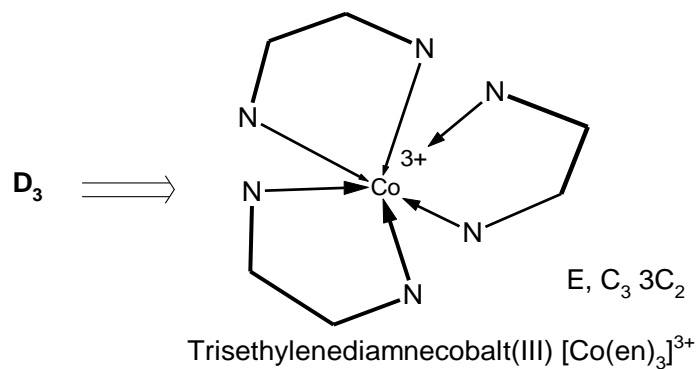
7. C_{nv} : here there is the E , a C_n axis, and might have more than one vertical mirror planes σ_v



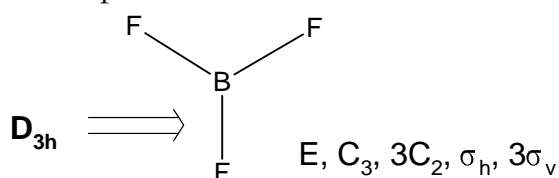
8. C_{nh} : contains E , a C_n axis, and might have more than one horizontal mirror planes σ_h . Note that it might have centre of inversion



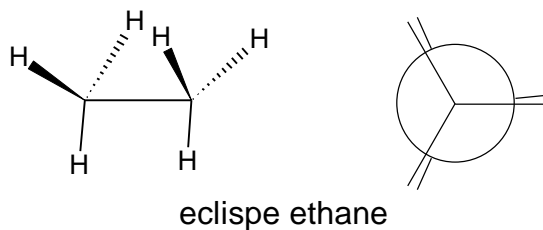
9. D_n : In this is identity E and an n-fold axis of rotation C_n and might have more than one 2-fold rotational axes which are perpendicular to the principle axis



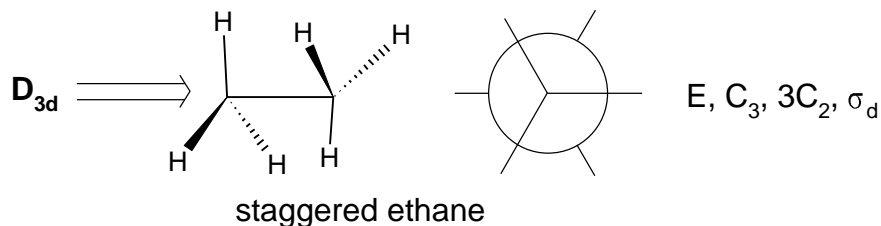
10. D_{nh} : contains the same symmetry elements as D_n with the addition of one or more horizontal mirror planes σ_h



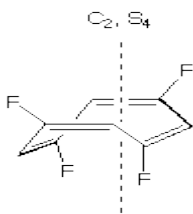
- eclipse ethane $D_{3h} = E, C_3, 3C_2, \sigma_h, 3\sigma_v$
- benzene $D_{6h} = E, C_6, 6C_2, \sigma_h, 6\sigma_v$



11. D_{nd} : contains the same symmetry elements and D_n with the addition of one or more dihedral mirror planes σ_d



12. S_n : In this is identity E and one S_n axis



$$S_4 = E, C_2, S_4$$

The following groups contain more than one principle axis and they all meet at the centre of the molecule. and are referred to as the cubic group. They are high symmetry groups. The more common ones are divided into the Tetrahedral groups (T_d , T_h and T) and the Octahedral groups (O_h and O) and there are other that do not fall under these categories.

13. **T_d** : contains all the symmetry element of a regular tetrahedron – 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes and 4 S_6 axes e.g. CH_4
14. **T** : same as T_d but no planes of reflection
15. **T_h** : same T but contains has a centre of inversion i
16. **O_h** : group of regular octahedron e.g. $SF_6 = E, 8C_3, 6C_2, 6C_4, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$

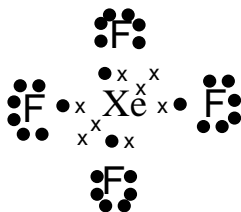
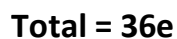
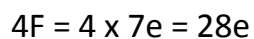
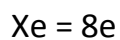


17. **O** : same as O_h but with no planes of reflection.
18. **I_h** : $E, 12C_5, 20C_3, 15C_2, i, 12S_{10}, 20S_6, 15s$ in Icosahedron e.g. C_{60} , dedocahedrane molecule ($C_{20}H_{20}$).
19. **R_3** : it has an infinity number of C_n axes with all the possible values of n and is the symmetry of sphere. Atoms belong to this group.

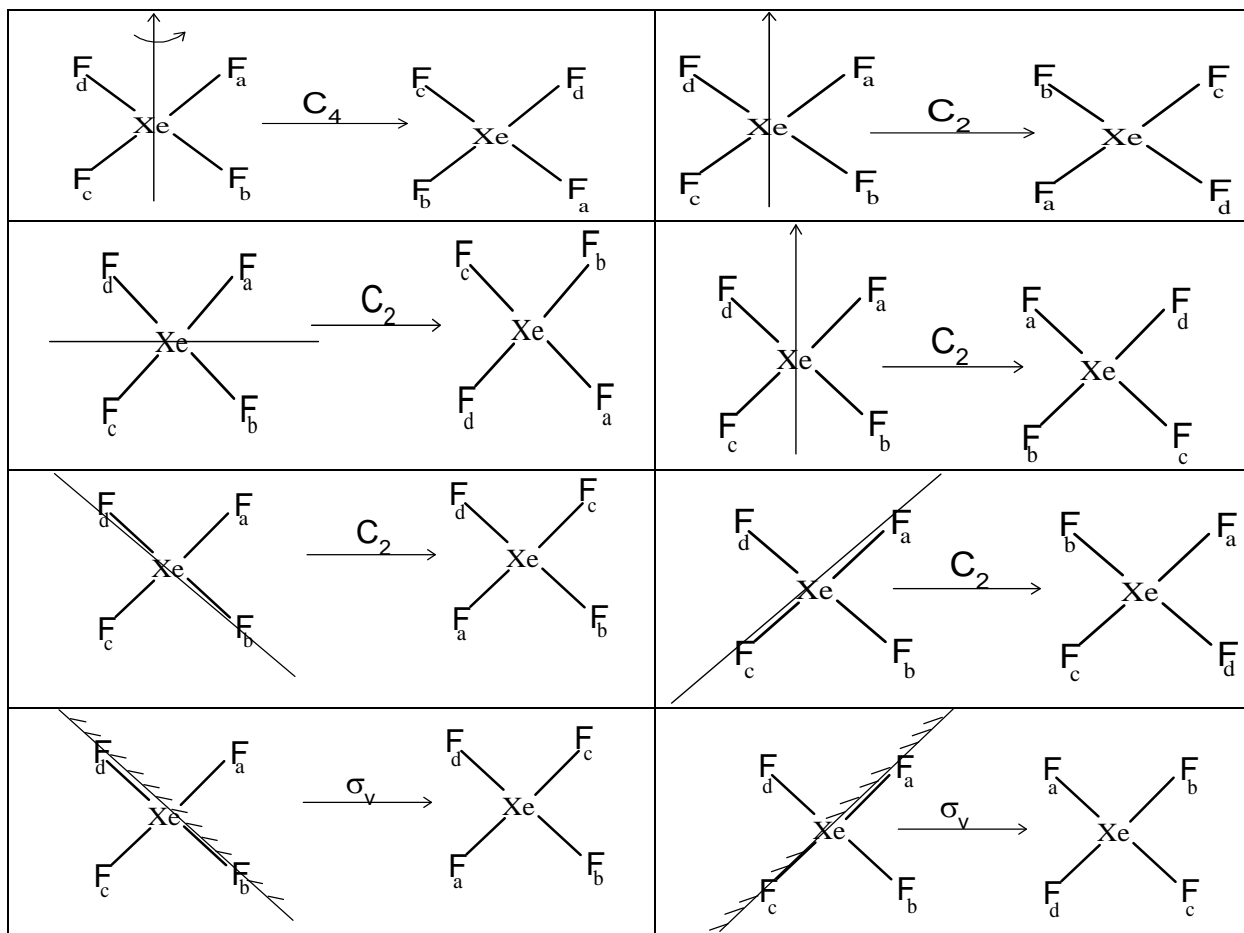
Assignment #2

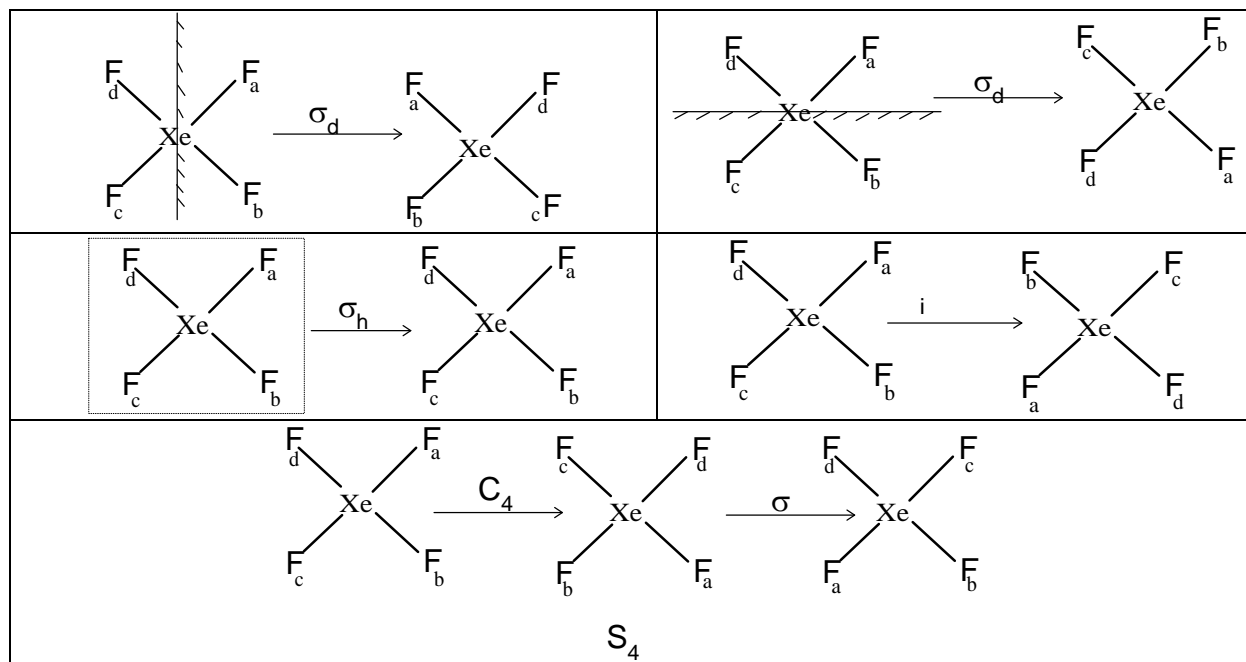
- Illustrate the operation of the all the symmetry elements in each molecule. (Hint: Label the F atoms to distinguish them).
 - NF₃
 - BrF₅
 - PF₅
- Following the point group chart determine their point group.

Here are two examples showing you how you should proceed:



XeF₄ has 4 bond pair and 2 lone pairs. It shape is square planar





Symmetry elements are $E, C_4, C_2, 4C_2, 2\sigma_v, 2\sigma_d, \sigma_h, S_4, i$

Following the point group chart

Is the molecule linear? No

Does it have a high symmetry? No it is square planar

Is there a principle axis C_n ? Yes

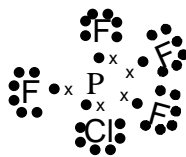
Are there any nC_2 axes \perp to the C_n axis? Yes

Is there a plane \perp to the C_n axis?

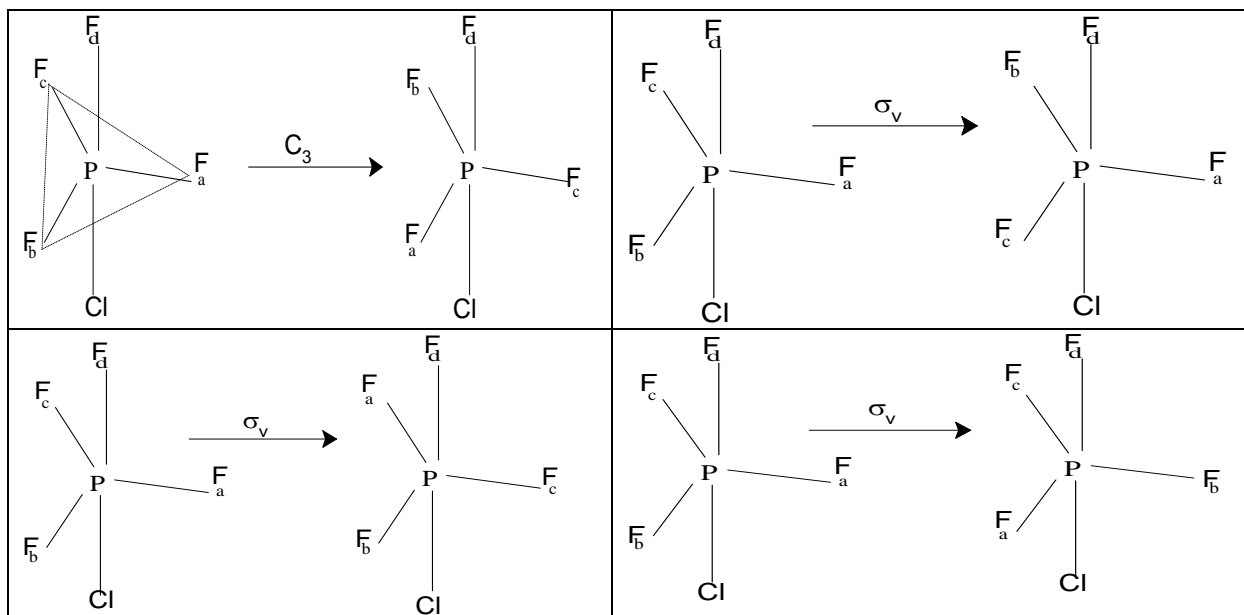
It belongs D_{nh} , i.e. is the **D_{4h}**

No need to draw the lines just do the operations and indicate movement with the labelled atoms. See the example below.

PF_4Cl
 $P = 5e$
 $4F = 4 \times 7e = 28e$
 $Cl = 7e$
Total = 40e



PF_4Cl has 5 bond pair
 and 0 lone pair. Its
 shape is Trigonal
 bipyramid



Symmetry elements are $E, C_3, 3\sigma_v,$

Following the point group chart

Is the molecule linear? No

Does it have a high symmetry? No it is trigonal bipyramid

Is there a principle axis C_n ? Yes

Are there any nC_2 axes \perp to the C_n axis? No

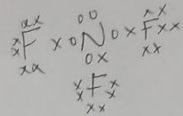
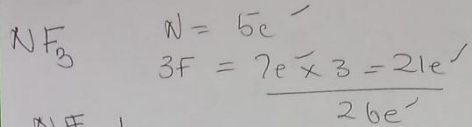
Is there a plane \perp to the C_n axis? No

It belongs C_{nv} , i.e. is the C_{3v}

Solution to Assignment 2

Dr RC George

①

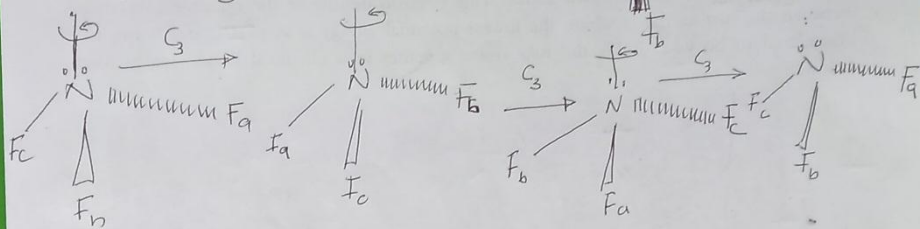


1.

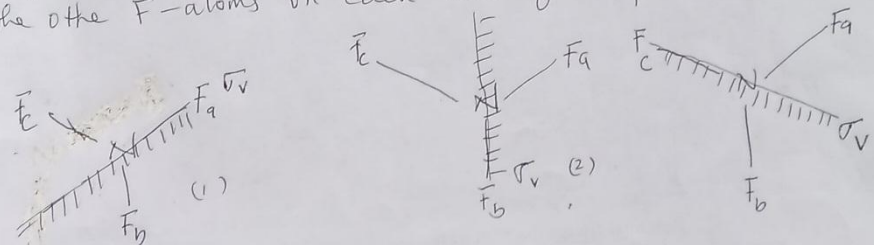
NF_3 has 3bp and 1lp
 Its shape is trigonal pyramidal

It has E

It has a C_3



It has 3 vertical mirror (plane). These planes are parallel (in-line) with the principle axis of rotation. They ~~be of each N~~ pass through each N-F bond with the other F-atoms on each side of the plane.



Is the molecule linear? NO

Does it have a high symmetry? NO, it trigonal pyramidal

Is there a principle axis C_n ? Yes

Are there any nC_2 axis \perp to the C_n axis? NO

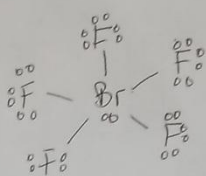
Is there a plane \perp to the C_n axis? NO

Are there $n\sigma_v$ planes? Yes

Point Group
 C_{3v}

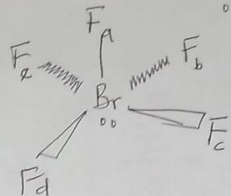
BrF_5

$\text{Br} = 7e^-$ (29)
 $5\text{F} = 7e^- \times 5 = 35e^-$
 $\frac{42e^-}{42e^-}$

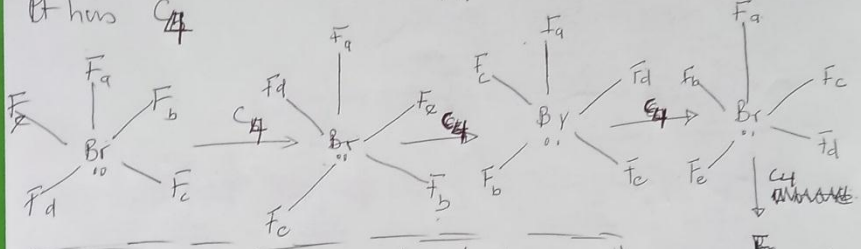


BrF_5 has 5 bp and 1 lp
 Its shape is square pyramidal

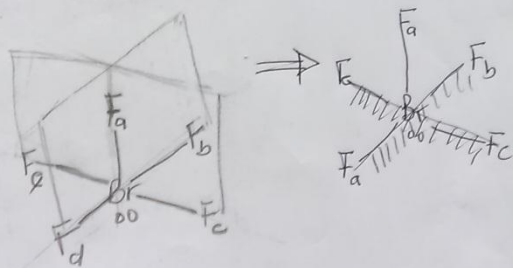
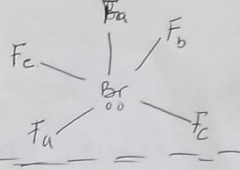
It has E



It has C_4

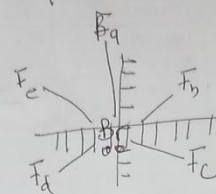


It has vertical planes σ_v the planes are parallel to the principle axis of rotation; in line with $\text{F}_d - \text{Br} - \text{F}_b$ and $\text{F}_e - \text{Br} - \text{F}_c$



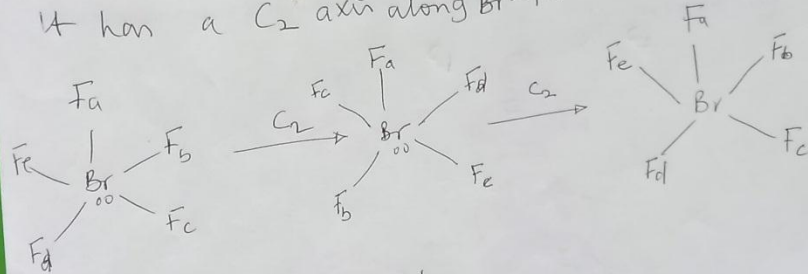
2.

It also has $2\sigma_d$ (dihedral planes). They lie parallel to the ~~principle~~ principal axis of rotation i.e. C_4 but bisect the angles ~~between~~ $\text{F}_b - \text{Br} - \text{F}_c$ and $\text{F}_d - \text{Br} - \text{F}_e$, also bisect the α angles ~~between~~ between $\text{F}_d - \text{Br} - \text{F}_c$ and $\text{F}_e - \text{Br} - \text{F}_b$ also



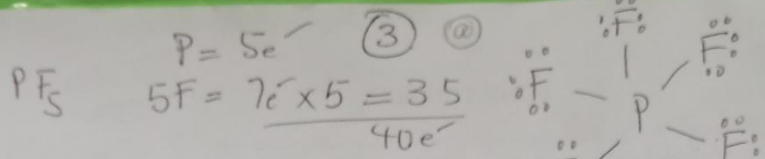
It has E

It has a C_2 axis along $\text{Br} - \text{F}_a$

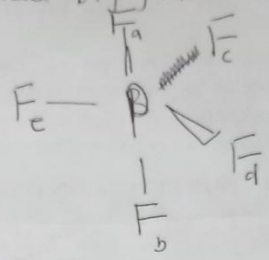


- Is the molecule linear? NO
- Does it have a high symmetry? NO
- Is there a principle axis of rotation? Yes C_4
- Are the nC_2 axis \perp to the C_n axis? NO
- Is there a σ_h \perp to the C_n axis? NO
- Are there $n\sigma_v$ planes? Yes

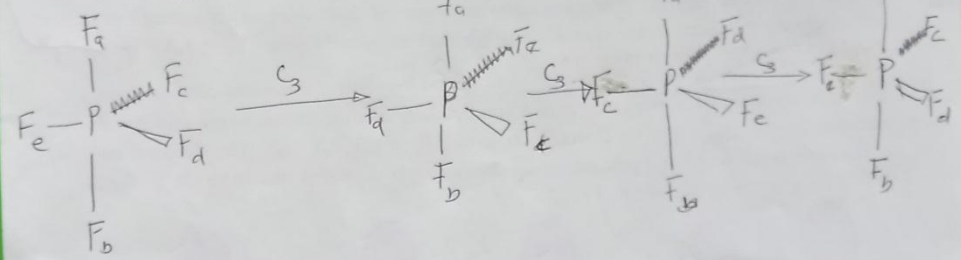
Point group C_{4v}



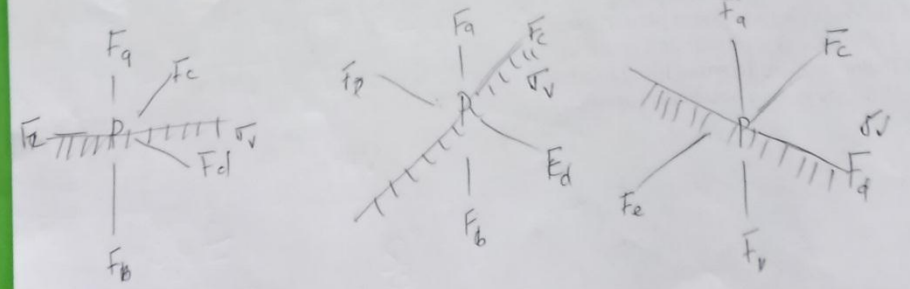
PF_5 has 5 bp and no lone pair
 shape is trigonal bipyramidal



It has C_3

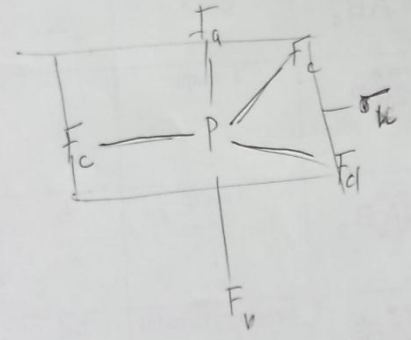


It has 3 vertical planes parallel to the principle axis of rotation (C_3). They lie on each of the equatorial F (F_c, F_d, F_e) while the other will be on each side of the plane

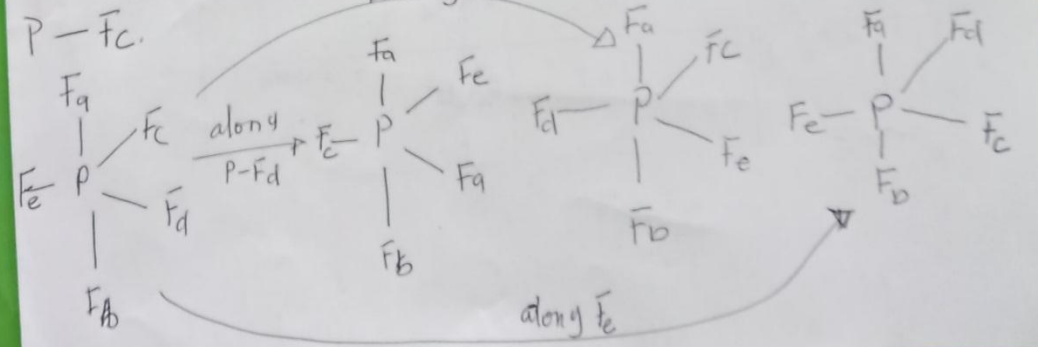


3.

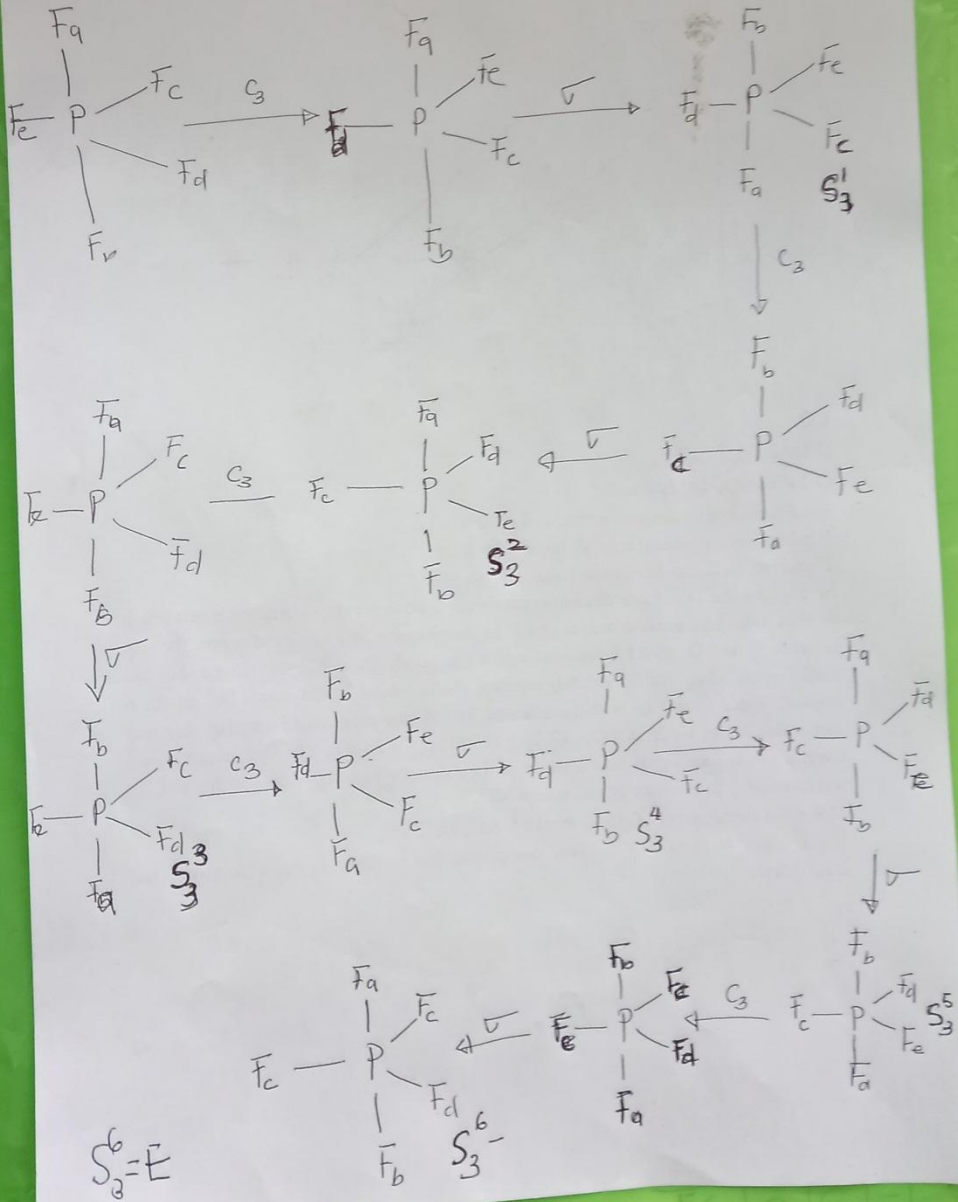
They have σ_h (a ~~horizontal~~ horizontal plane that lies on $F_c - F_d - F_e - P$ with F_a above and F_b below



It has 3 C_2 axis along each of $P-F_d, P-F_e, P-F_c$ which are \perp to the C_3



It also has improper rotation (S_3). (c)



3. cont'

(d)

Is the molecule linear? NO

Does it have a high symmetry? NO

Is there a principle axis of rotation C_n ? Yes.

Are there $n C_2$ axis \perp to the C_n axis? Yes.

Is there a σ_h plane \perp to C_n axis? Yes.

PF_5 belong to the D_{3h} point group

MODULE THREE

INTRODUCTION TO COORDINATION COMPOUNDS (II)

- ❖ **Unit One** – What are coordination compounds?
- ❖ **Unit Two** – Naming coordination compounds
- ❖ **Unit Three** – (A) Coordination number and molecular structure
(B) Types of ligands
- ❖ **Unit Four** – Isomerism in coordination compounds
- ❖ **Unit Five** – Crystal field theory

What are Coordination Compounds?

Coordination complexes are compounds which consist of a central metal atom or ions surrounded by a definite number of electron donating molecules or ions

These molecules or ions surrounding the metals are referred to as **ligands**.

The central metal is usually **transition metals** this is because of the presence of vacant d or f orbitals for the ligands to donate their electrons.

A coordination complex maybe a neutral molecule or an ion and if it is positively charged it is called a cationic complex while the negatively charged complex is called an anionic complex.

Coordination compound are coloured. They exhibit magnetic properties such as being diamagnetic (no unpaired electrons) or paramagnetic (one or more unpaired electrons).

Double salts vs Coordination complexes

- Double salts and coordination complexes can appear similar especially in writing their formulae e.g. $\text{KCl.MgCl.6H}_2\text{O}$ and $\text{Fe(CN)}_2.4\text{KCN}$.
- However, $\text{KCl.MgCl.6H}_2\text{O}$ is a double salt when it's dissolved in water it gives rise to K^+ , Mg^{2+} , Cl^- ions.
- Whereas $\text{Fe(CN)}_2.4\text{KCN}$ when dissolved in water does not form K^+ , Fe^{2+} , and CN^- ions but rather K^+ and $[\text{Fe(CN)}_6]^{4-}$.
- $[\text{Fe(CN)}_6]^{4-}$ is a complex ion, hence $\text{Fe(CN)}_2.4\text{KCN}$ is a coordination compound and is better written as $\text{K}_4[\text{Fe(CN)}_6]$.

The charge on the complex ion must be equal to the sum of the charge on the central ions and the charges (if any) on the ligand e.g. $[\text{Fe}(\text{CN})_6]^{4-}$ charge on Fe is +2 and charge on CN is -1

$$+2 + (6 \times -1) = -4$$

That is why there are 4 counter ion (K^+), $\text{K}_4[\text{Fe}(\text{CN})_6]$ and not $4\text{K}[\text{Fe}(\text{CN})_6]$

The number of ligands surrounding the central metal is called the **coordination number** of the complex and this is different from oxidation number of the complex.



-4 is the oxidation number of the complex ion

6 is the coordination number.

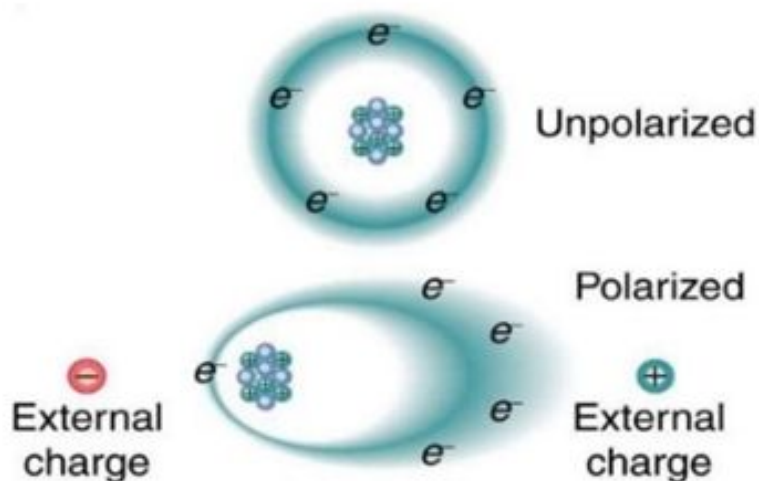
Oxidation number is referred to as the Primary/Principle Valence while coordination number is referred to as Secondary/Auxiliary valence

Hard and Soft Acids and Bases in Transition Metal Complexes.

- The interaction between the metal atom and the ligands are considered to be Lewis acid – base reactions.
- A Lewis base is an electron pair donor while Lewis acids are electron pair acceptor.
- So ligands are Lewis bases and the central metals are Lewis acids.
- The acids and the bases are classified as hard or soft.
- Hardness means that acid or base is not easily polarized.
- Softness means that they are easily polarized.

Acid	Mn ²⁺ , Zn ²⁺ etc
Base	F ⁻ , Cl ⁻ , NH ₃

Hard acids re

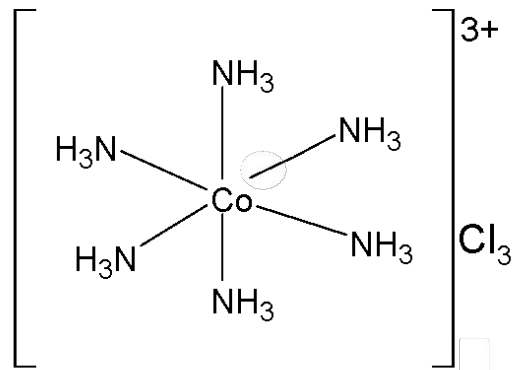


Soft
Pd ²⁺ , Fe ²⁺ , Co ²⁺ ,

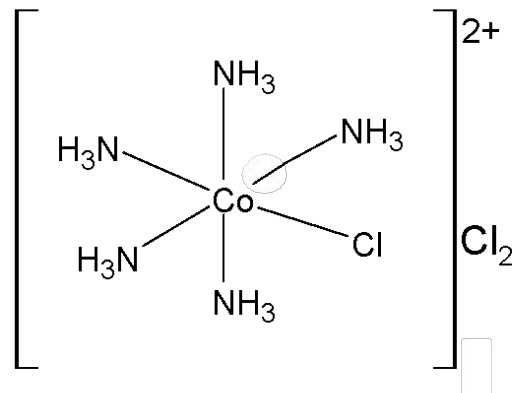
binds to soft bases.

WERNER'S THEORY OF COORDINATION COMPOUNDS

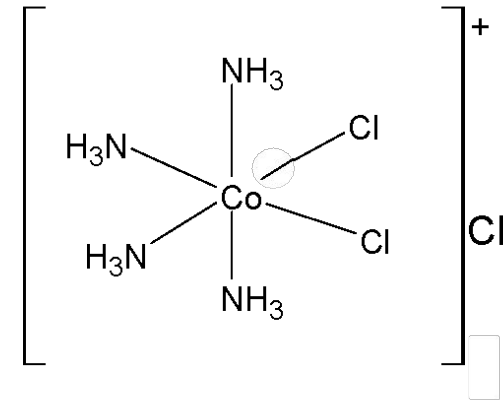
Alfred Werner got the Nobel prize of chemistry in 1913 for his coordination theory of transition metal-amine complexes.



In solution 3 moles of Cl⁻ is produced



In solution 2 moles of Cl⁻ is produced



In solution 1 mole of Cl⁻ is produced



Just like NaCl will dissociate in water to produce Na⁺ and Cl⁻ same thing with AlCl₃
Al³⁺ + 3Cl⁻ →

Postulate of Werner's theory

- In coordination compounds, the central metal atoms exhibit primary valence and secondary valence. The primary valence is ionizable and the secondary one is not. The primary valence corresponds to oxidation state the secondary valence corresponds to the coordination number.
- Every metal atom has a fixed number of secondary valences (coordination number(s)).
- The metal atom tends to satisfy both its primary valence as well as the secondary valence. The primary valence is satisfied by negative ions because the metal ion has positive charge whereas the secondary valence is satisfied either by negative ions or by neutral molecules.
- The secondary valences are always directed towards the fixed position in the space and this lead to definite geometry of the coordination compound.

Limitation of Werner's theory

- It failed to explain why all elements do not form coordination compounds.
- It failed to explain the directional properties of bond in coordination compounds.
- It does not explain the colour, magnetic and optical properties of these compounds.

END OF UNIT ONE

UNIT TWO

Naming Coordination Complexes

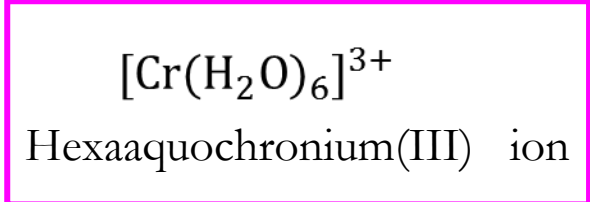
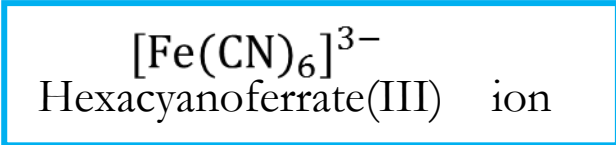
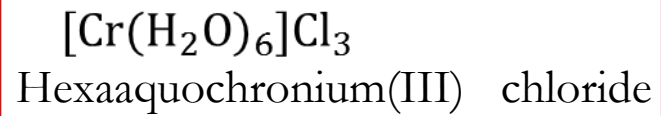
The rules for naming coordination compounds are as following:

1. The **cation** is named before the anion. This rule holds whether the complex ion is negatively charged or positively charge. For example, in $\mathbf{K}_4[\text{Fe}(\text{CN})_6]$ and $\mathbf{[Co(NH}_3)_4\text{Cl}_2]\text{Cl}$; \mathbf{K}^+ and $\mathbf{[Co(NH}_3)_4\text{Cl}_2]^+}$ are the cations and are named first.
2. Within a complex ion the ligands are named first, and the metal ion is named last.
3. The names of the anionic ligand end with the letter o, whereas a neutral ligand is usually called by the name of the molecule except for H_2O , CO , and NH_3 .

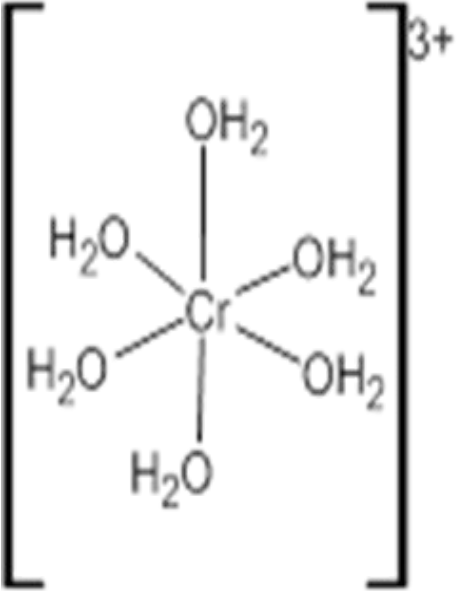
4. When there are more than one ligands present, we use the Greek prefixes di-(2), tri-(3), tetra-(4), penta-(5), and hexa- (6) to name. For example $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ will be *hexaaquocobalt* or *hexaaquacobalt*.
5. When there are different ligands the ligands are names in alphabetical order. Thus the ligands in the cation $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ are “*tetraamminedichloro*”.
6. If the name of the ligand contains a Greek prefix, we use the prefixes *bis*-(2), *tris*-(3), and *tetrakis*-(4) to indicate the number of ligands present. For example, the ligand *ethylenediamine* already contain the word ‘*di*’ which is a Greek word therefore if two of such ligands are present, the name will be *bis(ethylenediamine)*.

7. The oxidation number of the metal in Roman numerals following the name of the metal. For example the Roman numerals III is used to indicate the +3 oxidation state of Co in $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ which is called *tetraaminedichlorocobalt(III) ion*. (no space between the name of the metal and its oxidation state).
8. If the complex is an anion, its name ends in **-ate**. For example, in $\text{K}_4[\text{Fe}(\text{CN})_6]$, the anion $[\text{Fe}(\text{CN})_6]^{4-}$ is called hexacyanoferrate(II) ion. Note that the Roman numeral II indicates the oxidation state of iron.
9. In writing the name of the **complex ion** there must be **no space between the name**.

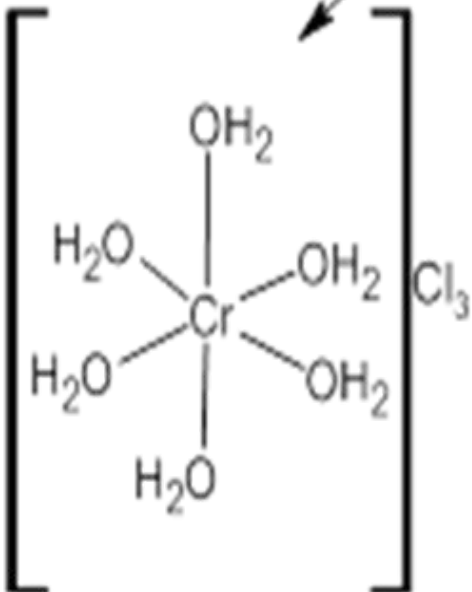
10. In writing the chemical formula of a complex the ligands are written in circle brackets () while the complex ion is written in square brackets [].
11. The counter ion (if present) are written outside the square brackets – before the square brackets if it is a cation e.g. $\text{K}_3[\text{Fe}(\text{CN})_6]$ and after the square brackets if it is an anion e.g. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$.
12. Structurally the complex ion is drawn showing all bonds between the metal and the ligands. This are then placed a large square bracket forming what is called the coordination sphere while its counter ion placed before or after the bracket (outside the coordination sphere).



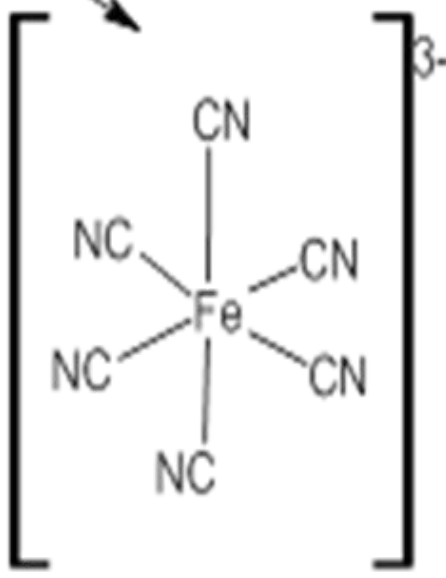
Inside coordination sphere



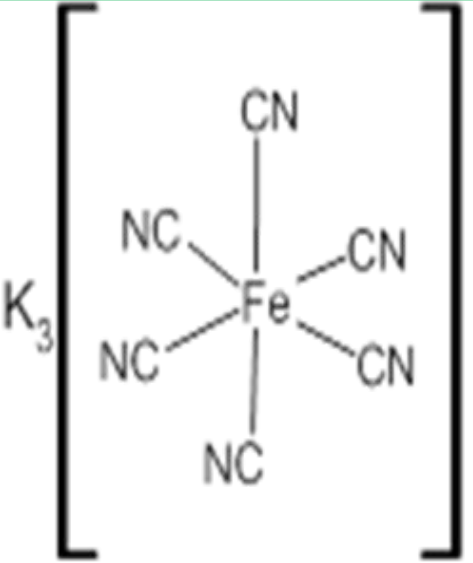
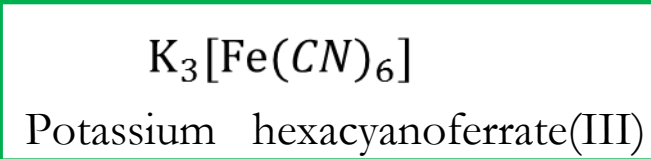
Cationic complex



Complex salt



Anionic complex



Complex salt

END OF UNIT TWO

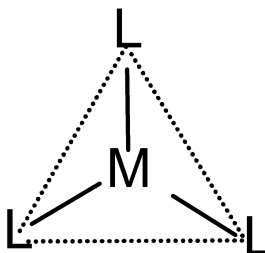
UNIT THREE

(A) Coordination Number and Molecular Structure



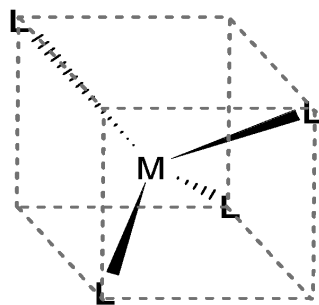
Coordination $n_{\phi} = 2$

Shape = Linear



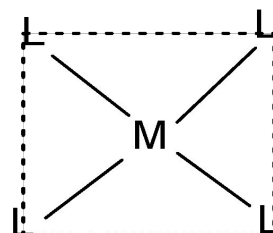
Coordination $n_{\phi} = 3$

Shape = Trigonal Planar

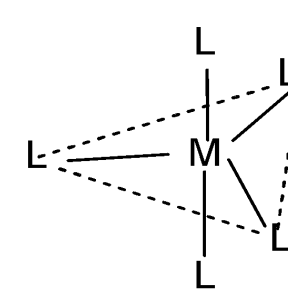


Tetrahedral

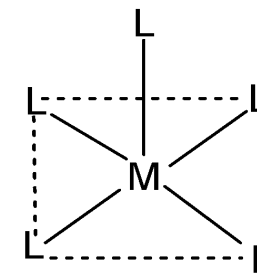
Coordination $n_{\phi} = 4$



Square Planar

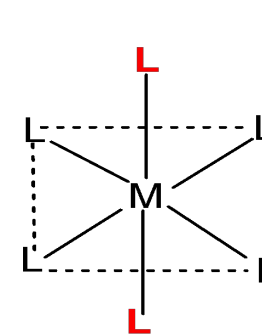


Trigonal bipyramidal

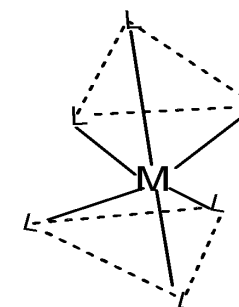


Square-based pyramid

Coordination $n_{\phi} = 5$



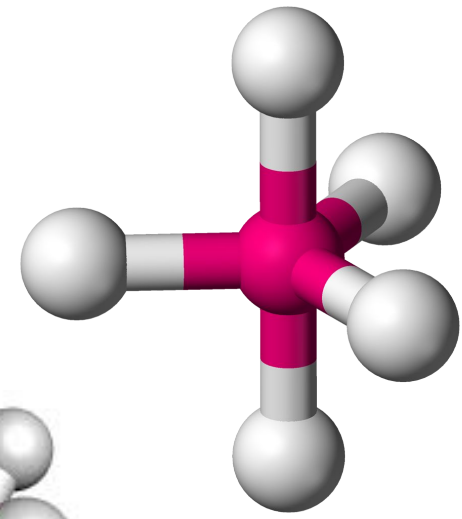
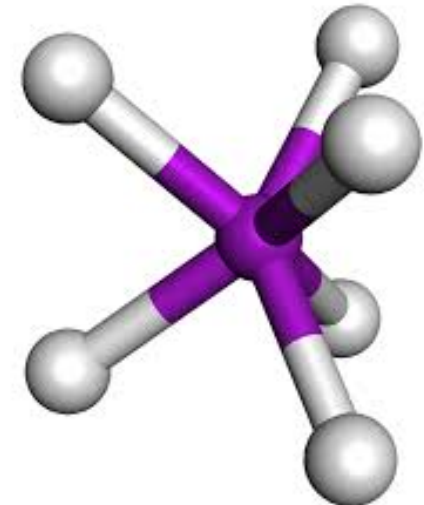
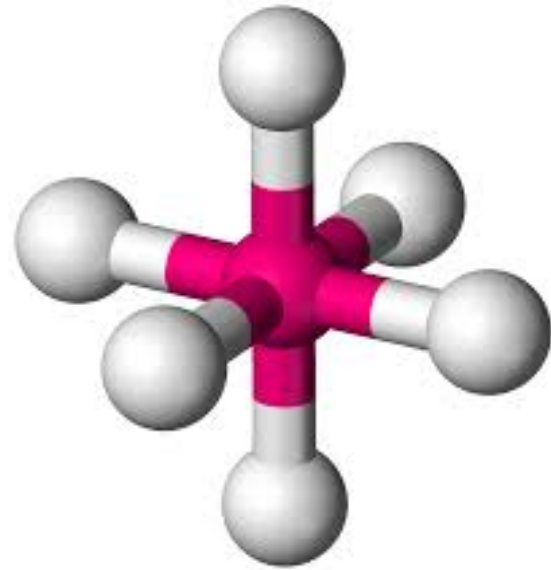
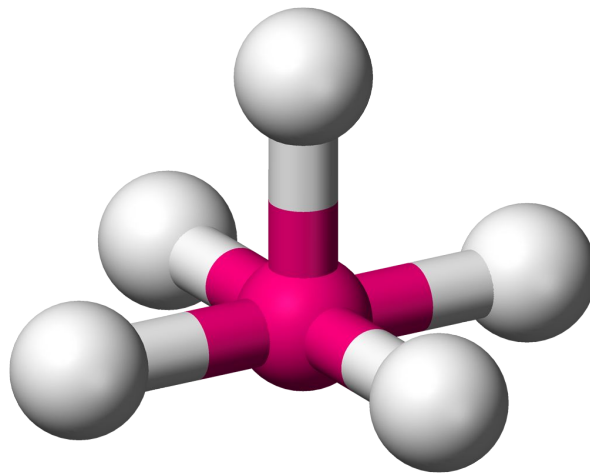
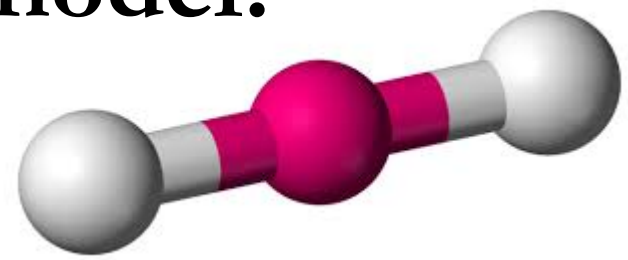
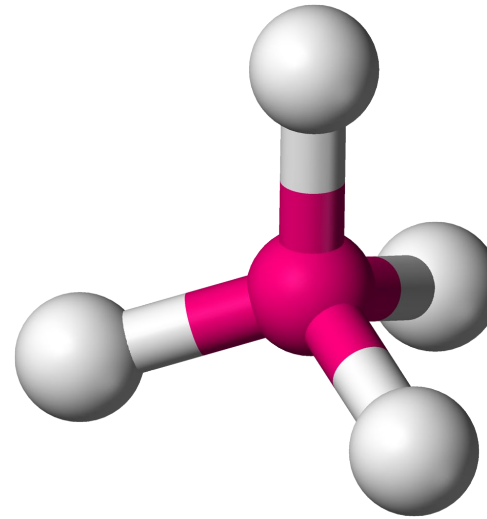
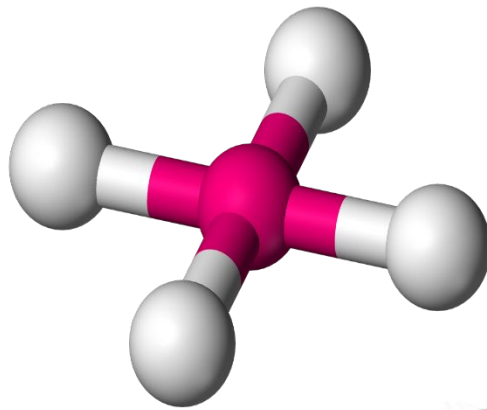
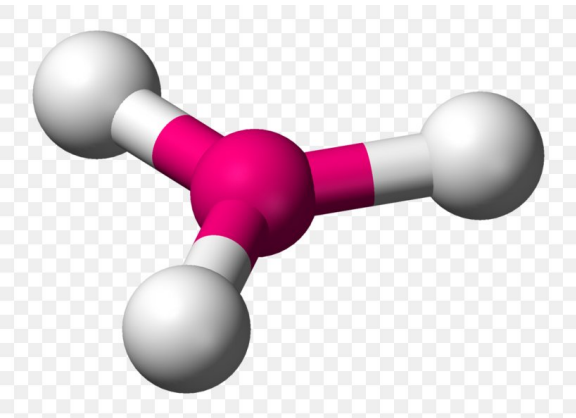
Octahedral



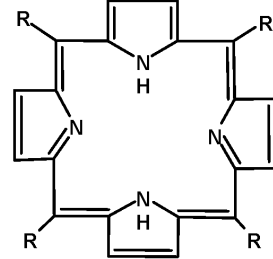
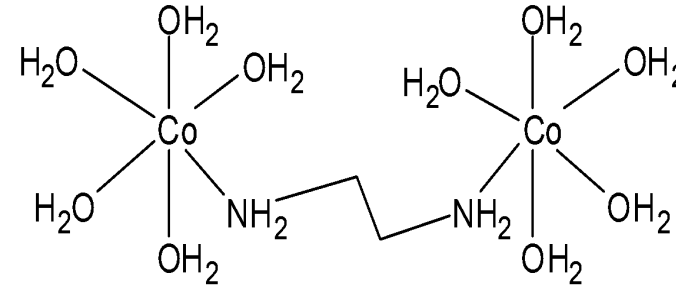
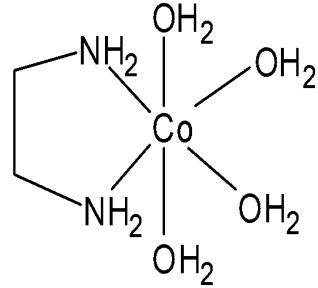
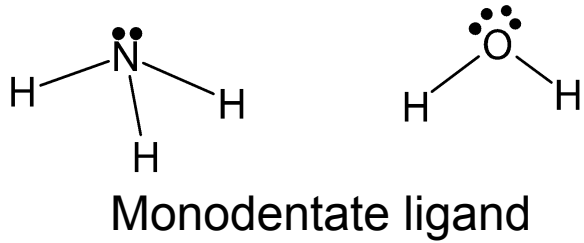
Trigonal prism

Coordination $n_{\phi} = 6$

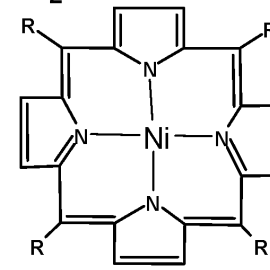
Can you identify the shape of each 3-d model?



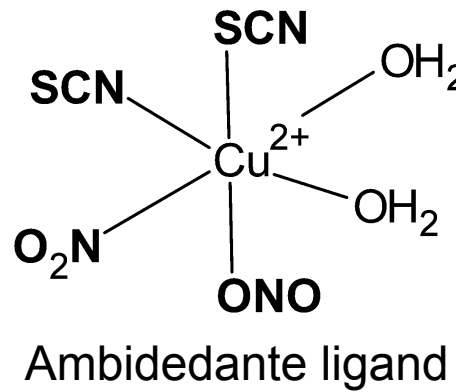
(B) Types of Ligand



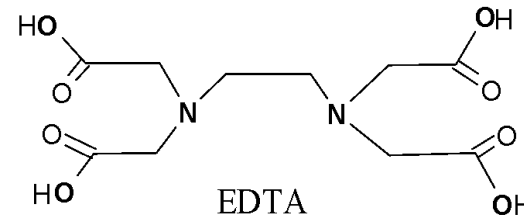
a. Porphyrin



b. Metalloporphyrin

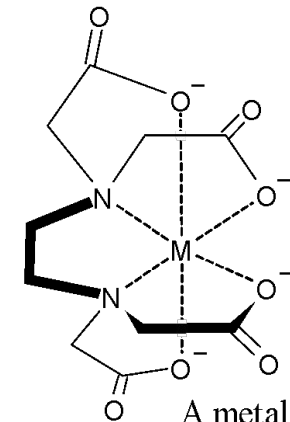


Ambidentate ligand



EDTA

Chelating ligands

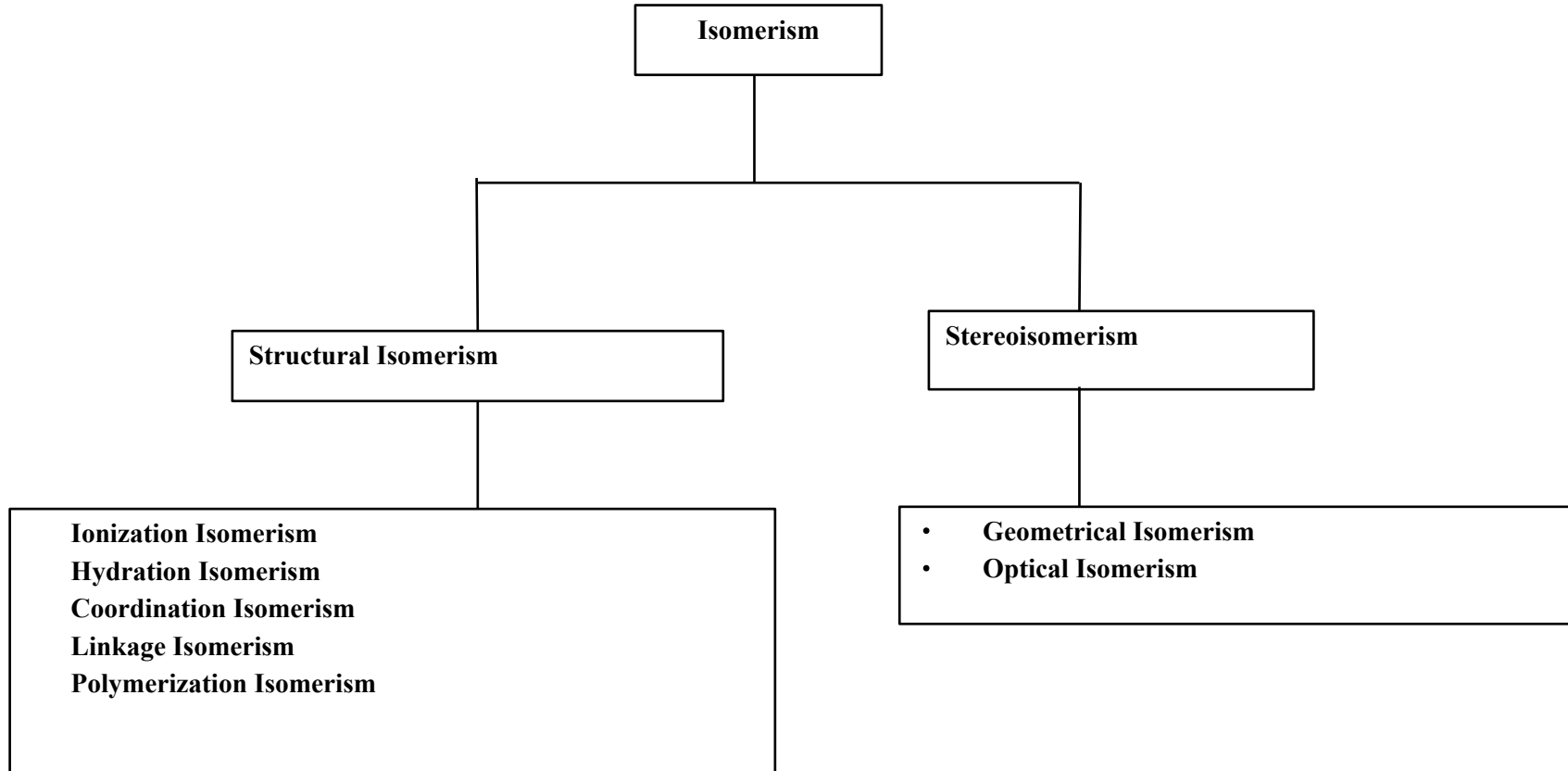


A metal coordinated to the EDTA, forming a chelate

END OF UNIT THREE

UNIT FOUR

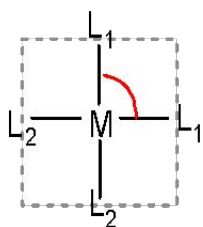
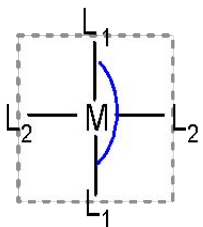
Isomerism in Coordination Compounds



Structural Isomerism

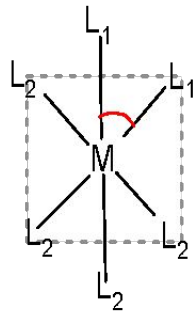
Type of isomerism	Examples
Ionization Isomerism	$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ (violet in colour) $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (red in colour)
Hydration Isomerism	$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ – Green $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ – Blue green $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ – Violet
Coordination Isomerism	$[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$ $[\text{Co}(\text{NH}_3)_6] [\text{Co}(\text{NO}_2)_6]$ and $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2] [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
Linkage Isomerism	Co–NCS Isothiocyanate Co–SCN Thiocyanate
Polymerization Isomerism	$[\text{Pt}(\text{NH}_3)_2(\text{Cl})_2]$ $(\text{Pt}_n\text{N}_{2n}\text{H}_6\text{Cl}_{2n}) \{n=1\}$ $[\text{Pt}(\text{NH}_3)_4] [\text{Pt}(\text{Cl})_4]$ $(\text{Pt}_n\text{N}_{2n}\text{H}_6\text{Cl}_{2n}) \{n=2\}$

Geometrical Isomerism

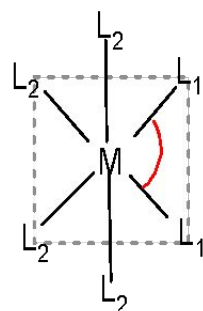


Trans - isomer **Cis - isomer**
Square planar complexes

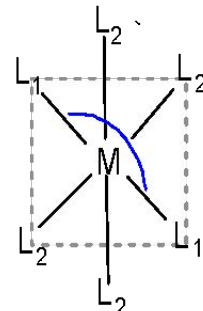
M - central metal
L₁ and L₂ are different ligands
Using L₁ as reference point
90° - represented in red
180° - represented in blue



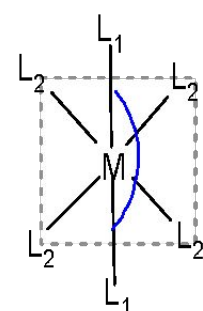
(a)



(b)



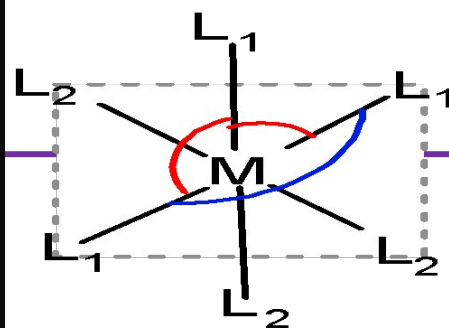
(c)



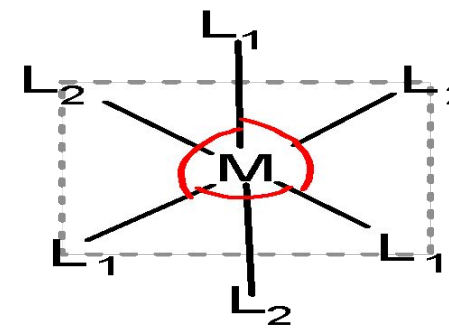
(d)

Cis - isomer **Trans - isomer**

Octahedral complexes



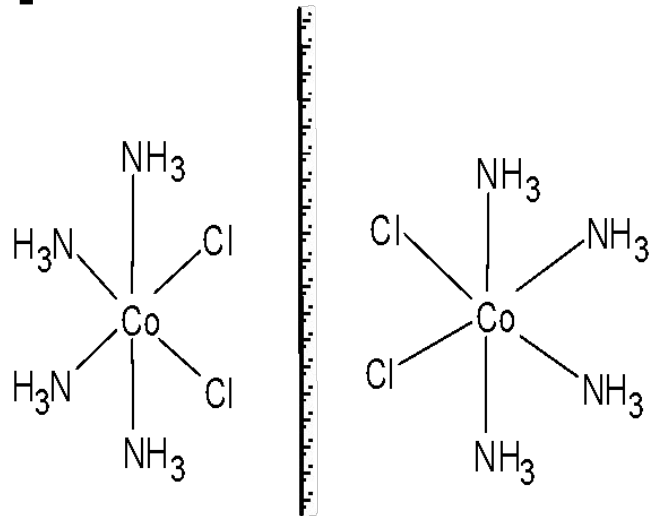
mer -



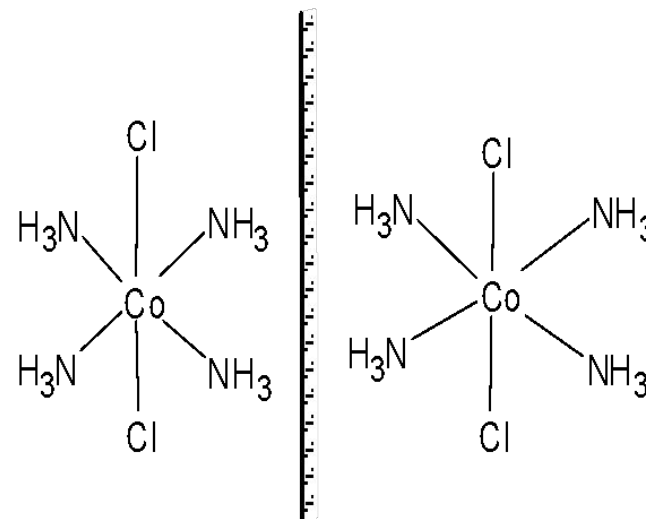
fac-

M - central metal
L₁ and L₂ are different ligands
Using L₁ as reference point
90° - represented in red
180° - represented in blue

Optical Isomerism

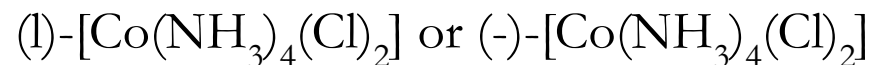


These are non-superimposable mirror image hence they are optically active and are enantiomers

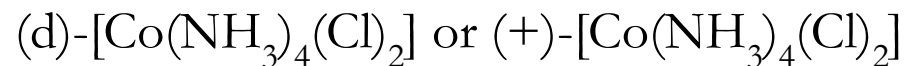


These are superimposable mirror image therefore are not optically active and are diastereomers

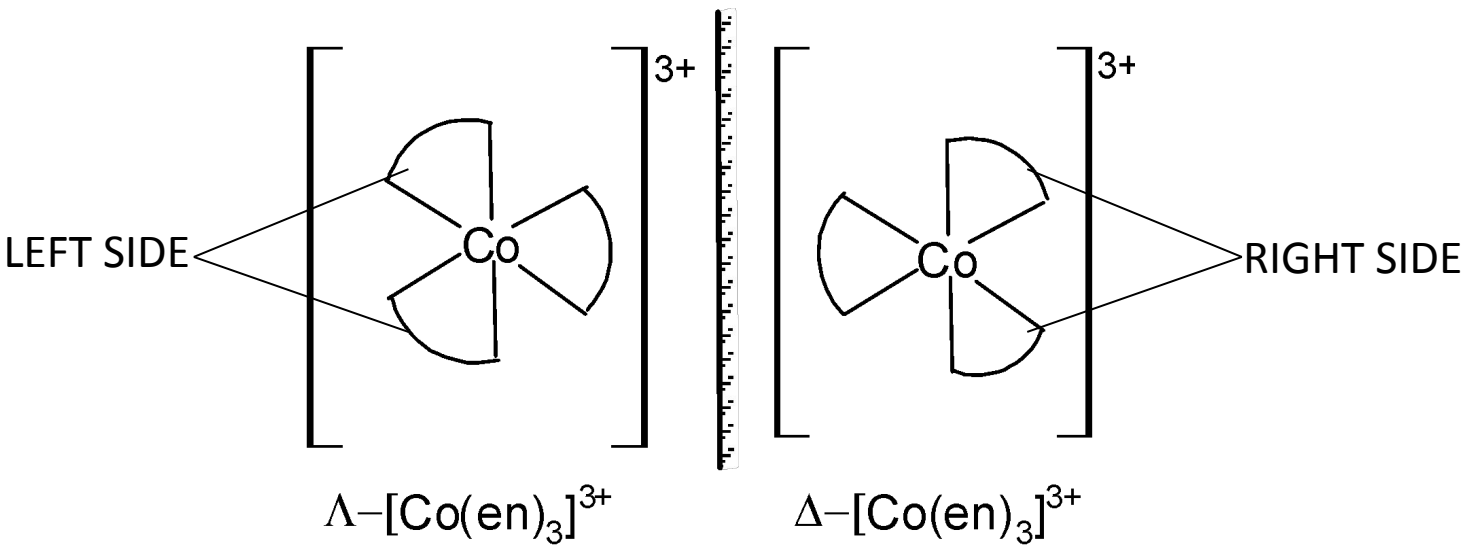
One rotates towards the left would be labeled as



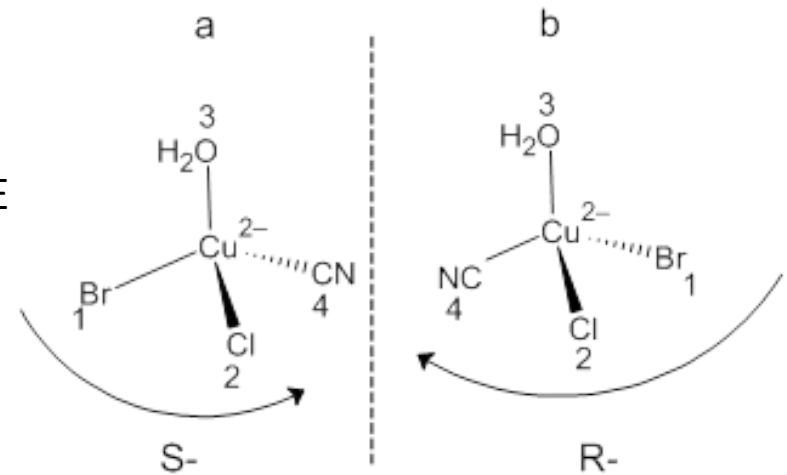
The one that rotate right would be labeled as



More on Optical Isomerism



Λ - and Δ - isomerism



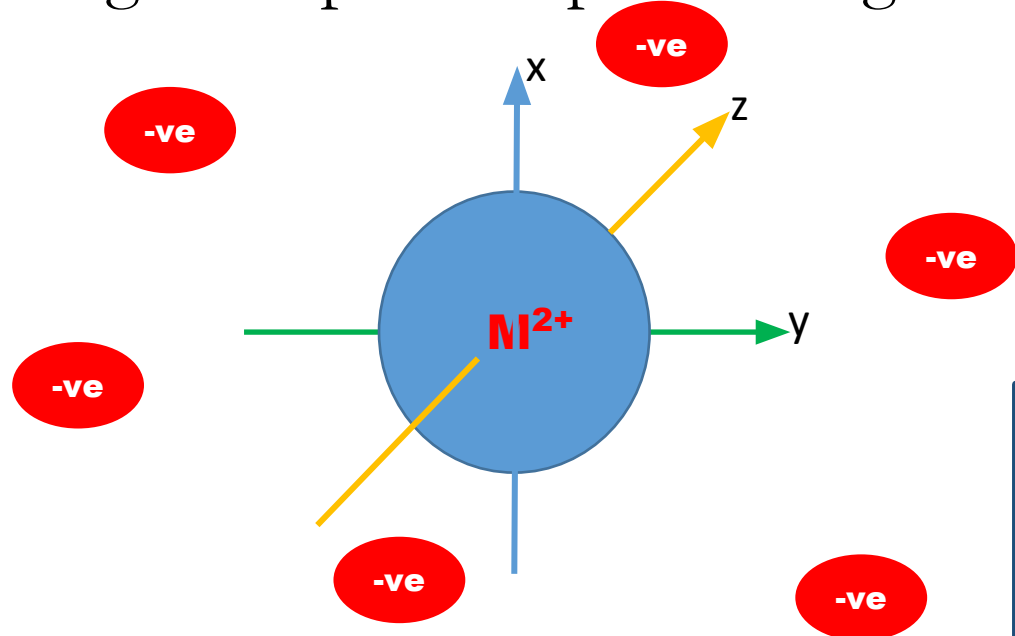
R- and S- isomerism

END OF UNIT FOUR

UNIT FIVE

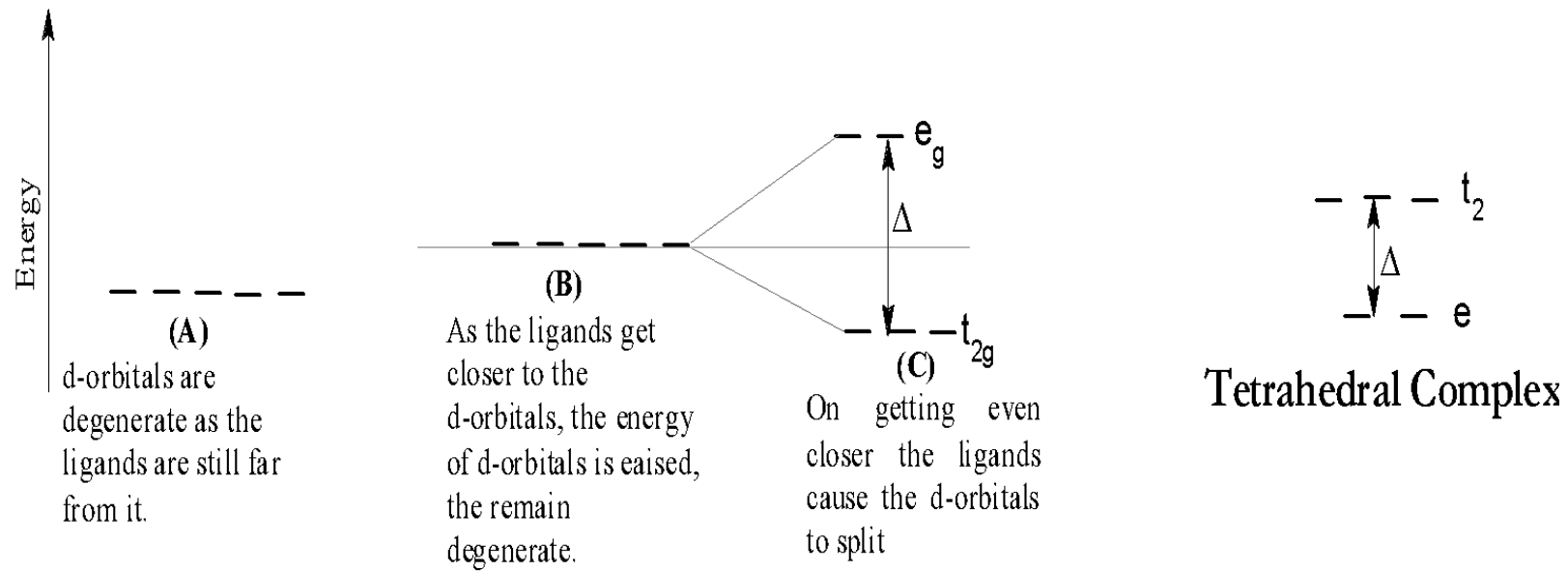
Crystal Field Theory (CFT)

This theory explains the bonding between metals and ligands to be electrostatic where the metal is positively charged and the ligands are negative spherical point charge.



***Valence Bond theory (VBT)** describes the bonds between the metal and the ligand as coordinate bond, where the ligand donates lone pair(s) of electrons to the vacant d or f orbital of the metal.

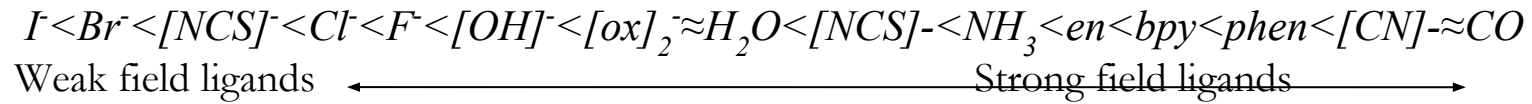
***Ligand Field theory (LFT)** describes the bonds between metal and ligand overlapping of the atomic orbitals of metal with ligand group of orbitals to form molecular orbitals. It is based on molecular orbital theory. It takes into account both ionic and covalent interactions.



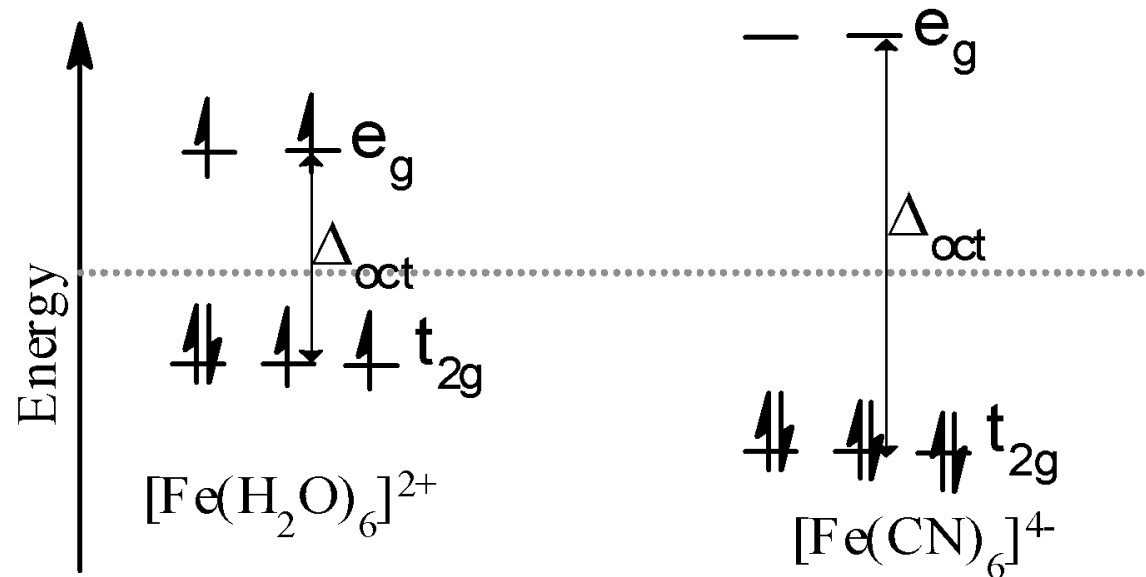
Octahedral Complex

- A. Before the ligands approach the metal the d-orbitals are degenerate (i.e. equal in energy).
- B. Although the electrons of the ligands are attracted to the central ion but as the ligands approach closer to the metal ion there is also repulsion between the electrons in d-orbitals and the electrons of the ligands.
- C. This effect raises the energy of the d-orbital and consequently split them. The direction of approach of the ligand to the d-orbitals affect the type of splitting that occurs.

- The magnitude (size) of Δ depends on the strength of the ligands.

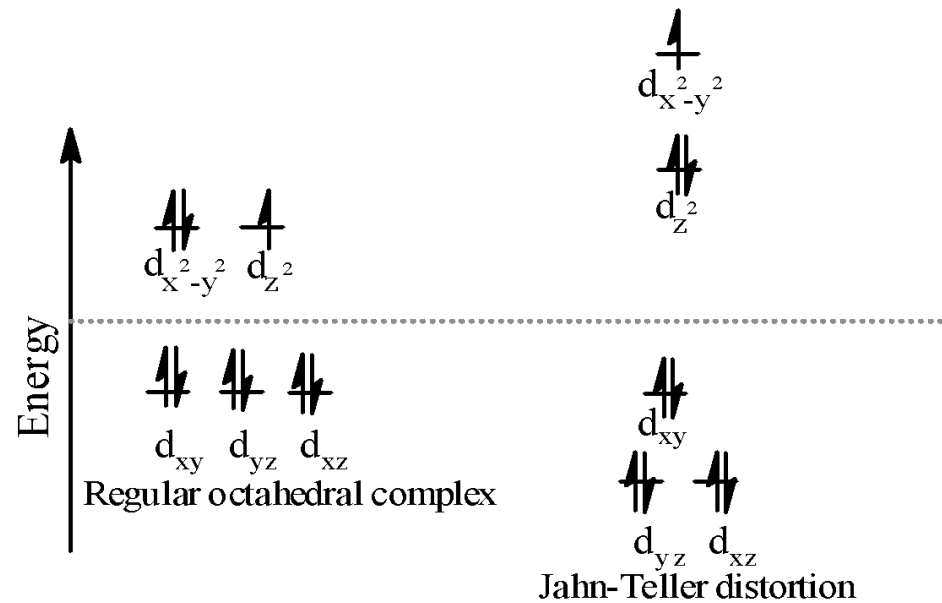
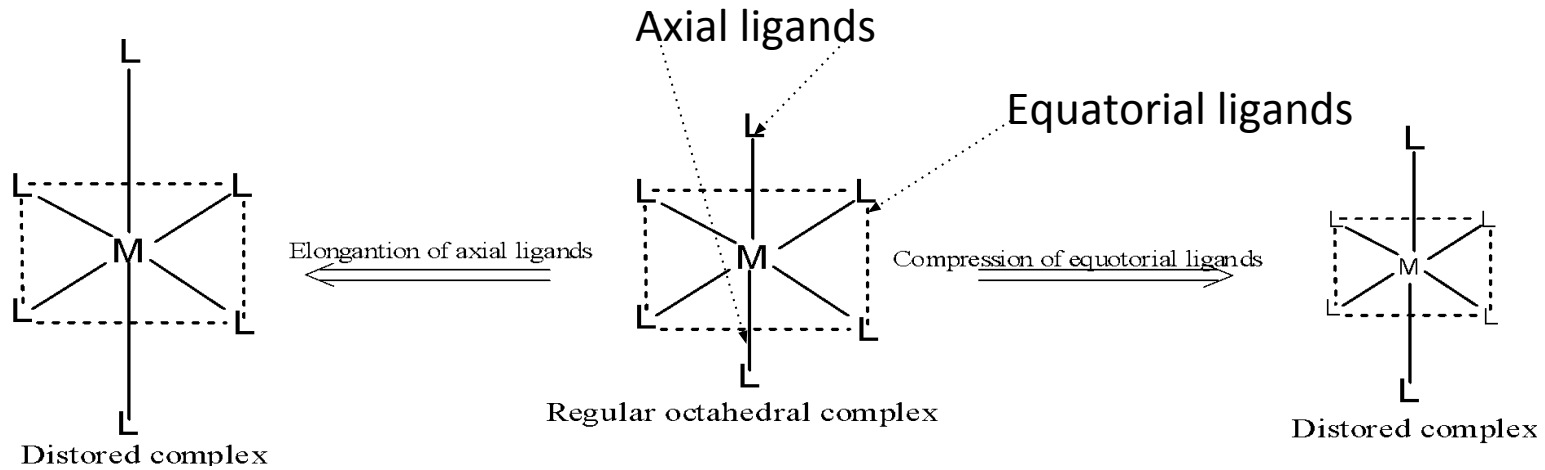


- Strong field ligands force



- In the presence of weak field ligands the complex is high spin because there is no force pairing
- In strong field ligands which then forces pairing the complex is described as being low spin.

Jahn-Teller Distortion



The asymmetrical filling of the e_g orbital caused the distortion

Lability and Inertness

- If the crystal field splitting is wide an incoming ligand will not be able to substitute it such a complex is inert.
- chelating ligand cause inertness.
- The more filled the d-orbitals the more labile hence d^{10} ion of Zn^{2+} , Cd^{2+} and Hg^{2+} are very labile.
- Across the 3d period, M^{2+} ions are labile and Cu^{2+} is most labile due to distortions.
- d-metal complexes with d^3 (Cr^{3+}), and low-spin d^6 configuration like Fe^{2+} and Co^{3+} are inert.
- High charge and small size results in inertness.

THE END

MODULE THREE

INTRODUCTION TO COORDINATION COMPOUNDS II

- **Unit One** – What are coordination compounds?
- **Unit Two** – Naming coordination compounds
- **Unit Three** – (A) Coordination number and molecular structure
(B) Types of ligands
- **Unit Four** – Isomerism in coordination compounds
- **Unit Five** – Crystal field theory

UNIT ONE: What are Coordination Compounds?

Double salts and coordination complexes can appear similar especially in writing their formulae e.g. $\text{KCl.MgCl.6H}_2\text{O}$ and $\text{Fe(CN)}_2.4\text{KCN}$. However, $\text{KCl.MgCl.6H}_2\text{O}$ is a double salt when it's dissolved in water it gives rise to K^+ , Mg^{2+} , Cl^- ions. Whereas $\text{Fe(CN)}_2.4\text{KCN}$ when dissolved in water does not form K^+ , Fe^{2+} , and CN^- ions but rather K^+ and $[\text{Fe(CN)}_6]^{4-}$. $[\text{Fe(CN)}_6]^{4-}$ is a complex ion, hence $\text{Fe(CN)}_2.4\text{KCN}$ is a coordination compound and is better written as $\text{K}_4[\text{Fe(CN)}_6]$.

Coordination complexes are compounds which consist of a central metal atom or ions surrounded by a definite number of electron donating molecules or ions. These molecules or ions surrounding the metals are referred to as ligands. The central metal is usually transition metals this is because of the presence of vacant d or f orbitals for the ligands to donate their electrons. A coordination complex may be a neutral molecule or an ion and if it is positively charged it is called a cationic complex while the negatively charged complex is called an anionic complex.

The interaction between the metal atom and ligand are considered to be as Lewis acid-base reaction. Lewis bases are electron pair donor while Lewis acids are electron pair acceptor. So the ligands are Lewis base and the central metals are Lewis acid.

The charge on the complex must be equal to the sum of the charge on the central ions and the charges (if any) on the ligand e.g. $[\text{Fe(CN)}_6]^{4-}$ charge on Fe is +2 and charge on CN is -1

$$+2 + (6 \times -1) = -4$$

The number of ligands surrounding the central metal is called the **coordination number** of the complex and this is different from oxidation number of the complex.



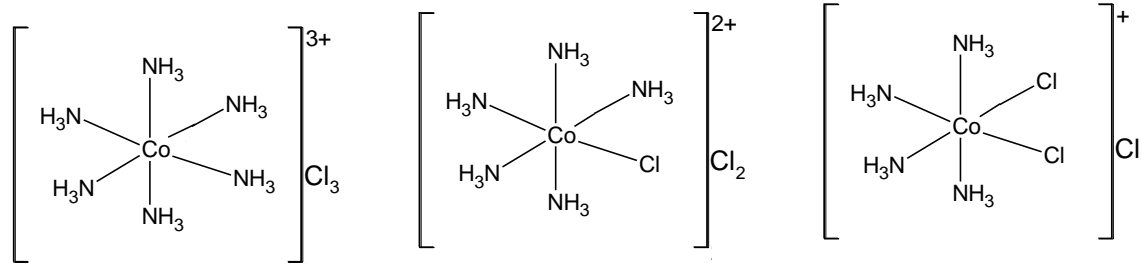
-4 is the oxidation number of the complex ion

6 is the coordination number.

Oxidation number is referred to as the Primary/Principle Valence while coordination number is referred to as Secondary/Auxiliary valence. Primary valences are non-directional while secondary valences are directional.

Werner's Theory of Coordination Compounds

Alfred Werner got the Nobel prize of chemistry in 1913 for his coordination theory of transition metal-amine complexes. He carried out a series of experiments with reacting CoCl_3 and various concentrations of ammonia form various amminechlorocobalt(III) complexes then titrating against AgNO_3 to determine the amount of chloride in the solution. For 3 different solutions he found that each had varied concentration of chloride ion. One had an equivalent of 3 moles of chloride ion, the other 2 moles and another just 1 mole. He concluded that the structure of these complexes were as



In solution 3 moles of Cl^- is produced

In solution 2 moles of Cl^- is produced

In solution 1 mole of Cl^- is produced

Postulate of Werner's theory

1. In coordination compounds, the central metal atoms exhibit primary valence and secondary valence. The primary valence is ionizable and the secondary one is not. The primary valence corresponds to oxidation state the secondary valence corresponds to the coordination number.
2. Every metal atom has a fixed number of secondary valences (coordination number(s)).
3. The metal atom tends to satisfy both its primary valence as well as the secondary valence. The primary valence is satisfied by negative ions because the metal ion

has positive charge whereas the secondary valence is satisfied either by negative ions or by neutral molecules.

4. The secondary valences are always directed towards the fixed position in the space and this lead to definite geometry of the coordination compound.

Limitation of Werner's theory

1. It failed to explain why all elements do not form coordination compounds.
2. It failed to explain the directional properties of bond in coordination compounds.
3. It does not explain the colour, magnetic and optical properties of these compounds.

UNIT TWO - Naming Coordination Compounds

The rules for naming coordination compounds are as following:

1. The cation is named before the anion. This rule holds whether the complex ion is negatively charged or positively charge. For example, in $K_4[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$; K^+ and $[Co(NH_3)_4Cl_2]^+$ are the cations and are named first.
2. Within a complex ion the ligands are named first, in alphabetical order, and the metal ion is named last.

Ligand	Abbreviation	Name of ligand in coordination compound
Bromide Br^-		Bromo
Chloride Cl^-		Chloro
Cyanide CN^-		Cyano
Hydroxide OH^-		Hydroxo
Oxide O^{2-}		Oxo
Carbonate CO_3^{2-}		Carbonate
Nitrite NO_2^-		Nitro
Oxalate $C_2O_4^{2-}$	$[ox]^{2-}$	Oxalato
Ammonia NH_3		Ammine
Carbon monoxide CO		Carbonyl
Water H_2O		Aquo
Ethylenediamine $H_2NCH_2CH_2NH_2$	en	Ethylenediamine
Acetylacetonate $CH_3COCH_2COCH_3$	$[acac]^-$	Acetoacetate
Ethylenediaminetetraacetate $(^-OOC)_2NCH_2CH_2N(COO^-)_2$	$[EDTA]^{4-}$	Ethylenediaminetetraacetate

3. The names of the anionic ligand end with the letter o, whereas a neutral ligand is usually called by the name of the molecule except for H_2O , CO , and NH_3 .
4. When there are more than one ligands present, we use the Greek prefixes di-(2), tri-(3), tetra-(4), penta-(5), and hexa- (6) to name. For example $[Co(H_2O)_6]^{3+}$ will be *hexaaquocobalt*.
5. When there are different ligands the ligands are names in alphabetical order. Thus the ligands in the cation $[Co(NH_3)_4Cl_2]^+$ are “*tetraamminedichloro*”.

6. If the name of the ligand contains a Greek prefix, we use the prefixes *bis*-(2), *tris*-(3), and *tetrakis*-(4) to indicate the number of ligands present. For example, the ligand *ethylenediammine* already contain the word '*d*' which is a Greek word therefore if two of such ligands are present, the name will be *bis(ethylenediammine)*.
7. The oxidation number of the metal in Roman numerals following the name of the metal. For example the Roman numerals III is used to indicate the +3 oxidation state of Co in $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ which is called *tetraaminedichlorocobalt(III) ion*.
8. If the complex is an anion, its name ends in *-ate*. For example, in $\text{K}_4[\text{Fe}(\text{CN})_6]$, the anion $[\text{Fe}(\text{CN})_6]^{4-}$ is called *hexacyanoferrate(II) ion*. Note that the Roman numeral II indicates the oxidation state of iron.

Metal	Names of metal in anionic complex
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Manganese	Manganate
Molybdenum	Molybdate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate

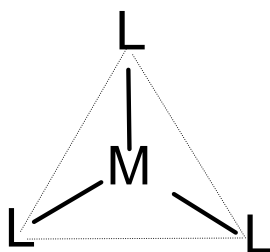
UNIT THREE – (A) Coordination Number and Molecular Structure

With the coordination number it is possible to predict the shape/structure of a complex. However further experimental data will be required to confirm the structure. Note here we will discuss only coordination number 2 - 6, however there are high coordination numbers up to 10.

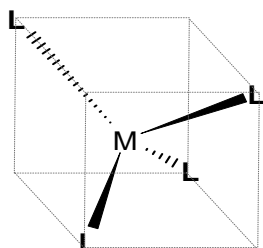
Coordination number 2: They are uncommon and generally restricted to Cu(I), Ag(I), Au(I), and Hg(II) and all are d^{10} ions e.g. $[\text{CuCl}_2]^-$, $[\text{Ag}(\text{NH}_3)_2]^{2+}$, $[\text{Au}(\text{CN})_2]^-$, $\text{Hg}(\text{CN})_2$. The shape is LINEAR.



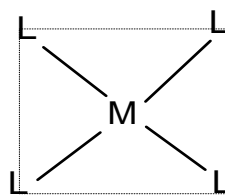
Coordination number 3: Their shape is TRIGONAL PLANAR e.g. $[\text{Cu}(\text{CN})_3]^{2-}$, $[\text{HgI}_3]^-$



Coordination number 4: The shape is usually TETRAHEDRAL or SQUARE PLANAR but the tetrahedral is more common e.g. $[\text{CoCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$ -tetrahedral geometry, $[\text{PdCl}_4]^{2-}$, $[\text{AuCl}_4]^-$ $[\text{PtCl}_4]^{2-}$ square planar.

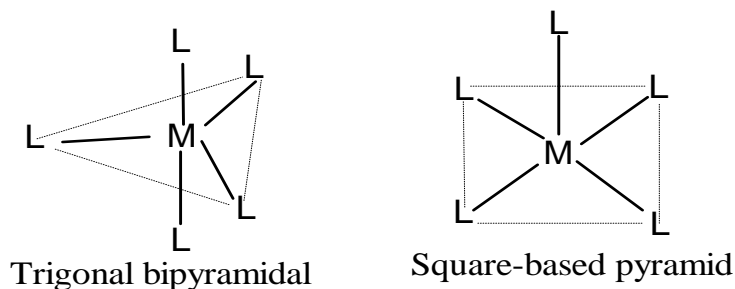


Tetrahedral

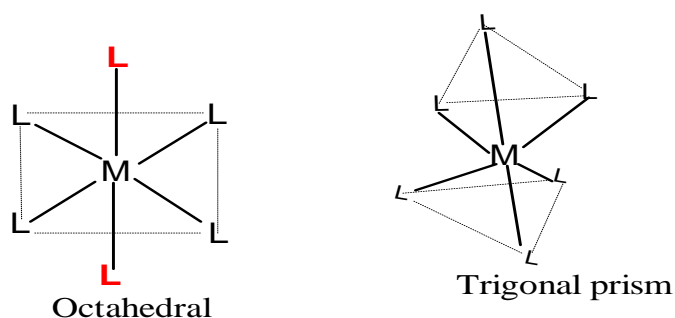


Square Planar

Coordination number 5: The usual shape is TRIGONAL BIPYRAMID or SQUARE BASED PYRAMID. For example, $[\text{CdCl}_5]^{3-}$, $[\text{CuCl}_5]^{3-}$ - trigonal bipyramid, $[\text{WCl}_4\text{O}]^-$, $[\text{TcCl}_4\text{N}]^-$ - square based pyramid.



Coordination number 6: This is another common coordination number. There shapes are usually OCTAHEDRAL or TRIGONAL PRISM. For example, $[\text{TiF}_6]^{2-}$, $[\text{Ti}(\text{OH}_2)_6]^{3+}$, $[\text{Co}(\text{OH}_2)_6]^{2+}$ - octahedral, $[\text{Zr}(\text{CH}_3)_6]^{2-}$ - trigonal prism



In octahedral complexes the 4 ligands (in black) that lie in the plane are the equatorial ligands and the two that are above and below the plane (in red) are axial ligands. The most commonly studied complexes are the octahedral, square planar and tetrahedral complexes

(B) TYPES OF LIGAND

Monodentate Ligands: these are ligands that use only 1 pair of electrons to bond to the central metal, for example H_2O , NH_3 , Cl^- etc.

Ambidentate Ligands: are monodentate ligands that can bond to the central atom through either of the two or more donor atoms e.g. NO_2^- it can bond through the oxygen (ONO^- nitrito) or through the nitrogen (NO_2 nitro). Another example is CSN^-

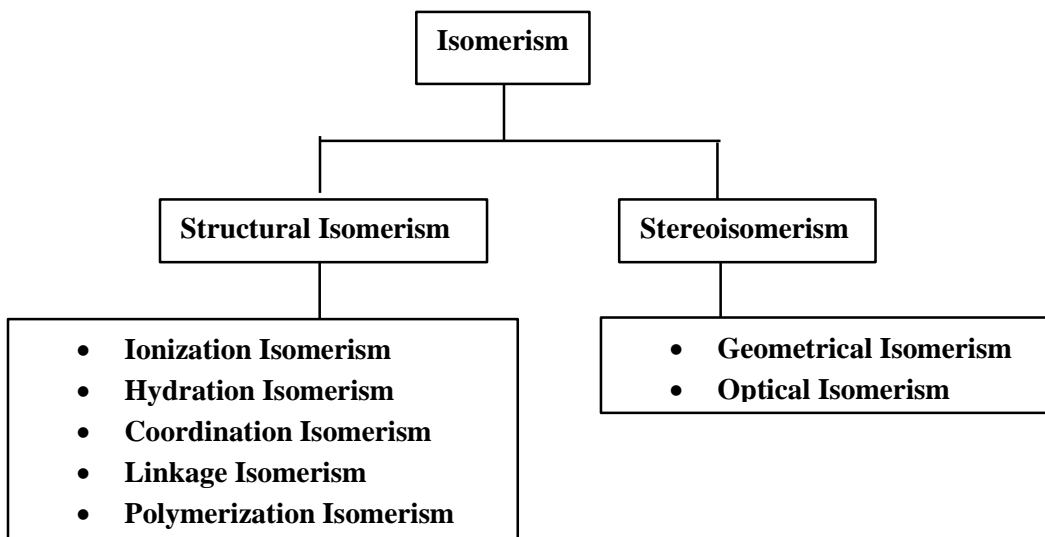
. This can bond through the Nitrogen ($\underline{\text{NCS}}^-$ isothiocyanate) or through the sulphur ($\underline{\text{SCN}}^-$ thiocyanate).

Polydentate Ligands: These ligands donate two or more pairs of electrons from different atoms in the ligand and to different sites in the structure of the complex. The specific names of such ligands are based on the number of donating sites. Below are few examples

- a. Bidentate Ligands: the ligands donate two pairs of electrons e.g. ethylenediamine $\text{H}_2\underline{\text{N}}\text{CH}_2\text{CH}_2\underline{\text{N}}\text{H}_2$, oxalate ion $\text{O}_2\underline{\text{C}}-\text{C}\underline{\text{O}}_2^-$.
- b. Tridentate Ligand: 3 pair of electrons e.g. diethylenetriamine $\text{H}_2\underline{\text{N}}\text{CH}_2\text{CH}_2\underline{\text{N}}\text{HCH}_2\text{CH}_2\underline{\text{N}}\text{H}_2$
- c. Tetradentate Ligand: Porphyrin
- d. Hexadentate Ligand: 6 pairs of electron e.g. ethylenediaminetetraacetate ion (EDTA) $[(\underline{\text{OOC}}\text{CH}_2)_2\underline{\text{N}}\text{CH}_2\text{CH}_2\underline{\text{N}}(\text{CH}_2\underline{\text{COO}}^-)_2]^{4-}$

Chelating Ligands: When a ligand attaches to the same central metal by two or more atoms forming a ring structure. The complex formed is called a chelate. Chelating ligands increase the stability of the complex.

UNIT FOUR - Isomerism in coordination compounds



Ionization Isomer: This occurs when there is an interchange of an anionic ligand that is inside the coordination sphere with another anionic ligand outside the coordination sphere e.g.

- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ (violet in colour)
- $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (red in colour)

Hydration Isomer: This arises when there is an interchange of H_2O and another ligand between the coordination sphere and outside of it e.g.

- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ – Green
- $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2\cdot \text{H}_2\text{O}$ – Blue green
- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ – Violet

Coordination Isomer: These isomers are formed from the interchange of ligand between 2 different metal centers and can only happen if the salts which form the cation and anions are themselves complex ions e.g.

- $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$
- $[\text{Co}(\text{NH}_3)_6] [\text{Co}(\text{NO}_2)_6]$ and $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2] [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$

Linkage Isomer: this arises when one or more ligands can coordinate to a metal ion in more than one way e.g.

- $[\text{Co}(\text{NH}_3)_5(\text{CSN})]\text{Cl}_2$ coordination can occur through S – atom or N – atom of the CSN ligand
 Co–**N**CS Isothiocyanate
 Co–**S**CN Thiocyanate
- $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ coordination can occur through O – atom or N – atom of the NO_2 ligand
 Co–**O**NO Nitrito
 Co–**N** O_2 Nitro

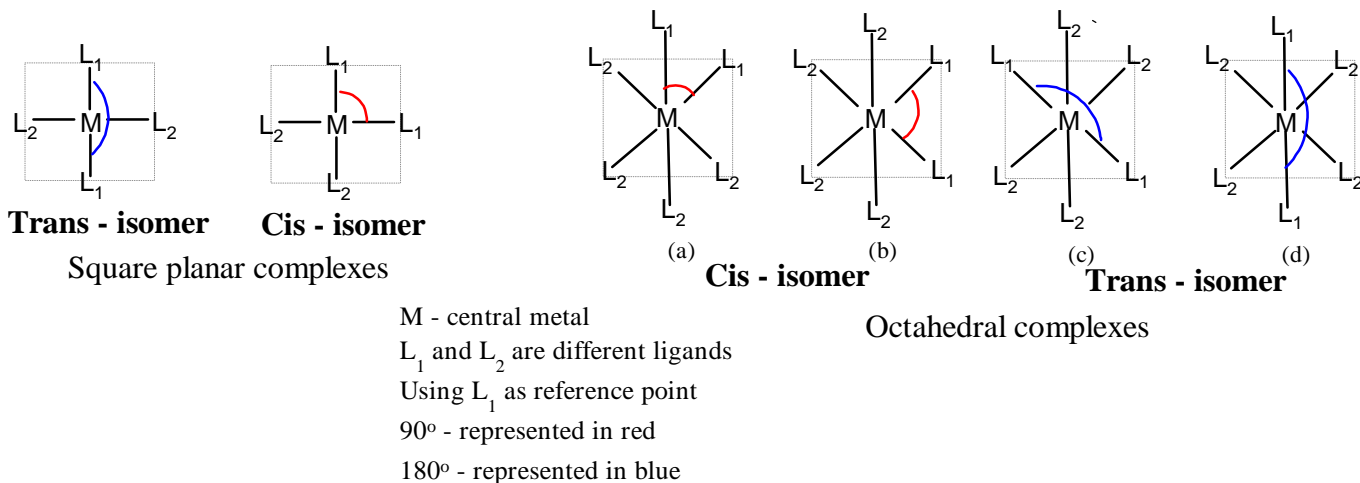
Polymerization Isomer: These isomers have the same empirical formulae but different molecular masses e.g.

- $[\text{Pt}(\text{NH}_3)_2(\text{Cl})_2]$ ($\text{Pt}_n\text{N}_{2n}\text{H}_6\text{Cl}_{2n}$) $\{n = 1\}$
- $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{Cl})_4]$ ($\text{Pt}_n\text{N}_{2n}\text{H}_6\text{Cl}_{2n}$) $\{n = 2\}$

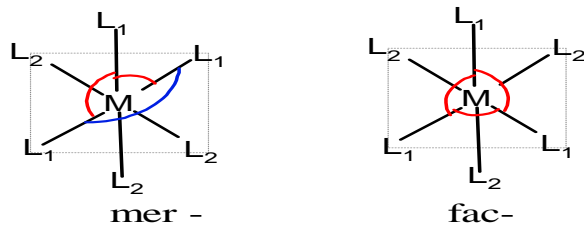
Geometrical Isomer: They have the same molecular formulae but different arrangement of their ligands in space. For coordination complexes there are two kinds.

a. Cis-Trans isomerism: here is the spatial arrangement of only 2 of the ligand especially in square planar and octahedral complexes.

- For the cis- isomer the two ligands are at 90° to each other with respect to the central atom and so the bond angle between the 2 ligands is 90° .
- Trans- isomers have the 2 ligands at 180° to each other i.e. opposite each other.



- b. Mer-Fac isomerism: here the spatial arrangement involves only 3 of the ligands and occurs in only octahedral complexes. For the fac- isomer the 3 ligands are at 90° to each other. For the mer- isomer 2 of the ligand would be at 90° to each other while the third one will be at 180° to one of the other 2.

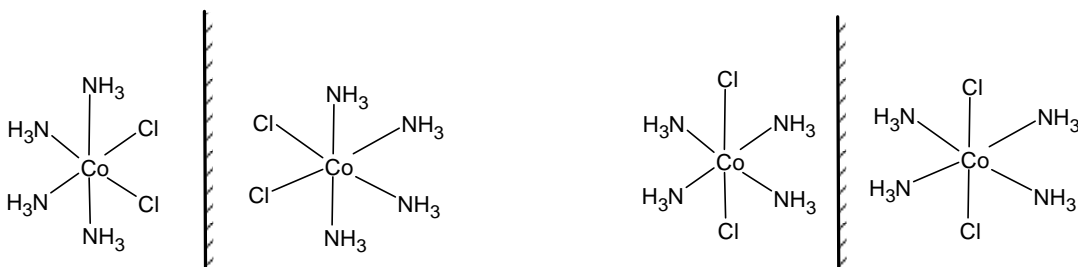


M - central metal
 L_1 and L_2 are different ligands
 Using L_1 as reference point
 90° - represented in red
 180° - represented in blue

Optical Isomers: these are two complexes that are mirror images of each other. When these mirror images are not superimposable they are called enantiomers and if they are superimposable they are called diastereomer.

The mirror images can be distinguished by the direction they rotate in the presence of polarized light. The one that rotate towards the left direction is called Laevorotatory (l or -) and other will rotate toward the right called Dextrorotatory (d or +). The degree of rotation of enantiomers will be the same but in opposite direction (left and right) hence are optically active.

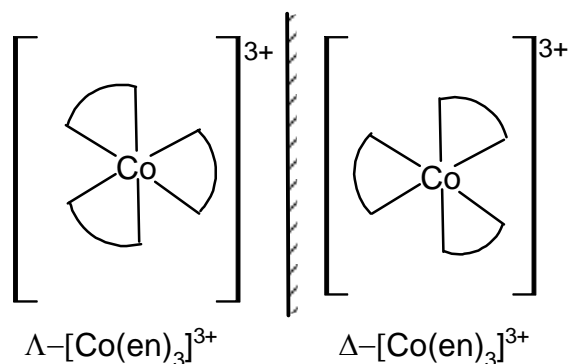
While for diastereomers they would move in the same direction and therefore optically inactive. So if $[\text{Co}(\text{NH}_3)_4(\text{Cl})_2]$ is an enantiomer and have a degree of rotation of 24° , the one that rotate towards the left would be labeled as (l)- $[\text{Co}(\text{NH}_3)_4(\text{Cl})_2]$ or (-)- $[\text{Co}(\text{NH}_3)_4(\text{Cl})_2]$ and the one that rotate right would be labeled as (d)- $[\text{Co}(\text{NH}_3)_4(\text{Cl})_2]$ or (+)- $[\text{Co}(\text{NH}_3)_4(\text{Cl})_2]$



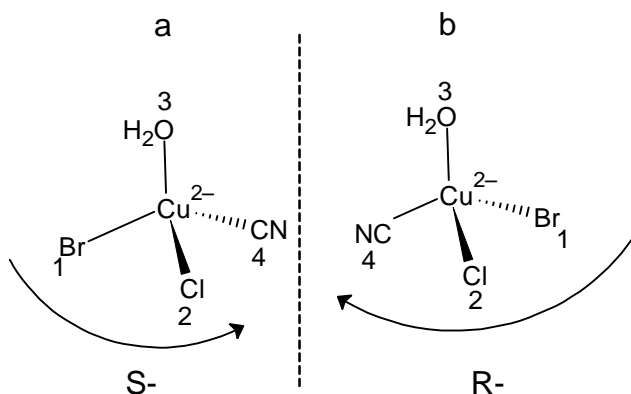
These are non-superimposable mirror image hence they are optically active and are enantiomers

These are superimposable mirror image therefore are not optically active and are diastereomers

For octahedral chelating ligand containing 3 equivalent ligands the prefix would be Δ (delta) right handedness and Λ (lamda) for left handedness.



R and S prefixes is the convention for labelling tetrahedral complexes with four different groups attached. The four groups attached to metal atom are prioritized according to the atomic number of the attached atoms, highest priority being assigned to highest atomic number and the one with the lowest atomic number has the lowest priority and it is ignored. Here the atoms attached directly to the metal (Cu) are Br (35), Cl (17), O (8) and C (6). These atoms have been labelled 1 to 4 from highest to lowest. In 'a' moving from 1 to 3 is anticlockwise and in 'b' it is clockwise. The R- and S-labels for the enantiomers refer to a clockwise (rectus) and anticlockwise (sinister) moving from high to low priority:

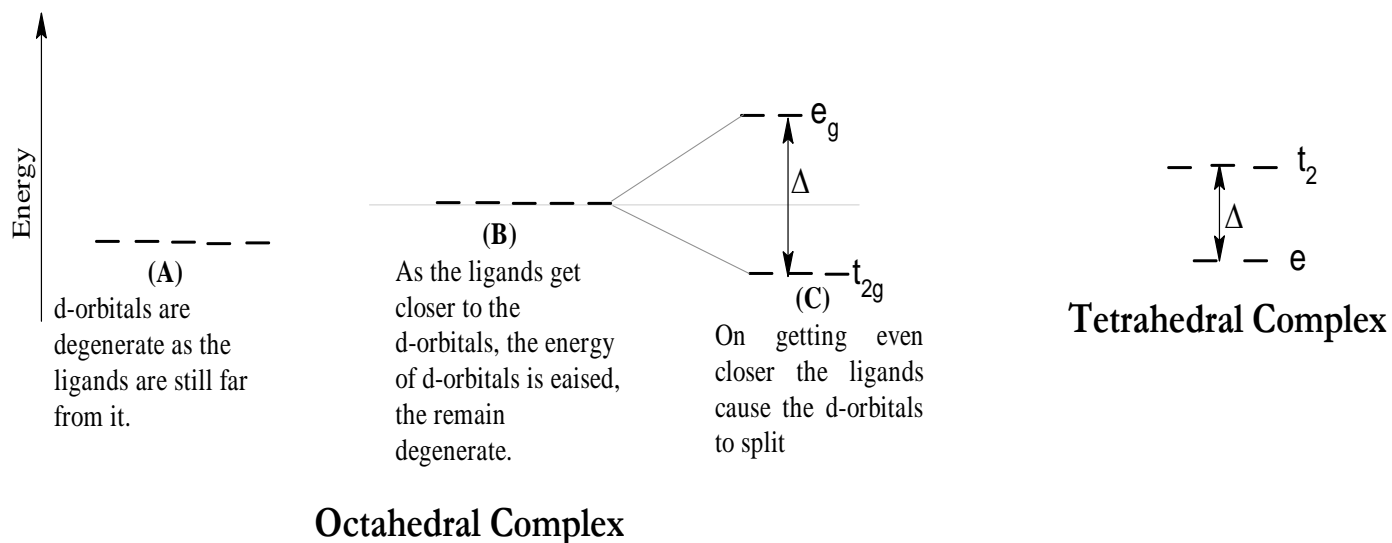


UNIT FIVE – Crystal Field Theory (CFT)

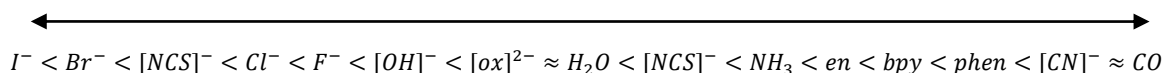
This is one of the theories used to explain the bonding in Transition metal complexes. Most of what has been discussed above is based on another theory, which is the Valence Bond theory (VBT). VBT describes the bond between the metal and the ligand as coordinate bond, where the ligand donates lone pair(s) of electrons to the vacant d or f orbital of the metal.

In CFT the bond is described to be purely electrostatic. Here the metal being positively charged attracts the ligands which are negatively charged spheres. Ligands of course are usually ions (Cl^- , Br^- etc) but for neutral ligands like ammonia or water, they are dipoles. N and O are more electronegative than H and would draw the electron they share more towards themselves giving them a partial $-ve$ charge ($-\delta$) and the H would have a partial $+ve$ charge ($+\delta$). The $-ve$ charged portion would now be attracted to the central metal (which is a cation).

- Before the ligands approach the metal the d-orbitals are degenerate (i.e. equal in energy).
- Although the electrons of the ligands are attracted to the central ion but as the ligands approach closer to the metal ion there is also repulsion between the electrons in d-orbitals and the electrons of the ligands.
- This effect raises the energy of the d-orbital and consequently splits them. The direction of approach of the ligand to the d-orbitals affects the type of splitting that occurs.



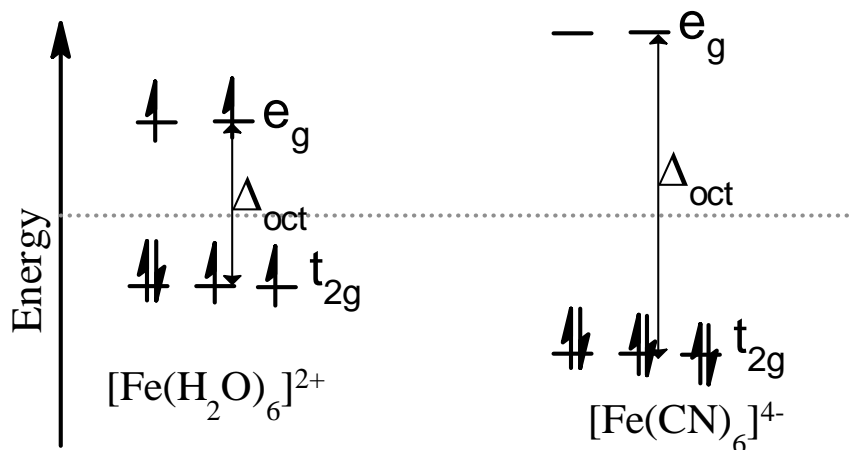
The magnitude (size) of Δ depends on the strength of the ligands. Ligands that result in large values of Δ are referred to as strong field ligands and those that result in small values of Δ are called weak field ligands. The arrangement of ligands according to their field strength is called the spectrochemical series



Weak field ligands

Strong field ligands

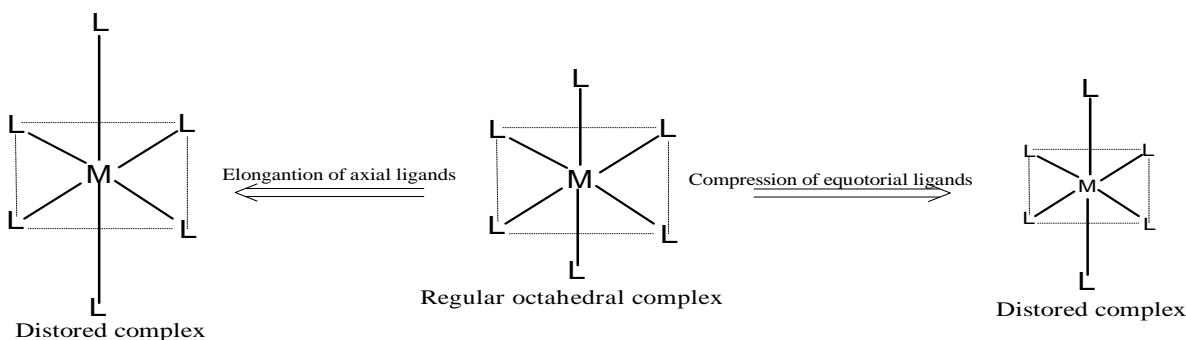
An increase in the crystal field splitting would result in force the electrons to pair. Strong field ligands force pairing because they cause the crystal field to split very wide such the electrons cannot move into e_g -orbitals and would rather be forced to pair in the t_{2g} . The same is applicable in a tetrahedral environment only this time instead of Δ_{oct} ; Δ_{tet} would be used. (Remember to reverse the orbitals i.e. e comes down and t_2 goes up).



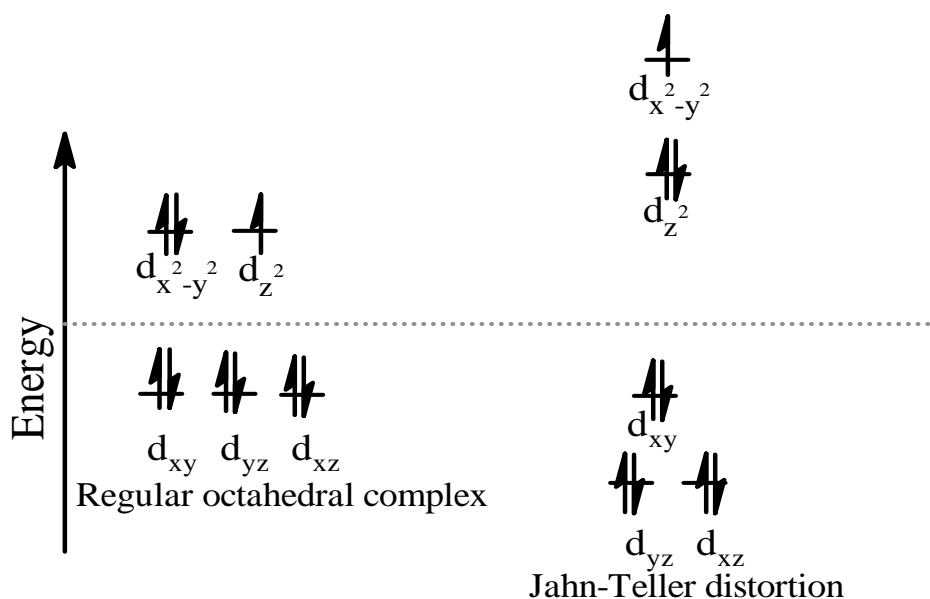
Coordination compound apart from being coloured they exhibit magnetic properties such as being diamagnetic (no unpaired electrons) or paramagnetic (one or more unpaired electrons). In the presence of weak field ligands the complex is said to have high spin however due to effect of strong field ligands which then forces pairing the complex is described as being low spin.

Jahn-Teller Distortion

Sometimes an octahedral complex undergoes distortion in its shape. This distortion can take place either by the elongation of the axial ligands or the compression of equatorial ligands.



This distortion is a manifestation of the Jahn-Teller effect and is referred to as tetragonal distortion. This effect occurs when the ground electronic configuration is asymmetrically filled, making the geometry unstable and in order to bring about stability, the distortion occurs. A common example is d^9 complexes of Cu(II).



The asymmetrical filling of the e_g orbital caused the distortion

Lability and Inertness

Any metal complex that undergoes reactions with $t_{1/2} \leq 1 \text{ min}$ at ordinary conditions (room temperature and about 0.1 M solution) is described as being kinetically labile. If the reaction takes significantly longer than this, the complex is kinetically inert. For example, iron(II) chloride dissolved in water gives a green solution; on addition of a few drops of cyanide solution, it changes to purple. If concentrated NH_3 is added or water, there will be no change in the colour of the solution. This is because the cyano complex is inert and the aquo complex is labile.

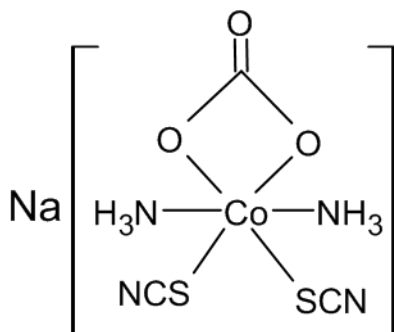
1. If the crystal field splitting is wide an incoming ligand will not be able to substitute it such a complex is inert.
2. Very small ions are often less labile because they have greater M-L bond energy and it becomes sterically difficult for incoming ligands to approach the metal ion
3. chelating ligand cause inertness
4. d^{10} ion of Zn^{2+} , Cd^{2+} and Hg^{2+} are very labile
5. Across the 3d period, M^{2+} ions are labile and Cu^{2+} is most labile due to distortions.
6. d-metal complexes with d^3 and low-spin d^6 configuration like Cr^{3+} , Fe^{2+} and Co^{3+} are inert
7. High charge and small size results in inertness.
8. The more filled the d-orbitals the more labile.

Assignment #3

1.

- What is the name of this complex $[Pt(2\text{HNCH}_2\text{CH}_2\text{NH}_2)_2\text{BrCl}]\text{Cl}_2$?
- What is the primary valence of the complex?
- What is the secondary valence of the complex?
- What is the oxidation state of the central metal?
- Draw the structure
- What shape will the complex likely have?

2.



- What is the name of this complex?
- What types of ligands are attached to the Co and give reasons for your choice?
- How many members make up the ring ligand?
- Draw the enantiomer of the complex (if it has one)
- What shape would the complex adopt?

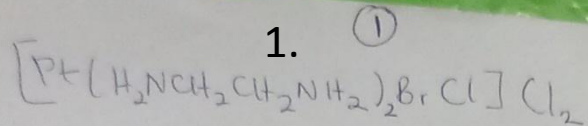
3.

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 5 ml of H_2O resulted in a purple coloured solution of $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$. To 2 ml of this solution 4 ml of *conc HCl* and 10 ml *NaCl* were added. This solution changed to deep green colour, of $\text{Na}_2[\text{CoCl}_4]$. To another 2 ml of the aquo complex, 1.5 ml *conc NH₃* and 10 ml of NH_4Cl were added, to form $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. This time the solution changed from purple to orange.

- Write the formula of the complex ions
- Which of these complexes would have high spin and which one would be low spin?
- Draw the splitting pattern of each and fill in the electrons to show the high spin and low spin states
- Which one would be inert and why?
- Which one of the complexes would be most labile and why?

Solution to Assignment 3

Dr. George



To be able to name this complex, one needs to know the oxidation state of Pt in the complex.

oxidation state of $H_2NCH_2CH_2NH_2 = 0$

✓ ✓ ✓ Br = -1

✓ ✓ ✓ Cl = -1

Let the oxidation state of Pt = x
 Total oxidation state of the complex = 0 [not charged]

d. $x + 2(0) + (-1) + (-1) + 2(-1) = 0$

d. $x - 1 - 1 - 2 = 0$

$x = +4$

a. Name of complex \rightarrow Bromochlorobis(ethylenediamine)platinum(IV)
Bromochlorobis(ethylenediamine)platinum(IV) chloride

b. Outside of the square bracket is 2 chloride ions, $(2Cl^-)$

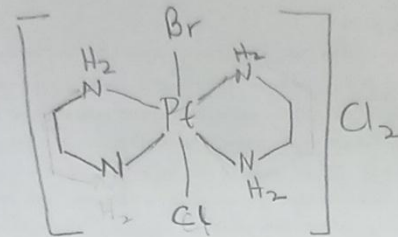
This means that the complex ion is a cation.
 Therefore the primary valence, (which is same as oxidation state) = +2

c. The secondary valence (coordination number) = 6.

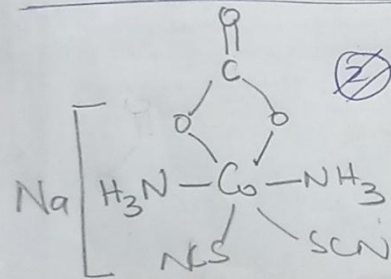
This is because ~~the~~ bromo & chloro ligands are both monodentate, while ethylenediamine is bidentate, therefore it coordinates ~~at 2~~ ^{through} 2 of its N-atoms, there are 2 of them.
 Hence the ~~coordination~~ secondary valence ^{number}

= 6

e. ②



f. Since the coordination number of this complex is 6, it is likely to be have an octahedral shape.



CO_3^{2-} is a carbonate ion. Please change it in the note [it was written in CO_2]

1. Sodium is outside the square brackets it means that the complex ion is an anion [i.e. ~~very~~ ^{very} charged]

2. Since it only has 1 Na^+ ion then the charge on the complex ion is -1 (Na^+ has a charge of +1)

- Charge on $CO_3^{2-} = -2$ carbonate
- Charge on $NH_3 = 0$ ammine
- Charge on $NCS = -1$ thiocyanate
- Charge on $Na = +1$
- Charge on $Co = x$

To determine the oxidation state of Co in the complex.

a.

$$+1 + x + 2(0) + 2(-1) + (-2) = 0$$

$$x + 1 - 2 - 2 = 0$$

$$x - 3 = 0$$

$$x = +3$$

Name of complex is \rightarrow

Sodium diammine-carbonate dithiocyanate cobaltate(III)

b.

1. Monodentate ligands, \Rightarrow NH_3 ~~\Rightarrow SCN^-~~

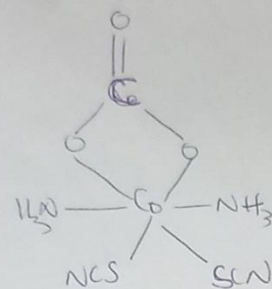
2. CO_3^{2-} is a bidentate, chelating ligand.

3. SCN^- is an ambidentate ligand. It can also bond through the N (NCS).

NH_3 is monodentate because only 1 pair of electrons to coordinate with.

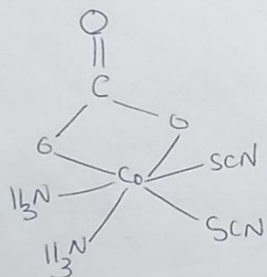
CO_3^{2-} is bidentate because it can donate 2 pairs of electrons. It is chelating ligand because it forms a ring when coordinated to the same metal.

c. It forms a 4 member ring.

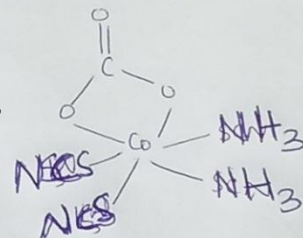


d.

It has a mirror image but they are superimposable. Therefore they are not enantiomers but diastereomers.



2.



These are enantiomers.

e.

The coordination number of this complex is 6. Therefore it is likely to be octahedral.

**CHM 201 LECTURE SERIES.
2022/2023 SESSION
DR T. A. AJAYEOBA.**

LECTURE I

How Philosophers thoughts of Atom

- **Philosopher Aristotle thoughts on Atom.**

The question posed was: into how small of pieces can you divide a grain of sand? The prevailing thought at the time, pushed by Aristotle, was that the grain of sand could be divided indefinitely, that you could always get a smaller particle by dividing a larger one and there was no limit to how small the resulting particle could be.

- **Democritus on Atom**

Since Aristotle was such an influential philosopher, very few people disagreed with him. However, there were some philosophers who believed that there was a limit to how small a grain of sand could be divided. One of these philosophers was Democritus (~460-370 B.C.E.). **He taught that there were substances called atoms and that these atoms made up all material things. The atoms were unchangeable, indestructible, and always existed.**

Dalton's Atomic Theory

The modern atomic theory, proposed about 1803 by the English chemist John Dalton, is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

Key points of Dalton's Atomic Theory

- All matter is composed of extremely small particles called atoms.
- Atoms of a given element are identical in size, mass, and other properties. Atoms of different elements differ in size, mass, and other properties.
- Atoms cannot be subdivided, created, or destroyed.
- Atoms of different elements can combine in simple whole number ratios to form chemical compounds.
- In chemical reactions, atoms are combined, separated, or rearranged.

Validity of Dalton's Atomic Theory

- Modern science had however shown that the only valid point in Dalton's atomic theory is that:
 - Atom is very small.
- Other points have been disproved by modern science. We now know that atoms are made up of sub atomic particles, of which, the electron, proton and neutron are very important. Other sub atomic particles include k-positron, neutrino etc.
- Atoms can be created or destroyed by the process of nuclear reactions or radioactivity
- Also, the phenomenon of isotopy has made it known that atoms of the same element are not necessarily identical in size, mass and other properties. For example, ^{12}C , ^{13}C , and ^{14}C are all atoms of the same element having different masses.
- Similarly, ^{14}C and ^{14}N are atoms of different element having the same mass.
- The existence of giant molecules is now known which are not just simple combination of atoms in a simple whole ratio.

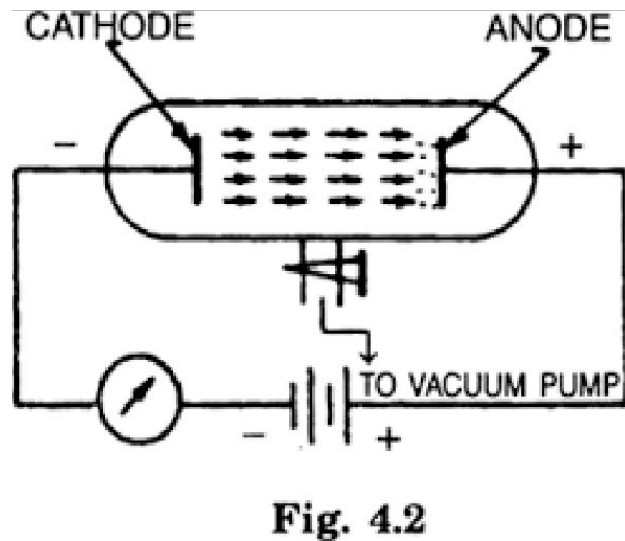
Production of Cathode Rays. Discovery of Electrons.

- The first indication of the complex nature of atom was obtained from a study of "*conduction of electricity through gases at reduced pressure*" by Julius Plucker in 1859. He took a cylindrical glass tube, called discharge tube (30 cm long and 4 cm in diameter) closed at both ends, provided with metallic electrodes and connected the tube with a high vacuum pump and low pressure gauge, to obtain very low pressures.
- The electrodes were connected to a high voltage battery of the order 10,000 volts or more. He observed when the tube was connected, the walls of the tube began to glow with a bluish or greenish light depending on the composition of the glass. It was found that the rays of light were emitted from the cathode and moved towards the anode at right angles and with large velocity. The rays were called cathode rays by Goldstein in 1876, since these originated from the cathode.

Discovery and Properties of Electrons : J. J Thomson

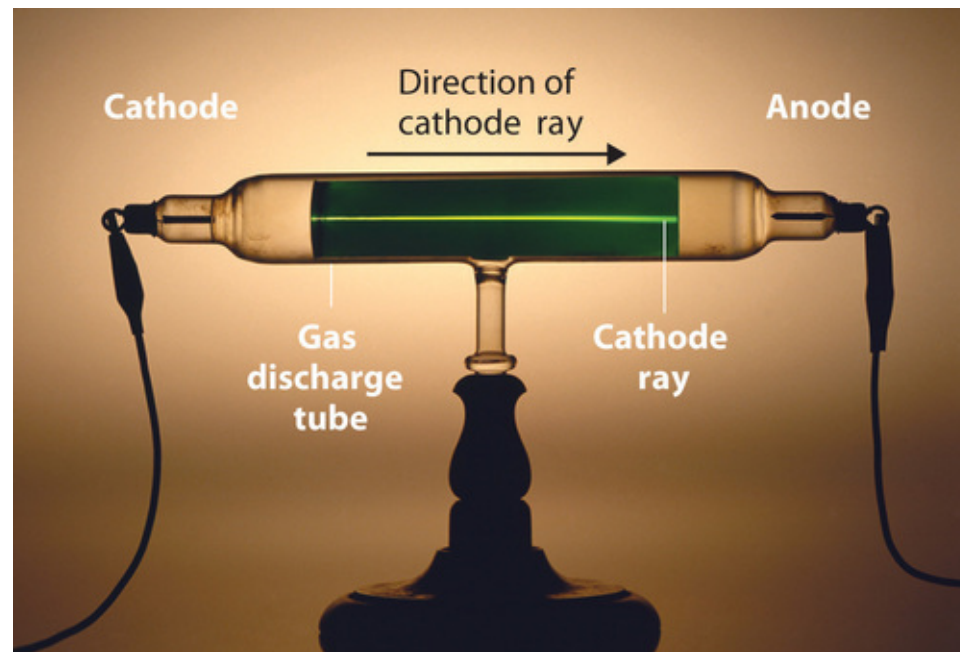
- J.J. Thomson and some other researchers, modified the Discharge tube and carry out various experiment on the cathode rays and came up with the properties of cathode rays. J.J. Thomson later called cathode ray, electron.
- Properties of cathode rays:
 - 1. The particles constituting the cathode rays are negatively charged. J.J Thomson showed that when they were passed through an electric field, they were deflected towards the positively charged plates. Similarly, when a magnetic field was applied on cathode rays, they were deflected
 - 2. They produce a greenish fluorescence on the walls of the glass tube. They also produce fluorescence in rare earths elements like cerium, natural minerals, sulphides and sulphates. When placed in the path of these rays, alumina glows red, tin stone glows yellow and willemite green.
 - 3. The rays travel in straight line perpendicular to the surface of the cathode. This was shown by the fact that if a metallic object like hinged aluminum cross is placed in the path of the rays a sharp shadow of this object is cast on the walls opposite the cathode.
 - 4. Cathode rays consist of moving material particles with definite mass and velocity i. e they have momentum. When a small paddle wheel is placed in the path of these rays, the wheel was set in motion.

DIAGRAM OF DISCHARGE TUBE.



Culled from <https://www.zigya.com/study/book?class>

A TYPICAL DISCHARGE TUBE



- https://chem.libretexts.org/Courses/Pasadena_City_College/CHEM_001A%3A_General_Chemistry_and_Chemical_Analysis/02%3A_Atoms_and_Elements/2.04%3A_The_Discovery_of_the_Electron

Discovery and Properties of Electrons : J. J Thomson cont'd.

- 5. Cathode rays produce heat when they fall on matter. When cathode rays from a concave cathode are focused on a platinum foil, it begins to glow. The kinetic energy of the cathode rays is transformed into heat energy by their stoppage.
- 6. Cathode rays produce X-rays. When cathode rays strike a solid substance, particularly one with a large atomic weight, they give rise to penetrating radiations, called X-rays which have the same nature as light does.
- 7. They ionize the gas through which they pass.
- 8. They cause chemical changes e.g. they have reducing effect.
- 9 They pass through thin metal foil e.g. they pass through thin aluminum foil
- . Thomson carried out a number of experiments for the determination of charge - to - mass ratio ($\frac{e}{m}$) value of an electron in which he varied the metal forming the cathode as well as the gas in the evacuated discharge bulb. In every case, he found the value of $\frac{e}{m}$ to be equal to 1.76×10^{11} coulomb/kg

Millikan's oil drop Experiment

- Millikan conducted the experiment to determine the elementary electric charge on an electron (e value) in 1909. This experiment provided essential insights into quantisation of electric charge.
- He set up a chamber with parallel metal plates, where small oil droplets were introduced. Initially the droplets experienced the force of gravity pulling them down. The upward force of buoyancy countered gravity until the droplets reached a constant velocity, indicating a balance of forces. An electric field was introduced between the plates. The droplets became charged as a result of ionization by X-rays.
- Millikan made the droplets hover in midair by adjusting the electric field strength. The electric force then balanced the gravitational force. This equilibrium of forces on the droplet can be expressed through the following equation:
 - $$q = \frac{mg}{E}$$
 - Where :
 - q is the charge of a single electron
 - m is the mass of the droplet
 - g is the acceleration due to gravity
 - E is the strength of the electric field
- Millikan experiment showed that the charges on the oil droplets were quantized and always occurred in multiples of fundamental unit. The charge on the electron was found to be 1.606×10^{-19} coulombs.
- Millikan results supported J.J. Thomson model of atom which propose the existence of a discrete, indivisible electrons

Millikan's oil drop Experiment cont'd

- Example 1:
- An oil droplet in Millikan's experiment has a mass of 5.6×10^{-14} kg. The electric field strength E is 2.0×10^3 N/C. Calculate the charge (e)

Using the equation:

$$q = \frac{mg}{E}$$

Put the values;

$$q = \frac{(5.6 \times 10^{-14} \text{ kg}) (9.8 \text{ m/s}^2)}{2.0 \times 10^3 \text{ N/C}}$$
$$q = \frac{5.488 \times 10^{-13} \text{ N}}{2.0 \times 10^3 \text{ N/C}}$$
$$q = 2.744 \times 10^{-16} \text{ C}$$

Millikan's oil drop Experiment cont'd

- Example 2:

An oil droplet having a net charge of $24 \mu\text{C}$ is placed in a uniform electric field of 610 N/C directed vertically. What is the mass of this object if it floats in the field?

$$\begin{aligned} \text{Given;} \quad q &= \frac{mg}{E} \\ \text{therefore,} \quad m &= \frac{qE}{g} \\ &= \frac{(24 \times 10^{-6} \text{ C}) \times (610 \frac{\text{N}}{\text{C}})}{9.80 \text{ m/s}^2} \\ m &= 1.5 \times 10^{-3} \text{ kg} \end{aligned}$$

Importance of the determination of charge on an electron (e)

- Determination of the charge on an electron has enabled the determination of other values such as:

1. Determination of Avogadro's number.

Avogadro's number is defined as the number of molecules per gram molecule of a substance, or it is the number of atoms per gram atom of a substance. Since the charge required to liberate one-gram ion of H^+ is equal to 95,000 coulombs, and the charge on one H^+ ion is equal (though of opposite sign) to that carried by an electron i. e 1.602×10^{-19} coulomb. Then:

$$\begin{aligned}\text{Avogadro's number} &= \frac{96,500 \text{ coulomb}}{1.602 \times 10^{-19} \text{ coulomb}} \\ &= 6.023 \times 10^{23}\end{aligned}$$

2. Mass of an electron in grams. The value of the electronic charge (e) and e/m enables the determination of mass of an electron:

$$\begin{aligned}m &= \frac{e}{e/m} = \frac{1.602 \times 10^{-19} \text{ coulomb}}{1.758 \times 10^8 \text{ coulomb/g}} \\ &= 9.108 \times 10^{-28} \text{ g} \quad (9.1 \times 10^{-31} \text{ kg})\end{aligned}$$

Importance of the determination of charge on an electron (e) cont'd.

- 3. Mass of an electron relative to that of hydrogen atom.

It has been found that the number of atoms in one mole of any element is equal to Avogadro's number, 6.023×10^{23} ,

Therefore, the weight of 6.023×10^{23} atoms of hydrogen = atomic weight of hydrogen = 1.008 g

$$\begin{aligned}\text{The weight of one atom of hydrogen} &= \frac{1.008}{6.023 \times 10^{23}} \text{ g} \\ &= 1.67 \times 10^{-24} \text{ g}\end{aligned}$$

Since the mass of an electron = 9.1×10^{-28} g

$$\text{Therefore, } \frac{\text{mass of hydrogen atom}}{\text{mass of an electron}} = \frac{1.67 \times 10^{-24} \text{ g}}{9.1 \times 10^{-28} \text{ g}}$$

$$= 1.835 \times 10^3 = 1835$$

That is, mass of hydrogen atom = 1835 x mass of an electron

Or mass of an electron = $\frac{1}{1835}$ x mass of hydrogen atom.

It means that the mass of an electron is $\frac{1}{1835}$ *th* of the mass of a hydrogen atom.

- please, note the units in all circumstance: 9.1×10^{-28} g is also 9.1×10^{-31} kg. The important thing is to make sure you are consistent in the units being used.

Importance of the determination of charge on an electron (e) cont'd

- 4. Mass of an electron in atomic mass units (a.m.u):
 - On the atomic weight scale, the mass of hydrogen atom has been found to be equal to 1.008 amu.

From equation (I) above, we have;

On atomic weight scale, the mass of an electron

$$= \frac{\text{mass of hydrogen atom in amu}}{1835}$$

$$\frac{1.008 \text{ amu}}{1835} = 0.0005493 \text{ amu.}$$

This mass is taken to be equal to zero. Therefore, electron is said to be a weightless particle.

Bohr's Atomic Model (1885-1962)

- Niels Bohr proposed an atomic model that helped solve the problem inherent in Rutherford's model.
- Bohr put forward an atomic model which is based on Planck's quantum theory of radiation.
- Bohr proposed a theory of atomic structure and provide a quantitative prediction of line spectra. He began with the planetary model but introduced certain assumptions which were:

Bohr's Atomic Model (1885-1962) cont'd

- (1). that the electron moves in an orbit around the central nucleus and only certain orbits are allowed.
- (II). Electron do not radiate energy when in these orbits, and it has associated with it, a definite amount of energy.
- (III). Under certain condition, transition between these stationary states (orbit) do occur and these transitions are accompanied by emmission or absorption.

Bohr's Atomic Model cont'd

- Niel Bohr (a Danish Physicist, 1913), put forward a new atomic model which is based on **Planck's** quantum theory of radiation:
 - In order to explain why electron revolving round the nucleus does not lose energy and consequently does not fall into the nucleus and how the spectral lines of the emission spectrum of H-atom are produced when electron jumps from one energy level to another
 - To deal with Bohr's atomic model, we should recall our understanding of:
 - i. Electromagnetic radiation (or waves) and nature of radiations emitted by electrons
 - ii. Emission spectrum, continuous spectrum and line spectrum
 - iii. Planck's quantum theory of radiation

Electromagnetic Radiation or Waves.

- Recall that waves are characterized by the following properties:
 - Wavelength (λ) expressed in cm, or m
 - Frequency (ν) expressed in Hertz (Hz or s^{-1}) or cycles (or waves) per second (cps)
 - Speed or velocity (c) ms^{-1}
 - wave number ($\tilde{\nu}$) cm^{-1} or m^{-1} $[1\ cm^{-1} = 10^2\ m^{-1}; 1\ cm = 10^{-2}\ m]$
- It has been known that the frequency of a wave is inversely proportional to its wavelength:
 - $\nu = \frac{c}{\lambda}$ 1.0
 - $C = \lambda \nu$ 1.1
 - Wavenumber ($\tilde{\nu}$) = $\frac{1}{\lambda}$;1.2
 - $\tilde{\nu} = \frac{1}{\lambda}$ since $\lambda = \frac{c}{\nu}$ 1.3
 - Therefore, Wavenumber ($\tilde{\nu}$) = $\frac{\text{frequency } \nu}{\text{velocity } c}$ 1.4

Electromagnetic Radiation or Waves cont'd

- E.g, calculate the wave number of the lines of frequencies 4×10^{14} Hz and 5×10^{16} Hz
- $c = 3 \times 10^8 \text{ m.s}^{-1}$

- $\tilde{\nu} = \frac{\nu}{c}; \quad \frac{4 \times 10^{14} \text{ Hz (Hz = s}^{-1}\text{)}}{3 \times 10^8 \text{ m.s}^{-1}}$

$$= 1.33 \times 10^6 \text{ m}^{-1}$$

Solve the other one.

Electromagnetic Radiation or Waves cont'd

- Calculate the wavelength of a wave of frequency 10^{11} Hz travelling with the speed of light.

Using equation 1.0,

$$v = \frac{c}{\lambda};$$

$$\lambda = \frac{c}{v},$$

$$\lambda = \frac{3 \times 10^8 \text{ m s}^{-1}}{10^{11} \text{ s}^{-1}}$$

$$= 3 \times 10^{-3} \text{ m}$$

Question: Calculate the frequency and wavenumber of yellow light having wavelength of 580 nm.

$$\lambda = 580 \text{ nm} = 580 \times 10^{-9} \text{ m}; \quad c = 3 \times 10^8 \text{ ms}^{-1}.$$

$$v = \frac{c}{\lambda}; \quad v = \text{frequency},$$

$$v = \frac{3 \times 10^8 \text{ ms}^{-1}}{580 \times 10^{-9} \text{ m}} = 5.172 \times 10^{14} \text{ s}^{-1} \text{ or Hz}$$

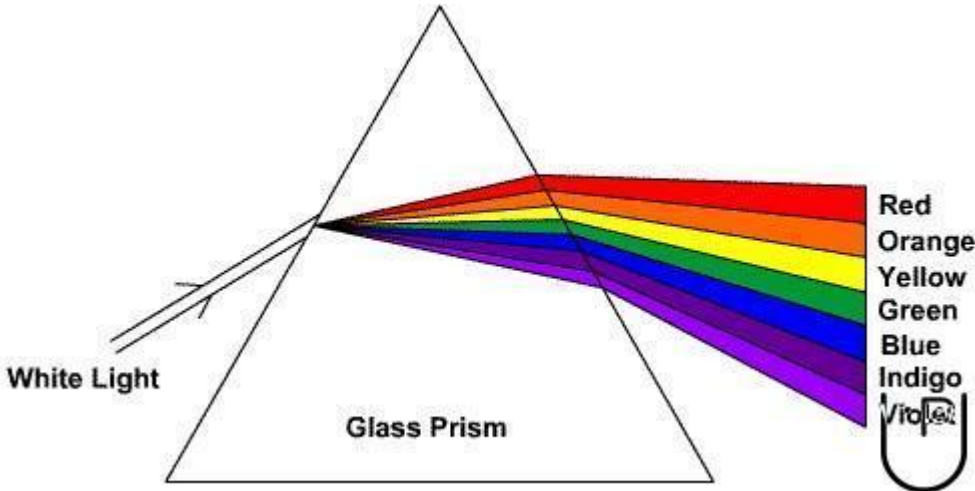
for the wavenumber;

$$\begin{aligned} \bar{v} &= \frac{1}{\lambda} \\ &= \frac{1}{580 \times 10^{-9} \text{ m}} \\ &= 1.724 \times 10^6 \text{ m}^{-1} \end{aligned}$$

Spectrum

- Spectrum is an array of waves or particles which is spread out according to the increasing or decreasing of some property such as wavelength or frequency.
- With a prism, we can spread out the light from a bulb to give continuous spectrum: that is a spectrum containing light of wavelength like a rainbow.

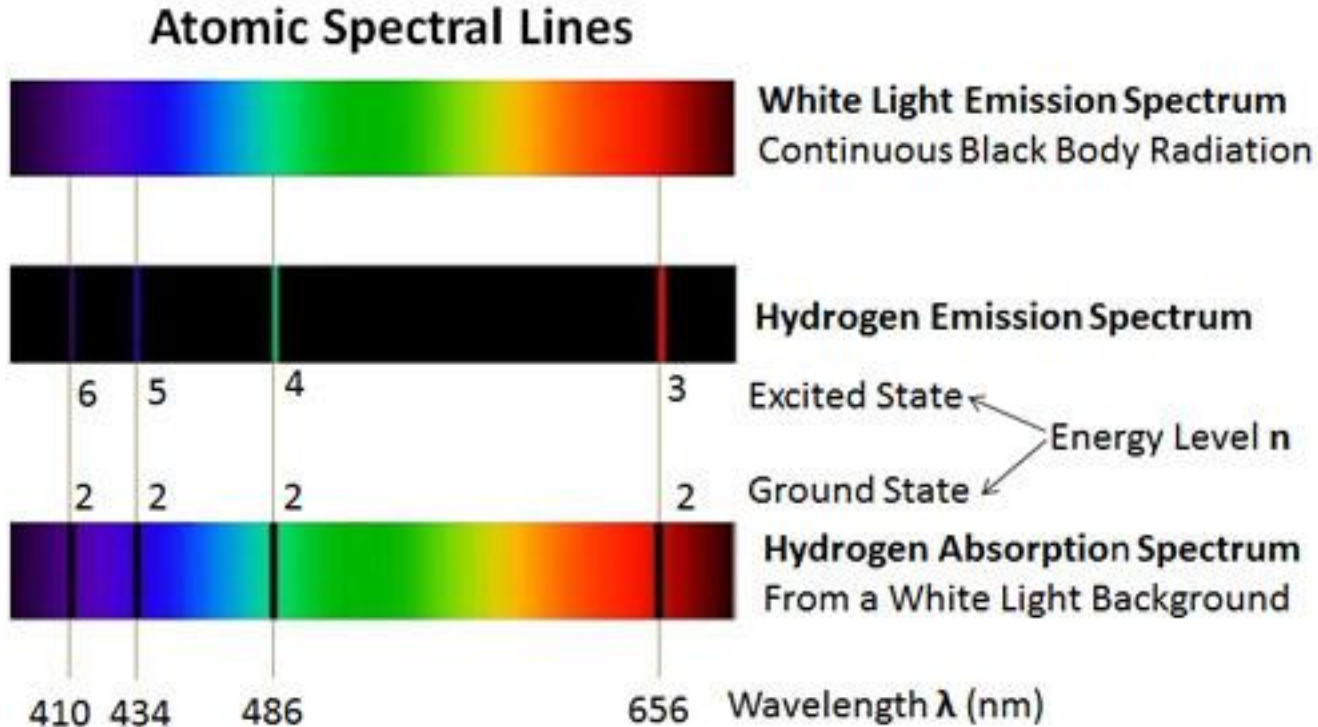
A continuous Spectrum of light through a Prism



Spectrum cont'd

- However, light emitted by a heated gas yielded different results. Rather than having a continuous spectrum, with all colours of the rainbow, we obtain what is called a Line Spectrum.
- A line spectrum, is a spectrum showing only certain colours or specific wavelength of light.
- When light from hydrogen gas discharge tube is separated into its components by a prism, it gives a spectrum of lines, each line correspond to light of a given wavelength.
- The line spectrum of the hydrogen atom in the visible region consist of only four lines which are Red, Blue-Green, Blue and a Violet), although, others appear in the infrared and ultraviolet region.

Atomic line spectra

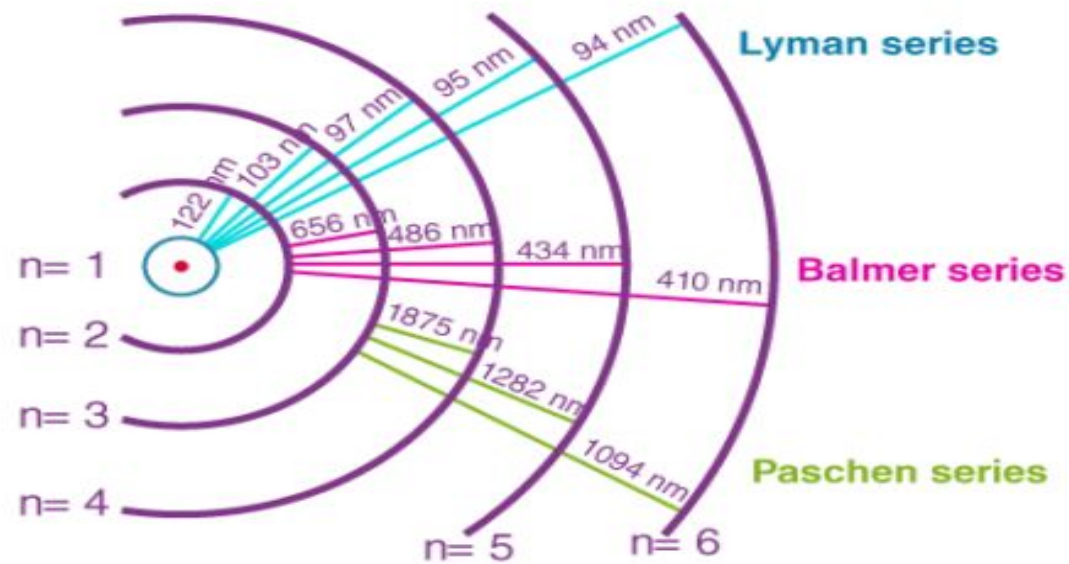


Classification of spectral lines in hydrogen spectrum.

- between. The wavelengths of various spectral lines seen in hydrogen spectrum show that these lines lie in visible, ultraviolet and infrared regions. All these spectral lines can be classified into five groups or series called spectral series which are named after their discoverers.

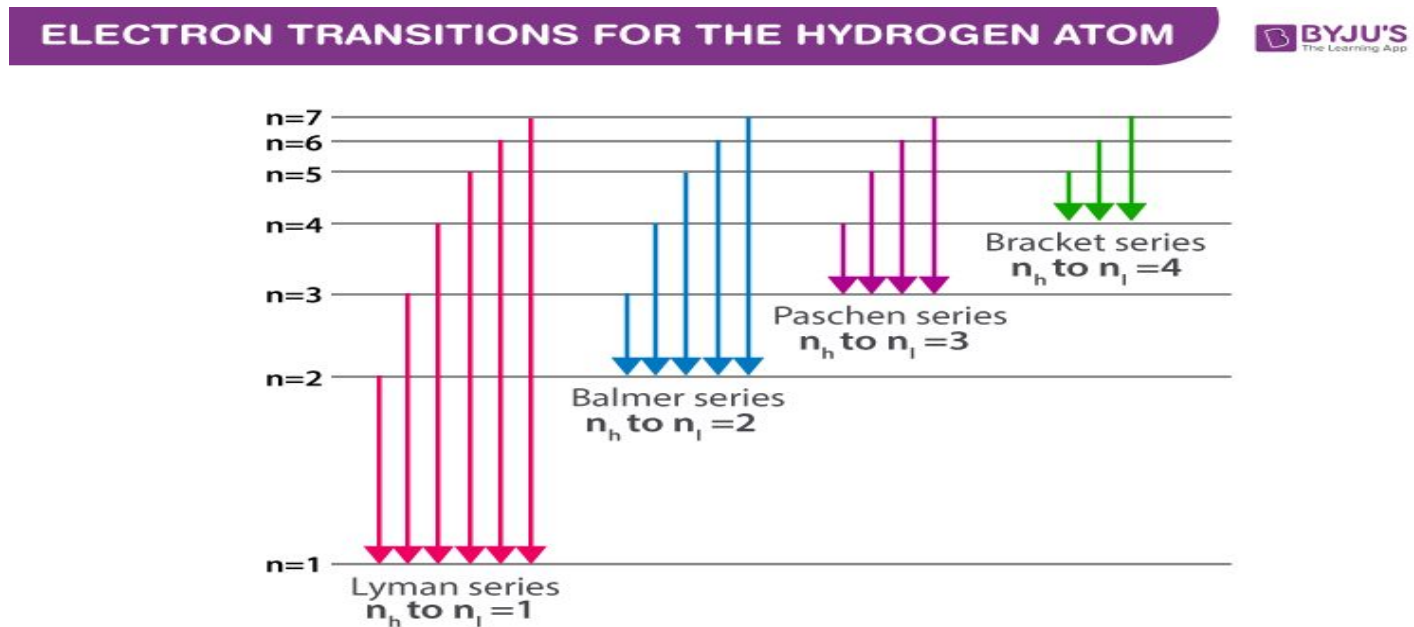
Spectral series	discovered by	appearing in
• Lyman series	Lyman	Ultraviolet region
• Balmer series	Balmer	Visible region
• Paschen series	Paschen	Infrared region
• Brackett series	Brackett	Infrared region
• Pfund series	Pfund	infrared region

- A spectral series is a collection of sequentially grouped wavelengths. Which describes light or any electromagnetic radiation released by energised atoms.



- <https://byjus.com/physics/spectral-series/>

- Transitions in hydrogen atom.



- <https://byjus.com/physics/spectral-series/>

Atomic line spectra

- In 1885, J.J Balmer showed that the wavelength λ , in the visible spectrum of hydrogen could be reproduced by a simple equation.
 - Balmer's formular;

Balmer's formular.

$$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

Where λ is the wavelength

R is the Rydberg's Constant and

n can have any integral value.

R = Rydberg's constant = $1.097 \times 10^7 \text{ m}^{-1}$

n = is some whole number (integers) greater than 2. i.e 3, 4, 5.....

For example, by substituting n= 3 into the equation,

$\lambda = 6.56 \times 6.56 \times 10^{-7} \text{ m}$ or 656 nm

This is the wavelength of red light in the line spectrum.

Planck's Quantum Theory of Radiation- Quantization of Energy .

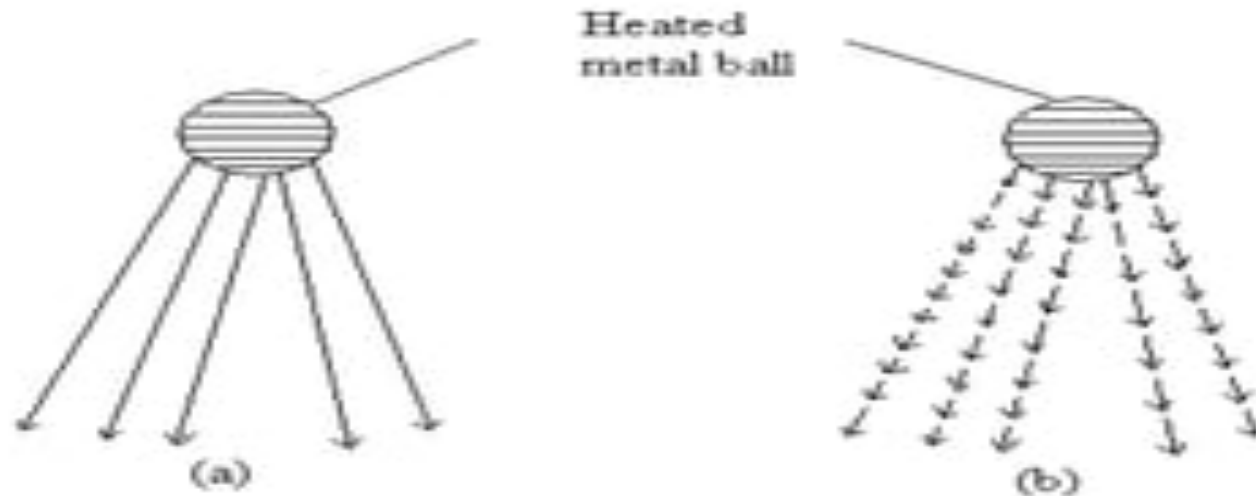
In 1900, Max Planck studied the spectral lines obtained from thermal radiations emitted by a hot(black) body at different temperatures and put forward a theory which is known as Planck's quantum theory of radiation. Various postulates of the theory are:

1. A hot body emits radiant energy not continuously (i.e. not as continuous waves as suggested by the classical Maxwell's wave theory) but discontinuously (discretely). In other words, this means that a hot body emits radiant energy not as continuous waves but as small packets or bundles or discrete (separate) units of waves. Each of these units are called a quantum (plural Quanta) which can independently exist. Thus, a quantum is defined as follows:
 - A quantum is the smallest unit of waves in the form of which a hot body emits radiant energy and which can exist independently.

hi

Planck's Quantum Theory of Radiation- Quantization of Energy

- a. continuous waves according to classical Maxwell's theory. (b). Discontinuous waves according to max planck's quantum theory



- <https://www.slideshare.net/ProfYogitaThakare/quantum-chemistryb-sc-iiisemvi>

Planck's Quantum Theory of Radiation- Quantization of Energy cont'd

- In case of light which is also a form of radiation, light energy (i.e. energy associated with light radiation) is emitted or absorbed in the form of packets or bundles each of which is called photon (instead of quantum). Photon is not a material body. It is considered to be a massless bundle of energy.
- In 1905, Albert Einstein while explaining the photoelectric effect, proved the existence of photons.
- (2). the energy (E) associated with each quantum or photon of a given radiation or light is proportional to the frequency (ν) of the emitted radiation or light, i.e

$$E \propto \nu$$

$$\text{or } E = h \nu;$$

where h is a constant known as Planck's constant = 6.624×10^{-34} j.s

$$\text{Since } \nu = \frac{c}{\lambda}$$

$$E = h \cdot \frac{c}{\lambda}$$

This equation shows that the smaller the wavelength (or higher the frequency) of radiation, the larger the energy associated with a quantum or a photon. For example, a photon transmitted by violet light, which has a higher frequency has more energy than that transmitted by red light which has lower frequency.

In 1905, Einstein said that the energy associated with a photon (E) with mass m and velocity c is also given by:

$$E = mc^2$$

This equation is called Einstein's equation or Einstein mass-energy relationship

Applications of Planck's quantum theory of radiation

- - i. in 1905, Einstein applied this theory to explain the photoelectric effect
 - ii. in 1913, Bohr used this theory to explain the structure of the atom and the origin of spectral lines in hydrogen spectrum.
 - iii. in 1922, Compton applied this theory to explain the phenomena incoherent scattering of x-rays (Compton effect).
- Examples: the violet line in a spectrum have wavelength equal to 4000 Å. calculate the energies of photons transmitted.

$$\lambda = 4000 \text{ \AA} = 4000 \times 10^{-10} \text{ m}$$

$$\begin{aligned} E &= h \cdot \frac{c}{\lambda} \\ &= \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s} \times 3 \times 10^8 \text{ ms}^{-1}}{4000 \times 10^{-10} \text{ m}} \\ &= 4.9695 \times 10^{-19} \text{ J} \end{aligned}$$

- Electromagnetic radiation of wavelength 242 nm is just sufficient to ionize the outermost electron of the sodium atom. Calculate the ionization energy of sodium atom.

($c = 3 \times 10^8 \text{ m.s}^{-1}$; $h = 6.626 \times 10^{-34} \text{ J.s}$; Avogadro's number = 6.023×10^{23})

- $E = h \cdot \frac{c}{\lambda}$

$$= 6.626 \times \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{242 \times 10^{-9}}$$

$$= 8.21 \times 10^{-19} \text{ J}$$

$$= 8.21 \times 10^{-22} \text{ kJ}$$

$$= 8.21 \times 10^{-22} \times (\text{Avogadro's number}) \text{ kJ/mole}$$

$$= 8.21 \times 10^{-22} \times 6.023 \times 10^{23} \text{ kJ/mole}$$

$$= 494.48 \text{ kJ/mole}$$

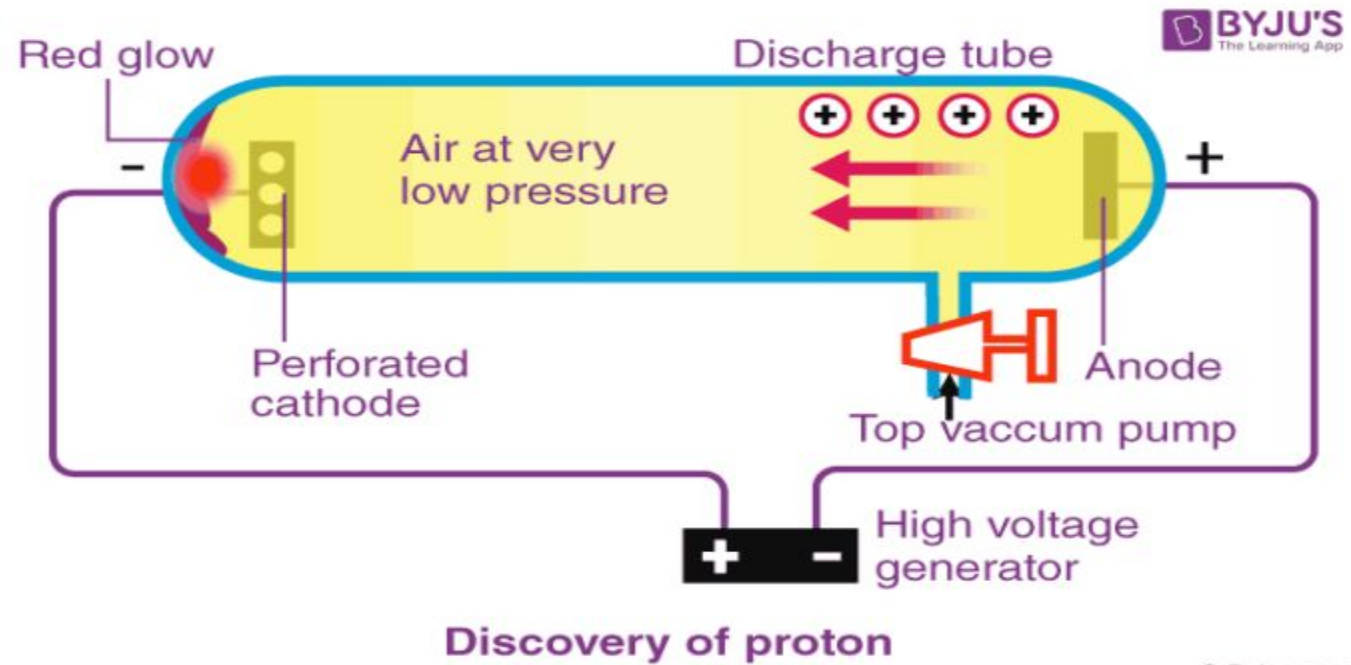
**CHM 201 LECTURE SERIES.
2022/2023 SESSION
DR T. A. AJAYEOBA.**

LECTURE II

Anode (positive) rays: Discovery of Protons.

- Atom is electrically neutral, and has been found to have negatively charged particles known as electrons, it should have some particles which should be positively charged. Attempts were made by many scientists to show the presence of positively charged particles. In 1886, German physicist, Goldstein took a discharge tube provided with a cathode perforated with extremely fine holes and observed that when a large potential difference was applied between the electrodes, not only cathode rays or electrons were originated from cathode, but also new type of colored rays was simultaneously originated from the anode, moving from anode towards cathode through the fine holes or canals in the cathode and causing a glow on the wall opposite to anode.
- The search for the predicted positive charge continued in order to counterbalance the negatively charged electrons. However, it was Rutherford that was also credited with the discovery of proton through his Gold foil experiment.

Production of positive rays in the discharge tube.



- <https://byjus.com/chemistry/proton-neutron-discovery>

CREDITING RUTHERFORD WITH DISCOVERY OF PROTON

- In 1909, Ernest Rutherford, along with collaborators Hans Geiger and Ernest Marsden, initiated the renowned gold foil experiment at the University of Manchester. Alpha particles were directed at a thin gold foil, with observations made on the scattering patterns.
- Contrary to expectations based on the prevailing model, some alpha particles experienced significant deflections or even rebounded. Rutherford astutely interpreted these outcomes as indicative of a concentrated, positively charged nucleus within the atom.
- **Identification of the Proton:** The subsequent step involved the identification of the specific particle responsible for the positive charge. Rutherford, in 1919, directed alpha particles at nitrogen gas, resulting in the emission of hydrogen nuclei. This established the presence of a positively charged particle, later confirmed as the proton.

CREDITING RUTHERFORD WITH DISCOVERY OF PROTON CONT'D

- Ernest Rutherford observed that his scintillation detectors detected hydrogen nuclei when a beam of alpha particles was shot into the air.
- After investigating further, Rutherford found that these hydrogen nuclei were produced from the nitrogen atoms present in the atmosphere.
- He then proceeded to fire beams of alpha particles into pure nitrogen gas and observed that a greater number of hydrogen nuclei were produced.
- He concluded that the hydrogen nuclei originated from the nitrogen atom, proving that the hydrogen nucleus was a part of all other atoms.
- This experiment was the first to report a [nuclear reaction](#), given by the equation: $^{14}\text{N} + \alpha \rightarrow ^{17}\text{O} + \text{p}$ [Where α is an alpha particle which contains two protons and two neutrons, and 'p' is a proton]
- The hydrogen nucleus was later named 'proton' and recognized as one of the building blocks of the atomic nucleus

Properties of positive rays as observed by JJ Thomson

1. The particles constituting positive rays are positively charged. They were deflected towards the negatively charged plate in an electromagnetic field.
2. The charge-to-mass ratio (e/m) for positive rays is smaller than that for an electron.
3. The positive rays produces flashes on ZnS plate.
4. The rays travel in a straight line in a direction opposite the cathode.
5. Charge-to-mass ratio value: it was found that e/m values for different gases filling the discharge tube was not the same. When hydrogen gas was filling the tube, the e/m value was found to be highest. Since the value of the charge (e) was the same for all gases, it means that the value of the (m) should be lowest for the positive particle obtained from hydrogen gas. Thus, positive particle of hydrogen gas is the lightest among all positive particles obtained from different gases. These particles were called protons, given by Rutherford.
6. Charge on a proton. Charge on a proton is equal in magnitude but opposite in sign to that of an electron. Thus, the charge carried by a proton is equal to $+1.602 \times 10^{-19}$ coulombs, which is taken to be equal to one units of positive charge (+1). Thus, a proton is said to carry one unit of positive charge on it.

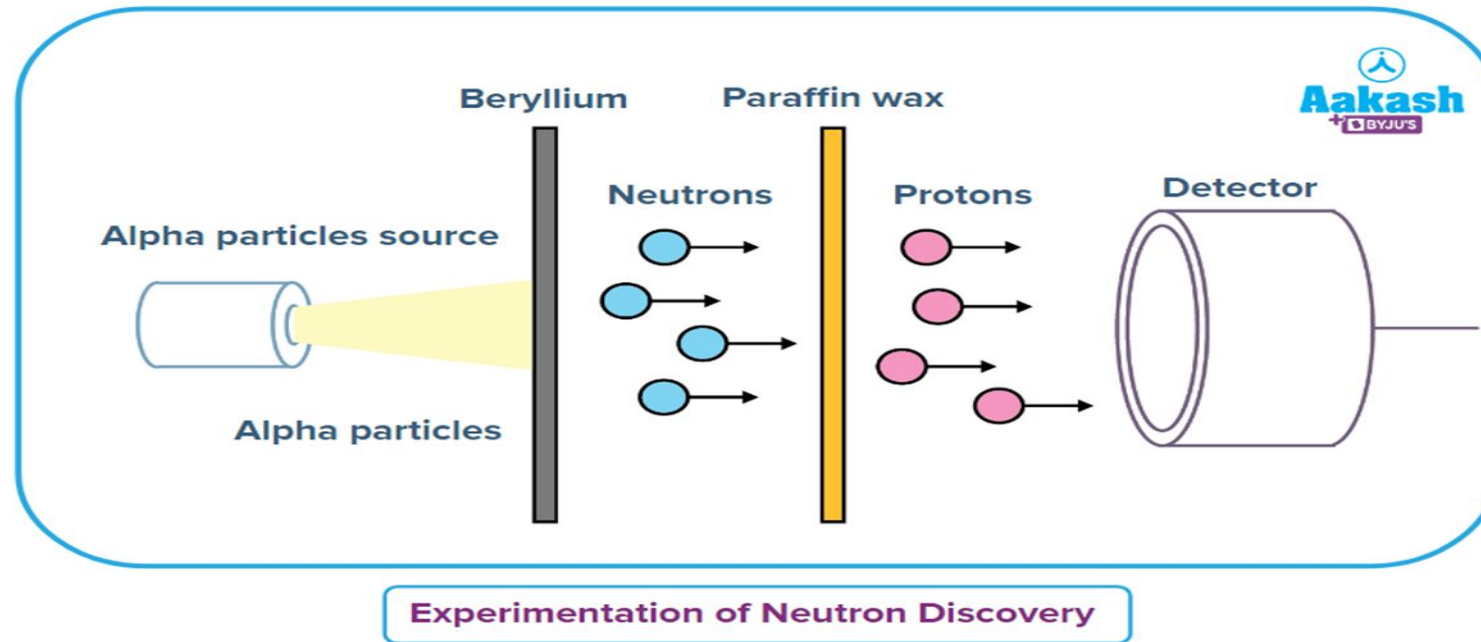
DISCOVERY OF NEUTRON

Up till 1932, it was predicted that the atom is composed only of electrons and proton, and that the mass of an atom is due to the mass of proton present in the nucleus, since the mass of electron is negligible. Mass of each proton is equal to 1.00375 atomic mass. Unit. (a.m.u). Rutherford noticed that the atomic masses of different atoms could not be explained if it is composed of only protons and electrons, and therefore, he predicted in 1920 that some kind of neutral particles having mass equal to protons must be present.

DISCOVERY OF NEUTRON, CONT'D.

- The discovery of neutrons can be traced back to the year 1930 when the German nuclear physicists Herbert Becker and Walther Bothe observed that a penetrating form of radiation was produced when the alpha particles emitted by polonium was incident on relatively light elements such as lithium, beryllium, and boron. This penetrating radiation was unaffected by electric fields and was, therefore, assumed to be gamma radiation.
- The British physicist Sir James Chadwick discovered neutrons in the year 1932. He was awarded the Nobel Prize in Physics in the year 1935 for this discovery.

DISCOVERY OF NEUTRON, CONT'D



- <https://www.aakash.ac.in/important-concepts/chemistry/discovery-of-protons-and-neutrons>

Properties of Neutrons

- 1. Mass and Charge of Neutrons: The mass of a neutron is equal to that of a proton. On the relative scale, since the mass of a proton is taken to be equal to 1 a. m. u. although, the exact mass of a neutron is 1.00898 a.m.u, in grams, the mass of a neutron is equal to 1.672×10^{-24} g. Neutron has no charge.
- 2. Decay of Neutrons: A free neutron decays into a proton (${}_{+1}^1p$) with the emission of an electron and an antineutrino. Nuclei are made up of protons and neutrons. While neutrons are stable inside many nuclei, free neutrons decay with a lifetime of about 15 minutes. This makes them a radiation problem around nuclear reactors, since they can leak out of the reactor and decay. **The neutron decays into a proton, an electron, and an antineutrino of the electron type.**



Properties of Neutrons

- Neutrons are very penetrating. The intensity of their penetration is reduced to half in passing through thickness of 1.5 cm. neutrons are however less penetrating than cosmic ray.
-
- Uses of neutrons
- Almost all elements are transmuted by neutrons. A fast-moving neutron ejects an alpha particle from nitrogen nucleus, thereby converting it into boron nucleus.
- ${}^{14}_7N + {}^1_0n \rightarrow {}^{11}_6B + {}^4_2He$
-
- Whereas, when a slow-moving neutron falls on certain substances, they are captured with the emission of high energy gamma radiation. The new substances formed are radioactive e.g.
- ${}^{65}_{29}Cu + {}^1_0n \rightarrow {}^{66}_{29}Cu + hv$
- ${}^{66}_{29}Cu \rightarrow {}^{66}_{30}Zn + {}^0_{-1}e$

Henry Moseley and Atomic number.

- Moseley in 1913, bombarded a number of elements with cathode rays (electron). The energy provided by the cathode rays caused the elements to give off X-rays. Moseley investigated the connection between the frequency of the X-rays and the nature of the elements giving them off.
- He found that as the atomic mass increases, the wavelength of the resultant x-ray decreases. From this results, it was deduced that there must be a fundamental property of the atom of elements which increases regularly as the atomic mass increases.
- Moseley called this, the number of proton in the nucleus of the atom.

Values of the charge and Mass protons, neutrons and electrons

Particles	Charge/coulomb	Actual mass/Kg	Ratio of mass
Proton	1.602×10^{-19} positive (+)	1.673×10^{-27}	1
Neutron	0.0 Nil	1.675×10^{-27}	1
Electron	-1.602×10^{-19} Negative (-)	9.109×10^{-31}	

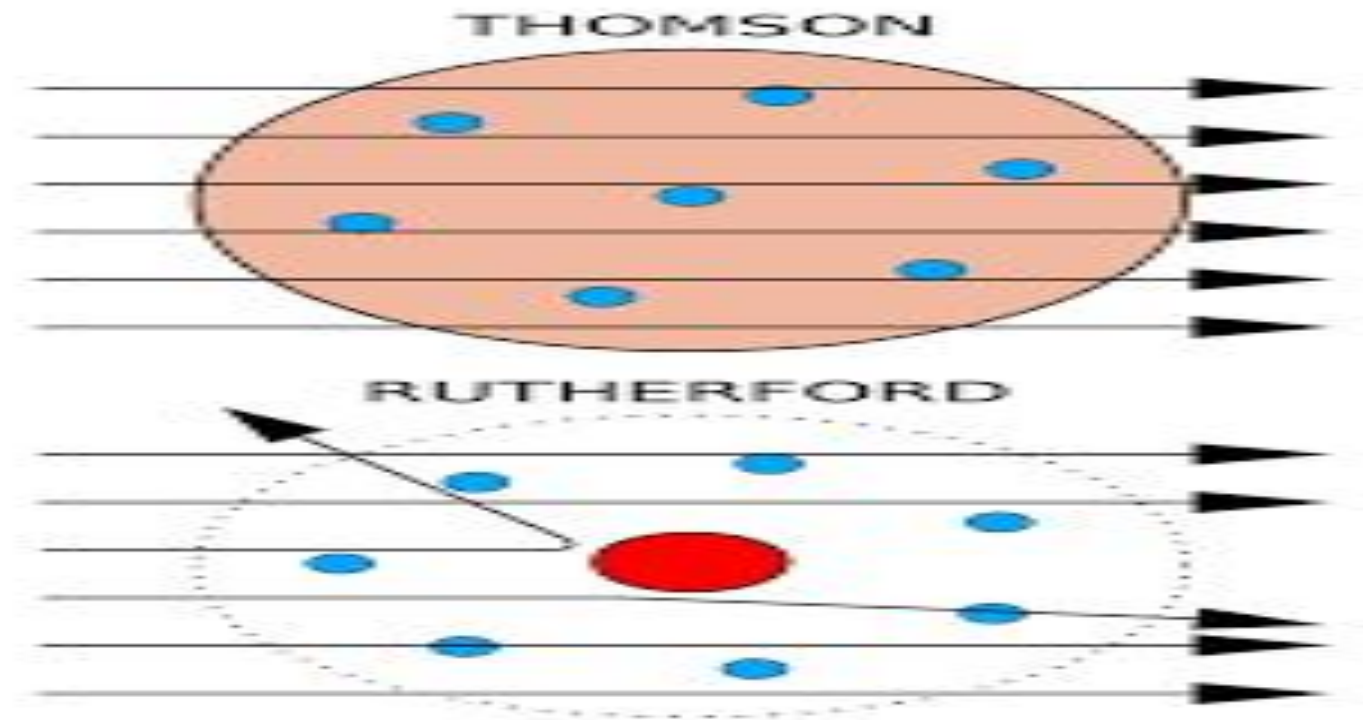
Ernest Rutherford's Gold Foil Experiment

- Ernest Rutherford and his co-workers in (1911) performed the gold foil experiment that gave direction to the modeling of the atomic structure
- He bombarded a thin gold foil with alpha particles (generated from a radioactive source). He found out that most of the alpha particles (α) passed through the foil in a straight line (undeflected) while a few of the particles (about 1 out of 8000) were deflected back at various degrees.
- A scintillation plate was used to locate the ray after passing through the foil.
- The explanation is that most alpha particles were able to pass through because the atom consist mainly of empty space. A few of α -particles were deflected because they approached the positively charged nucleus. The deflections were few because the nucleus is very small such that only few particles got near it.

Ernest Rutherford's Gold Foil Experiment cont'd.

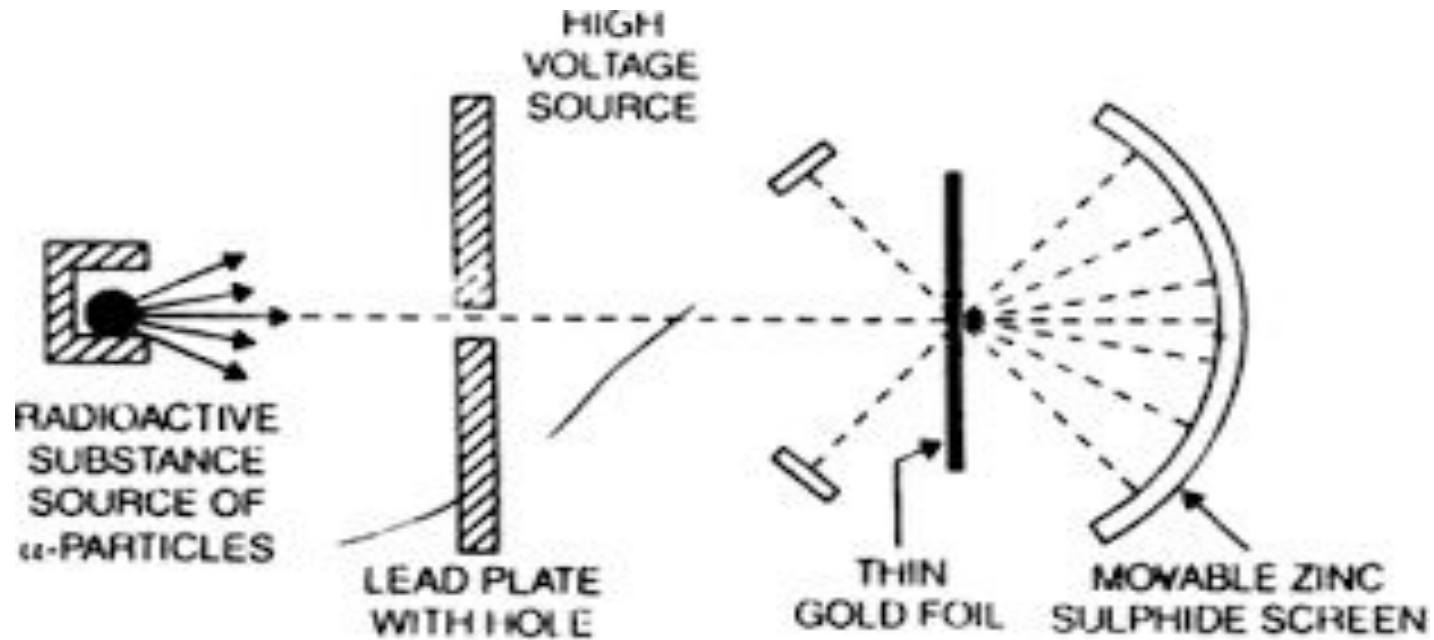
- Rutherford then suggested an atomic model called the nuclear model in which an atom has a small positively charged centre (nucleus) where nearly all the mass are concentrated, and large space (extra nuclear space) that surrounds the nucleus containing the electrons.
- He posited that:
 - (1) the mass and the positive charge must be concentrated in a tiny fraction of the atom called the nucleus.
 - (2). Negatively charged electrons revolve around the nucleus in closed orbits with a fast speed and hence, almost all the space round the nucleus is occupied by the revolving electrons. (a comparison with solar system).

Thomson's Plum pudding atomic model and Rutherford's Nuclear model of the Atom.

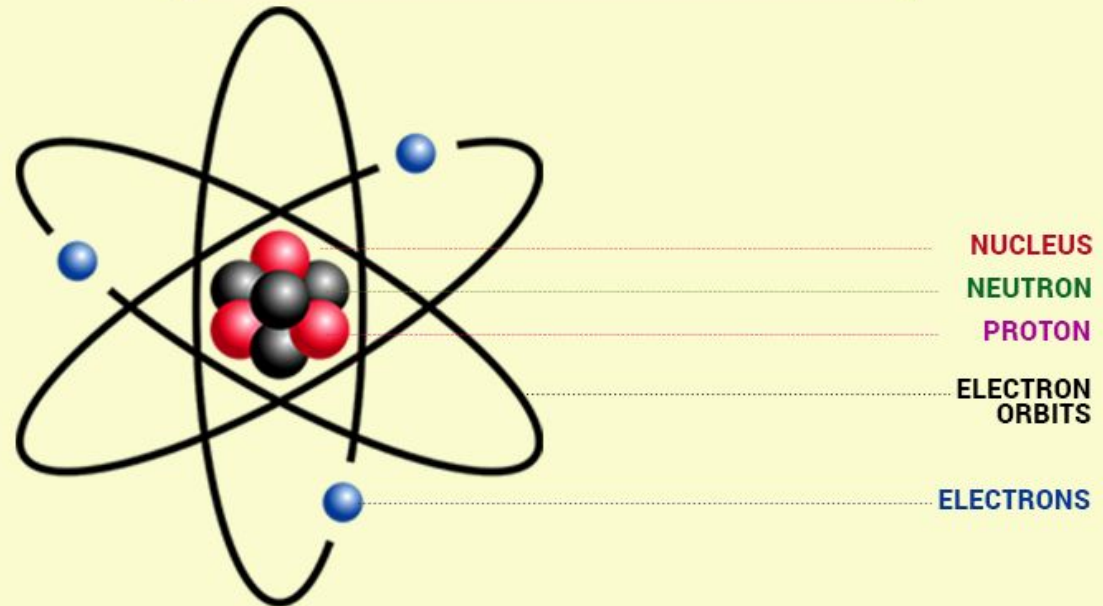


The two models suggested that atom is made up of largely empty space. Rutherford further suggested the presence of a positively charged nucleus in the centre where most of the mass is located. Cullled from *large.stamford.edu*

Rutherford's gold foil scattering experiment.



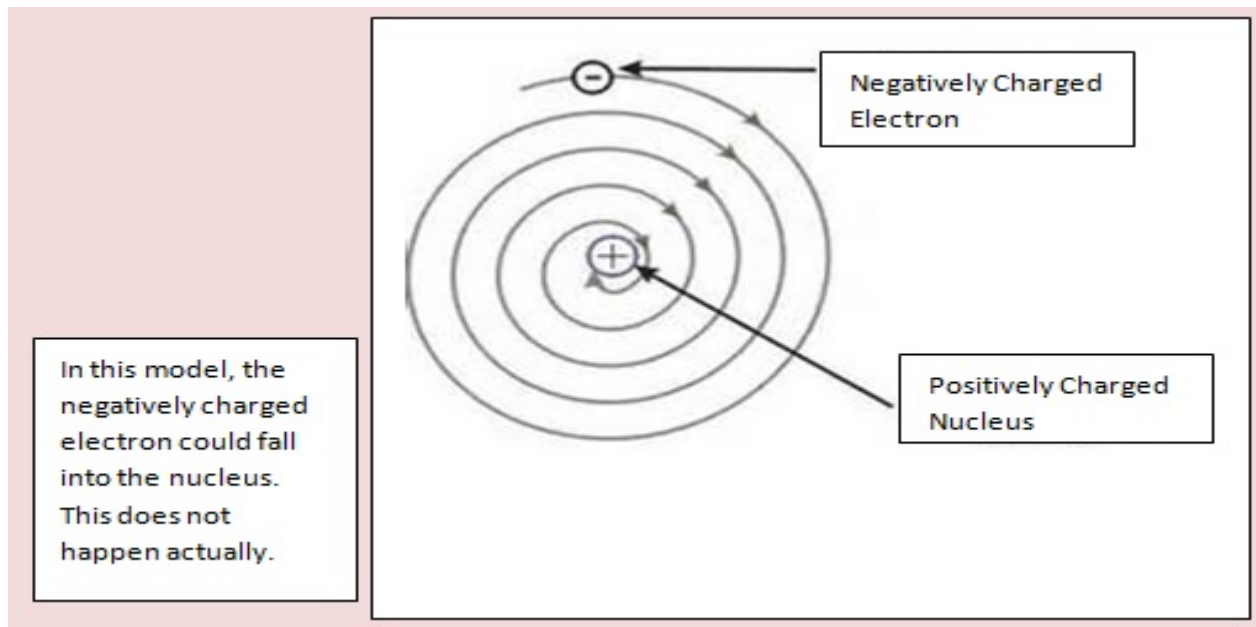
Rutherford's Model Of Atoms



Limitations of Rutherford's Nuclear Model of the Atom.

- As predicted by Rutherford that electrons are revolving round the nucleus, one could show that an electrically charged particles (such as electron) that revolved around a positively charged centre would continuously lose energy as electromagnetic radiation and it will spiral (collapse) into the nucleus (in about 10^{-10} sec).
- It then means atom would not be stable, hence there will be no matter. But that is actually not the situation. Atoms are stable hence we have matters.

Limitations of Rutherford's Nuclear Model of the Atom cont'd



Bohr's Atomic Model (1885-1962)

- Niels Bohr proposed an atomic model that helped solve the problem inherent in Rutherford's model.
- Bohr put forward an atomic model which is based on Planck's quantum theory of radiation.
- Bohr proposed a theory of atomic structure and provide a quantitative prediction of line spectra. He began with the planetary model but introduced certain assumptions which were:

Bohr's Atomic Model (1885-1962) cont'd

- (1). that the electron moves in an orbit around the central nucleus and only certain orbits are allowed.
- (II). Electron do not radiate energy when in these orbits, and it has associated with it, a definite amount of energy.
- (III). Under certain condition, transition between these stationary states (orbit) do occur and these transitions are accompanied by emmission or absorption.

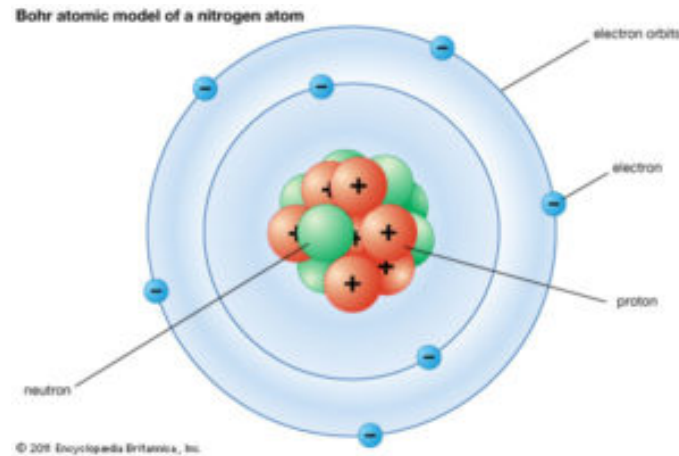
TO BE CONTINUED IN THE NEXT SLIDE

Postulates of Bohr's Atomic Model

- A Danish physicist named Neil Bohr in 1913 proposed the Bohr atomic model. He modified the problems and limitations associated with Rutherford's model of an atom. Earlier in Rutherford Model, Rutherford explained in an atom a nucleus is positively charged and is surrounded by electrons (negatively charged particles).
- The electrons move around in a predictable path called orbits. Bohr modified Rutherford's model where he explained that electrons move around in fixed orbital shells. Furthermore, he explained that each orbital shell has fixed energy levels. Therefore, Rutherford basically explained a nucleus of an atom whereas Bohr took the model one step ahead. He explained about electrons and the different energy levels associated with them.

What is Bohr's Model of an Atom

- According to the Bohr Atomic model, a small positively charged nucleus is surrounded by revolving negatively charged electrons in fixed orbits. He concluded that electron will have more energy if it is located away from the nucleus whereas electrons will have less energy if it located near the nucleus.



- *Bohr's Model of an Atom (Source Credit: Britannica)*

Postulates of Bohr Atomic Model

- Electrons revolve around the nucleus in a fixed circular path termed “orbits” or “shells” or “energy level.”
- The orbits are termed as “stationary orbit.”
- Every circular orbit will have a certain amount of fixed energy and these circular orbits were termed orbital shells. The electrons will not radiate energy as long as they continue to revolve around the nucleus in the fixed orbital shells.
- Jumping of an electron from one energy level to the other- Ground state and excited state: as long as an electron remains in a particular orbit, it neither emits nor absorbs energy. But when an electron is excited from a lower energy level to a higher energy level, it absorbs energy. On the other hand, when it comes back from a higher energy level to a lower energy level, it emits energy.

The different energy levels are denoted by integers such as $n=1$ or $n=2$ or $n=3$ and so on. These are called quantum numbers. The range of quantum numbers may vary and begin from the lowest energy level (nucleus side $n=1$) to the highest energy level.

The different energy levels or orbits are represented in two ways such as 1, 2, 3, 4... or K, L, M, N..... shells. The lowest energy level of the electron is called the ground state.

The change in energy occurs when the electrons jump from one energy level to other. In an atom, the electrons move from lower to higher energy level by acquiring the required energy. However, when an electron loses energy it moves from higher to lower energy level.

Therefore,

- 1st orbit (energy level) is represented as K shell and it can hold up to 2 electrons.
- 2nd orbit (energy level) is represented as L shell and it can hold up to 8 electrons.
- 3rd orbit (energy level) is represented as M shell and it can contain up to 18 electrons.
- 4th orbit (energy level) is represented as N Shell and it can contain maximum 32 electrons.

Distribution of Electrons in Orbits or Shells

- Electronic distribution of various orbits or energy levels can be calculated by the formula $2n^2$. Here, 'n' denotes the number of orbits.
- The number of electrons in K shell (1st orbit) can be calculated by $2n^2 = 2 \times 1^2 = 2$. Thus, maximum number of electrons in 1st orbit = 2
- Similarly, The number of electrons in L shell (2nd orbit) = $2 \times 2^2 = 8$. Thus, maximum number of electrons in 2nd orbit = 8
- We can determine the maximum number of electrons in a similar way.

Bohr's theory of the atomic spectrum of hydrogen

- In the postulations about stationary state in which the energy of the electron is constant; such state is characterized by circular orbits about the nucleus in which the electron has angular momentum given below where n is the principal quantum number

- $mvr = n\left(\frac{h}{2\pi}\right);$

- where $m =$ mass of electron; $v =$ velocity of electron; $r =$ radius of the orbit; $h =$ the planck's constant; $\frac{h}{2\pi}$ may be written as \hbar

- Energy is absorbed or emitted only when an electron moves from one stationary state to another and the energy change is given as

-

- $\Delta E = En_2 - En_1 = hv$

- If we apply the bohr model to the hydrogen atom, the radius of each allowed circular orbit can be determined from the equation below:

-

- $$r_n = \frac{\epsilon_0 h^2 n^2}{\pi m_e e^2}$$

- Where, $\epsilon_0 =$ permittivity of a vacuum = $8.854 \times 10^{-12} \text{ Fm}^{-1}$

- $h =$ planck constant = $6.626 \times 10^{-34} \text{ J.s}$

- $n = 1, 2, 3, \dots$ Describing a given orbit

- $m_e =$ electron rest mass = $9.109 \times 10^{-31} \text{ kg}$

- $e =$ charge on an electron = $1.602 \times 10^{-19} \text{ C}$.

Limitations of Bohr's Model of an Atom

- Bohr's model no longer observes the Heisenberg Uncertainty Principle.
- The Neils Bohr atomic version speculation considers electrons to have each recognised function and momentum simultaneously, that's unthinkable as indicated with the aid of using Heisenberg.
- The Bohr atomic version no longer makes an accurate prediction of large-sized atoms and furnishes enough statistics that are simplest for smaller atoms.
- Bohr's model does not make clear the Zeeman effect whilst the spectrum is cut up into some wavelengths in the sight of a magnetic field.
- It does not state the Stark effect whilst the spectrum receives separated into nearly negligible strains in the sight of an electric powered field

de Broglie Relation.

- Bohr's theory firmly established the concept of atomic energy levels. it was however unsuccessful in accounting for the details of atomic structure and in predicting energy levels for atoms other than hydrogen.
- According to Albert Einstein, light has a wave-particle dual properties which we characterise by frequency and wavelength. E.g, a particle of light, the photon has a definite energy
- $E = h\nu = h \cdot \frac{c}{\lambda}$;1.0
- $h \cdot \frac{c}{\lambda} = mc^2$;1.1
- Therefore, $\frac{h}{\lambda} = mc$;.....1.2
- $\lambda = \frac{h}{mc}$ 1.3 .

de Broglie Relation

- In 1924, Louis de Broglie argued that if light were composed of particles and yet showed wave-like properties, the same should be true of electrons and other particles. This phenomenon is referred to as wave-particle duality. The de-Broglie relationship combines concepts of classical mechanics with the idea of wave-like properties by showing that a particle with momentum (mass, m and velocity, v) possesses an associated wave of wavelength λ .
- $\lambda = \frac{h}{mv}$

de Broglie Relation

- De broglie reasoned that if light (considered as a wave) exhibits particles aspects, then perhaps, particles of matter show characteristics of waves under proper circumstances. He therefore postulated that a particle of matter of mass m , and speed v has an associated wavelength, by analogy with light.

$$\bullet \lambda = \frac{h}{mv}$$

λ is the de broglie wavelength

- h is the planck's constant = 6.626×10^{-34}
- v = velocity of the particle
- M = mass of the object.

de Broglie Relation

- Question: Hydrogen molecules are among the most massive particles to produce a diffraction pattern. The mass of a hydrogen molecule is about 3.4×10^{-27} Kg. if the molecules
● move at a speed of 1700 m.s^{-1}

what is the de broglie wavelenght?

Answer: using the de broglie equation $\lambda = \frac{h}{mv}$

$$\begin{aligned} & \bullet \frac{6.626 \times 10^{-34}}{3.4 \times 10^{-27} \times 1700} \\ & = 1.15 \times 10^{-10} \text{ m} \end{aligned}$$

- Question: Calculate the wavelength of a body of mass 1 mg moving with a velocity of 3 m.s^{-1}

$$\lambda = \frac{h}{mv}; \quad h = 6.626 \times 10^{-34} \text{ J.s}, m = 1 \text{ mg} = 1 \times 10^{-6} \text{ kg}, v = 3 \text{ m.s}^{-1}$$

$$\begin{aligned} & \bullet \lambda = \frac{6.626 \times 10^{-34} \text{ J.s}}{1 \times 10^{-6} \text{ kg} \times 3 \text{ m.s}^{-1}} && \text{note } (J = \text{kg.m}^2.\text{s}^{-2}) \\ & = 2.20 \times 10^{-28} \text{ m} \end{aligned}$$

Question: what is the de broglie wavelenght of a neon particle of 2.2×10^{-21} Kg travelling at a speed of 4500 m.s^{-1}

Heisenberg's uncertainty principle

- If an electron has wave like properties, there is an important and difficult consequence: it becomes impossible to know exactly both momentum and position of the electron at the same instant time.
- This is what is known as Heisenberg's uncertainty principle. That is, if we measure the momentum of an electron accurately, then, we cannot know its position with certainty and if we know the position of the electron, we cannot measure the momentum with certainty.
- Mathematical expression of the principle: if Δx represents the error (or uncertainty) in the measurement of the position and Δp represents the uncertainty in the measurement of the momentum of a sub-atomic particle like electron and neutron, then according to these principle; these two quantities are related as:

- $\Delta x \cdot \Delta p \geq \frac{h}{2\pi}$ [uncertainty relation]
- Where Δp (momentum) = $\Delta v \cdot m$
- $\Delta x \cdot \Delta v \geq \frac{h}{2\pi m}$

v = velocity; m = mass of the particle,

Heisenberg's uncertainty principle

- therefore, the equation can be written as:

- $\Delta v = \frac{h}{2\pi \cdot m \cdot \Delta x}$ uncertainty relation.

- question: what is the uncertainty in the measurement of the velocity of an electron in H-atom with mass = 9.108×10^{-31} kg, whose uncertainty in position (Δx) is equal to 1.0×10^{-10} m.

- answer: Δv (uncertainty in measurement of velocity) = $\frac{h}{2\pi \cdot m \cdot \Delta x}$

- $\frac{6.626 \times 10^{-34}}{2 \times 3.14 \times 1.0 \times 10^{-10} \times 9.108 \times 10^{-31}}$

- = $1.16 \times 10^6 \text{ m.s}^{-1}$

QUANTUM NUMBERS, ATOMIC ORBITALS, AND ELECTRON CONFIGURATIONS

Quantum Numbers and Atomic Orbitals

By solving the Schrödinger equation ($H\psi = E\psi$), we obtain a set of mathematical equations, called **wave functions** (ψ), which describe the probability of finding electrons at certain energy levels within an atom.

A wave function for an electron in an atom is called an **atomic orbital**; this atomic orbital describes a region of space in which there is a high probability of finding the electron. Energy changes within an atom are the result of an electron changing from a wave pattern with one energy to a wave pattern with a different energy (usually accompanied by the absorption or emission of a photon of light).

Each electron in an atom is described by four different **quantum numbers**. The first three (n , l , m_l) specify the particular orbital of interest, and the fourth (m_s) specifies how many electrons can occupy that orbital.

1. **Principal Quantum Number (n): $n = 1, 2, 3, \dots, 8$.**

Specifies the **energy** of an electron and the **size** of the orbital (the distance from the nucleus of the peak in a radial probability distribution plot). All orbitals that have the same value of n are said to be in the same **shell (level)**. For a hydrogen atom with $n=1$, the electron is in its *ground state*; if the electron is in the $n=2$ orbital, it is in an *excited state*. The total number of orbitals for a given n value is n^2 .

2. **Angular Momentum (Secondary, Azimunthal) Quantum Number (l): $l = 0, \dots, n-1$.**

Specifies the **shape** of an orbital with a particular principal quantum number. The secondary quantum number divides the shells into smaller groups of orbitals called **subshells (sublevels)**. Usually, a letter code is used to identify l to avoid confusion with n :

l	0	1	2	3	4	5	...
Letter	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	...

The subshell with $n=2$ and $l=1$ is the $2p$ subshell; if $n=3$ and $l=0$, it is the $3s$ subshell, and so on. The value of l also has a slight effect on the energy of the subshell; the energy of the subshell increases with l ($s < p < d < f$).

3. **Magnetic Quantum Number (m_l): $m_l = -l, \dots, 0, \dots, +l$.**

Specifies the **orientation in space** of an orbital of a given energy (n) and shape (l). This number divides the subshell into individual **orbitals** which hold the electrons; there are $2l+1$ orbitals in each subshell. Thus the s subshell has only one orbital, the p subshell has three orbitals, and so on.

4. **Spin Quantum Number (m_s):** $m_s = +1/2$ or $-1/2$.

Specifies the **orientation of the spin axis** of an electron. An electron can spin in only one of two directions (sometimes called *up* and *down*).

The **Pauli exclusion principle** (Wolfgang Pauli, Nobel Prize 1945) states that *no two electrons in the same atom can have identical values for all four of their quantum numbers*. What this means is that no more than **two** electrons can occupy the same orbital, and that two electrons in the same orbital must have **opposite spins**.

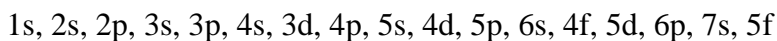
Because an electron spins, it creates a magnetic field, which can be oriented in one of two directions. For two electrons in the same orbital, the spins must be opposite to each other; the spins are said to be **paired**. These substances are not attracted to magnets and are said to be **diamagnetic**. Atoms with more electrons that spin in one direction than another contain **unpaired** electrons. These substances *are* weakly attracted to magnets and are said to be **paramagnetic**.

Table of Allowed Quantum Numbers

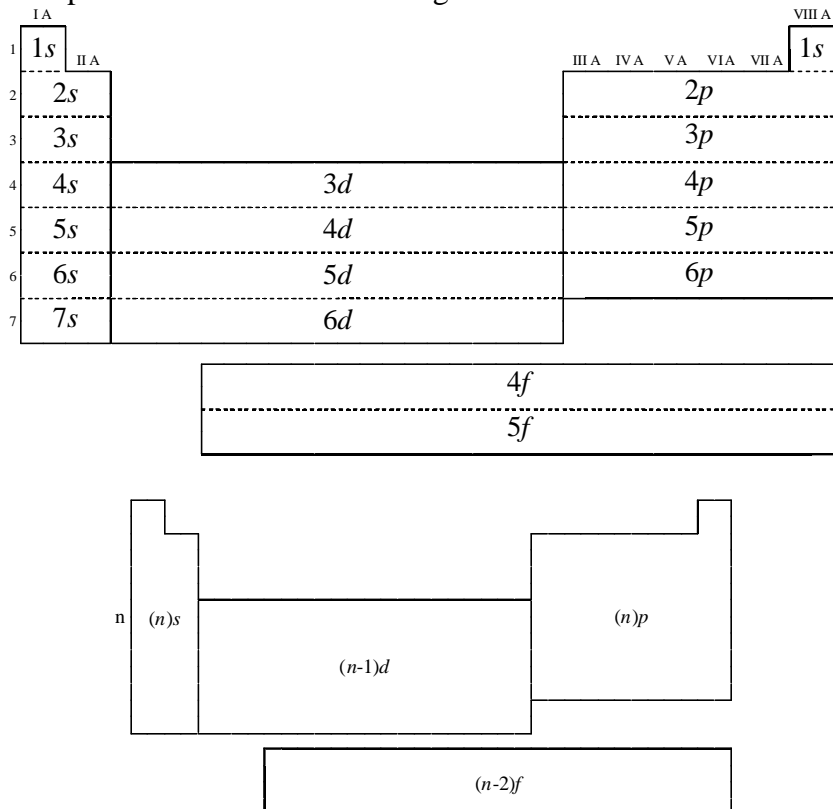
<u>n</u>	<u>l</u>	<u>m_l</u>	<u>Number of orbitals</u>	<u>Orbital Name</u>	<u>Number of electrons</u>
1	0	0	1	1s	2
2	0	0	1	2s	2
	1	-1, 0, +1	3	2p	6
3	_____	_____	_____	_____	_____
	_____	_____	_____	_____	_____
	_____	_____	_____	_____	_____
4	_____	_____	_____	_____	_____
	_____	_____	_____	_____	_____
	_____	_____	_____	_____	_____
5	_____	_____	_____	_____	_____
	_____	_____	_____	_____	_____
	_____	_____	_____	_____	_____
	_____	_____	_____	_____	_____

Writing Electron Configurations

The distribution of electrons among the orbitals of an atom is called the **electron configuration**. The electrons are filled in according to a scheme known as the **Aufbau principle** (“building-up”), which corresponds (for the most part) to increasing energy of the subshells:



It is not necessary to memorize this listing, because the order in which the electrons are filled in can be read from the periodic table in the following fashion:



In electron configurations, write in the orbitals that are occupied by electrons, followed by a superscript to indicate how many electrons are in the set of orbitals (e.g., H $1s^1$)

Another way to indicate the placement of electrons is an **orbital diagram**, in which each orbital is represented by a square (or circle), and the electrons as arrows pointing up or down (indicating the electron spin). When electrons are placed in a set of orbitals of equal energy, they are spread out as much as possible to give as few paired electrons as possible (**Hund’s rule**).

In a **ground state** configuration, all of the electrons are in as low an energy level as it is possible for them to be. When an electron absorbs energy, it occupies a higher energy orbital, and is said to be in an **excited state**.

Properties of Monatomic Ions

The electrons in the *outermost shell* (the ones with the highest value of n) are the most energetic, and are the ones which are exposed to other atoms. This shell is known as the **valence shell**. The inner, *core* electrons (*inner shell*) do not usually play a role in chemical bonding.

Elements with similar properties generally have similar outer shell configurations. For instance, we already know that the alkali metals (Group I) always form ions with a +1 charge; the “extra” s^1 electron is the one that’s lost:

IA	Li	$1s^2 2s^1$	Li^+	$1s^2$
IA	Na	$1s^2 2s^2 2p^6 3s^1$	Na^+	$1s^2 2s^2 2p^6$
IA	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	K^+	$1s^2 2s^2 2p^6 3s^2 3p^6$

The next shell down is now the outermost shell, which is now full — meaning there is very little tendency to gain or lose more electrons. The ion’s electron configuration is the same as the nearest noble gas — the ion is said to be **isoelectronic** with the nearest noble gas. Atoms “prefer” to have a filled outermost shell because this is more electronically stable.

- The Group IIA and IIIA metals also tend to lose all of their valence electrons to form cations.

IIA	Be	$1s^2 2s^2$	Be^{2+}	$1s^2$
IIA	Mg	$1s^2 2s^2 2p^6 3s^2$	Mg^{2+}	$1s^2 2s^2 2p^6$
IIIA	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	Al^{3+}	$1s^2 2s^2 2p^6$

- The Group IV and V metals can lose either the electrons from the p subshell, or from both the s and p subshells, thus attaining a **pseudo-noble gas configuration**.

IVA	Sn	$[\text{Kr}] 4d^{10} 5s^2 5p^2$	Sn^{2+}	$[\text{Kr}] 4d^{10} 5s^2$
			Sn^{4+}	$[\text{Kr}] 4d^{10}$
IVA	Pb	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^2$	Pb^{2+}	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2$
			Pb^{4+}	$[\text{Xe}] 4f^{14} 5d^{10}$
VA	Bi	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^3$	Bi^{3+}	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2$
			Bi^{5+}	$[\text{Xe}] 4f^{14} 5d^{10}$

- The Group IV - VII non-metals gain electrons until their valence shells are full (8 electrons).

IVA	C	$1s^2 2s^2 2p^2$	C^{4-}	$1s^2 2s^2 2p^6$
VA	N	$1s^2 2s^2 2p^3$	N^{3-}	$1s^2 2s^2 2p^6$
VIA	O	$1s^2 2s^2 2p^4$	O^{2-}	$1s^2 2s^2 2p^6$
VIIA	F	$1s^2 2s^2 2p^5$	F^-	$1s^2 2s^2 2p^6$

- The Group VIII noble gases already possess a full outer shell, so they have no tendency to form ions.

VIII A	Ne	$1s^2 2s^2 2p^6$
VIII A	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$

- Transition metals (B-group) usually form +2 charges from losing the valence s electrons, but can also lose electrons from the highest d level to form other charges.

B-group	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	Fe^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
			Fe^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

THE PERIODIC TABLE

- In 1869 and 1870, Dmitri Mendeleev and Lothar Meyer stated that the properties of the elements can be represented as periodic functions of their atomic weights. In other words, the periodic law states that: when elements are arranged in order of increasing atomic number, there is a periodic repetition of their chemical and physical properties. As new elements have been discovered, the original form of periodic table has been extensively modified and it is now recognized that periodicity is a consequence of the variation in ground state electronic configurations. A modern periodic table emphasizes the blocks of 2, 6, 10 and 14 elements which results from the filling of s, p, d, f atomic orbitals respectively. An exception is He, which for reasons of its chemistry, is placed in a group with Ne, Ar, Kr, Xe, and Rn

MODERN PERIODIC TABLE

Periodic table of the elements

period	group 1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr				

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

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THE PERIODIC TABLE CONT'D

- The IUPAC has produced guidelines for naming blocks and groups of elements in the periodic table. In summary:
- Blocks of elements may be designated by the use of the letters *s*, *p*, *d*, and *f*;
- Elements (except H) in groups 1, 2 and 13 – 18 are called *main group elements*;
- With the exception of 18, the first two elements of each main group are called *typical elements*;
- Elements in groups 3 – 12 (the d- block elements) are also commonly called the *transition elements*, although elements in group 12 are not always included;
- *The f-block elements are sometimes called the inner transition elements.*

NAMES OF GROUPS

- Collective names for some of the groups of elements in the periodic table are given in the table below.

Group number	Recommended name
1	Alkali metals
2	Alkaline earth metals
15	Pnictogens
16	Chalcogens
17	Halogens
18	Noble gases

SLATER'S RULE

Effective nuclear charges, Z_{eff} , experienced by electrons in different atomic orbitals may be estimated using Slater's rules. These rules are based on experimental data for electron promotion and ionization energies, and Z_{eff} is determined from the equation.

- $Z_{eff} = Z - S$
- Where Z = nuclear charge, Z_{eff} = effective nuclear charge, S = screening (or shielding) constant.
- Values of S may be estimated as follows:
- Write out the electronic configuration of the element in the following order and groupings: $(1s)$, $(2s, 2p)$, $(3s, 3p)$, $(3d)$, $(4s, 4p)$, $(4d)$, $(5s, 5p)$ etc.
- Electrons in any group higher in this sequence than the electron under consideration contribute nothing to S
- Consider a particular electron in an ns or np orbital:
 - Each of the other electrons in the (ns, np) group contributes $S = 0.35$.
 - Each of the electrons in the $(n-1)$ shell contributes $S = 0.85$
 - Each of the electrons in the $(n-2)$ or lower shells contributes $S = 1.00$
- Consider a particular electron in a nd or nf orbital.
 - Each of the other electrons in the (nd, nf) group contributes $S = 0.35$
 - Each of the electrons in a lower group than the one being considered contributes $S = 1.00$.

Table 2.6.12.6.1: Slater's Rules for calculating shieldings

Group	Other electrons in the same group	Electrons in group(s) with principal quantum number n and azimuthal quantum number $< l$	Electrons in group(s) with principal quantum number $n-1$	Electrons in all group(s) with principal quantum number $< n-1$
[1s]	0.30	-	-	-
[ns, np]	0.35	-	0.85	1
[nd] or [nf]	0.35	1	1	1

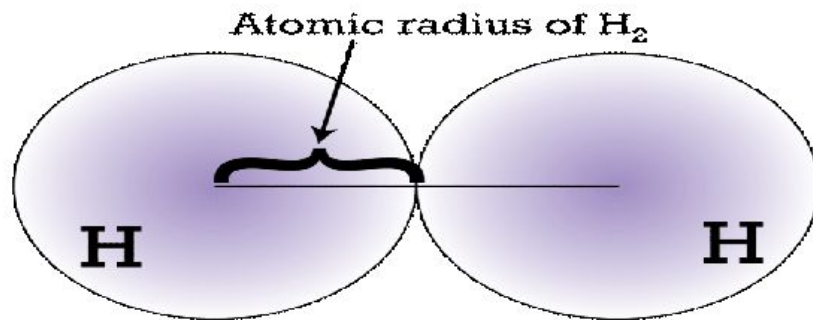
SLATER'S RULE

- Question: confirm that the experimentally observed electronic configuration of K, $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$, is energetically more stable than the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$.
-
- For K, $Z = 19$. Applying Slater's rules, the effective nuclear charge experienced by the 4s electron for the configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$ is:
 - $Z_{eff} = Z - S$
 - $= 19 - [(8 \times 0.85) + (10 \times 1.00)]$
 - $= 2.20$
-
- The effective nuclear charge experienced by the 3d electron for the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ is
 - $Z_{eff} = Z - S$
 - $19 - (18 \times 1.00)$
 - $= 1.00$
- Thus, an electron in the 4s (rather than the 3d) atomic orbital is under the influence of a greater effective nuclear charge and in the ground state of potassium, it is the 4s atomic orbital that is occupied.

ATOMIC RADIUS

- In the periodic table, there are a number of physical properties that are trend-like. This means that as you move down a group or across a period, you will see the properties changing in a general direction. The actual trends that are observed with atomic size have to do with three factors. These factors are:
 - the number of protons in the nucleus (called the **nuclear charge**).
 - the number of energy levels holding electrons and the number of electrons in the outer energy level.
 - the number of electrons held between the nucleus and its outermost electrons (called the **shielding effect**).

1. The gold foil experiment performed by Rutherford in 1911 was the first experiment that gave scientists an approximate measurement for the size of the atom. The atomic size is the distance from the nucleus to the valence shell, where the valence electrons are located.
2. Atomic size is defined in several different ways, which often produce some variations in the measurement of atomic sizes. One way that chemists define atomic size is by using the atomic radius. The **atomic radius** is one-half the distance between the centers of a homonuclear diatomic molecule, as illustrated below. A **diatomic molecule** is a molecule made of exactly two atoms, while homonuclear means both atoms are the same element.



3.

Group Trends in Atomic Radii

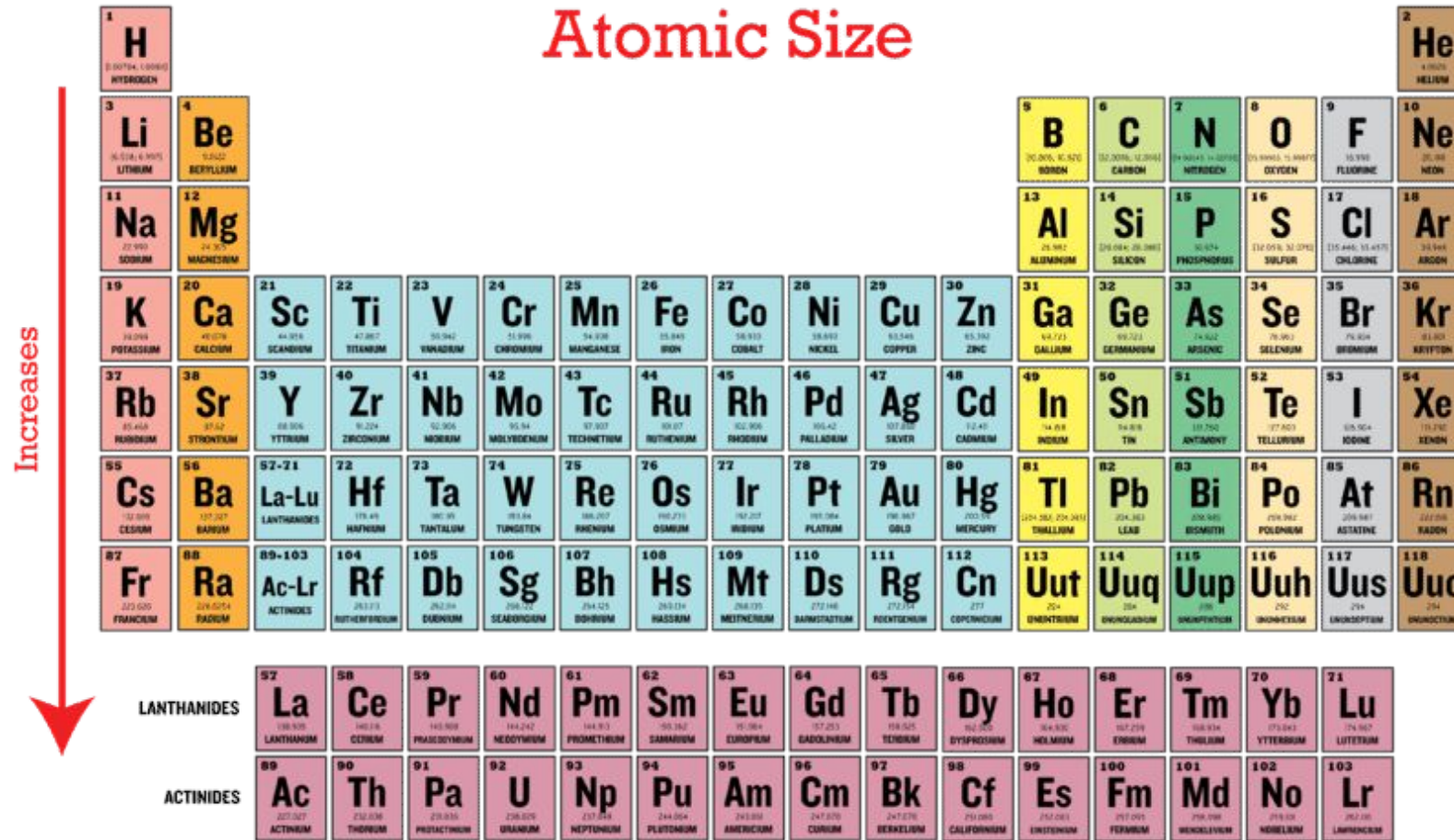
- Let's consider how the atomic radii changes from the top of a group to the bottom. Take, for example, the Group 1A metals. Every atom in this family has the same number of electrons in the outer energy level (true for all main group families). Each period in the periodic table represents another added energy level. Therefore, as we move down the periodic table, each successive period represents the addition of a larger energy level, thus increasing the atomic radius.
- **The shielding effect**
- One other contributing factor to atomic size is the shielding effect. The protons in the nucleus attract the valence electrons in the outer energy level, but the strength of this attraction depends on :
 - the size of the charges,
 - the distance between the charges, and
 - the number of electrons between the nucleus and the valence electrons.

Group Trends in Atomic Radii CONT'D

- The presence of the inner (core) electrons weakens the attraction between the nucleus and the valence electrons. **This weakening is called the shielding effect.** Note that although valence electrons do participate in shielding, electrons in the same energy level do not shield each other as effectively as the core electrons do. As a result, the amount of shielding primarily depends on the number of electrons between the nucleus and the valence electrons. When the nucleus pulls strongly on the valence electrons, the valence shell can be pulled in tighter and closer to the nucleus. When the attraction is weakened by shielding, the valence shell cannot be pulled in as close. The more shielding that occurs, the further the valence shell can spread out.

- For example, consider element **Sodium**, it has the electronic configuration: $1s^2 2s^2 2p^6 3s^1$. The outer energy level is $3s^1$. There is one valence electron, but the attraction between this lone valence electron and the nucleus, which has 11 protons, is shielded by the other 10 inner (core) electrons. When we compare an atom of sodium to one of **Caesium** ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$),
- we notice that the number of protons increases, as well as the number of energy levels occupied by electrons. The increase in the number of protons, however, is also accompanied by the same increase in the number of shielding electrons. The result is that the valence electron in both atoms feels a similar pull from the nucleus, but the valence electron in the caesium atom is further from the nucleus because it is in a higher energy level. Compared to the shielding effect, the increase in the number of energy levels has a greater impact on the atom's size. Consequently, the size of a caesium atom is larger than that of a sodium atom.
- This is true for, not only Group 1A metals, but for all of the groups across the periodic table. For any given group, as you move downward in the periodic table, the size of the atoms increases. For instance, the largest atoms in the halogen family are bromine and iodine (astatine is radioactive and only exists for short periods of time, so we won't include it in the discussion). You can imagine that with the increase in the number of energy levels, the size of the atom must increase. The increase in the number of energy levels in the electron cloud takes up more space.

THE ARROW INDICATE DIRECTION OF INCREASE IN ATOMIC RADII DOWN THE GROUP



Question.

- **Example:**
- Which of the following is larger? Explain.
- As or Sb
- Ca or Be
- Polonium or Sulphur

Trends in Atomic Radii Across the Period

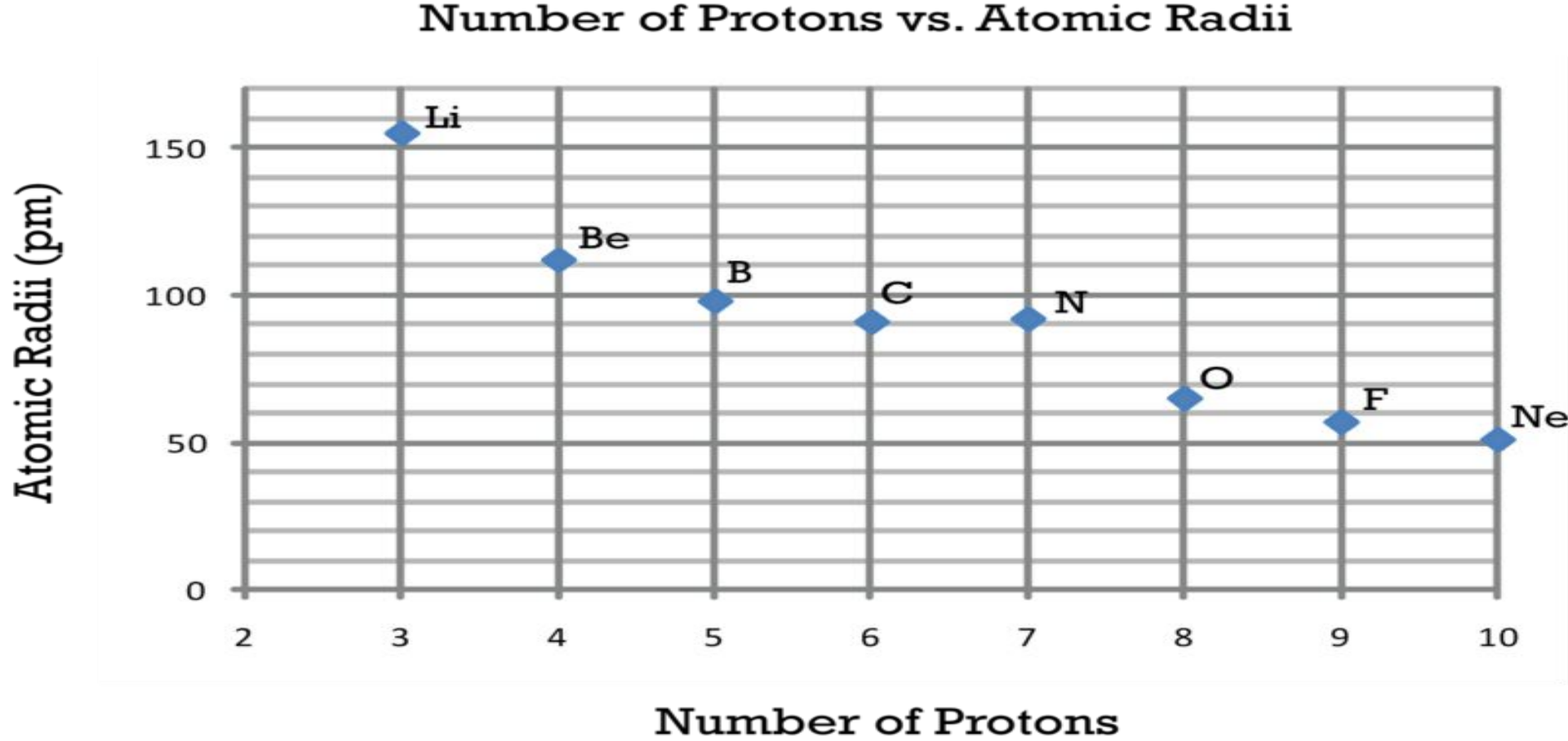
- In order to determine the trend for the periods, we need to look at the number of protons (nuclear charge), the number of energy levels, and the shielding effect. Across a row in the periodic table, the atomic number still increases, and thus the number of protons would increase. For a given period, however, we find that the outermost energy level does not change as the number of electrons increases. In period 2, for example, each additional electron goes into the second energy level, so the total number of energy levels does not go up.

Trends in Atomic Radii Across the Period

Cont'd

- Looking at the elements in period 2, the number of protons increases from three (for lithium) to nine (for fluorine). Therefore, the nuclear charge increases across a period. Meanwhile, the number of energy levels (n) occupied by the electrons remains the same. We know that every one of the elements in this period has two core electrons in the inner energy level ($n = 1$). The core electrons shield the outer electrons from the charge of the nucleus. Since the number of protons attracting the outer electrons increases while the shielding remains the same, the valence electrons are pulled closer to the nucleus, making the atom smaller.
- Consider the elements lithium, beryllium, and fluorine from period 2. With lithium, the two core electrons will shield the one valence electron from three protons. As the number of protons increases, the nuclear charge increases. With an increase in nuclear charge, there is an increase in the pull between the protons and the outer level, pulling the outer electrons toward the nucleus. The amount of shielding from the nucleus does not increase because the number of core electrons remains the same. The net result is that the atomic size decreases going across the row. In the graph below, the values are shown for the atomic radii for period 2

Trends in Atomic Radii Across the Period Cont'd

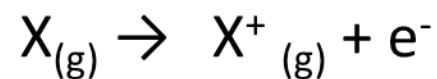


Ionization energy

- The amount of energy required by an isolated gaseous atom to lose an electron from its ground state is defined as the ionisation energy of an element
- in simple terms or to put it another way, the amount of energy required to remove an electron from an atom or an ion, or the proclivity of an atom or ion to surrender an electron, can be described as ionisation energy in simple terms. The loss of an electron occurs most frequently in the ground state of the chemical species in question. we can say that the measure of strength (attractive forces) by which an electron is held in a particular location is ionisation energy.
- **ionisation energy can be defined as the minimum amount of energy that an electron in an inert gaseous atom or ion must absorb in order to escape the influence of the nucleus. It is also referred to as the ionisation potential, and it is typically an endothermic reaction.**
- What we can deduce further is that the ionisation energy of a chemical compound provides us with an indication of its reactivity. It can also be used to determine the strength of chemical bonding. It is measured in either electron volts or kilojoules per mol (kJ mol) of substance.

IONISATION ENERGIES

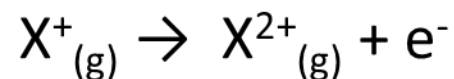
- The first ionization energy (IE_1) of a gaseous atom is the internal energy change, ΔU , at 0 K associated with the removal of the first valence electron:



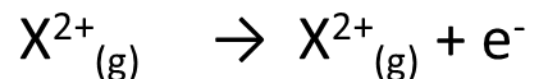
For thermochemical cycles, an associated change in enthalpy, ΔH , at 298K is used:

$$\Delta H (298 \text{ K}) \approx \Delta U (0 \text{ K}).$$

The second ionization energy, (IE_2) of an atom refers to the equation below:

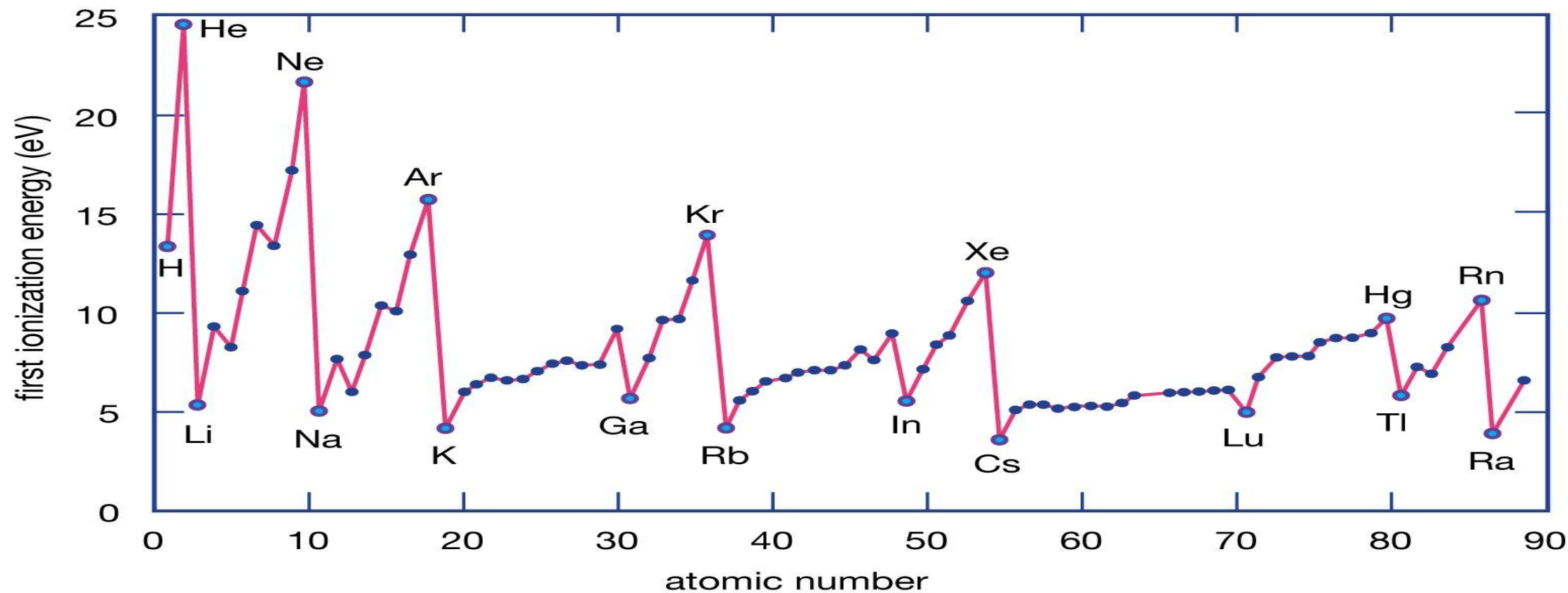


The third ionization energy, (IE_3) of an atom:



- And so on

FIRST IONIZATION ENERGY



Factors that influence the ionisation enthalpy of the elements

- The enthalpy of ionisation is determined by the following factors:
- **Nuclear charge:** As the nuclear charge increases, the ionisation enthalpy increases proportionally. This is owing to the fact that, as nuclear charge increases, the electrons in the outer shell become more tightly bound to the nucleus, requiring more energy to extricate an electron from the atom than previously existed.
- For example, as we move along a period from left to right, the ionisation enthalpy increases as a result of the increased nuclear charge.
- **Atomic size or radius:** As the atomic size or radius grows, the ionisation enthalpy falls. The attractive force on the outer electron reduces as the distance between the outer electrons and the nucleus grows with the growth in atomic radius.
- It is as a result of this that the outside electrons are held less tightly, and so a smaller amount of energy is required to knock them out. As a result, the ionisation enthalpy reduces as the size of the atoms increases. It has been discovered that the ionisation enthalpy decreases as one moves down a group

Factors that influence the ionisation enthalpy of the elements CONT'D

- **The electrons' penetrating impact.** The ionisation enthalpy increases in proportion to the increase in the penetration impact of the electrons. This well-known fact is that, in the case of multielectron atoms, the electrons of the s-orbital have the highest probability of being found near the nucleus, and this probability decreases as the p-, d- and f- orbitals of the same shell are added to the mix.
- In other words, s- electrons from any shell penetrate the nucleus more readily than p- electrons from the same shell. As a result, the penetration effect diminishes in the order $s > p > d > f$ within the same shell, for example, the enthalpy of first ionisation for aluminium is lower than that for magnesium. The reason for this is that in the case of aluminium ($1s^2, 2s^2, 2p^2, 3s^2, 3p^2$), we must remove a p-electron from the same energy shell in order to make Al^+ ion, whereas in the case of magnesium ($1s^2, 2s^2, 2p^6, 3s^2$), we must remove an s-electron from the same energy shell in order to produce Mg^+ ion.

Factors that influence the ionisation enthalpy of the elements CONT'D

- **The shielding or screening action of electrons in the inner shell.** Ionisation enthalpy reduces as the shielding effect of the inner electrons, (screening effect), grows stronger. As a result, the nucleus's force of attraction for the electrons in the valence shell reduces, and as a result, the ionisation enthalpy lowers.
- **The influence of the electrons' arrangement.** If an atom's orbitals are exactly half filled or completely filled, the arrangement is more stable than expected; as a result, removing an electron from such an atom requires more energy than would be expected. Example: Be ($1s^2, 2s^2$) has a greater ionisation enthalpy than B ($1s^2, 2s^2, 2p^1$) because it requires lesser energy to remove the valence one electron in the p-orbital of boron than removing one electron from the s-orbital of boron which already has a stable configuration.
- Similarly, N ($1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$) has higher ionisation enthalpy than O ($1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$) because the p-orbital in Nitrogen is half filled and stable, whereas, the $2p_x$ in oxygen could be experiencing some instability compared to other p-orbital, so is easier for electron to be removed there.

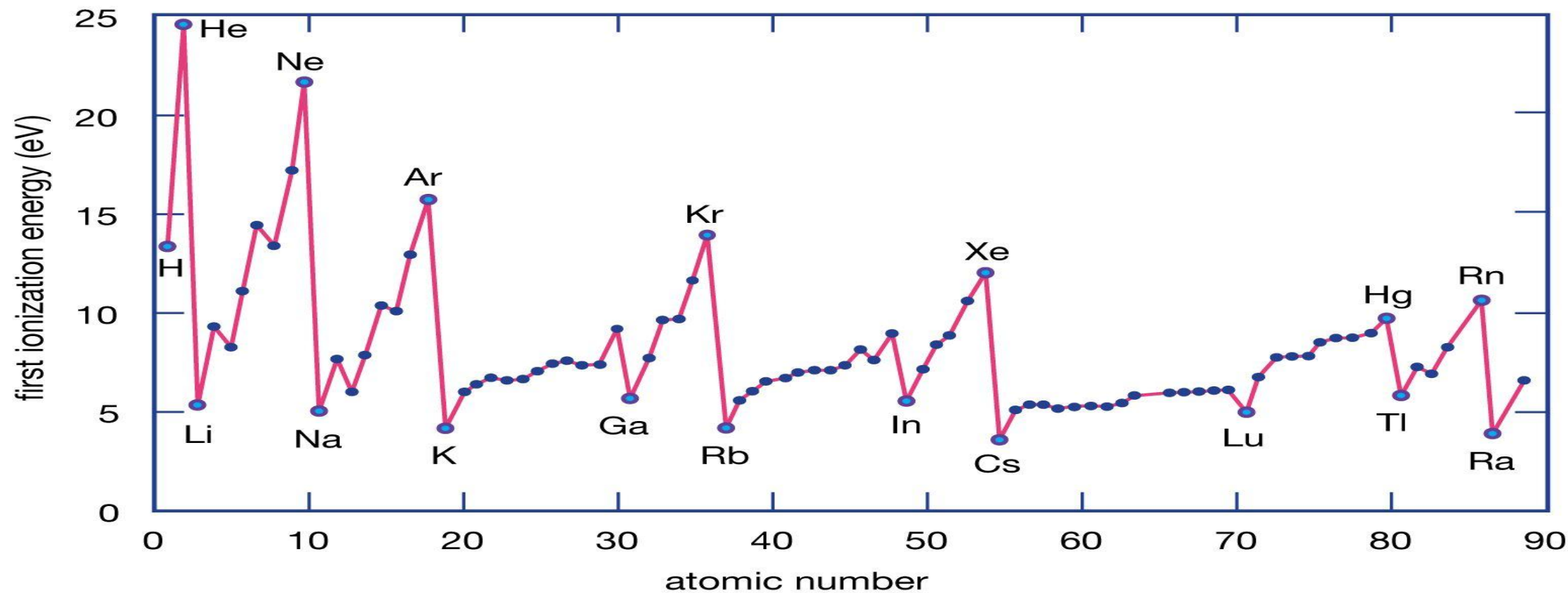
Factors that influence the ionisation enthalpy of the elements CONT'D

Overall, when we move from **left to right in a period**, the ionization energy (enthalpy) increases with rising atomic numbers, which is consistent with the trend of the period.

Oxygen, O, has a higher ionisation enthalpy than Be ($1s^2, 2s^2$); O ($1s^2, 2s^2 2p_x^2, 2p_y^1 2p_z^1$), which is expected

- As we proceed along a **group** of elements from one element to the next, the ionisation enthalpies continue to decrease on a regular basis.

FIRST IONIZATION ENERGY



Electron affinity

- Electron affinity is a measure of the energy change that occurs when an atom gains an electron to form a negative ion. Electron affinity is the ability of an atom to accept an electron. This is a quantitative measurement of the energy change occurring when an electron is added to a neutral gas atom.
- **The first electron affinity, EA_1 , of an atom is minus the internal energy change at 0 K associated with the gains of one electron by a gaseous atom.**
- $Y_{(g)} + e^- \rightarrow Y^-_{(g)}$
- For thermochemical cycles, an associated enthalpy change is used:
$$\Delta_{EA} H (298 \text{ K}) \approx \Delta_{EA} U (0 \text{ K}) = -EA$$
- Attachment of an electron to an atom is usually exothermic. E.g $\text{Li}_{(g)} + e^- \rightarrow \text{Li}^-_{(g)} \quad \Delta_{EA} H / -60 \text{ kJ mol}^{-1}$
- Two electrostatic forces oppose one another: the repulsion between the valence shell electrons and the additional electron, and the attraction between the nucleus and the incoming electron. In contrast, repulsive interactions are dominant when an electron is added to an anion and the process is endothermic.
- E.g $\text{S}^-_{(g)} + e^- \rightarrow \text{S}^{2-}_{(g)} \quad \Delta_{EA} H / \text{kJ mol}^{-1} (+640)$

Like ionization energy, there is an electron affinity measured for an atom for each successive electron added.

- Trends in first electron affinity

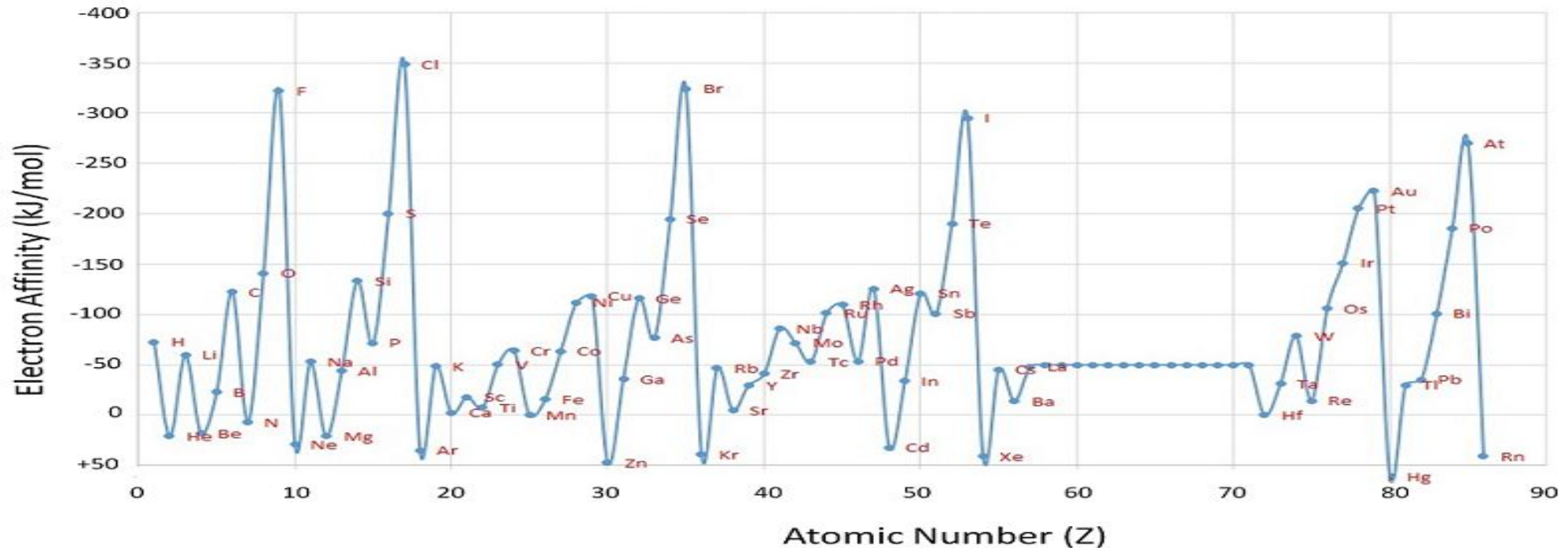
- o Tend to be negative, meaning energy is released when the electron is added.

- o The amount of energy released increases left to right across a period.

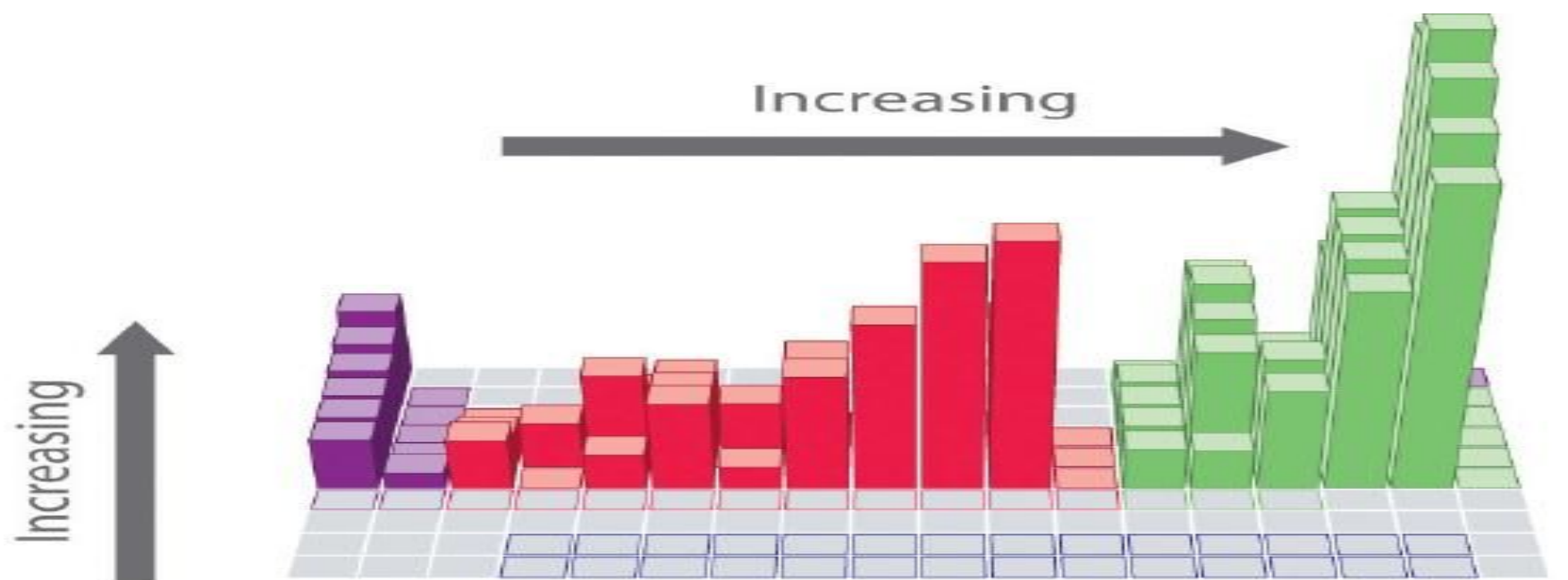
- o The amount of energy released decreases down a group.

- o The noble gases have positive first electron affinities, meaning they require energy to accept an electron.

A Plot of Periodic Variation of Electron Affinity with Atomic Number



- A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies).



Magnitude of electron affinity (kJ/mol),
s-, *p*-, and *d*-block elements

■ *s* block

■ *p* block

■ *d* block

■ *f* block

Factors that affects electron affinity

- **Atomic size:** across a period, moving from left to right, the atomic size decreases. This is due to the increasing effective nuclear charge, pulling the electrons closer to the nucleus.
- The smaller atomic size results in higher electron affinity because the incoming electron is added to a smaller atomic volume, leading to a stronger attraction between the electron and the nucleus.
- **Effective Nuclear Charge:** the effective nuclear charge is the net positive charge experienced by an electron in the outermost shell. The effective nuclear charge increases across the period from left to right.
- The increasing nuclear charge enhances the attractive force between the electrons and the nucleus, making it more favorable for an atom to accept an additional electron.

Factors that affects electron affinity

3 Shielding effect: the electron affinity generally decreases down the group due to the shielding effect. Electrons in inner energy levels partially shield the outer electrons from the attractive force of the nucleus.

- With increased shielding, the outer electrons experience a weaker attraction to the nucleus, making it less energetically favorable for an atom to gain an electron.

4 Electron Repulsion: as an electron is added to an atom, there is an increase in electron-electron repulsion. This repulsion opposes the addition of another electron.

- The repulsion between electrons contributes to the overall energy change associated with gaining an electron. The balance between attractive forces (nuclear attraction) and repulsive forces (electron-electron repulsion) ultimately determines the electron affinity of an atom. Smaller atoms, with their higher electron density and closer-packed electrons may experience more pronounced electron repulsion effects during the process of gaining an electron

In Summary

- In summary, the **electron affinity** (EA) of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table

BONDING

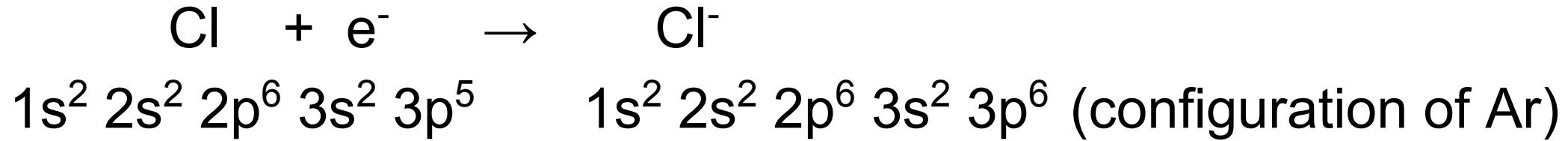
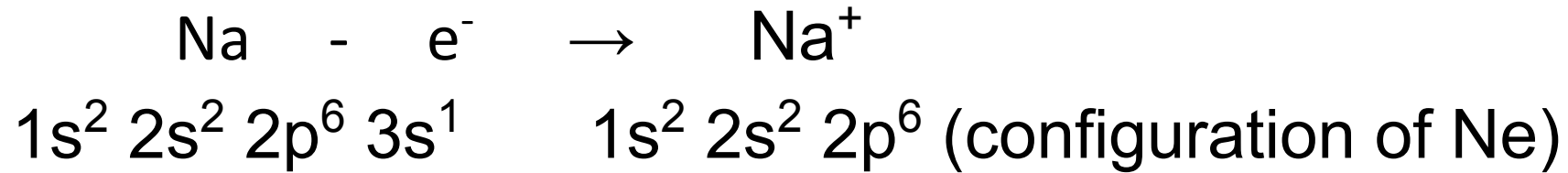
BONDING

- The chemical behaviour of an atom is determined to a large extent by the number and arrangement of the electrons in the outermost shell(s) of the atom.
- Valence electrons are electrons in the outer orbitals which are involved in chemical combination.
- Based on the electronic theory of valency the stability of the noble gases is related to their chemical inertness, a result of filled outermost shell.
- Atoms therefore combine to attain this type of noble electronic configuration.

□ Types of bonding

- Ionic electrovalent bonding: This is formed by the electrostatic force of attraction between positive and negative ions.
 - It involves the transfer of one or more electron from a metal to a non-metal.

- Forming ions
- E.g NaCl



□ Factors that favours ionic bonding

- ✓ Low ionization potential for the electron donating atom
- ✓ High electron affinity for the electron accepting atom
- ✓ High lattice energy of the resultant ionic compound.

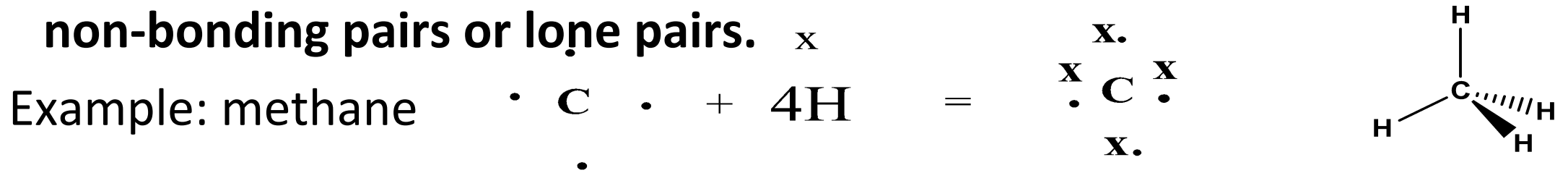
□ General properties of compounds formed by electrovalent bond

- ✓ They exist as crystalline solids at RT
- ✓ They have high m.pt and b.pt due to the strong electrostatic attraction between the oppositely charged ions
- ✓ They conduct electricity in solution, molten/fused form; electrolyte.
- ✓ ionic compounds are soluble in water and other similar polar solvents. This is due to the electrostatic attraction between the ions and the polar molecules of the solvent.
- ✓ However, they are generally insoluble in non-polar solvents.
- ✓ The chemical properties are those of its constituent ions.

□ **Covalent bond**

- This involves the sharing of one or more pairs of electrons of either the same element or two different elements in so doing the atoms often obtain the electronic configuration of the nearest noble gas.

- The electron pairs shared between the two atoms are called **bonding pairs** while those that remain on each atom which were not shared are called **non-bonding pairs or lone pairs**.



HCH bond angle = $109^{\circ} 28'$. structure is tetrahedral

□ General Properties

- ✓ They exist as separate discrete molecules or big giant molecules.
- ✓ At RT covalent compounds are usually gases, liquids or low m.pt solids. However the more complex compounds have much higher m.pt e.g proteins and plastics.
- ✓ They are non-electrolyte.
- ✓ They are insoluble in non-polar solvents at RT.
- ✓ They react slowly together.

□ Coordinate covalent bonding

- ✓ This is a type of covalent bond in which both electrons shared are donated by one atom only.
- ✓ eg ammonium ion

- the shape of ammonium ion is tetrahedral with bond angle of $109^{\circ} 28'$ as in methane molecules. The repulsion between the bound electron pairs is equal. The positive charge on the ammonium ion is delocalized over the ion to give the tetrahedral structures.
- This bond type occurs in transition metal ion complexes. In such cases the ligands (Lewis base) are the electron pair donors, forming coordinate covalent bonds with the transition metal ions e.g $\text{Cu}(\text{NH}_3)_6^{2+}$

- From the foregoing it can be inferred that the atoms tend to obtain noble gas configuration through the sharing or transferring of electrons.
- The tendency of atoms to have in molecules eight electrons in their valence shells (two for hydrogen atoms) is known as octet rule. (in particular atoms present prior to the 4th period).
- A number of atoms in most molecules do not satisfy the octet rule. These include:
 - a. electron-deficient molecules. e.g BF_3
 - b. molecules with central atom with more than eight valence electrons around it e.g PCl_5 , SO_2 , CO_3^{2-} , NO_3^- . These involve the delocalization or spreading of bonding pairs of electrons and the distribution of charge over a number of atoms rather than being localized between two atoms. The resonance structure is a hybrid of the various possible distributions of electrons.

- a non ideal nature occurs in both covalent and ionic bonds.

□ ionic character of covalent bond

- In molecules formed between different atoms the tendency to attract bonding electron-pairs differ, therefore, the bonding electron pairs in a covalent bond are unequally shared between the two atoms concerned, then it is said to be polarized and the molecule containing the bond may have a permanent electrostatic dipole moment.
- The degree of polarization depends on the relative electronegativities of the atoms concerned

□ covalent character of ionic bond

- Consider NaCl
- As a result of the charge the Na^+ ion attracts the outer electrons of Cl^-
- This leads to deformation or distortion of the outer electrons of the chloride anions



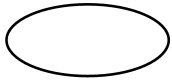
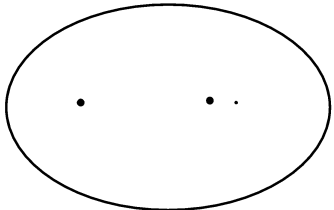


- The cation is said to polarize the anion because the electrical center of gravity of the negative charges in the anion no longer coincides with that of the positive charges.
- The degree of polarization of an ionic bond is a measure of degree of covalent character

□ Pauling electronegativity scale

Electronegativity is a measure of the ability of an atom in a molecule to draw bonding electrons to itself, leading to an inductive terms (Pauling values) and from ionization energies and electron affinities (Mulliken values).

- The absolute value of the difference in electronegativity of two bonded atoms gives a rough measure of the polarity to be expected in a bond.
- Based on Pauling electronegativity :
- a difference of 2.1 corresponds to about 50% ionic character
- bond with absolute value of the difference in electronegativity of 2.1 or more are almost entirely ionic
- those with lower values are polar covalent and zero value indicates zero ionic character and is pure; y covalent bond.

S/N	Bond	Shape
1.	Ionic Bond	
2.	Ionic bond with partial covalent character	
3.	Polar covalent bond	 $\delta+$ $\delta-$
4.	Pure covalent bond	

- Table 1 above indicating types of bonds and their shapes.

□ Fajan's rule

- Fajan summarized the factors that favour bond formation:
 - a. ionic bonds are favoured by
 - i. large cation with small charge, bonding with
 - ii. small anion with small charge
 - b. covalent bonds are favoured by
 - i. atoms with small cations and high charge bonding with
 - ii. atoms with large anions and high charge

CHEMICAL BONDING 2

Metallic Bond

- Metallic bond is primarily observed in metals
- Three main concepts may be used to describe metallic bond; they are:
 - ✓ Free electron theory
 - ✓ valence bond theory
 - ✓ molecular orbital or band theory

□ Metallic Bond (free electron theory)

- This model explains metallic bond as involving the positive cores of the atoms of the metals held together by a surrounding electron cloud of valence electrons.
- (the positive cores are cations, i.e, ions formed by the metals, formed by the fact that the valence electrons are not localized within the atom, but they are delocalized within the crystal lattice of the metal, shared by more than one core)
- The valence electrons are free to move throughout the crystal.
- The freedom of these electrons to move throughout the crystal is responsible for the electrical conductivity of metals
- increased number of valency electrons results in an increased cohesive force between the electron cloud and the positive core of the atoms

□ Band theory

- Another theory used to explain metallic bonding is based on molecular orbital concept. Generally, when two atomic orbitals combine, two molecular orbitals are formed.
- one having lower energy than the parent atomic orbitals called bonding molecular orbital and the other having higher energy than the parent atomic orbitals called anti-bonding molecular orbital.
- according to the band theory the highest energy electrons of metallic crystals occupy either a partially filled valence band or a completely filled valence band that overlaps with an conduction band.
- NB: Many closely spaced MO levels constitute a band

- **The conduction band** is the band of MO that electrons can jump up into from the valence band when excited. When the electrons are in these orbitals they have enough energy to move freely in the material.
- **The valence band** is the outermost electron molecular orbital of an atom of a specific material that electrons can occupy.
- The energy difference between the highest occupied energy state of the valence band and the lowest unoccupied state of the conduction band is called the band gap and is indicative of the electrical conductivity of a material.
- A large band gap means that a lot of energy is required to excite valence electrons to the conduction band.
- In conductors (metals) the valence and conduction bands may overlap

- Therefore electrons can readily jump between the two bands
- When one end of a piece of metal is heated, electrons at that end gain energy and move to an unoccupied MO, where they can travel rapidly to any other part of the metal, which becomes hot too.
- This is because on absorbing heat the electrons become thermally excited and are promoted to conduction band.
- The reverse process is accompanied by the release of heat.
- Metals have lustrous appearance because mobile electrons can absorb visible light, as a result they jump to the conduction band.

- On reverting to their original position, they emit photons of visible light making the surface shiny.
- **Insulators** are characterized by a large band gap, prohibitively large amount of energy is required to move electrons into the conduction bands.
- This energy gap called forbidden zone, is too large for electrons to jump to reach the conduction band. e.g diamond and phosphorus
- **Semi conductors** have small band gaps that allows for a meaningful fraction of the valence electrons of the material to move into the conduction band given a certain amount of energy.
- They do not conduct electricity at low temperatures.
- However, a small increase in temperature is sufficient to raise the electrons to the conduction bands. e.g silicon

- This property gives them a conductivity between conductors and insulators

□ **Comparison of metallic, ionic and covalent bond**

- ✓ Metallic bond differs from ionic bond in that there are no ions present but it resembles it in that the bonding forces are non-rigid and non-directional.
- ✓ Metallic bond differs from covalent bond in that metal atoms do not form separate (discrete) molecules but resembles it in that the atomic cores are bound together by being attracted to the electron cloud between them.

❑ Structures of metals

- In solid metals the atoms are packed closely together in regular array in either close-packed or body-centred cubic systems

❑ Close-packed structures

- In this case each atom is surrounded by six neighbours in the plane of the first layer and every alternate layer lies directly on top of each other i.e of the type ABABAB....., where A represents the arrangement in the first layer and B in the second, then the building order is described as ABABAB.....The types of close-packed structure include:

✓ Hexagonal close packing

✓ Face-centered cubic packing

□ Body-centered cubic

- This is not close-packed but contains about one third empty space. There is a sphere at the centre of the cube with eight other spheres at the corners of the cube in contact with the central sphere. It has a coordination number of 8 and the packing is not quite so close as in the other two metallic structures.

□ Properties of metallic compounds

- They are good conductors of heat and electricity
- Pure metals are malleable and ductile
- Pure metals have high melting points

□ Intermolecular forces

- These are forces of interaction between molecules. These forces are normally weakly attractive.
- Two main types exist between neutral molecules

✓ van-der Waal forces and

✓ hydrogen bond

- van-der Waal forces originates from three main interactions.

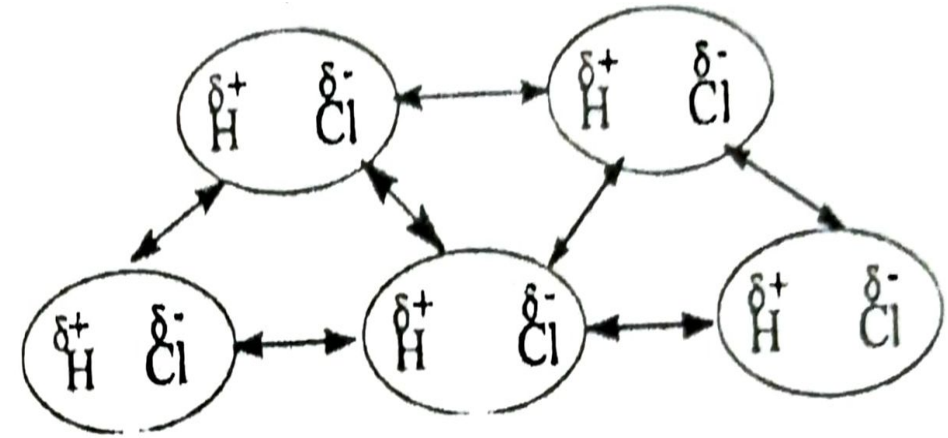
□ Dipole-Dipole forces

- This is an attractive intermolecular force resulting from the tendency of polar covalent molecules to align themselves in such a way that the positive end of one dipole is near the negative end of another dipole.

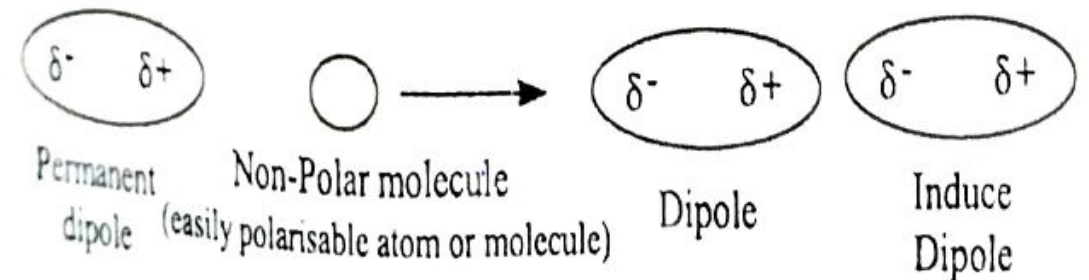
□ Permanent Dipole-Induced Dipole

✓ Dipole attractions also occurs between non-polar molecules. The electron cloud of non-polar molecules could easily be distorted when close to the positive end of a permanent dipole.

✓ The electron cloud will be drawn towards the permanent dipole; this disturbs the electron cloud in the non-polar molecules and thus induces a temporary dipole. The electron cloud distortion is called polarization.



example of dipole-dipole forces
permanent dipole-induced dipole (below)



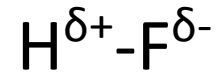
□ Induced Dipole-Induced Dipole (London Forces)

- These are weak attractive forces between molecules resulting from the small instantaneous dipoles that occur because of the varying positions of the electrons during their motion about nuclei.

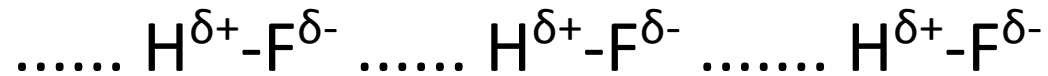
□ Hydrogen bonding

- This may be defined as an electrostatic force of attraction in which hydrogen atom links highly electronegative elements, such as fluorine, oxygen or nitrogen.
- It is not a bond in true sense of the term. Rather it is a form of fairly strong dipole-dipole interaction.
- Example, HF
- The electron pair which links the two atoms is unequally shared. It is displaced more towards F atom and away from H atom.
- This is because F has much higher electronegativity than H.

- As a result, F acquires a small negative charge, while H acquires a small positive charge.



- The negative centre of one molecule attracts the positive centre of the other.



- This attraction leads to the property of association.

□ Factors affecting H-bonding

- Electronegativity of the atom other than hydrogen
- Size of the atom other than hydrogen

- The small size of the electronegative atoms allows the atom to come sufficiently close for the resultant attraction to have significant effects on properties such as melting and boiling points.
- The higher the electronegativity of the heteroatom X, the stronger the bond and the higher the m.pt and b.pt.
- The more the number of hydrogen bonds in a molecule the higher the m.pt or b.pt

□ Properties affected by H-bonding

- Physical state
- Melting point and boiling point
- Solubility
- Strength of acids and bases
- Dimerization of carboxylic acids

□ Types of H-bond

- Intermolecular hydrogen bonding
- Intramolecular hydrogen bonding.

□ Anomalous character of water.

- The solid state of a substance is more dense than the liquid state. Water shows anomalous character. Ice has a lower density than liquid water. It therefore floats on the water surface and freezing of aquatic systems occurs from surface downwards. As a result aquatic life in oceans, rivers or lakes do not perish in winter. Hydrogen bonding is responsible for this unusual property of water.
- In ice, each water molecule is hydrogen-bonded to four other water molecules. Two of the hydrogen bonds are formed through the two H atoms covalently bound to oxygen, while the other two are formed through the two lone pairs on O atom.
- The tetrahedral coordination around each water molecule results in a cage-like structure. Due to cage formation, the volume is unusually large and therefore, density is abnormally low.
- As the temperature is increased some of the hydrogen bonds break and the cage-like structure tends to become dismantled. The volume progressively decreases and density consistently increases.

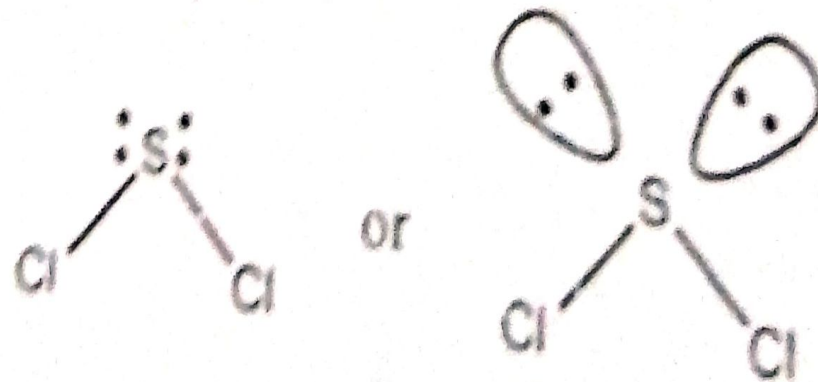
- At 277 K, the cage-like structure completely breaks down. The volume is now at a minimum and density at a **maximum**. Beyond 277K , thermal expansion of water increases the volume. The density once again registers a decline. Thus water has the maximum density at 277 K.
- Since the hydrogen-bonded cage breaks slowly, water has high specific heat, meaning that water absorbs more heat per unit of temperature rise than almost any other liquid. Hence the high boiling point of water
- It also means that as water cools it gives off more heat to its surroundings than any other substance.
- As a result water acts as a large thermostat, confining the temperatures on earth within moderate limits.
- ❖ With >70% of the earth surface water, God is indeed awesome!!!
- ❖ **Teaser:** can you relate this with the phenomenon of land and sea breeze and why at times fishermen prefer to fish at night. (you may include other bond types in the explanation)

□ Shape of Simple Molecules and Ions

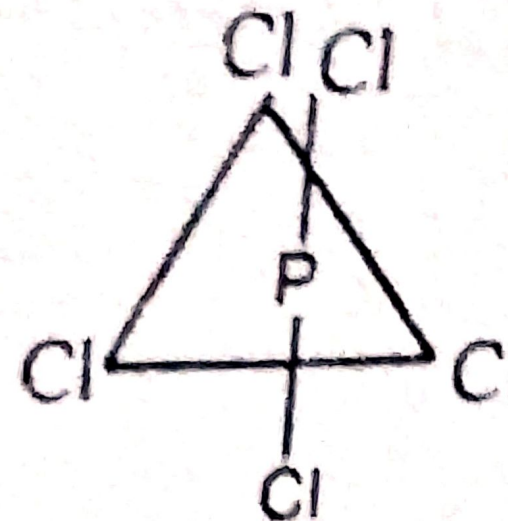
□ Valence Shell Electron Repulsion Model

- This is a model for predicting the shapes of molecules and ions in which valence shell electrons pairs are arranged about each atom so that the electron pairs are kept far apart from each other thus minimizing electron pair repulsion.
- The number of electron pairs primarily determines the shape and bond angles of the molecules and ions.
- This include both bonding and non bonding
- example SCl_2 valence electron= 6
 - electron shared = 2
 - total number of electrons=8
 - number of electron pairs = $8/2= 4$

- Here only two bonds are formed therefore there are two bond pairs,
- Hence the 4 electron pairs obtained from the above calculation is equivalent to 2 bond pairs and 2 lone pairs,
- therefore the structure is tetrahedral.



- PCl_5
 - valence electron = 5
 - electron shared = 5
 - total number of electrons = 10
 - number of electron pairs = $10/2 = 5$
 - there are five bond pairs
 - Hence the 5 electron pairs are used to form the five bond pairs.
 - Therefore the structure is trigonal bipyramid with bond angles of 120°



- However the number of electron pairs alone does not completely account for the shapes and bond angles.
- For example it does not account for the differences between the shapes and bond angles of methane, water and ammonia.
- Although, all these molecules contain four electron pairs.
- In VSEPR theory, the strength of repulsion between electron pairs decreases as follows:
 - lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair
- Methane, ammonia and water contain four electron pairs.
- Methane is tetrahedral, whereas both ammonia and water molecules have distorted tetrahedral shapes.
- This is because the lone pairs take up more space than the bonding electron pairs.
- Therefore the bond angles for methane ammonia and water is 109.5° , 106.7° , 104.5° respectively.

□ Valence Bond Theory

- ✓ Generally in the formation of covalent bond atoms with unpaired electrons tend to combine with other atoms which also have unpaired electrons.
- ✓ In this way the unpaired electrons are paired up and the atoms involved all attain a stable electronic arrangement.
- ✓ However some case exist such that the number of bonds formed is more than the number of unpaired electrons
- ✓ Formation of hybrid orbitals are used in valence bond theory to explain this.

- ✓ Hybridization refers to the mixing of two or more orbitals that have comparable energies followed by their splitting into equal number of degenerate orbitals. The new orbitals are called hybrid orbitals.
- ✓ The energy of the hybrid orbitals are lower than the parent orbitals.
- ✓ bonding occurs by the excitation of the atom, then electrons that were paired in the ground state are unpaired and promoted into suitable empty orbitals
- ✓ This increases the number of unpaired electrons and hence the number of bonds which will be formed.

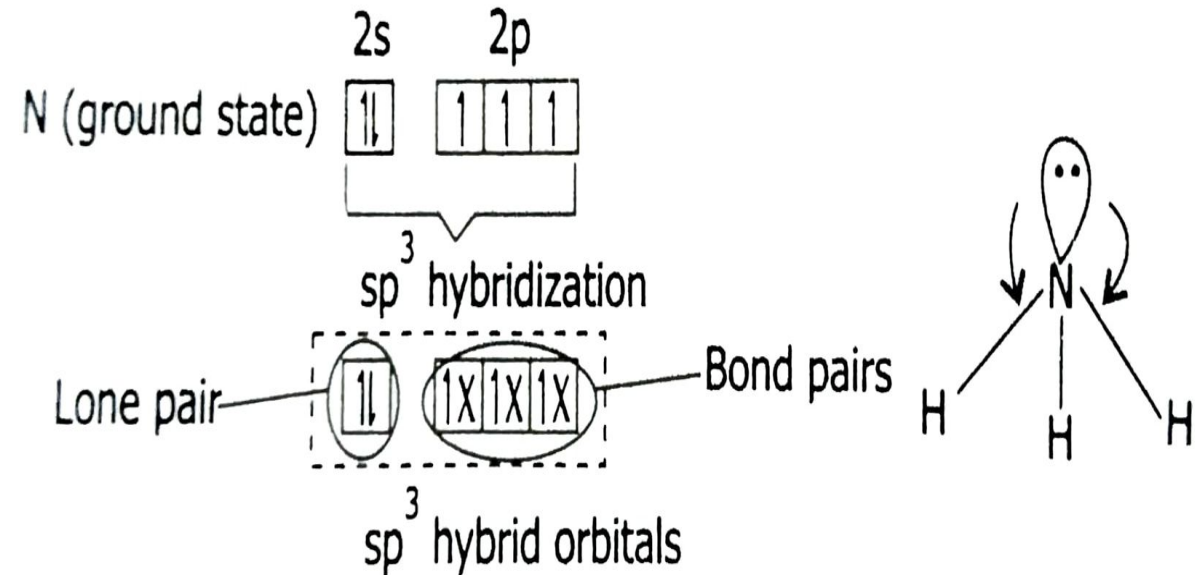
Approximate strengths of bonds formed by various orbitals

orbital	relative bond strength
s	1.0
p	1.73
sp	1.93
sp ²	1.99
sp ³	2.00

Geometry of some molecules and their hybridization

□ ammonia

- the central atom N has three unpaired electrons in its ground state
- the geometry is tetrahedral pyramid
- there are three bond pairs and one lone pair around N
- repulsion between the lone pair and bond pair causes a decrease in bond angle to 109.28°



□ Boron(III) chloride BCl_3

- B forms bond with three chlorine atoms.
- with the formation of sp^2 hybrid orbitals
- repulsion is minimized if the three chlorine atoms coordinate to the B atom at an angle of 120°
- The geometry is plane triangular

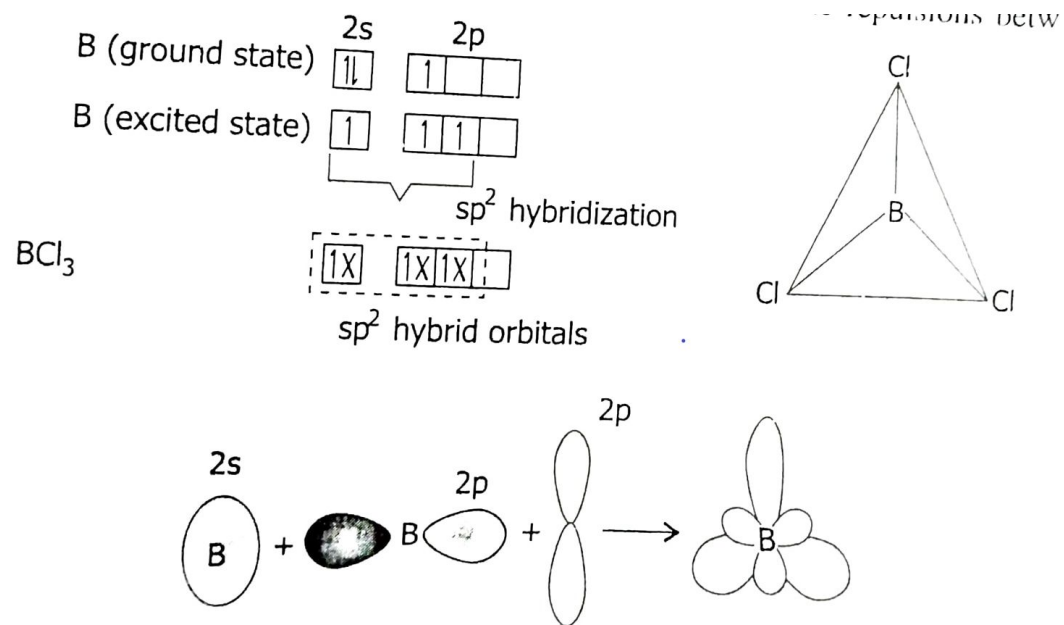
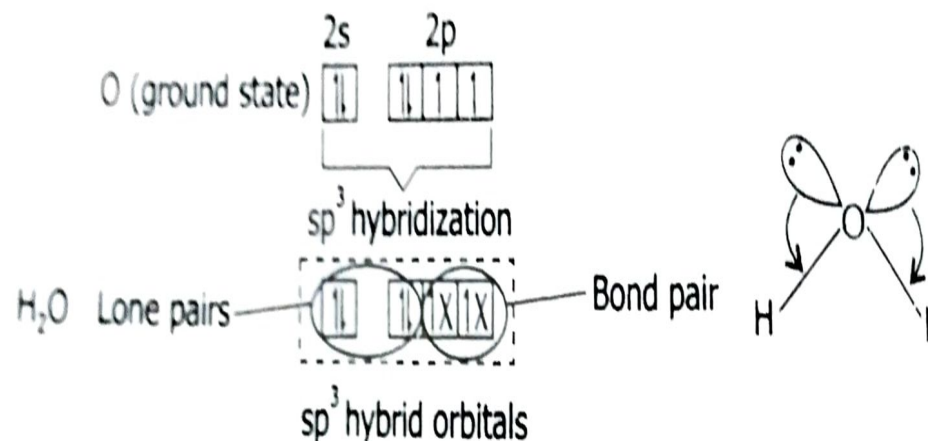


Fig. 3.20 Formation of sp^2 hybrid orbitals

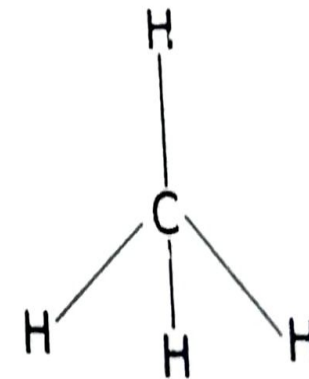
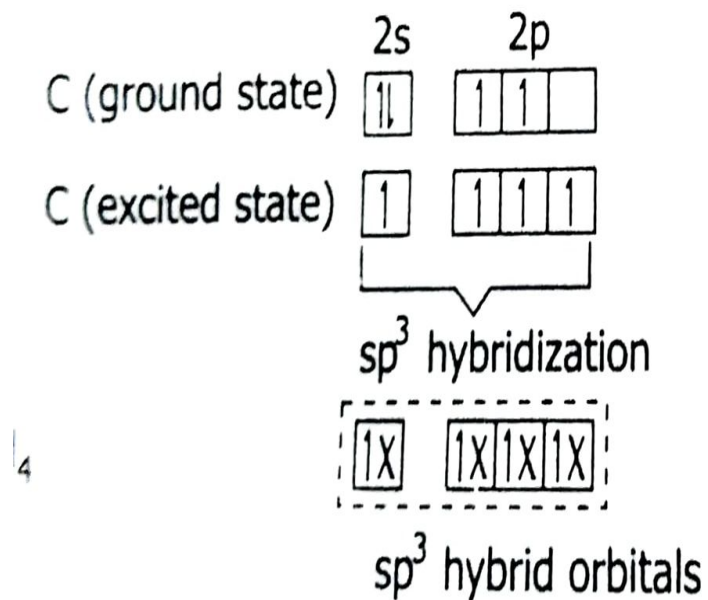
□ water

- the O atom of a water molecule has two unpaired electrons in its ground state
- oxygen becomes sp^3 hybridized bonding with two H atoms.
- the geometry is tetrahedral (V-shaped)
- as the two lone bond pairs repel each other strongly they are closer to each of the bond pairs
- they then repel the bond pairs closing down the bond angle to 104°

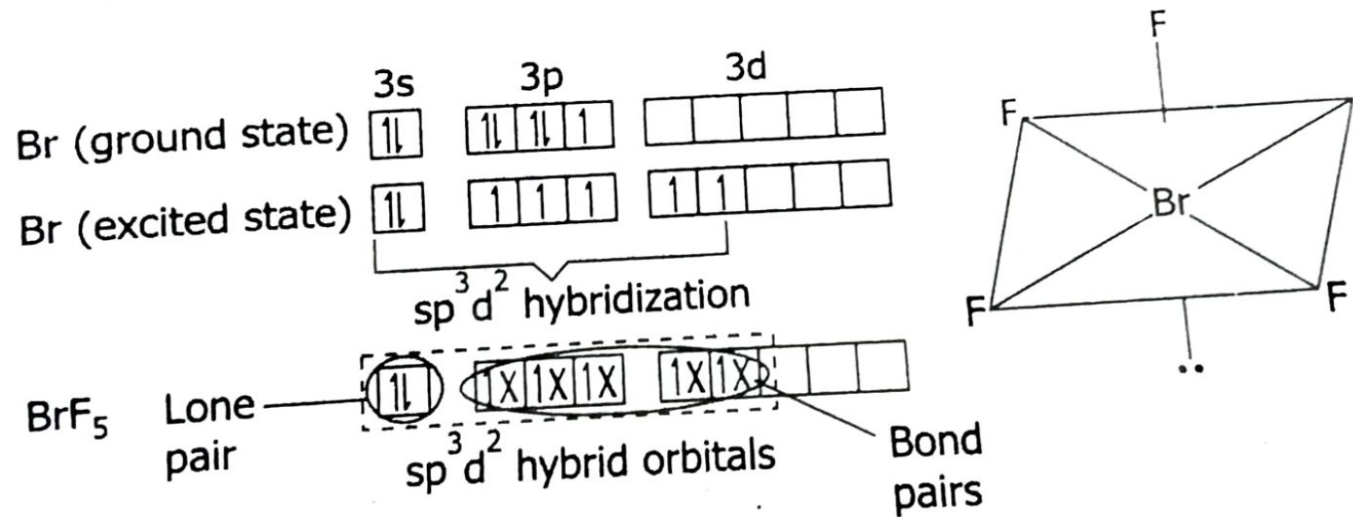


□ CH₄ methane

- the carbon atom is sp³ hybridized
- with tetrahedral geometry
- bond angle of 109.5°



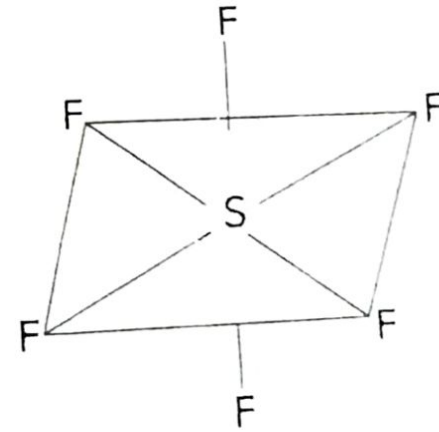
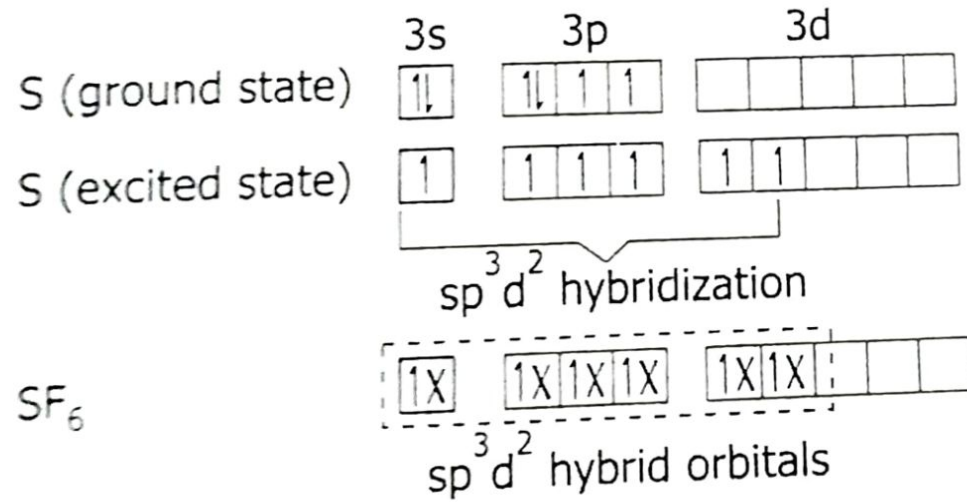
Bromine pentafluoride (BrF₅) The central atom, Br, in bromine pentafluoride is sp^3d^2 hybridized.



octahedral geometry with one position occupied by lone pairs of electrons

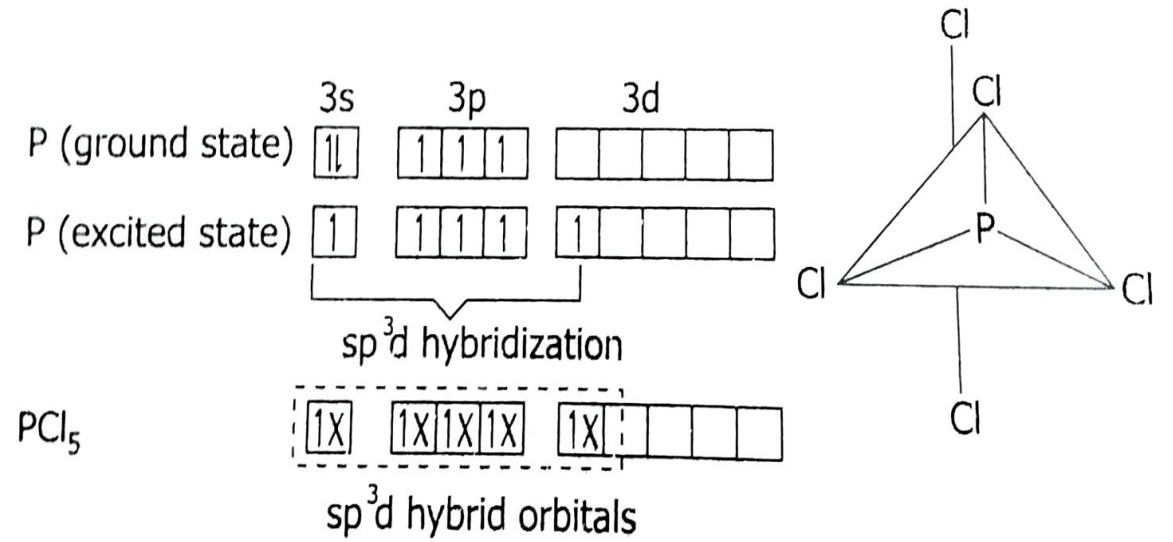
SF₆

energy levels, orbitals



The six sp^3d^2 hybrid orbitals are directed along the apex of a regular octahedron where they overlap with the F orbitals. All the bond angles are 90°.

- PCl_5
- trigonal bipyramid



Worked Example

Question 1

Use electronegativity values to predict the nature of bond in the following molecules

- (i) CCl_4 (ii) LiF (iii) H_2O (iv) PH_3 (v) Cl_2

Solution

Molecule	Bond	Electronegativity Difference	Nature of Bond
CCl_4	C - Cl	$3.0 - 2.5 = 0.5$	Polar covalent
LiF	Li - F	$4.0 - 1.0 = 3.0$	Ionic
H_2O	O - H	$3.5 - 2.1 = 1.4$	Polar covalent
PH_3	P - H	$2.1 - 2.1 = 0$	Purely covalent (non-polar)
Cl_2	Cl - Cl	$3.0 - 3.0 = 0$	Purely covalent (non-polar)

**Electronegativities of the elements in the Periodic Table
(Pauling electronegativity scale)**

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca	-	Ge	As	Se	Br
0.8	1.0	-	1.8	2.0	2.4	2.8
Rb	Sr	-	Sn	Sb	Te	I
0.8	1.0	-	1.8	1.9	2.1	2.5
Cs	Ba	-	Pb	Bi	Po	At
0.7	0.9	-	1.8	1.9	2.0	2.2

Assignment

1. With the aid of annotated diagrams give two examples of induced dipole-induced dipole forces

❖ Teaser 2

- From the earlier teaser question can you extrapolate your answer to why sand is used to fry/roast ground nut.

2. Define the term crystal lattice

3a. Draw the structure of water in, solid, liquid and gaseous form indicating its intermolecular bonding (hydrogen bond)

3b. Highlight the effect of hydrogen bond in each state of water relating this with their structure.

4. Compare and contrast covalent, electrovalent and metallic bonding.

❖ Teaser 3

- The electrical conductivity of a metal decreases with increasing temperature, use band theory to explain this.
- ❖ 4. Graphite is an allotrope of carbon, a non-metal, however it does conduct electricity. Suggest reasons for this observation.

5. Discuss the anomalous high boiling point of water.

CHM201

ACIDS AND BASES

Definition

- There are several theories to define the terms acids and bases
- The most relevant is a function of the system considered

[1] Arrhenius theory: Substances that produce H^+ in aqueous medium are called acids and those producing OH^- are bases

e.g $HCl \rightleftharpoons H^+ + Cl^-$; $NaOH \rightleftharpoons Na^+ + OH^-$

□ Hydrogen ion concentration may be given in terms of pH

$$pH = -\log_{10}[H^+]$$

- Consider: $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$
- $K_a = [\text{H}_3\text{O}^+] + [\text{OH}^-] / [\text{H}_2\text{O}]^2$ (K_a = equilibrium const)
- $K_w = [\text{H}_3\text{O}^+] + [\text{OH}^-] = 1 \times 10^{-14} \text{ mol}^2\text{L}^{-2}$ ($[\text{H}_2\text{O}]$ is constant)
- Similarly the $\text{p}K_a = -\log K_a$
- $\text{p}K_a$ may also serve as a measure of the strength of an acid
- High acid strength = large K_a = small value of $\text{p}K_a$
 - Variations in acid strength
 - i. Strength increases on moving from left to right on the PT

E,g: methyl ammonia water hydrogen fluoride

pK_a 46 35 16 3

ii. Acid strength increases on moving down a group

HF HCl HBr HI

pK_a 3 -7 -9 -10

iii. For oxoacids that contain more than one hydrogen atom, successive dissociation constant become more positive

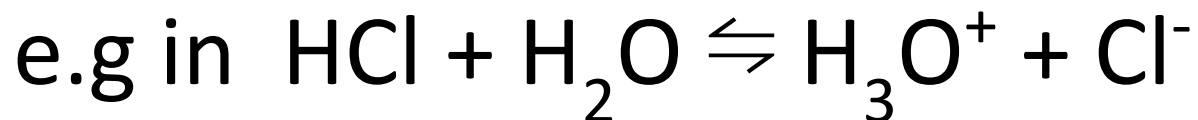
Jv. When an element forms a series of oxoacids the more the oxygen atom the more acidic it is

[2] Bronsted Lowry theory: Acids are proton donors and bases are proton acceptors

□ This extends to non-aqueous systems e.g liquid NH_3 e.g: $\text{NH}_4\text{Cl} + \text{NaNH}_2 \rightarrow \text{NaCl} + 2\text{NH}_3$

- Identify the acid/base in the above reaction with reasons

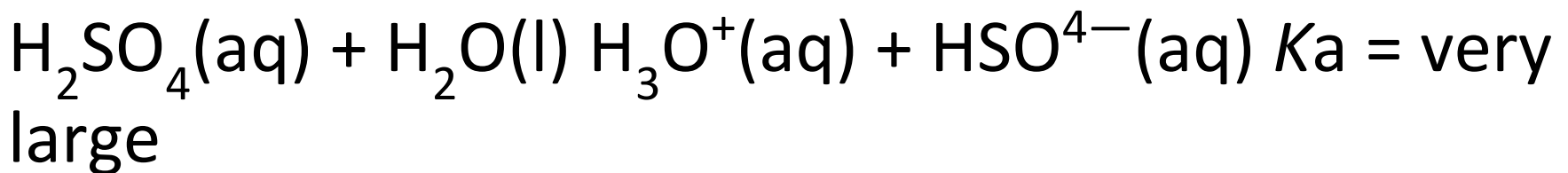
- Conjugate pairs are species that differ in composition only by a proton



Here Cl^- is the conjugate base of HCl
and H_3O^+ is the conjugate acid of H_2O

- Acids are classified by the number of hydrogen ions available to be donated.
- *Monoprotic acids* have one hydrogen ion to donate.
- *Polyprotic acids* have two or more hydrogen ions to donate.
- All polyprotic acids donate one hydrogen ion at a time.

E.g:



- Homework:

1. Compare and contrast both theories
2. Give two limitations of the Bronsted-Lowry theory
3. List four examples of
 - i. Strong acids
 - ii. Weak acids
 - iii. Strong bases
 - iv. Weak bases
4. Suggest reasons why you classified each compound in question 3 above as such.

5. Consider the CHM 201 past questions and answers booklet and give answers to questions 48-54 for 2019/2020 session in your own words.

6. Consider question 53 and arrange the solutions given assuming:

a. the acids are in aqueous solutions

b. in concentrated forms

Give reasons to buttress your point.

NB: Kindly submit answers to the questions on or before 14th February to your individual class reps; who in turn should submit them to the Secretary to the Department of Chemistry to place them in my pigeon hole.

Levelling and differentiating solvents

- Levelling solvents are solvents in which the strength of any acid or base in them are the same strength.
- ❖ As an example oxalic, sulphuric and nitric acid all ionize in water and have varying acid strength
 - However, in liquid ammonia, they all ionize completely.
 - ie they are all levelled (have similar strength) in liquid ammonia
 - In differentiating solvents acids/bases dissociate to varying degrees, ie, they exhibit different strength.
 - Eg, acetic acid; many mineral acids ionize partially in it,
 - However, (usual) bases, e.g NaOH ionize completely in it.
 - Therefore we may infer that a differentiating solvent for acids will act as a levelling solvent for bases and vice versa.

Lewis definition for acids and bases

- Acids are substances which accept electron pairs

These include:

- Positive ions : Cu^{2+} , Ag^+ , Co^{2+}
 - Molecules formed by elements in the first row of the periodic table with incomplete octet: BF_3 , BeCl_2
 - Compounds in which the central atom may exceed its octet by use of d-orbital, TiCl_4 , SiCl_4 ,
- Bases donate electron pairs
- Negative ions F^- , OH^- , CN^-
 - molecules with lone pairs of electrons, e-g ammonia
 - molecules with C-C multiple bonds, $\text{CH}_2=\text{CH}_2$

Hard and soft acids and bases

- This theory proposes that soft acids react faster and form stronger bonds with soft bases. And hard acids react faster and form stronger bonds with hard bases, all other factors being equal.
- Hard acids have the following characteristics:
 - Small atomic/ionic radius
 - High oxidation state
 - Polarizing in nature
 - Eg: Ti^{4+} , Cr^{3+} , BF_3 , Cr^{6+}
- Hard bases : have high electronegativity, slightly polarizable: NH_3 , CO_3^{2-} , F^- , OH^- , CH_3COO^-
- The affinity of hard acids and hard bases for each other is mainly ionic in nature.

- Soft acids and bases tends to have the following characteristics:
- Large atomic/ ionic radius
- Low/zero oxidation state
- Acids: negligible polarizability and bases: highly polarizable
- Low electronegativity (bases)
- Soft acids: Ag^+ , CH_3Hg^+ , BH_3 , Cd^{2+} , Pt^{2+} , Pd^{2+} , Hg^{2+}
- Soft bases: I^- , H^- , SCN^- , R_3P

The affinity of soft acids and bases for each other is mainly covalent in nature

Oxidation and Reduction

- Many reactions occur by formal loss of electron by one atom and gain of electron by another.
- The process of electron gain is called reduction while that of loss of electron is known as oxidation
- Both are jointly called redox reaction
- Species that supply electrons are called reducing agent
- While the one that receives electrons is called oxidizing agent (Oxidant)
- $$\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightleftharpoons \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$$
$$\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} \text{ (oxidation; o.s of 0 to +2)}$$
$$\text{Cu}^{2+}_{(aq)} \rightarrow \text{Cu}_{(s)} \text{ (reduction; o.s of +2 to 0)}$$

Electrochemical cell

- An electrochemical cell is a device that produces an electric current from energy.
- They are of two types
 - I. Converts chemical energy to electrical energy: galvanic cell
 - II. Converts electrical energy to chemical energy: electrolytic cell
- Galvanic cell
 - Consists of two conductive electrodes (the anode and cathode)
 - Anode is the electrode where oxidation occurs
 - Cathode is where reduction occurs
 - In between both electrodes is the electrolyte that contains free moving ions.
 - The metal of the anode oxidizes from 0 to a positive oxidation state
 - The metal ion in solution will accept electrons from the cathode and the oxidation state of the ions becomes zero; resulting in solid metal deposited on the cathode.

- The two electrodes are electrically connected to each other allowing for a flow of electrons that leave the metal of the anode and flow through this connection to the ions at the surface of the cathode.
- A voltmeter measures the change of electrical potential between the anode and cathode, this voltage is termed emf .
- The path of electrons in an electrochemical cell is shown using a cell diagram



H/W

1. Draw an annotated diagram of a galvanic cell (Daniel cell) using the cell diagram shown above.
2. What does the double line (||) and (1M) from the cell diagram above represent

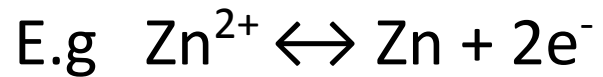
Electrode Potential and Standard Electrode Potential

- The potential difference between a metal and a solution containing its own ions (in equilibrium) is called electrode potential of that metal (electrode).
- The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons.
- This implies that it is a measure of the relative tendency of the metal to undergo oxidation or reduction.
- Depending on the tendency of a metal to lose or gain electrons the electrode potential may be of two types namely oxidation potential and reduction potential
- Oxidation potential of a metal indicates its electron losing tendency, while reduction potential represents the electron gaining capacity of the metal.
- However, according to IUPAC convention electrode potentials are given as reduction potentials.
- The unit of the electrode potential is the volt.

- Factors affecting the magnitude of electrode potential

- a. The nature of metal or electrode: metals have different tendency to lose or accept electrons.

- b. Concentration of metal ions in solution



As the concentration of Zn^{2+} ions increases the equilibrium will shift to the left side and the electrode potential decrease. Similarly as the concentration of Zn^{2+} ions decreases electrode potential increases.

- c, Temperature

- d. Complexation: Complex formation may also bring down the effective concentration of one of the species involved in an electrode process, thereby altering the potential of the system

- e. pH: When hydrogen or hydroxyl ions are involved in a half-cell reaction, their concentrations appear in the Nerst equation and accordingly the potential is influenced by the pH of the medium.

- Standard electrode potential (E°) may be defined as the potential difference between the standard hydrogen half cell and the half cell that is being studied, provided that:

- i. All the dissolved species are at unit concentration (1M)

- ii. Gases are at 1 atm pressure.

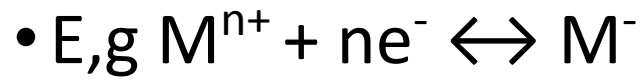
- iii. All solids are in their most stable form

iv The temperature is maintained at 25 °C

- The standard emf of a given cell (E°_{cell}) is equal to the difference of standard reduction potential of the cathode ($E^{\circ}_{\text{cathode}}$) and the standard reduction potential of the anode (E°_{anode}).

- $E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{\text{cell}}$

- The emf of any cell can be calculated using the Nerst equation



- $E = E^{\circ} + RT/nF \ln(1/a_m^{n+})$

If both oxidized and reduced form are in solution

- $E = E^{\circ} + RT/nF \ln(a_{\text{oxidized}}/a_{\text{reduced}})$

- Where: R= gas constant; T= absolute temperature; a_m^{n+} = the activity of the ion in solution; n= valency of the ion; F= Faraday.

- NB: a_m^{n+} may be replaced by the concentration of the ions in solution

- Emf is also related to the free energy change of a system by the equation
- $\Delta G = -nFE$
- Or standard electrode potential: $\Delta G^\circ = -nFE^\circ$
- An arrangement of element in order of increasing E° values is called the electrochemical series
- In this series the most electropositive elements are at the top and the least electropositive at the bottom
- Couples containing powerful reducing agents have negative potentials
- Strong oxidizing agents have positive potentials.
- E° value is affected by complexation
- In certain cases E° also depends on pH.

Electrode potential and equilibrium constant

- The free energy change of a chemical reaction is dependent on the activity of the reactant and products.
- Accordingly the emf of a cell should also depend on the activity of the species taking part in the cell reaction.
- $\Delta G^\circ = -nFE^\circ$
- $\Delta G^\circ = -RT \ln K$
- Therefore; $RT \ln K = nFE^\circ$
- $\ln K = nFE^\circ / RT$
- Or $2.303 \log K = nFE^\circ / RT$
- Hence if E° is known K can be obtained for an equation
- Furthermore,
- $E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{ox}]}{[\text{redu.}]}$
- $= E^\circ + \frac{0.059}{n} \log \frac{[\text{oxidized form}]}{[\text{reduced form.}]}$ At 298K

- Using this for the two half cell reactions. At equilibrium net emf must be zero. Therefore the net emf is zero.
- Example: $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \leftrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$
- For $\text{MnO}_4^- / \text{Mn}^{2+}$
- $E_1 = E_1^0 + 0.059/5 \log [\text{MnO}_4^-][\text{H}^+]/[\text{Mn}^{2+}]$
- For $\text{Fe}^{2+}/\text{Fe}^{3+}$
- $E_2 = E_2^0 + 0.059/5 \log [\text{Fe}^{3+}]^5/[\text{Fe}^{2+}]^5$
- However, at equilibrium $E_1 = E_2$
- $E_1^0 - E_2^0 = \{ 0.059/5 \log [\text{Fe}^{3+}]^5/[\text{Fe}^{2+}]^5 \} - \{ 0.059/5 \log [\text{MnO}_4^-][\text{H}^+]/[\text{Mn}^{2+}] \}$
- $= 0.059/5 \log [\text{Fe}^{3+}]^5 [\text{Mn}^{2+}] / [\text{Fe}^{2+}]^5 [\text{MnO}_4^-][\text{H}^+]$
- $= 0.059/5 \log K$
- But $E_1^0 = 1.51$ and $E_2^0 = 0.77$
- $\log K = 5(1.51 - 0.77)$
- $K = 10^{62.6}$ H/W suggest the implication of the K value obtained.

- Assignment

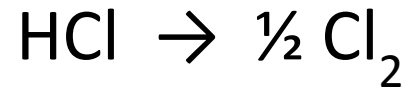
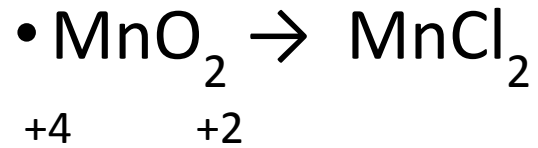
1. Give 3 properties of hard and soft acids and bases each.
2. Give 4 examples each of hard and soft acids and bases
3. Predict whether Fe will be oxidized to Fe^{2+} by the reaction with 1.0 HCl (Fe/ Fe^{2+})
4. Define an acid in terms of the following theories:
 - I. Arrhenius
 - II. Brownsted Lowry
 - III. Lewis
4. Distinguish between levelling and differentiating agents and give two examples of each.
5. Give two possible practical applications of electrochemistry.
6. Balance the equation representing the redox reaction of the reduction of potassium permanganate solution to manganous salt in acidic medium by hydrogen peroxide.

Balancing redox equation

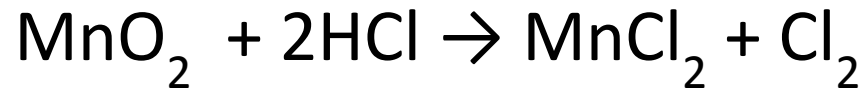
- Redox reactions involves the transfer of electrons from reducing agent to oxidizing agent,
- Balancing redox equations may be carried out using either of two ways
 - a. The oxidation no method
 - b. The ion-electron method
 - a. Oxidation no method
 - Step1: Ascertain the mole ratio of the oxidant and reductant
 - Step 2: All the species appearing on the reactant and product side are considered; adjustment is made for atoms which do not undergo any change of oxidation number. Acid, alkali or water may be inserted depending on the condition and medium of the reaction.

- Step 3: The balancing is closed by inspection of the reactant and product side, i.e. that it is balanced.
- Example: manganese dioxide oxidizes concentrated hydrochloric acid to chlorine, manganous chloride and water.

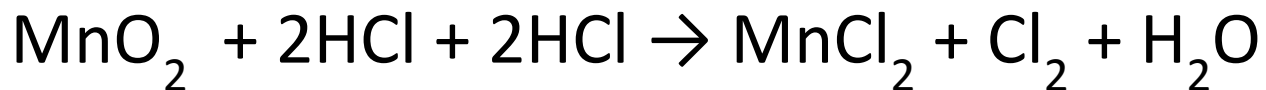
• Step 1

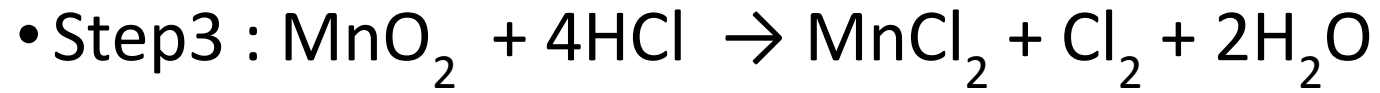


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• Step 2



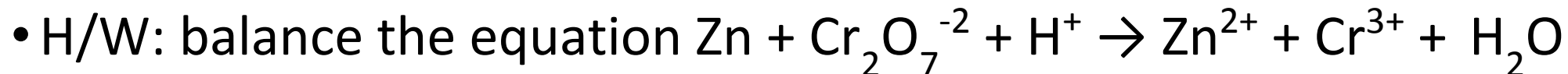
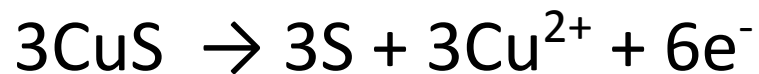
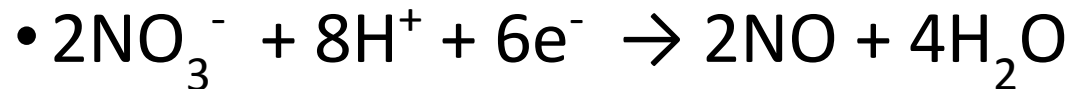
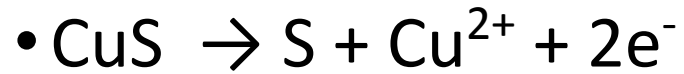
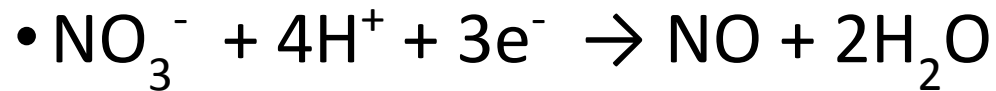
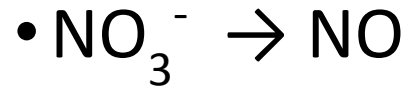


b. Ion-electron method

This method is based on the electronic theory of oxidation and reduction. However, it is particularly limited to ionic reactions in aqueous solutions.

- Step 1 : The products of the reaction are ascertained and the loss of electrons by the reductant and the gain of electrons by the oxidant are expressed separately by partial equations
- Step 2: The individual partial equations are balanced separately with respect to different atoms as well as with respect to the electrical charge on both sides. H^+ and OH^- are inserted as appropriate. For electrical balance the total charge of all the ions appearing on the two sides of the half reactions are considered and the difference adjusted by adding electrons on the appropriate side.
- Step 3: The two partial equations obtained are multiplied by suitable factors to equalize the number of electrons in them. These are added after the electrons cancel out. The ions are replaced by molecules with necessary adjustment.

• Example: Cupric sulfide dissolves in hot nitric acid forming cupric nitrate, nitric oxide and sulphur



Electrolysis

- Electrolysis means literally taking apart with electricity.
- It is a non-spontaneous chemical change produced by electrical energy.
- It is used commercially to prepare many reactive metals in their elemental form
- and to prepare fluorine and chlorine gas.
- Electrolysis involves the use of electrical energy to drive a non-spontaneous redox reaction.

- In electrolysis, an electric current is sent through an electrolyte in order to stimulate the flow of ions necessary to run an otherwise non-spontaneous reaction.
- Processes involving electrolysis include: electro-refining, electro-synthesis, and the chloro-alkali process.
- The voltage that is needed for electrolysis to occur is called the decomposition potential.
- Electrolysis can also be described to involve the passing of a direct electric current through an electrolyte which produces chemical reactions at the electrodes and decomposition of the materials.

- The main components required to achieve electrolysis are an electrolyte, electrodes, and an external power source.
- A partition (e.g. an ion-exchange membrane or a salt bridge) is optional to keep the products from diffusing to the vicinity of the opposite electrode.
- The electrodes are immersed separated by a distance such that a current flows between them through the electrolyte and are connected to the power source which completes the electrical circuit.
- A direct current supplied by the power source drives the reaction causing ions in the electrolyte to be attracted toward the respective oppositely charged electrode.

- The desired products of electrolysis are often in a different physical state from the electrolyte and can be removed by mechanical processes (e.g. by collecting gas above an electrode or precipitating a product out of the electrolyte).

- Each electrode attracts ions that are of the opposite charge.
- Positively charged ions (cations) move towards the electron-providing (negative) cathode.
- Negatively charged ions (anions) move towards the electron-extracting (positive) anode.
- In this process electrons are effectively introduced at the cathode (reduction) as a reactant and removed at the anode (oxidation) as a product.
- When neutral atoms or molecules, such as those on the surface of an electrode, gain or lose electrons they become ions and may dissolve in the electrolyte and react with other ions.

- When ions gain or lose electrons and become neutral, they will form compounds that separate from the electrolyte.
- Positive metal ions like Cu^{2+} deposit onto the cathode in a layer. The terms for this are electroplating, electrowinning, and electrorefining.
- When an ion gains or loses electrons without becoming neutral, its electronic charge is altered in the process.
- For example, the electrolysis of brine produces hydrogen and chlorine gases which bubble from the electrolyte and are collected. The initial overall reaction is thus:
 - $2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 + \text{Cl}_2$
 - The reaction at the anode results in chlorine gas from chlorine ions:

- $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
- The reaction at the cathode results in hydrogen gas and hydroxide ions:
- $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
- Without a partition between the electrodes, the OH^- ions produced at the cathode are free to diffuse throughout the electrolyte to the anode.
- As the electrolyte becomes more basic due to the production of OH^- , less Cl_2 emerges from the solution as it begins to react with the hydroxide producing hypochlorite (ClO^-) at the anode:

- $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$
- The more opportunity the Cl_2 has to interact with NaOH in the solution, the less Cl_2 emerges at the surface of the solution and the faster the production of hypochlorite progresses.
- This depends on factors such as solution temperature, the amount of time the Cl_2 molecule is in contact with the solution, and concentration of NaOH.
- Likewise, as hypochlorite increases in concentration, chlorates are produced from them:
- $3\text{NaClO} \rightarrow \text{NaClO}_3 + 2\text{NaCl}$
- Other reactions occur, such as the self-ionization of water and the decomposition of hypochlorite at the cathode, t

□ Decomposition potential

- Decomposition potential or decomposition voltage refers to the minimum voltage (difference in electrode potential) between anode and cathode of an electrolytic cell that is needed for electrolysis to occur.[21]
- The voltage at which electrolysis is thermodynamically preferred is the difference of the electrode potentials as calculated using the Nernst equation. Applying additional voltage, referred to as overpotential, can increase the rate of reaction and is often needed above the thermodynamic value. It is especially necessary for electrolysis reactions involving gases, such as oxygen, hydrogen or chlorine.

□ Oxidation and reduction at the electrodes

- Oxidation of ions or neutral molecules occurs at the anode.
- Reduction of ions or neutral molecules occurs at the cathode. |

□ Electrolytic Cell vs Voltaic Cell

- An electrolytic cell is essentially the non-spontaneous reaction's voltaic cell, (in fact if we reversed the flow of electricity within a voltaic cell by exceeding a required voltage, we would create an electrolytic cell). Electrolytic cells consist of two electrodes (one that acts as a cathode and one that acts as an anode), and an electrolyte.
- Unlike a voltaic cell, reactions using electrolytic cells must be electrically induced and its anode and cathode are reversed (anode on the left, cathode on the right).

VOLTAIC CELL	ELECTROLYTIC CEL
Oxidation: $X \rightarrow X^+ + e^-$ (Negative Anode)	$Y \rightarrow Y^+ + e^-$ (Positive Anode)
Reduction: $Y^+ + e^- \rightarrow Y$ (Positive Cathode)	$X^+ + e^- \rightarrow X$ (Negative Cathode)
Overall: $X + Y^+ \rightarrow X^+ + Y$ ($G < 0$)	$X^+ + Y \rightarrow X + Y^+$ ($G > 0$)
This reaction is spontaneous and will release energy	This reaction is non-spontaneous and will absorb energy

□ Electrolysis of Molten Sodium Fluoride

- Anode: $2\text{F}_{(l)}^{-1} \rightarrow \text{F}_{(g)}^2 + 2\text{e}$
- Cathode: $2\text{Na}_{(l)}^{+1} + 2\text{e} \rightarrow 2\text{Na}_{(l)}$
- $E^{\circ} = E_{\text{anode}} - E_{\text{cathode}} = -2.87 \text{ V} - (+2.71 \text{ V}) = -5.58 \text{ V}$
- This is a large negative E°
- This shows it is a highly endothermic process requiring a large energy input to drive it.

- This is the commercial method typically used to prepare pure alkali metals which otherwise could

□ Electrolysis of Water

- $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta\text{G} = + 474.4 \text{ KJ}$
- The reaction can be easily driven by an electrical current. Pure water is made conductive with sulfuric acid, chosen because sulfate anion is not easily oxidized.
- Anode: $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^{+1}(\text{aq}) + 4\text{e}$
- Cathode: $4\text{H}^{+1}(\text{aq}) + 4\text{e} \rightarrow 2\text{H}_2(\text{g})$

□ Quantitative Aspects of Electrolysis

□ Faraday observed that the mass of metal deposited by electrolysis was proportional to the amount of current that flowed through the cell. (**Faraday First law of electrolysis**)

- $m \propto Q \equiv m / Q = Z$

- m = mass of the substance deposited or liberated at the electrode

- Q = charge (coulombs); Z = electrochemical equivalent i.e. mass of the substance deposited or liberated per unit charge.

- Electric current flow is expressed in amperes, and by definition,

- Charge(coulombs) = Current(amperes) x Time(s) and

- 1 mole of electrons = 96500 coulombs \equiv 1 Faraday

- $Z = E/F$, E = equivalent weight and $F = 1$ Faraday; therefore $m = E \cdot I \cdot t(s) / F$

- **Example 1:** A 0.430 amp current flowed through a molten magnesium fluoride electrolysis cell for 1 hour, 35.0 minutes. What mass of magnesium and what mass of fluorine was produced?

- The overall reaction is: $\text{MgF}_{2(l)} \rightarrow \text{Mg}_{(l)} + \text{F}_{2(g)}$
- Anode (oxidation) $2\text{F}_{(l)}^{-1} \rightarrow \text{F}_{2(g)} + 2e$
- Cathode (reduction) $\text{Mg}_{(l)}^{+2} + 2e \rightarrow \text{Mg}_{(l)}$
- First, calculate moles of electrons, then calculate moles of fluorine and magnesium.
- Charge(coulombs) = Current(amperes) x Time(s)
- = 0.430 amp x 5700 s = 1.05×10^3 coulomb (Total charge that flowed through the cell.)
- 1.05×10^3 coulomb x 1 mole of electrons/96500 coulombs = 1.09×10^{-2} mol of electrons
- 1.09×10^{-2} mol electrons x (1 mol Mg/2 mol electrons) x (24.31 g Mg/mol Mg) =
- = 0.133 g of Mg

$$1.09 \times 10^{-2} \text{ mol electrons} \times (1 \text{ mol F}_2 / 2 \text{ mol electrons}) \times (38.00 \text{ g F}_2 / \text{mol F}_2) =$$

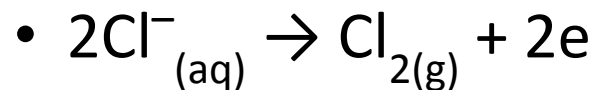
- = 0.207 g F₂

□ **Faraday second Law of Electrolysis** states that when the same amount of electric current is passed through different electrolytes connected in series the masses of the substances deposited or liberated at the electrodes are directly proportional to their respective chemical equivalent/ equivalent weight (their molar mass divided by the valence)

- Mathematically, $m_1/m_2 = E_1/E_2$

- **Example 2:** A constant current is passed through an electrolytic cell containing molten MgCl₂ for 12 h. If 4.83 L of Cl₂ (at STP) is produced at the anode, what is the current in amperes?

- Solution:



- First we convert 4.83 L of Cl₂ to moles
- $PV = nRT$
- but $n = (1 \text{ atm})(4.83 \text{ L}) / (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(273 \text{ K}) = 0.216 \text{ mol}$

Answer= 0.965 A

- Using the formulas given can you complete example 2.?

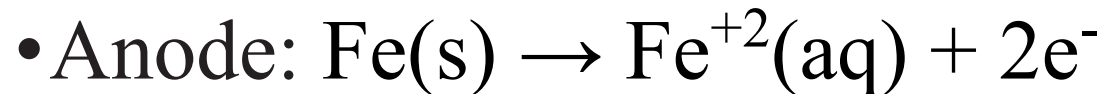
□ Corrosion

- Corrosion can be defined as the deterioration of materials by chemical processes. The most important by far is electrochemical corrosion of metals, in which the oxidation process $M \rightarrow M^+ + e^-$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a **depolarizer**.
- Examples of corrosion include the rusting of iron, tarnishing of silver, development of green coating on copper and bronze.
- It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron.
- A lot of money is lost every year on account of corrosion.

- The economic aspects of corrosion are far greater than most people realize; according to a report published in 2001, the cost of corrosion in the U.S. alone was \$276 billion per year. Of this, about \$121 billion was spent to control corrosion, leaving the difference of \$155 billion as the net loss to the economy.

- Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon.

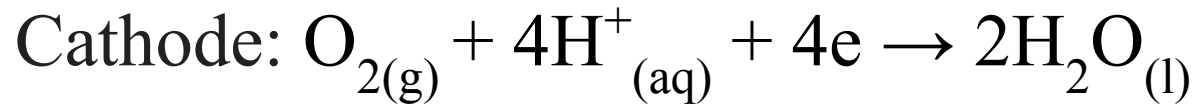
- At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction



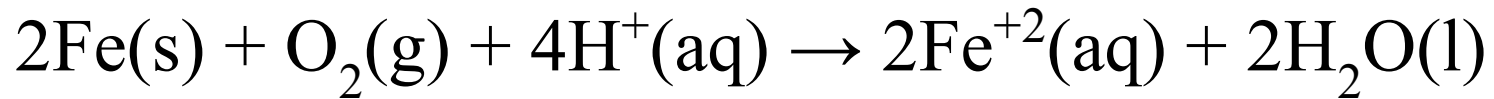
Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in the presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water).

- Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere.

- This spot behaves as cathode with the reaction



- The overall reaction being:



- **$E_o \text{ cell} = E_o \text{ cathode} - E_o \text{ anode} = 1.23 \text{ V} - (-0.44\text{V}) = + 1.67 \text{ V}$**

The ferrous ions are further oxidized by atmospheric oxygen to ferric ions

- which come out as rust in the form of hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$) and with further production of hydrogen ions.
- Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion.
- One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol).
- Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object.
- An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

Assignment

- “In a sense, corrosion can be viewed as the spontaneous return of metals to their ores.” Suggest reasons why this statement may be correct.
- The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. What characteristic of metals enables this to occur?

BATTERIES

- A battery serves as a source of electrical energy
- It is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy.
- They are usually a series or pile of cells that can be used as a source of direct current at a constant voltage
- However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use.

a. **The Mercury Battery**

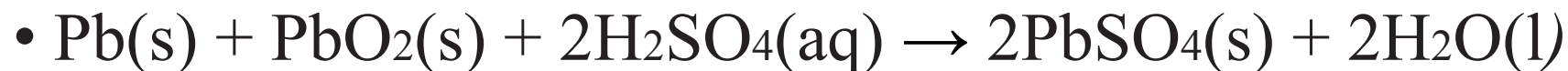
Consists of *amalgamated* zinc anode and a stainless steel casing which supports the mercuric oxide

- cathodic material. Only the solid components change, not the electrolyte, keeping volume and internal pressure constant.
- It is used in high-end applications where removing battery is inconvenient.
 Anode: $\text{Zn(Hg)} + 2\text{OH}^-(\text{aq}) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2\text{e}$ (plus unchanged Hg)
 Cathode: $\text{HgO(s)} + \text{H}_2\text{O} + 2\text{e} \rightarrow \text{Hg(l)} + 2\text{OH}^-(\text{aq})$

b. The Lead Storage Battery

- It is commonly used in automobiles and invertors.
- It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.
 Anode: $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}$
 Cathode: $\text{PbO(s)} + 4\text{H}^+ + \text{SO}_4^{2-}(\text{aq}) + 2\text{e} \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

Overall cell reaction :



- It can be recharged by passing current
- On charging the battery the reaction is reversed and $\text{PbSO}_4(\text{s})$ on anode and cathode is converted into Pb and PbO_2 , respectively

Assignment

- a. Give two other examples of batteries and their uses.
- b. Discuss on the energy changes in electrolysis
- c. Give five examples of metals that are extracted electrolytically.
- d. Predict the products of electrolysis for each of the following
 - i. An aqueous solution of AgNO_3 with silver electrodes
 - ii. An aqueous solution of AgNO_3 with platinum electrodes.
 - iii, A dilute solution of H_2SO_4 with platinum electrodes.