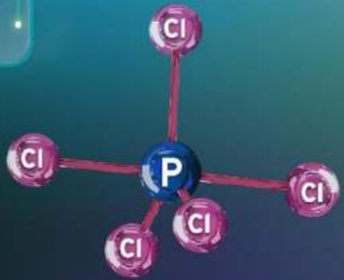
Welcome to

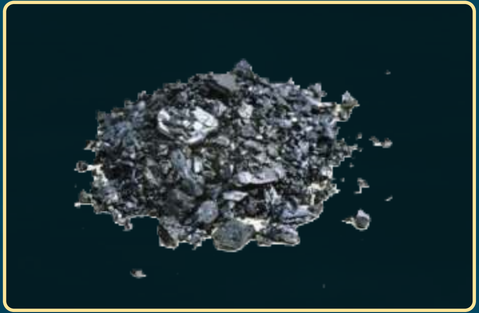
Aakash + BYJU'S LIVE

Chemical Bonding and Molecular Structure



NaCl

$CaCO_3$



Iodine crystals

Aluminium

The substances are formed as a result of combination of atoms or molecules or ions.

So Many Why?

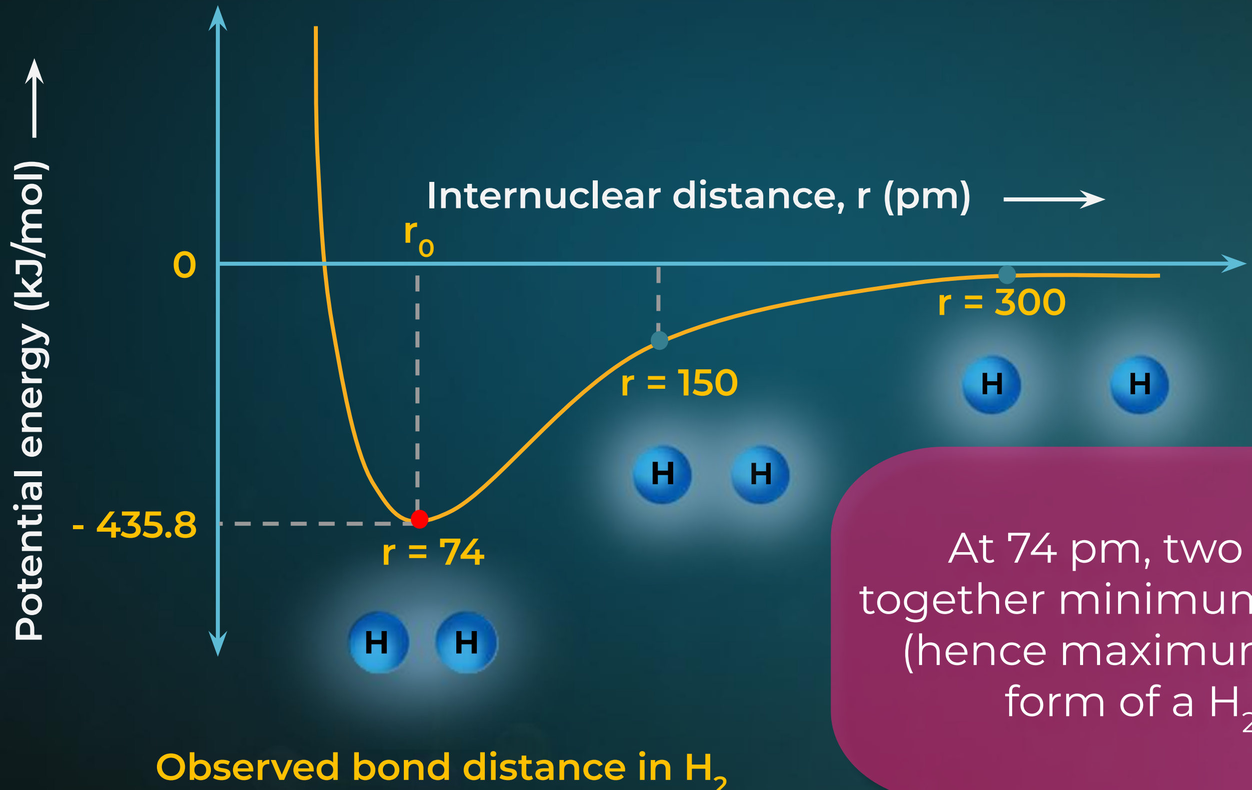
- Why do some atoms combine while certain others do not?
- What is the nature of the force that exists between combining atoms?
- Why does definite number of various atoms constitute a particular molecule?
- Why is it easy for some elements to lose electrons while it is harder for others?

Chemical Bond

The attractive force which holds various constituents (atoms, ions, etc.) together, in different chemical species.

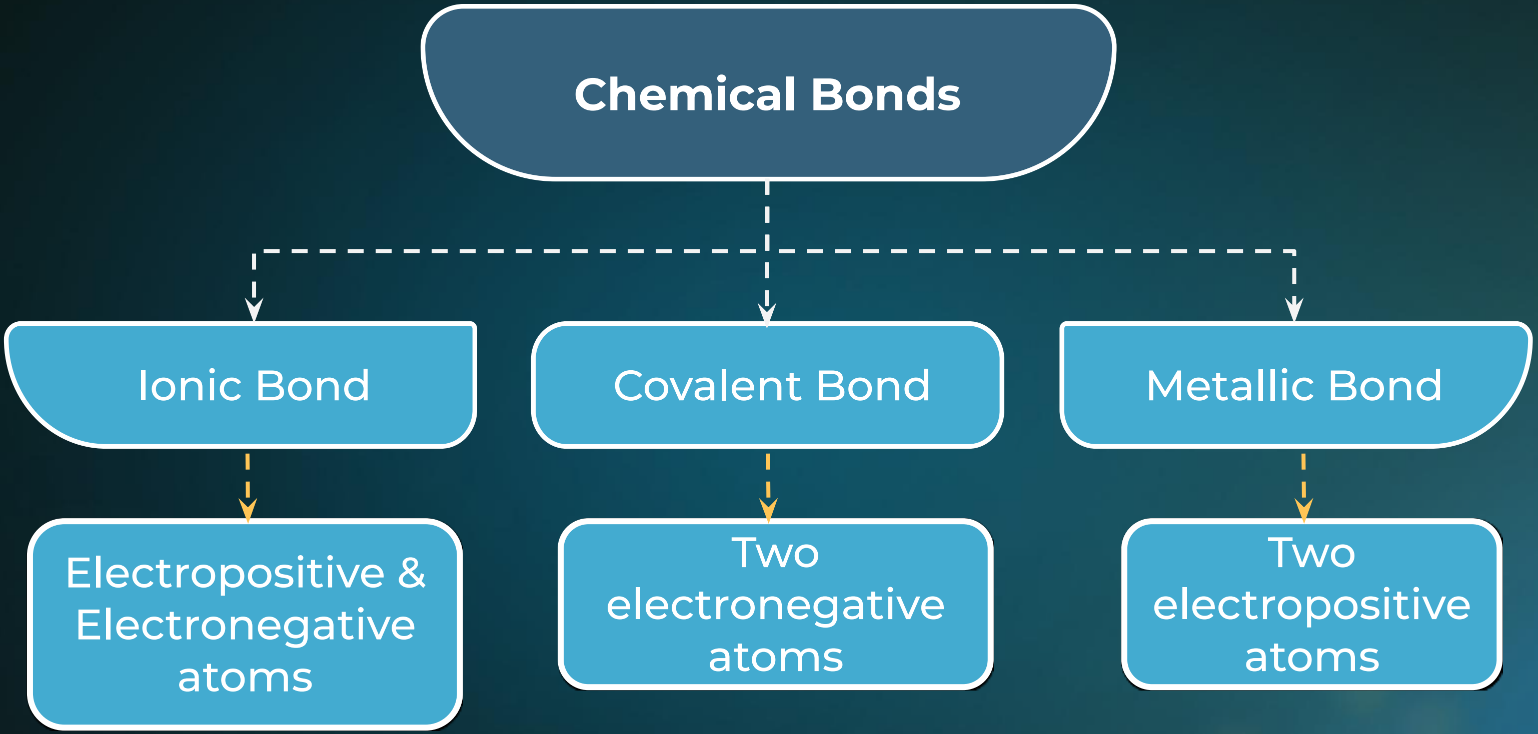
A chemical bond forms in order to reduce the energy of the chemical species involved in bonding, thereby increasing their stability.

Potential Energy Curve



Observed bond distance in H_2

At 74 pm, two H atoms have together minimum potential energy (hence maximum stability in the form of a H_2 molecule).



Chemical Bonds

Ionic Bond

Covalent Bond

Metallic Bond

Electropositive & Electronegative atoms

Two electronegative atoms

Two electropositive atoms

How Ionic Bonds are Formed?

Ionic Bond

Electrostatic force of attraction between oppositely charged ions.

To attain stable electronic configuration

Elements lose or gain electron(s) in order to have a stable electronic configuration in their valence shell

Formation of Ionic Bond

Elements involved in the ionic bond should possess

(1) The element losing electron should have **LOW ionisation enthalpy.**

(2) The element accepting electron should have **HIGH electron gain enthalpy.**

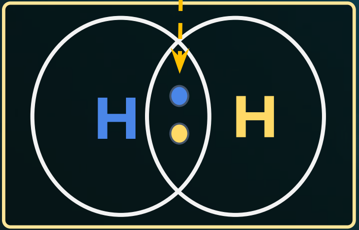
(3) **Large** difference in **electronegativity** of two elements

(4) **High Lattice enthalpy**

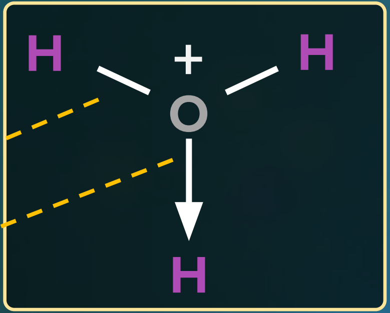
Covalent Bond and Coordinate Bond

A Covalent bond is formed by **sharing electrons.**

Shared pair of electrons



A bond in which the shared pair of electrons **originate from one atom** and none from the other is called coordinate bond.



Covalent Bond

Coordinate Bond

Metallic Bonds

Electrostatic force of attraction between a **metal kernel** and **valence electrons.**

Lattice Energy

Energy required to completely **separate one mole of solid** ionic compound into gaseous constituent ions.

$$\mathrm{NaCl\,(s)} \longrightarrow \mathrm{Na^{+}\,(g)} + \mathrm{Cl^{-}\,(g)}$$

$\mathrm{AB(s)} \longrightarrow \mathrm{A^{+}(g)} + \mathrm{B^{-}(g)}$; **Lattice Energy = Positive**

$\mathrm{A^{+}(g)} + \mathrm{B^{-}(g)} \longrightarrow \mathrm{AB(s)}$; **Lattice Energy = Negative**

Factors Affecting Lattice Energy

$$\text{Lattice Energy (L.E.)} \propto \frac{1}{r}$$

$$r^{+} + r^{-} = r$$

$$\text{Lattice Energy (L.E.)} \propto Z^{+} \times Z^{-}$$

r	Interionic distance
r^{+}	Radius of the cation
r^{-}	Radius of the anion

Z^{+}	Charge on the cation
Z^{-}	Charge on the anion

Lattice Energy

Charge is the deciding factor

Ionic compound	r (Å)	$Z^+ \times Z^-$	L.E. (kJ mol^{-1})
LiF	2.01	1	1004 kJ mol^{-1}
MgO	2.10	4	3933 kJ mol^{-1}

Order of Lattice Energy

KI < KBr < KCl < KF

BaO < SrO < CaO < MgO < BeO

NaF < MgF_2 < AlF_3

Properties of Ionic Compounds

01 **Soluble** in polar solvent

02 **High** Melting point and Boiling point

03 **Conduct Electricity** in aqueous & molten state

04 Exhibit **isomorphism** & **polymorphism**

05 Forms **crystal** in Solid state

06 Highly **Polar**

Isomorphism

Different ionic compounds having **similar crystal structure** are called isomorphs and this phenomenon is called **isomorphism.**

Isomorphous compounds have the **same type of formula .**

$FeSO_4.7H_2O$
Green vitriol

$MgSO_4.7H_2O$
Epsom salt

$ZnSO_4.7H_2O$
White vitriol

Polymorphism

Occurence of a particular substance in more than one **crystalline** form is called **polymorphism**

For example, ZnS exist as

(1) Sphalerite

(2) Wurtzite

Hydration Energy

Energy released when one mole of a **gaseous ion** is **hydrated** in large amount of water to form an **aqueous ion.**

Size of ion ↑ Hydration energy ↓

Charge of ion ↑ Hydration energy ↑

As the dielectric constant of solvent increases, **more energy is released** on **solvation**.

Solvation

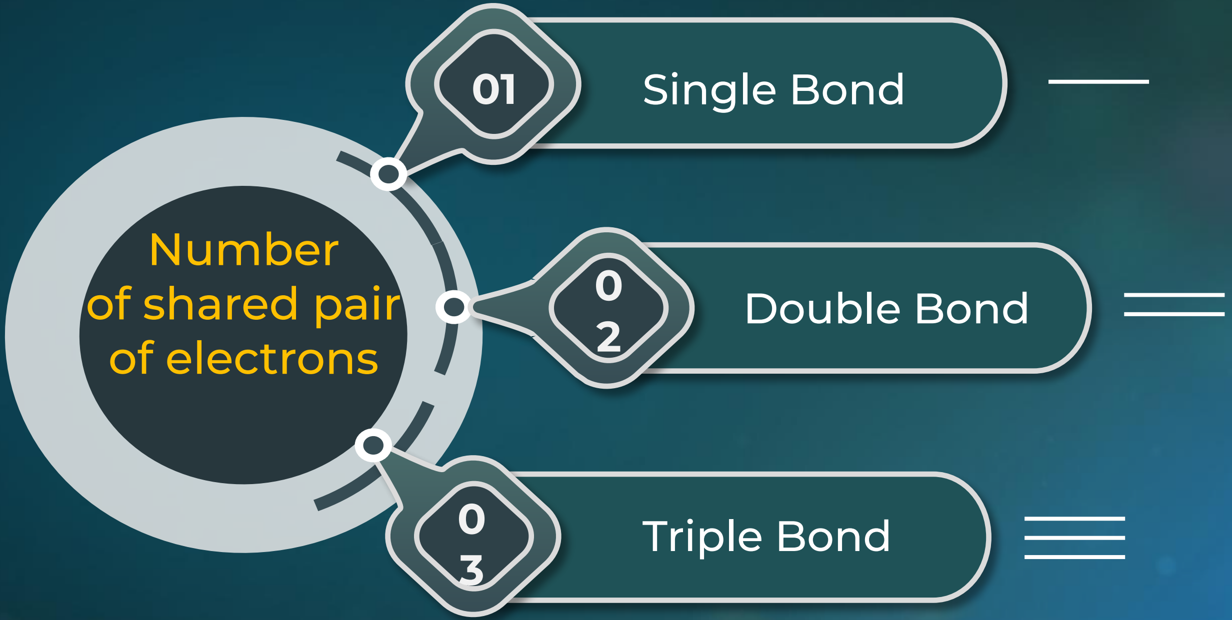
The interaction of the solute and the solvent molecules which **stabilizes the solute** in the solution

If the solvent is water, then it is known as Hydration

Dissolution of solute in water depends on **Lattice energy** and **Hydration energy**

Types of Covalent Bond

Formed by the **mutual sharing of electrons** between two atoms.



Number of shared pair of electrons

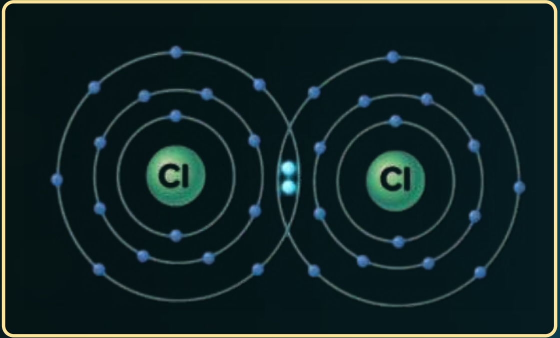
01 Single Bond

02 Double Bond

03 Triple Bond

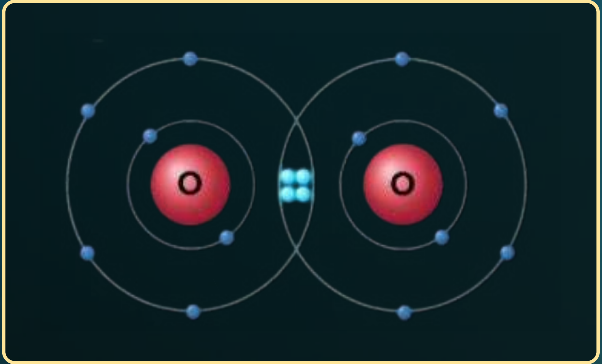
Types of Covalent Bond

(1) **One pair** of electrons is **shared**



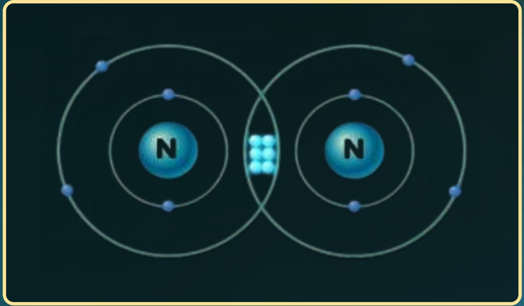
Single Covalent bond

(2) **Two pairs** of electrons are **shared**



Double Covalent bond

(3) **Three pairs** of electrons are **shared**



Triple Covalent bond

Theories of Covalent Bonding

- Kössel-Lewis Electronic theory
- VBT
- VSEPR
- MOT

Kossel Lewis Electronic Theory

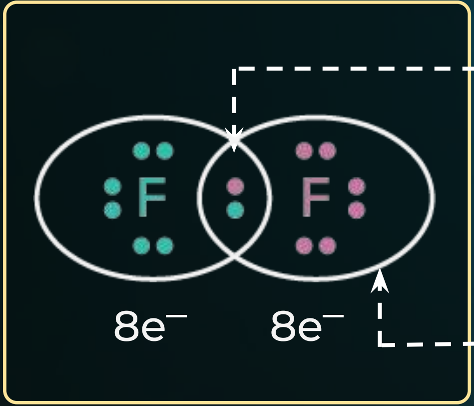
Atoms can combine by the **transfer of valence electrons** from one atom to another or by **sharing of electrons**.

Lewis Dot Structures

Combining **atoms contribute ≥ 1 electron(s)** to the shared pair

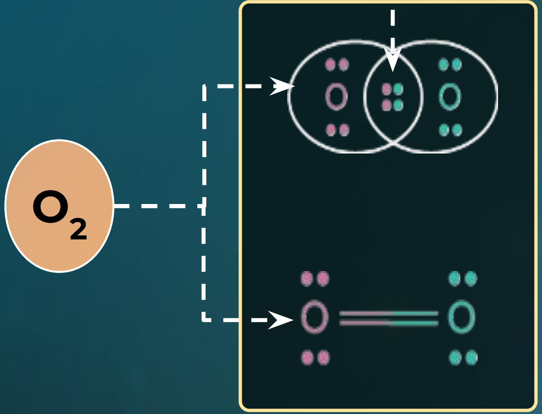
Covalent Bond

Attains **noble gas configuration**



Shared pair of electrons (e⁻)

Octet complete



Shared pair of electrons

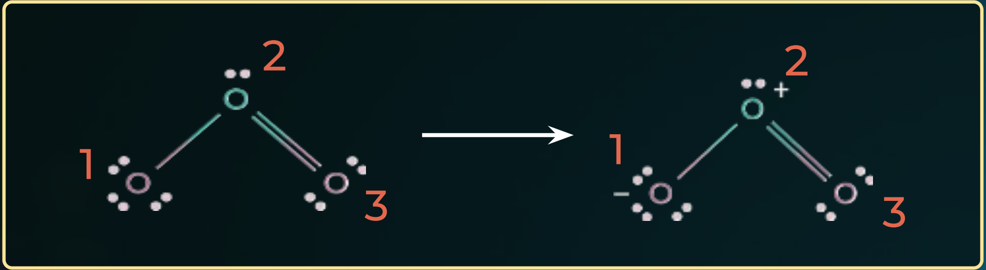
Formal Charge

01 It’s a theoretical charge over an individual atom of a molecule or an ion.

02 In polyatomic ions, the net charge is possessed by the whole ion.

03 Feasible to assign a formal charge on each atom.

Formal Charge



F.C. on O (1)	=	-1
F.C. on O (2)	=	+1
F.C. on O (3)	=	0

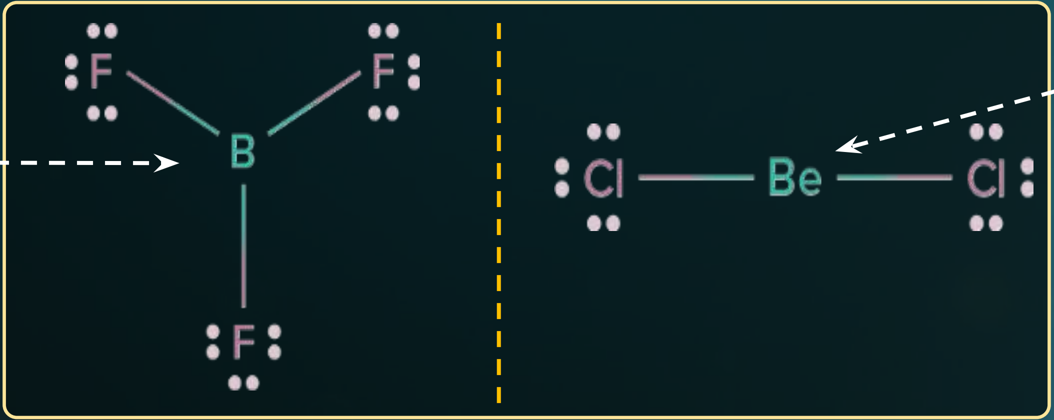
Used to give the **relative stability** of possible **Lewis structures**

Lowest energy structure:
Smallest formal charge on the atoms

Limitations of Octet Rule

1 Molecules with incomplete octet of the central atom

Hypovalent compound → **Electrons around central atom < 8**



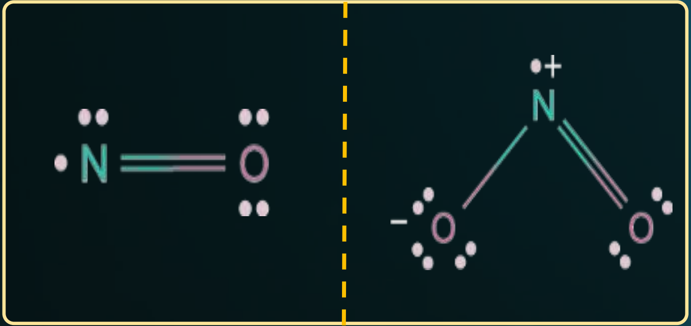
6 valence electrons

4 valence electrons

Limitations of Octet Rule

2 Molecules with odd electrons

NO, NO_2, ClO_2, ClO_3

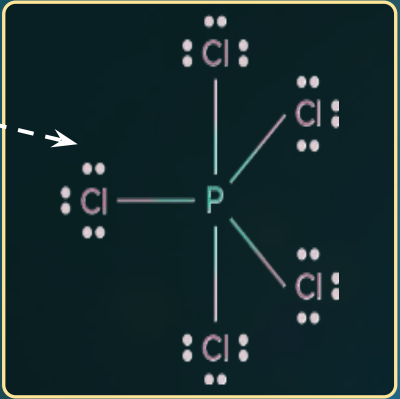


3 Molecules with expanded octet

Hypervalent compound

Electrons around central atom > 8

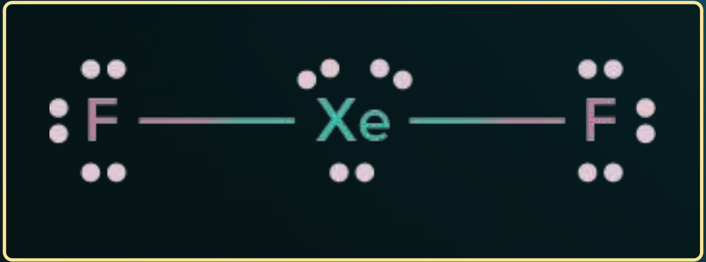
10 valence electrons



Limitations of Octet Rule

4 Formation of Xe & Kr compounds

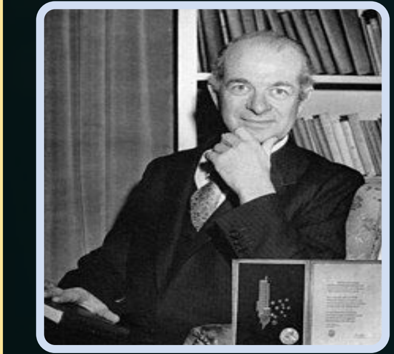
Xe and Kr form compounds with F and O even though their octet is already complete.



5 Doesn't account for the **shape** of the molecules

6 Doesn't explain about the **relative stability** of the molecules

Valence Bond Theory

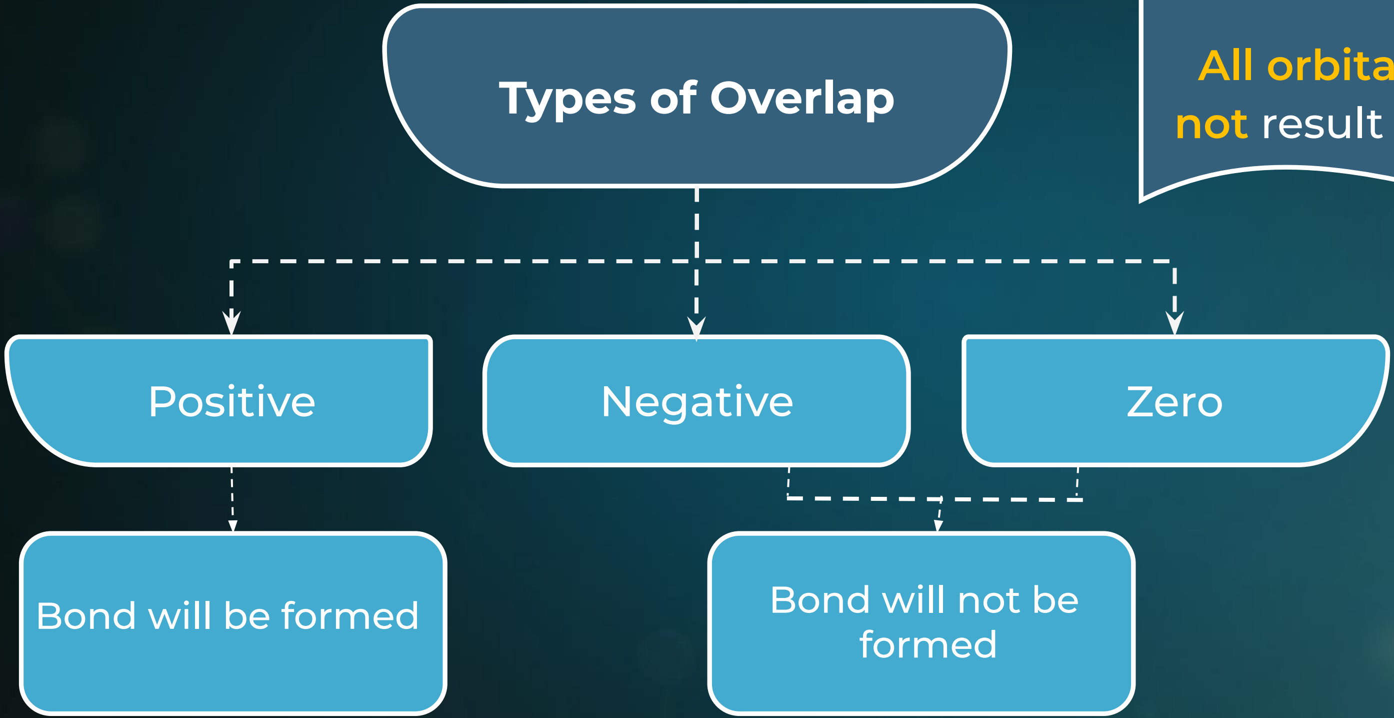


Linus Pauling

J.C. Slater

A covalent bond is formed by the **overlap** of half filled atomic orbitals that yield a pair of electrons shared between the two bonded atoms.

Orbital Overlap



Types of Overlap

Positive

Negative

Zero

Bond will be formed

Bond will not be formed

All orbital overlappings **do not** result in **bond formation**

Directional Properties of Bonds

Covalent Bond: **Directional**

Ionic Bond: **Non-Directional**

Coordinate or Dative Bond

Bond formed by sharing of electrons between two atoms. Shared pair of electrons is contributed by **only one of the two atoms.** Co ordinate bond once formed cannot be distinguished from covalent bond. Covalent and coordinate bond are same with respect to bond properties.

How to Identify Coordinate Bond?

Different covalency than usual

Example: N_2O

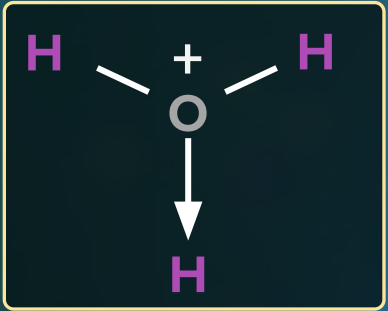
Fourth bond formed by **N** is always coordinate

$N \equiv \overset{+}{N} - \overset{-}{O}$

Presence of coordinate bond

Example: $[H_3O^+]$

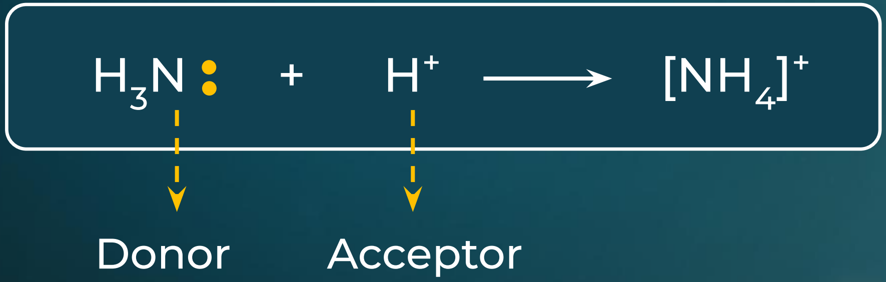
Third bond formed by **O** is always coordinate



Lewis Acid and Lewis Base

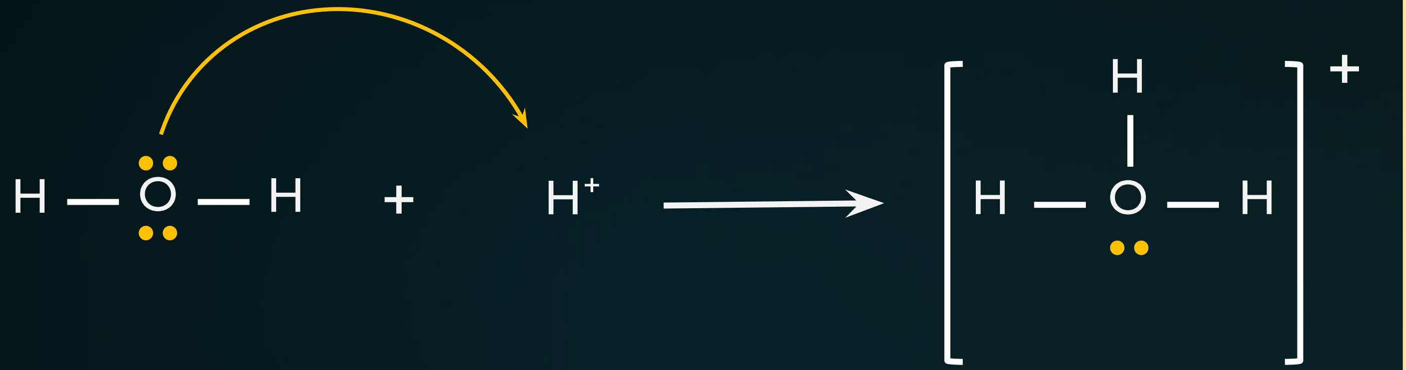
Lone pair donors are called **Lewis bases**

Lone pair acceptors are called **Lewis acids**



$$H_3N: + H^+ \longrightarrow [NH_4]^+$$

Co-ordinate Bond or Dative Bond



$$\mathrm{H-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}-H} + \mathrm{H^{+}} \longrightarrow \left[\mathrm{H-\underset{\bullet\bullet}{\overset{\overset{H}{|}}{O}}-H}\right]^{+}$$

or H_3O^+

Sigma and pi-bonds

Covalent Bond

Sigma (σ) bond

Sigma bond is formed when overlapping takes place along the **internuclear axis of orbitals** or when an **axial overlap** takes place.

Pi (π) bond

Pi (π) bond is formed when axes of combining orbitals are **perpendicular** to the internuclear axis i.e., **lateral** or **sidewise overlapping** takes place.

Axial or Head-on Overlapping

Cylindrically symmetrical about the internuclear axis

Can undergo **rotation** about the internuclear axis

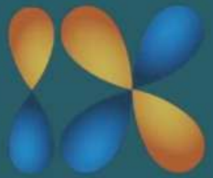
Generally, π bond between two atoms is formed in **addition to a σ bond**

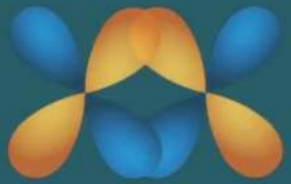
Types of π bond

pπ-pπ overlap

pπ-dπ overlap

dπ-dπ overlap





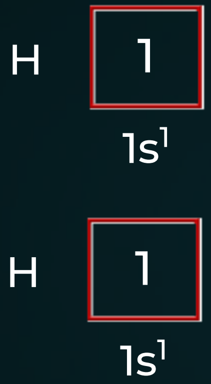
Bond Strength

In general, order of strength of bond

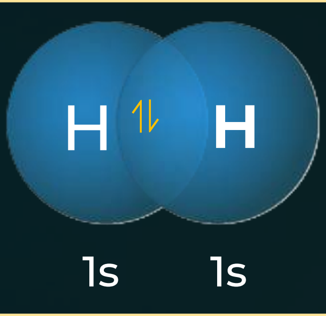
π < σ

- Greater the extent of overlapping, more will be the bond strength.
- For same value of n,
  s-s sigma overlap < s-p sigma overlap < p-p sigma overlap
- **Strength of π bonds:** 3p-3p π overlap < 2p-2p π overlap

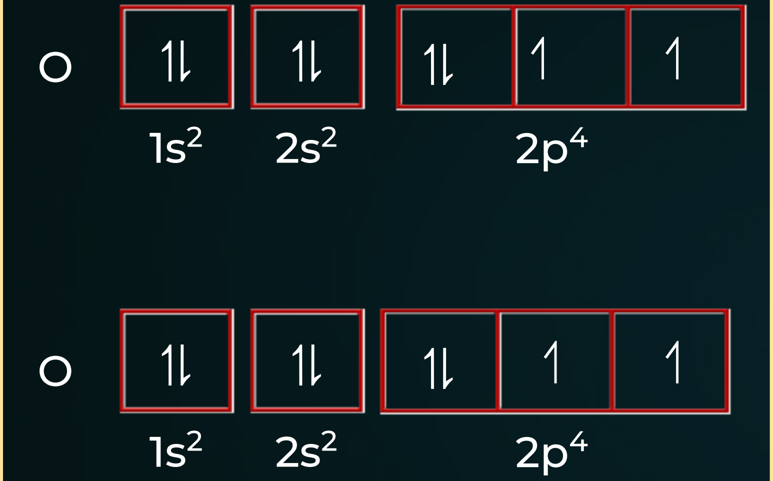
Bonding in H_2 Molecule



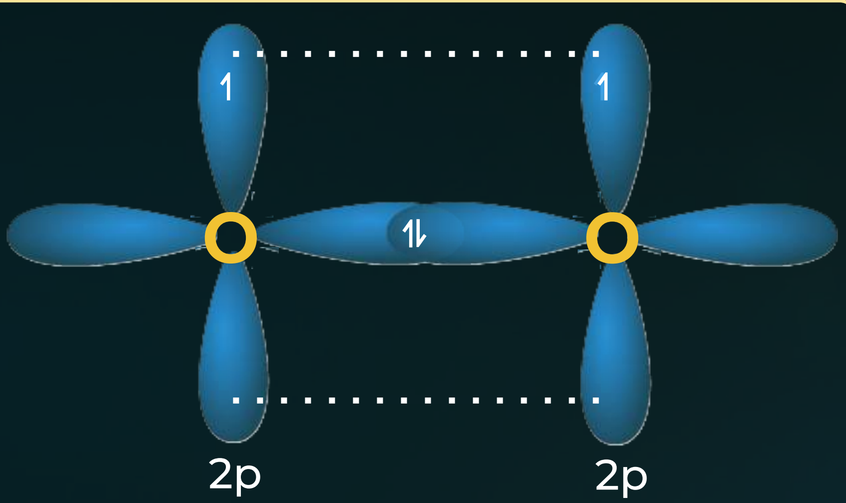
i.e. $\mathrm{H}\overset{\sigma}{-\!\!-\!\!-}\mathrm{H}$



Bonding in O_2 Molecule



i.e. $O \underset{\pi}{\overset{\sigma}{=}} O$

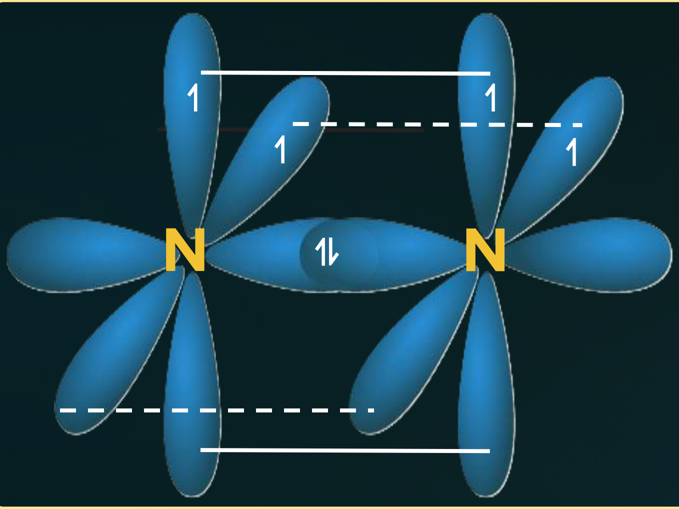


Bonding in N_2 Molecule

N	↑↓	↑↓	↑	↑	↑
	$1s^2$	$2s^2$		$2p^3$	

N	↑↓	↑↓	↑	↑	↑
	$1s^2$	$2s^2$		$2p^3$	

i.e. $N \overset{\sigma}{\underset{2\pi}{\equiv}} N$



Limitations of VBT

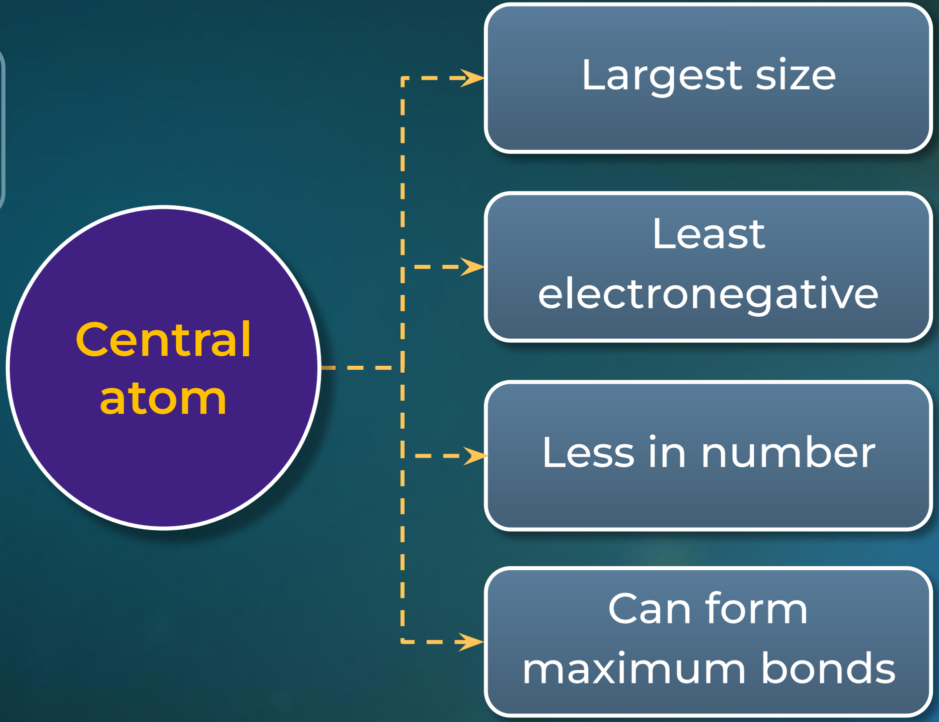
Paramagnetic nature of O_2 could not be explained.

Fails to account for the **geometry and shapes** of various molecules.

Steps to Draw Structures

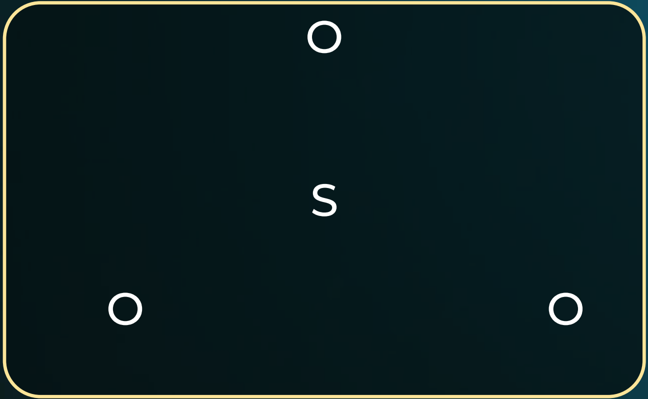
01 Select the central atom

SO_3 - Sulphur



Steps to Draw Structures

02 Draw a symmetrical skeleton of atoms.



03 Calculate the total number of valence electrons

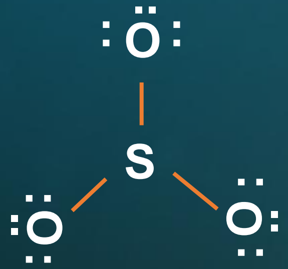
Valence electrons in SO_3 = $6 + (3 \times 6)$
= 24

Electron pairs = $\frac{24}{2}$ = 12

Steps to Draw Structures

04

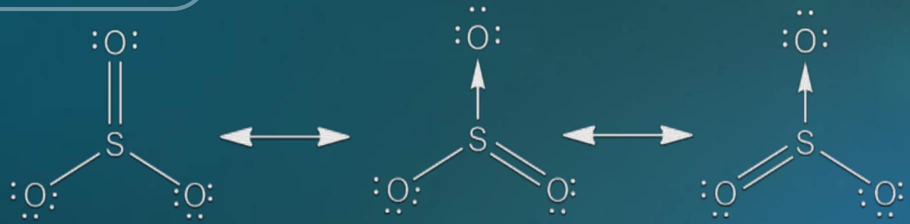
Make a single bond using the electron pairs. Then complete the octet of the side atoms. If any electron pair is left, assign it to the central atom.



Steps to Draw Structures

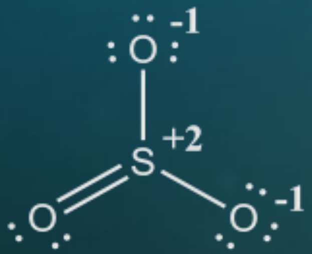
05

If the octet of central atom is not complete, use the lone pairs of side atoms to make the bonds and complete the octet.



06

Assign formal charge on each atom



VSEPR Theory

Used to provide **shape** and **electronic geometry** of covalent compounds.

1. Shape of a molecule depends upon the **number of valence shell electron pairs** around the **central atom**

2. Valence shell is taken as a sphere with the **electron pairs localising** on the **spherical surface**

3. **Electron pairs** in the **valence shell** repel one another since, they are all **negatively charged**

VSEPR Theory

4. Electron pairs occupy positions in space that tend to **minimise repulsion.**

5. **Lone pair** occupies more space on the sphere. So, the order of repulsion is:

lp-lp > lp-bp > bp-bp

(lp: Lone pair,
bp: Bonding pair)

VSEPR Theory

6. A **multiple bond** is treated as a **single bonding pair.**

There is **no effect** of **pi bond** on geometry and shape

Compound	Shape	π bond(s)
Cl - Be - Cl	Linear	0
$O = \overset{+}{C} - H$	Linear	1
O = C = O	Linear	2
H - C ≡ N	Linear	2

Point to Remember!!

For **electronic geometry** → Both **bond pairs** and **lone pairs** are considered

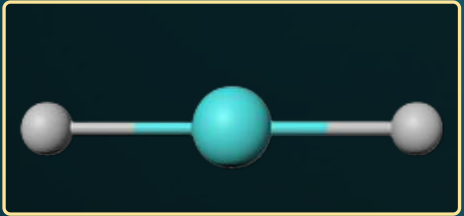
For **shape** → Only **bond pairs** are considered

VSEPR Theory

General Formula: AB_2

(A: Central atom, B: Side atom)

Electron pairs	Bonding pairs	Lone pairs	Electronic Geometry	Shape
2	2	0	Linear	Linear



Bond Angle = 180°

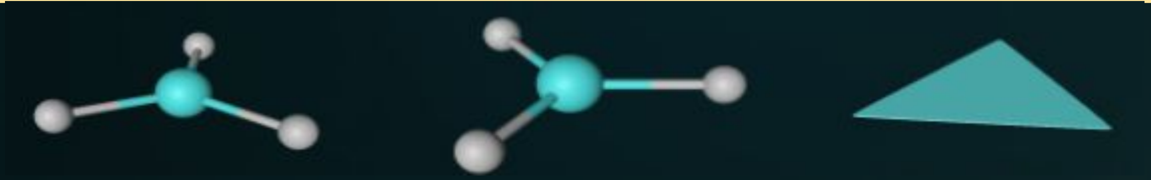
Example: CO_2, $BeCl_2$

VSEPR Theory

General Formula: AB_3

(A: Central atom, B: Side atom)

Electron pairs	Bonding pairs	Lone pairs	Electronic Geometry	Shape
3	3	0	Trigonal Planar	Trigonal Planar



Bond Angle = 120°

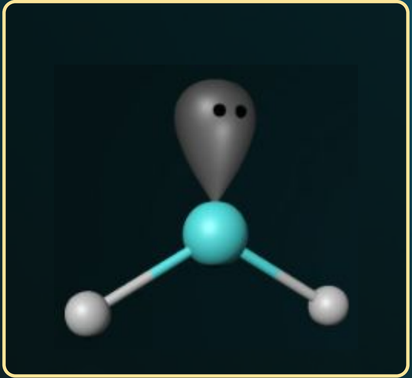
Example: BF_3, SO_3

VSEPR Theory

General Formula: **AB_2L**

(A: Central atom, B: Side atom, L: Lone pair)

Electron Pairs	Bonding Pairs	Lone Pairs	Electronic Geometry	Shape
3	2	1	Trigonal Planar	Bent/ V-Shape

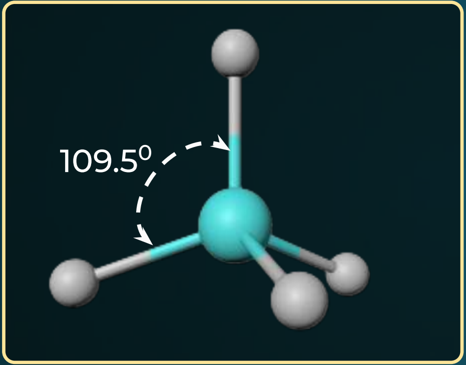


Bond Angle < 120°

Example: SO_2, $SnCl_2$

VSEPR Theory

Steric Number: 4 (sp^3)
(AB_4)



Bond Angle = 109.5°

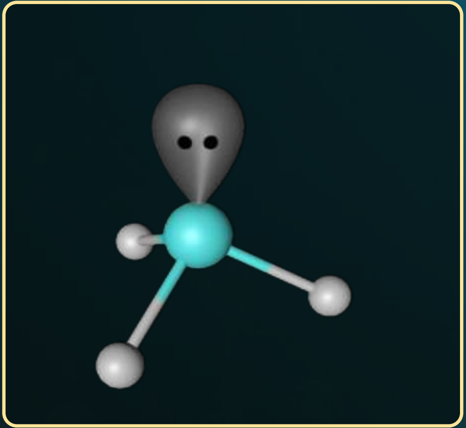
Example: CH_4, $[NH_4]^+$, XeO_4

VSEPR Theory

General Formula: **AB_3L**

(A: Central atom, B: Side atom, L: Lone pair)

Electron Pairs	Bonding Pairs	Lone Pairs	Electronic Geometry	Shape
4	3	1	Tetrahedral	Pyramidal



Bond Angle < 109.5°

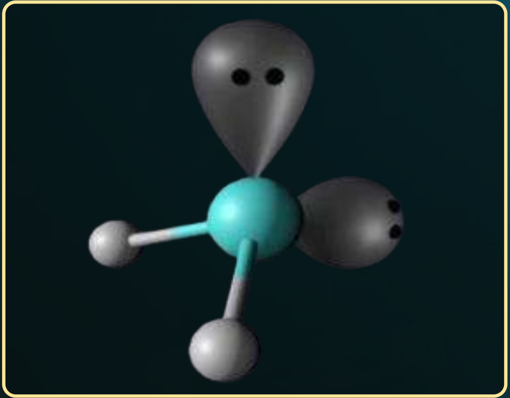
Example: NH_3, XeO_3, PCl_3

VSEPR Theory

General Formula: AB_2L_2

(A: Central atom, B: Side atom, L: Lone pair)

Electron Pairs	Bonding Pairs	Lone Pairs	Electronic Geometry	Shape
4	2	2	Tetrahedral	Bent or V-Shape



Bond Angle < 109.5°

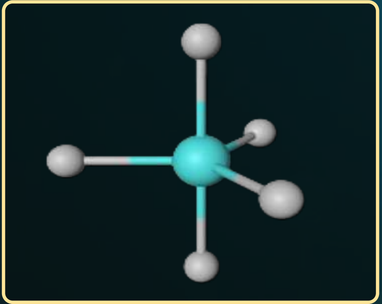
Example: H_2O, OF_2

VSEPR Theory

General Formula: AB_5

(A: Central atom, B: Side atom)

Electron Pairs	Bonding Pairs	Lone Pairs	Electronic Geometry	Shape
5	5	0	Trigonal Bipyramidal (T.B.P.)	Trigonal Bipyramidal (T.B.P.)

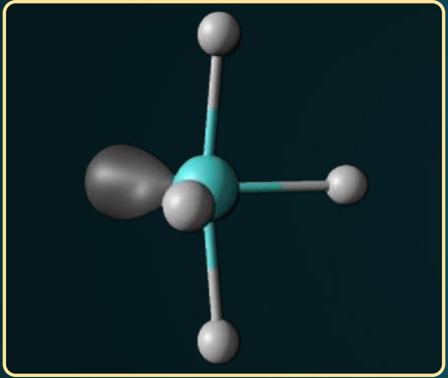


Bond Angle = 90°, 120°, 180°

Example: PCl_5, SOF_4

Valence Shell Electron Pair Repulsion Theory (VSEPR)

Steric Number: 5 (sp^3d) (AB_4L)



Bond Angle < 90° , 120°

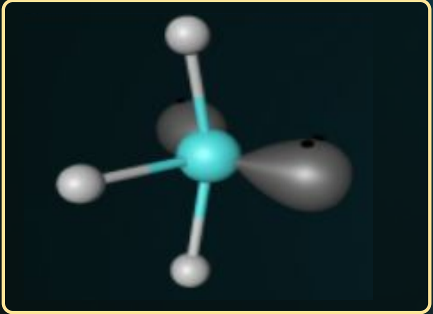
Example: SF_4, XeO_2F_2

VSEPR Theory

General Formula: AB_3L_2

(A: Central atom, B: Side atom, L: Lone pairs)

Electron Pairs	Bonding Pairs	Lone Pairs	Electronic Geometry	Shape
5	3	2	Trigonal Bipyramidal (T.B.P.)	T-Shape



Bond Angle < 90°, 180°

Example: ClF_3

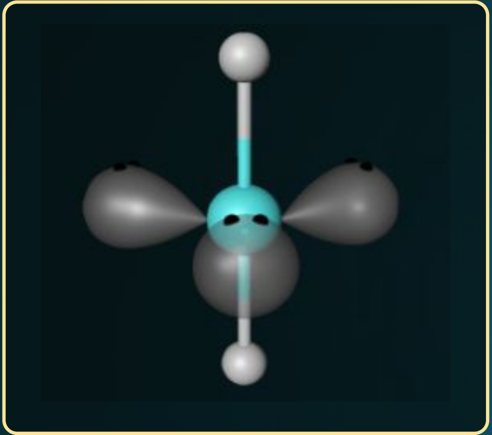
VSEPR Theory

General Formula: AB_2L_3

(A: Central atom, B: Side atom, L: Lone pairs)

Electron Pairs	Bonding Pairs	Lone Pairs	Electronic Geometry	Shape
5	2	3	Trigonal Bipyramidal (T.B.P.)	Linear

AB_2L_3

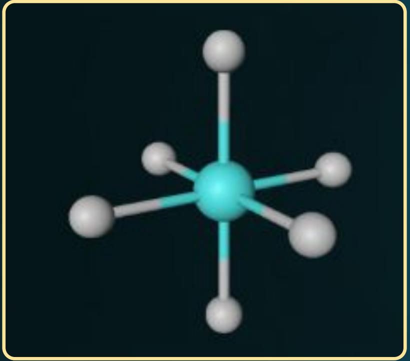
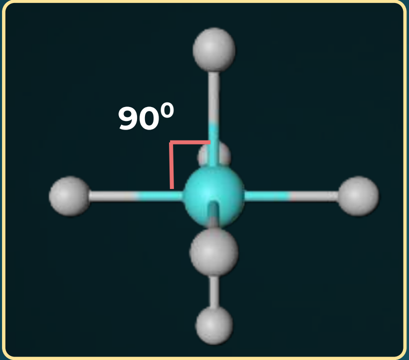


Bond Angle = 180°

Example: XeF_2, I_3^-

VSEPR Theory

Steric Number: 6 (sp^3d^2) (AB_6)

Bond Angle = 90°

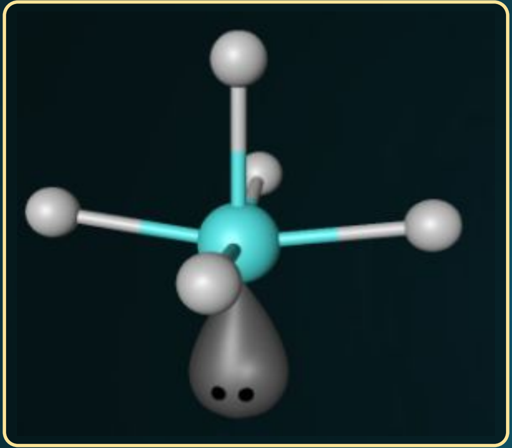
Example: SF_6

VSEPR Theory

General Formula	Electron Pairs	Bonding Pairs	Lone Pairs	Electronic Geometry	Shape
AB_5L	6	5	1	Octahedral	Square Pyramidal
AB_4L_2	6	4	2	Octahedral	Square Planar

(A: Central atom, B: Side atom, L: Lone pairs)

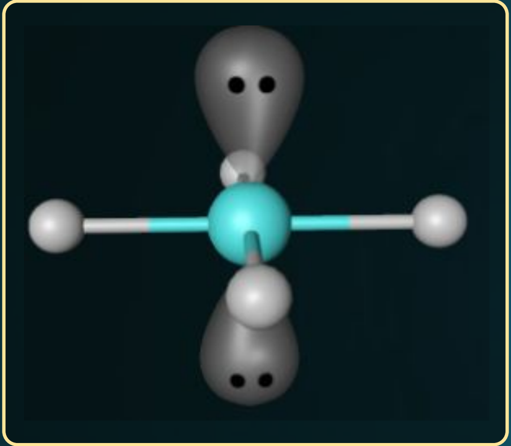
AB_5L



Bond Angle < 90°, 180°

Example: BrF_5, $XeOF_4$

AB_4L_2

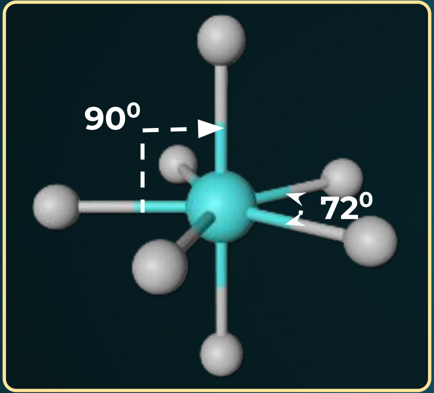


Bond Angle = 90°, 180°

Example: XeF_4

VSEPR Theory

Steric Number: 7 (sp^3d^3)
(AB_7)



Bond Angle = 72°, 90°

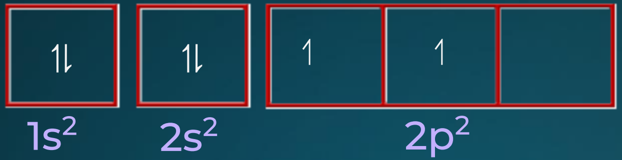
Example: IF_7

Need for Hybridisation

Shape of CH_4 Molecule

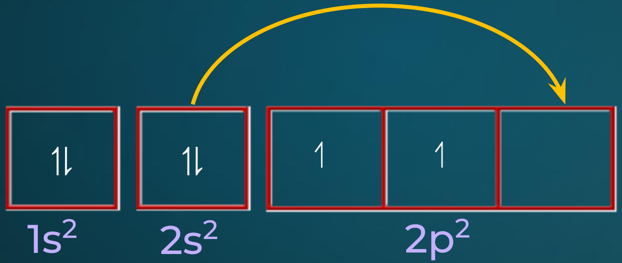
Electronic configuration of carbon is:

$C_{\text{Ground State}}$: [He] $2s^2\ 2p^2$

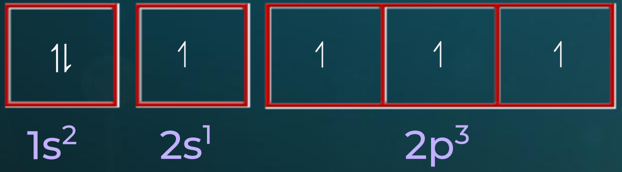


On excitation,

$C_{\text{Ground State}}$: [He] $2s^2\ 2p^2$

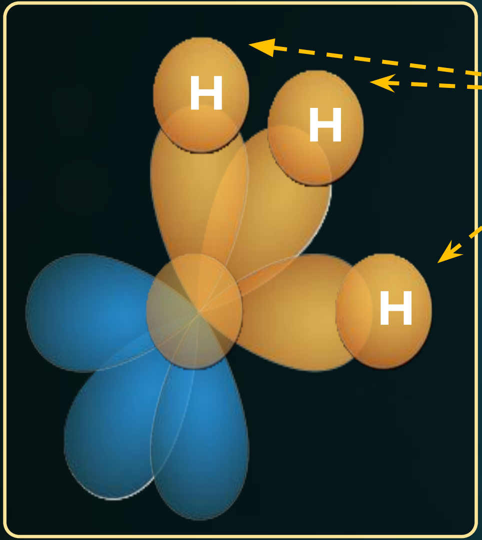


$C_{\text{Excited state}}$: [He] $2s^1\ 2p^3$



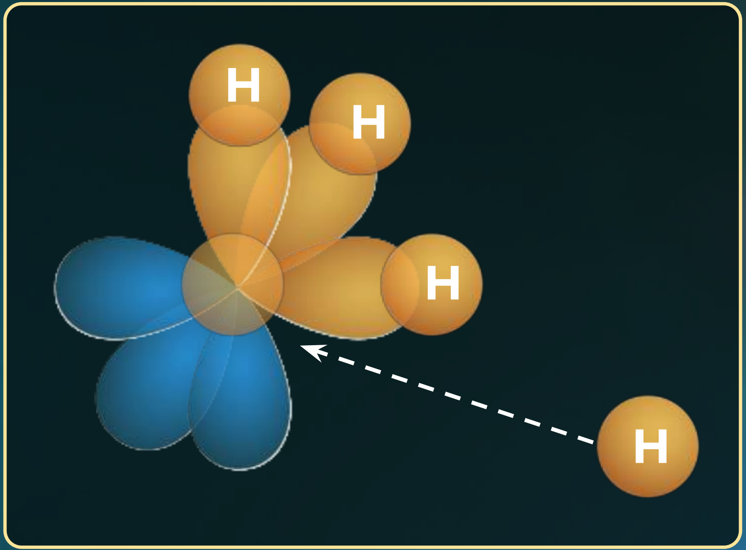
Release of energy due to **overlap between the orbitals** of **C and H**

Shape of CH_4 Molecule



C-H bonds formed by s (H)-p (C) overlapping

Angle between them will be 90°



4th C-H Bond will be formed by s (C)-s (H) overlap

Shape of CH_4 Molecule

s-orbital overlap can be in any direction

Direction of fourth C–H bond **cannot** be determined

Shape of CH_4 Molecule

Expected observations

All H-C-H bond angles are not certain

3 C-H bonds formed by s-p overlap are stronger than 1 C-H bond formed by s-s overlap

Experimental observations

All H-C-H bond angles are identical with a value of 109.5°

All C-H bond lengths and bond strengths are identical

Limitations of VBT

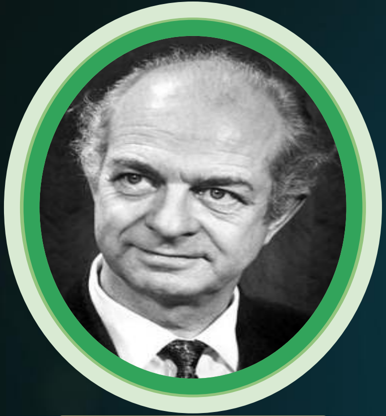
Formation of diatomic molecules are satisfactorily explained (except the paramagnetic nature of **O_2**)

VBT **fails to explain** the **bond properties** in polyatomic molecules

Hybridization + **VBT**

More complete theory to explain **polyatomic molecules**

Hybridisation



Pauling

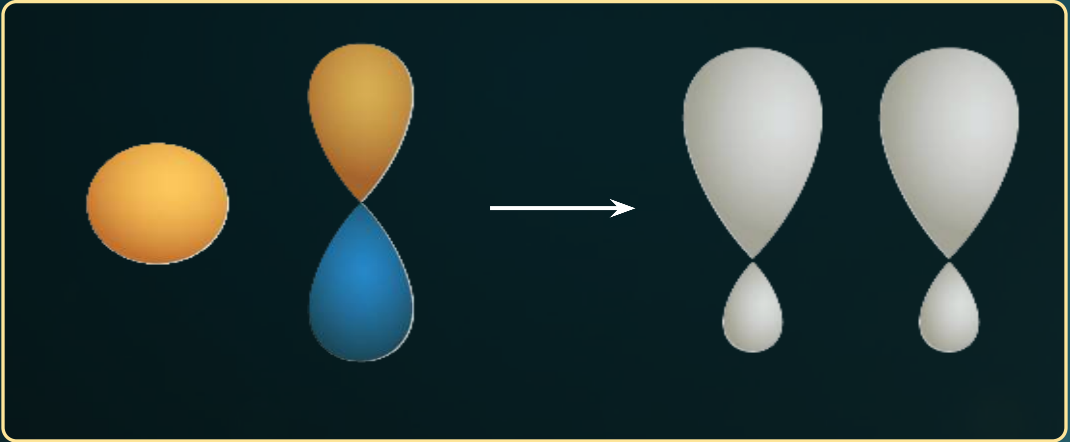
J.C. Slater

(1) **Intermixing** of atomic orbitals of equal **or slightly different energies,** results in the formation of **new set** of **orbitals of equivalent energies** and **shape.**

(2) The **orbitals** present in the **valence shell** (and sometimes **penultimate shell** also) of the atom can hybridise.

Hybridisation and Shape of Hybrid Orbitals

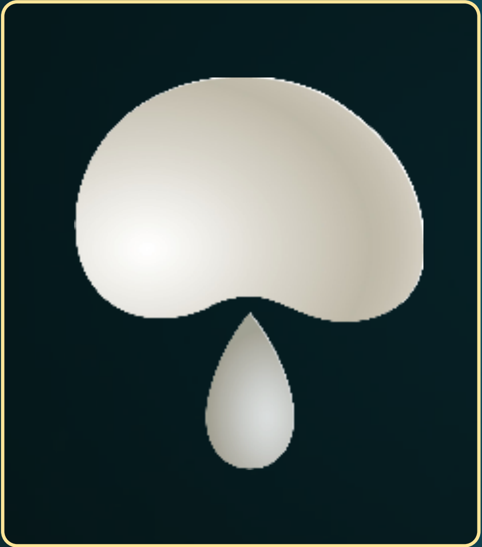
Number of **hybrid orbitals (H.O.)** = Number of **atomic orbitals intermixing**



Larger lobe of H.O. takes part in **bond formation** (σ-bond)

Did you Know?

Hybrid Orbital



Actual Shape

Shape used for representation

Naming of Hybrid Orbitals

On the basis of atomic orbitals participating in hybridization:

s-orbital + ‘n’ p-orbital + ‘m’ d-orbital

$\downarrow$

sp^nd^m hybrid orbital

Types of Hybridisation

sp

sp^2

sp^3

sp^3d

sp^3d^2

sp^3d^3

Important Conditions for Hybridisation

Orbitals can

- Have a pair of electrons
- Have an unpaired e^-
- Be vacant

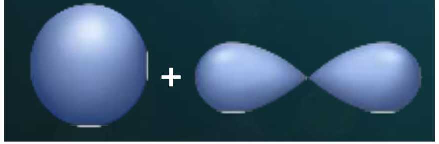
All three types can undergo hybridisation

Salient Features of Hybridisation

Promotion of electron is not an essential condition prior to hybridisation.

Orbitals undergo hybridisation and not the electrons.

Hybrid orbitals generally form σ bond.

Participating atomic orbitals	Number of hybridised orbitals	Hybridisation
One s + One p 	2	sp

% s Character

$$\%\ s\ \text{character} = \frac{\text{Number of s orbitals}}{\text{Number of (s+p) orbitals}} \times 100$$

sp > sp^2 > sp^3

Decreasing order of **s character**

Percentage Character of Orbitals

- sp
  - 50% s
  - 50% p
- sp^2
  - 33.33% s
  - 66.66% p
- sp^3
  - 25% s
  - 75% p

% s character increases	% p or % d character increases
Orbital becomes bulkier and shorter	Orbital becomes thinner and longer
Energy of hybrid orbital decreases	Energy of hybrid orbital increases
Electronegativity increases	Electronegativity decreases

Features of Hybridisation

% s character in hybrid orbital ↑ → Stability of hybrid orbital ↑ → Bond Strength ↑

$sp - p > sp^2 - p > sp^3 - p > p - p$

→

Decreasing order of **bond strength**

Hybrid orbitals are directed in space in a way to have **minimum repulsion** between the electron pairs → in order to obtain a **stable arrangement**

Steric Number

Type of hybridisation is estimated by steric number

Steric Number = Number of σ bonds of central atom + Number of lone pairs on central atom

$$\text{Steric Number} = \frac{V + M - q}{2}$$

Type of **hybridization** indicates the **geometry** of the molecule

Steric Number, Hybridization and Geometry

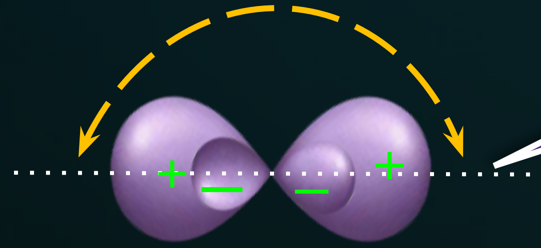
Steric number	Hybridization	Geometry	Involving Orbitals
2	sp	Linear	s, p_x/ p_z/ p_y
3	sp^2	Trigonal Planar	s, p_x, p_z/ p_y, p_z/p_x, p_y
4	sp^3	Tetrahedral	s, p_x, p_z, p_y
5	sp^3d	Trigonal bipyramidal	s, p_x, p_z, p_y, d_{z^2}
6	sp^3d^2	Octahedral	s, p_x, p_z, p_y, d_{z^2}, $d_{x^2-y^2}$
7	sp^3d^3	Pentagonal bipyramidal	s, p_x, p_z, p_y, d_{z^2}, $d_{x^2-y^2}$, d_{xy}

Methods for Finding Hybridisation

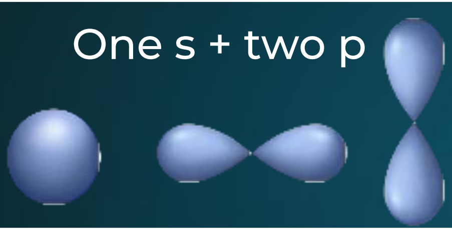
- Determination of type of hybridisation
  - Orbital Box Diagrams
  - Finding Steric Number
  - Formula for Steric Number

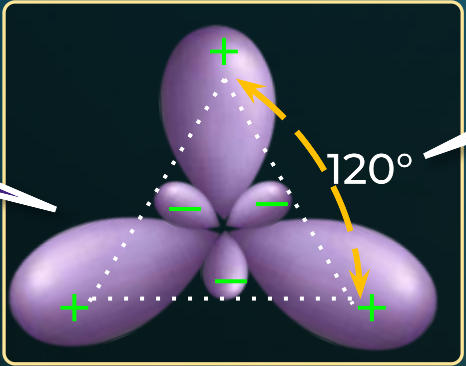
sp Hybridisation

Participating atomic orbitals	Number of hybridised orbitals	Hybridisation
One s + One p 	2	sp



sp^2 Hybridisation

Atomic orbitals participating in hybridisation	Number of hybridised orbitals	Hybridisation
One s + two p 	3	sp^2

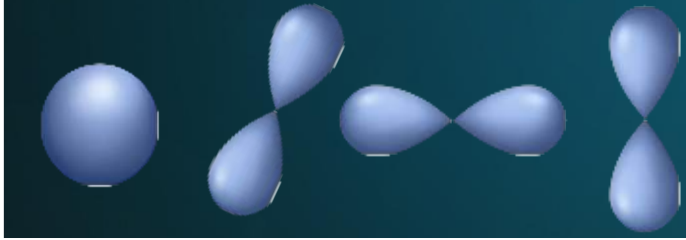


3 new sp^2 hybridised orbitals

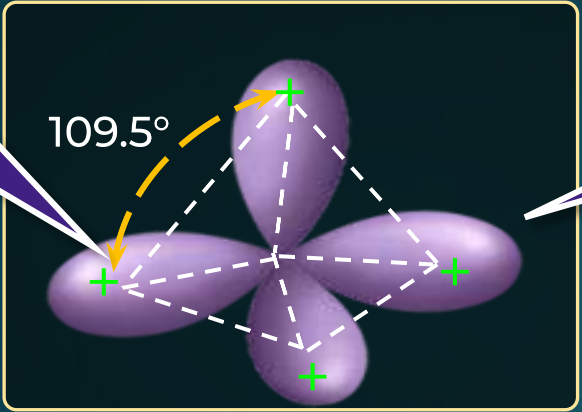
Trigonal planar

sp^2 Hybridisation

sp^3 Hybridisation

Atomic orbitals participating in hybridisation	Number of hybridised orbitals	Hybridisation
One s + three p 	4	sp^3

sp^3 Hybridisation



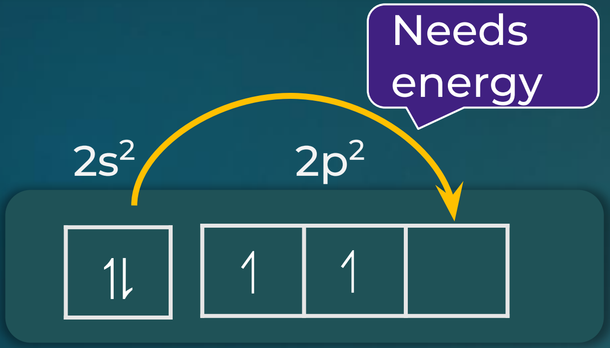
4 new sp^3 hybridised orbitals

Tetrahedral

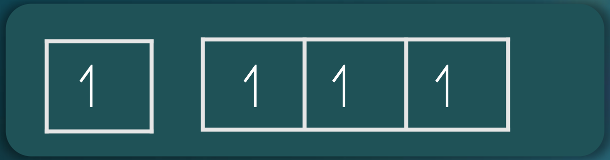
Bonding of CH_4 Molecule

Here, electronic configuration of carbon is

$C_{\text{Ground State}}$: [He] $2s^2\,2p^2$


Needs energy

$C_{\text{Excited state}}$: [He] $2s^1\,2p_x^1\,2p_y^1\,2p_z^1$



Bent’s Rule

In T.B.P. geometry,

Equatorial position

High % s character

Occupied by **lone pair, multiple bond**

Axial position

Low % s character

Occupied by more **electronegative** element

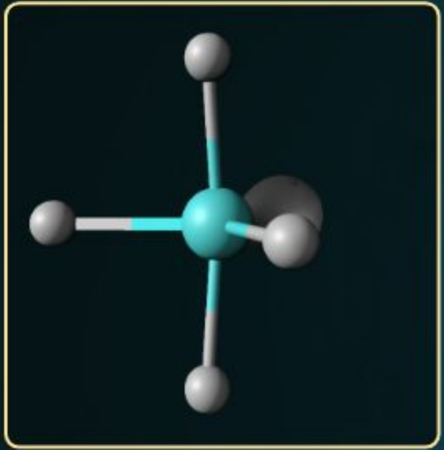
Berry Pseudorotation

Fluxional behaviour of **PF_5** due to fast exchange between axial and equatorial F atoms

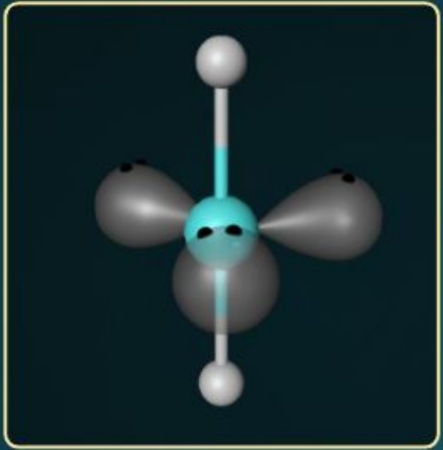
All P-F bonds are observed to be equivalent

Energy difference b/w **T.B.P.** and **square pyramidal** geometry < **Thermal energy** at room temperature

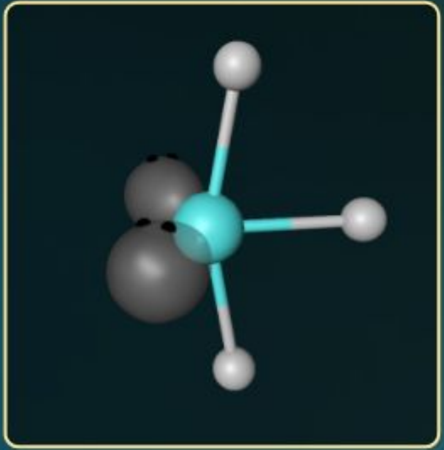
Examples of sp^3d Hybridisation



SF_4



XeF_2



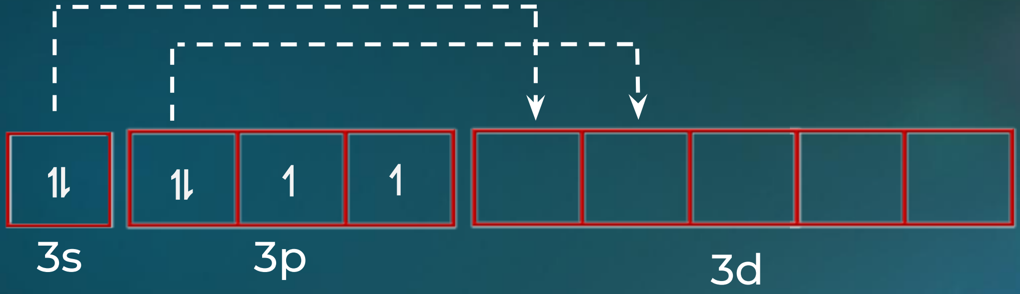
$XeOF_2$

sp^3d^2 Hybridisation

SF_6

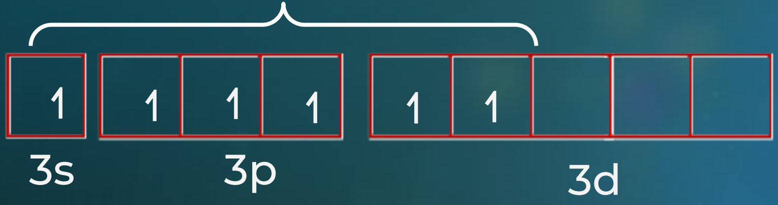
$S_{\text{Ground state}}$: [Ne] $3s^2 3p^4$

On excitation:



$S_{\text{Excited state}}$: [Ne] $3s^1 3p^3 3d^2$

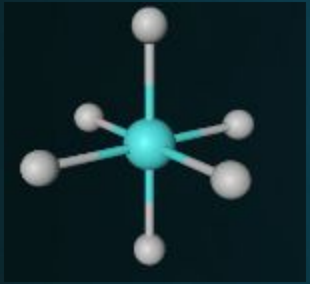
Hybridized orbitals



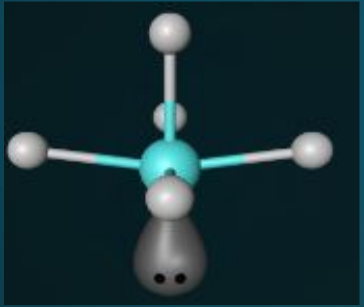
sp^3d^2 Hybridisation

No equatorial & no axial bonds

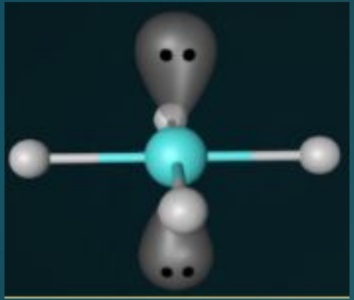
All Bond lengths are observed to be **identical**



SF_6

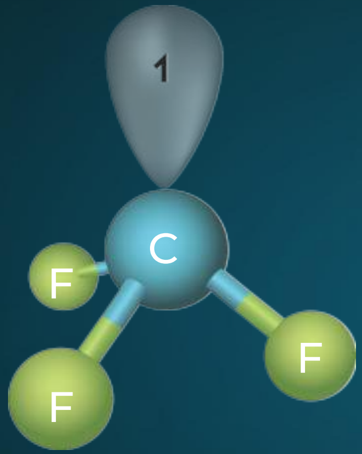


$XeOF_4$

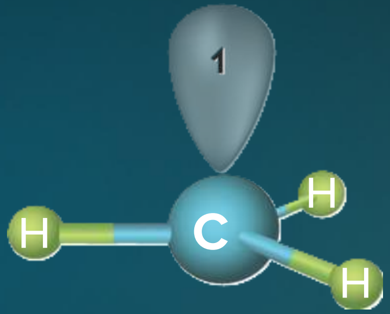


XeF_4

Hybridisation in Odd Electron Species



Hybridisation:
sp^3



Hybridisation:
sp^2

Did you Know?

$$PCl_5(s) \longrightarrow [PCl_4]^+ [PCl_6]^-$$

sp^3 sp^3d^2

$$PBr_5(s) \longrightarrow [PBr_4]^+ [Br]^-$$

sp^3

$$PI_5(s) \longrightarrow \text{Does not exist}$$

P cannot accomodate 6 large sized Br & I.
So, it cannot form PX_6^-.

Resonance

Phenomenon of delocalisation of π electrons

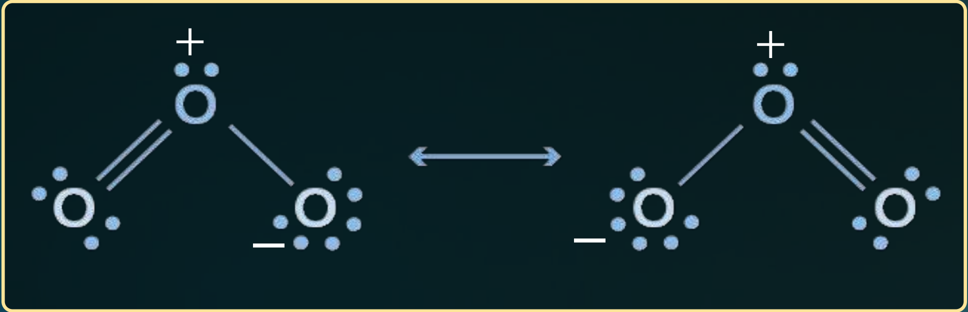
Most important parameter to explain the stability of certain molecule

If a single Lewis structure cannot represent a molecule

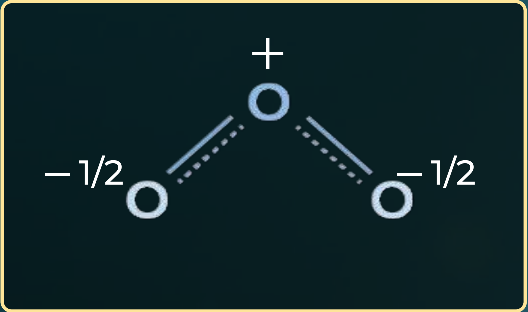
Resonance structures describe the molecule accurately

Need of the theory

Resonance Structures of O_3



Resonance Hybrid of O_3



Resonance

Molecules having Resonance

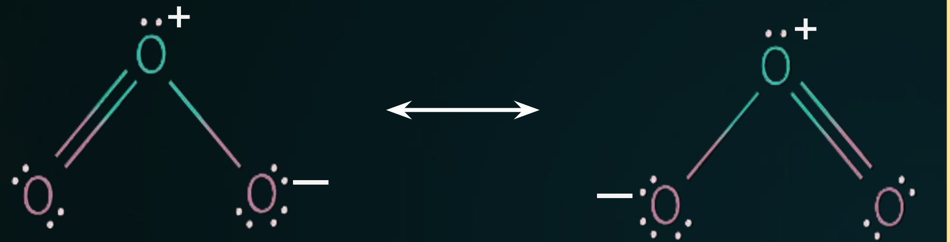
Resonance Structures (R.S.)

- Similar or **degenerate Energy**
- **Identical positions** of **nuclei**
- **Same** number of bonding & nonbonding **electron pairs**

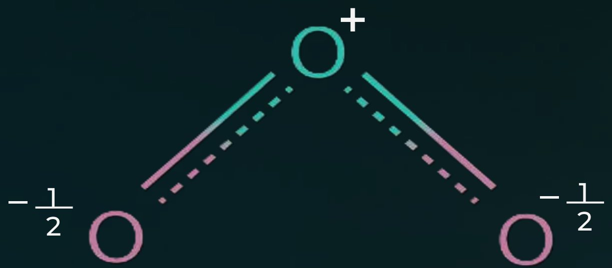
Resonance Hybrid (R.H.)

- Actual structure of **different possible** structures
- Does not violate the rules of **covalence maxima**
- **Most stable R.S.** contributes maximum towards **Resonance hybrid (R.H.)**

Resonance Structures (R.S.) and Resonance Hybrid (R.H.)



Resonance Structures of O_3



Resonance hybrid of O_3

Characteristics of Resonance

Resonance structures (R.S.) are hypothetical

Resonance hybrid (R.H.) has its **individual identity**

Bond lengths of R.H. are intermediate to those of **R.S.**

Conditions of Resonance

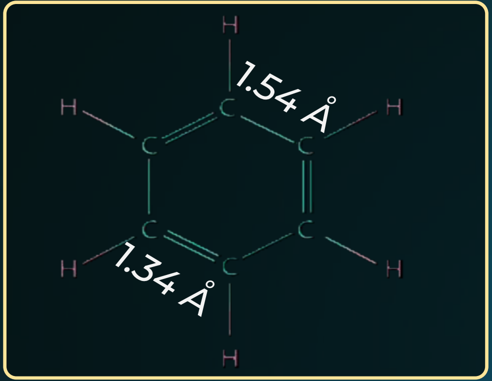
Structure should be **planar**

Occurs in adjacent parallel p-orbitals

Rules for Resonance Structures

- A Must have proper **Lewis structures**
- B Only **π electrons** or **lone pairs** can be moved
- C Overall **charge** of the system must **remain** the **same**
- D **Bonding framework** of a molecule must **remain intact**

Benzene



C_6H_6

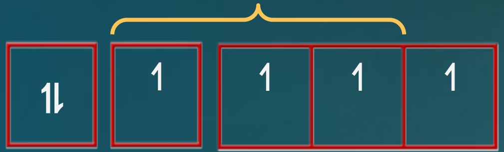
$C_{\text{Ground state}}: 1s^2\,2s^2\,2p^2$

$1s^2$ $2s^2$ $2p^2$

C_6H_6

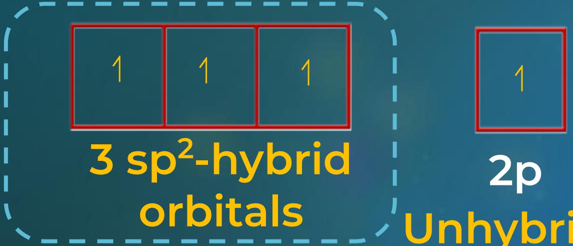
$C_{\text{Excited state}}: 1s^2\,2s^1\,2p^3$

Hybridize



$1s^2$ $2s^1$ $2p^3$

C (Excited and hybrid state)



3 sp^2-hybrid orbitals

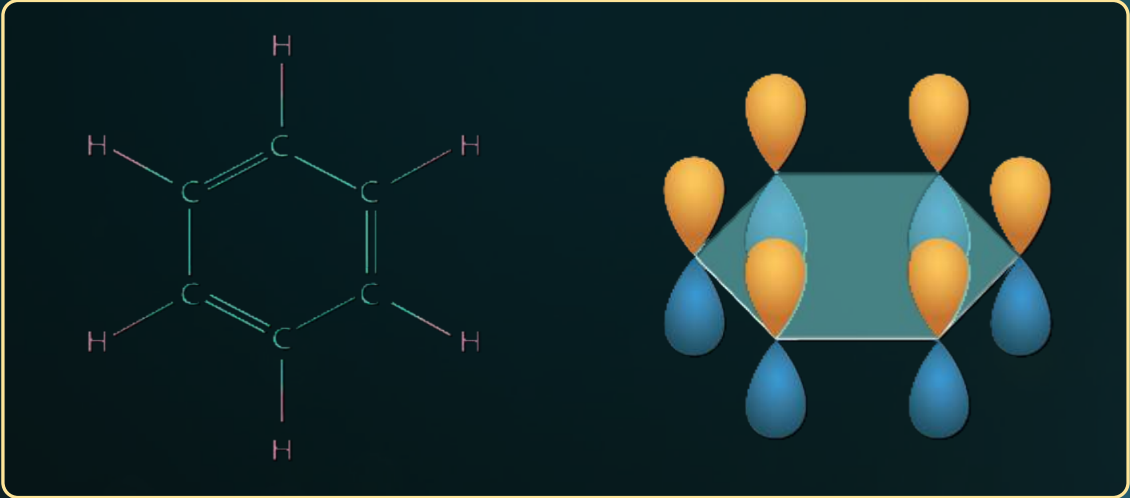
2p

Unhybridized p-orbital

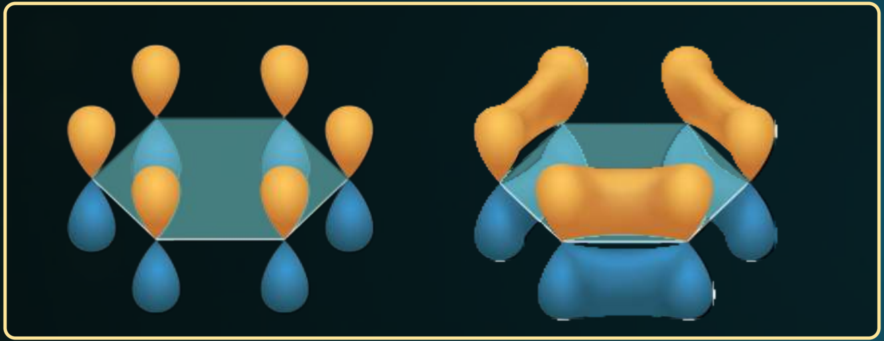
Benzene

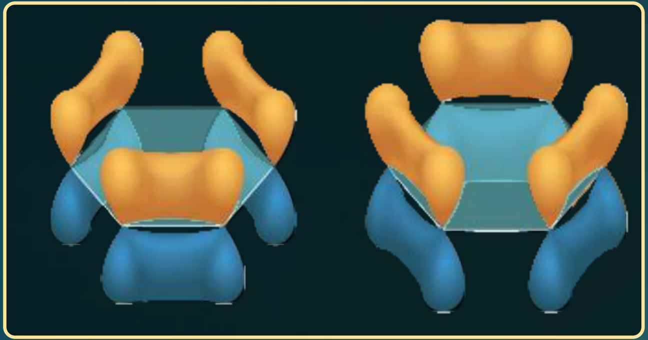
Each carbon of benzene has **one unhybridised p-orbital**

Unhybridised p-orbitals of each carbon are **parallel to each other**

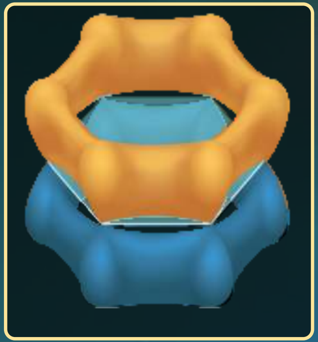


Benzene



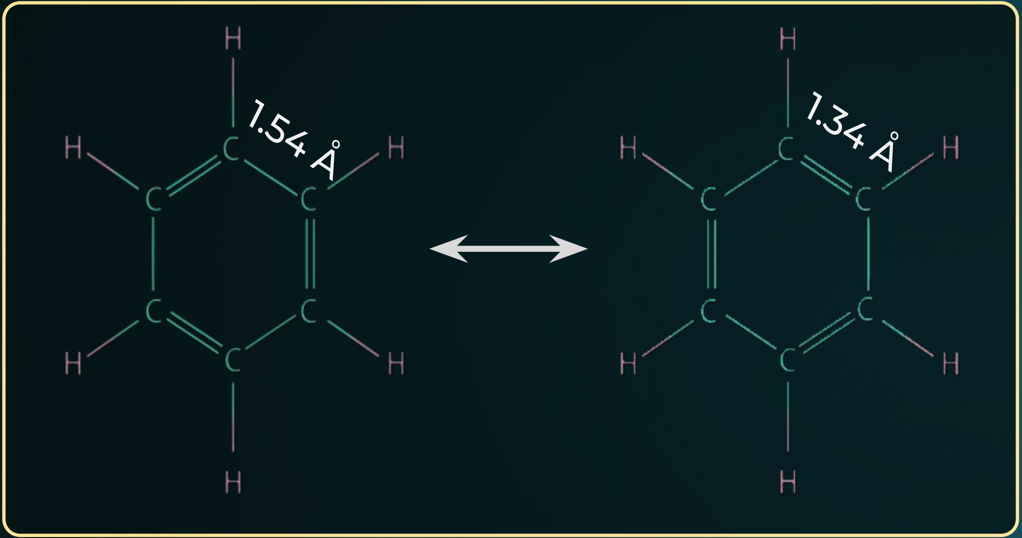


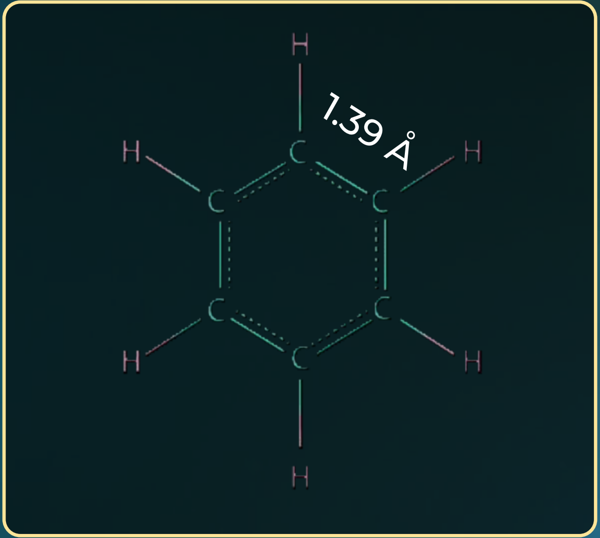
Localised π bonds



Delocalised π bonds

Resonance Structures and Resonance Hybrid of Benzene

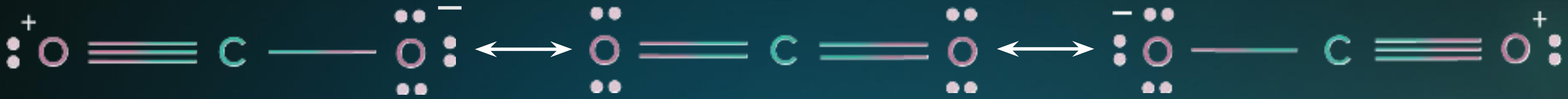




Bond order of Resonance Structures

For degenerate resonating structures:

Bond Order between two atoms = Total no. of bonds between 2 atoms in all structures ÷ Total no. of resonance structures



Less Contributing

Less Contributing

C = O bond length in CO_2 is **less than** expected because of **resonance**

Drago's Rule

- **Hybridization** does not take place for **compounds** of elements of **3rd period onwards**, bonded to a **less electronegative element** like **hydrogen**.
- It is because energy difference between participating orbitals is very high.

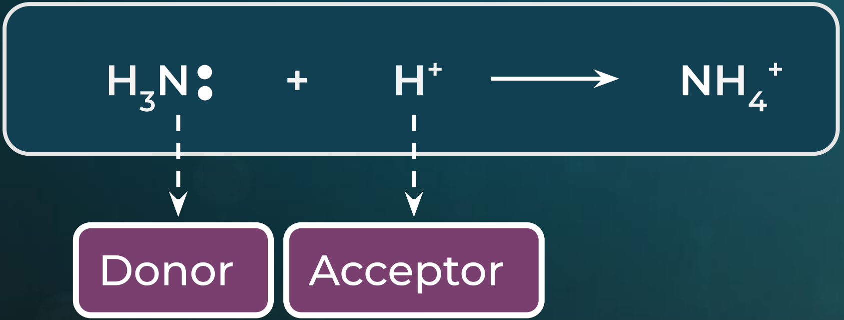
Lewis Acid and Lewis Base

01

Lone pair donors are also called as **Lewis base**

02

Lone pair acceptors are also called as **Lewis acid**



$$H_3N\!: \; + \; H^+ \longrightarrow NH_4^+$$

Lewis Acids

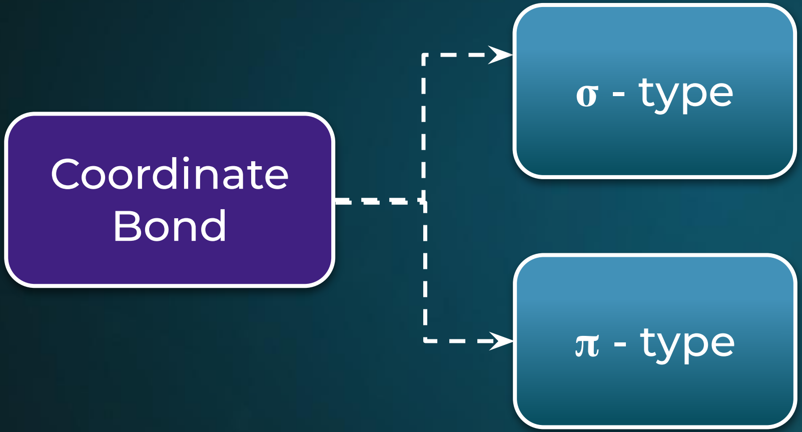
BF_3, $AlCl_3$, BCl_3	Incomplete octet
SiF_4, PCl_5, PF_5	Central atom has **vacant d-orbitals**
Mg^{2+}, Al^{3+}, Fe^{2+}, Zn^{2+}	**Metal cations**
CO_2, SO_2	Central atom is attached to a more **E.N. atom with multiple bonds**

Lewis Bases

NH_3, H_2O, ROH, RNH_2	Central atom has at least **one lone pair** and is surrounded by **less E.N. atom**
Cl^-, F^-, OH^-, NH_2^-	**Anions**

Back Bonding

Coordinate Bond

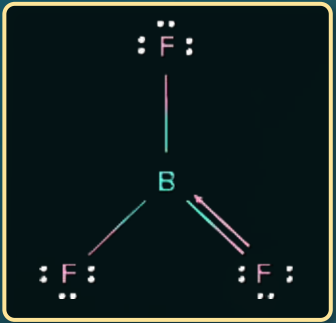


Coordinate Bond

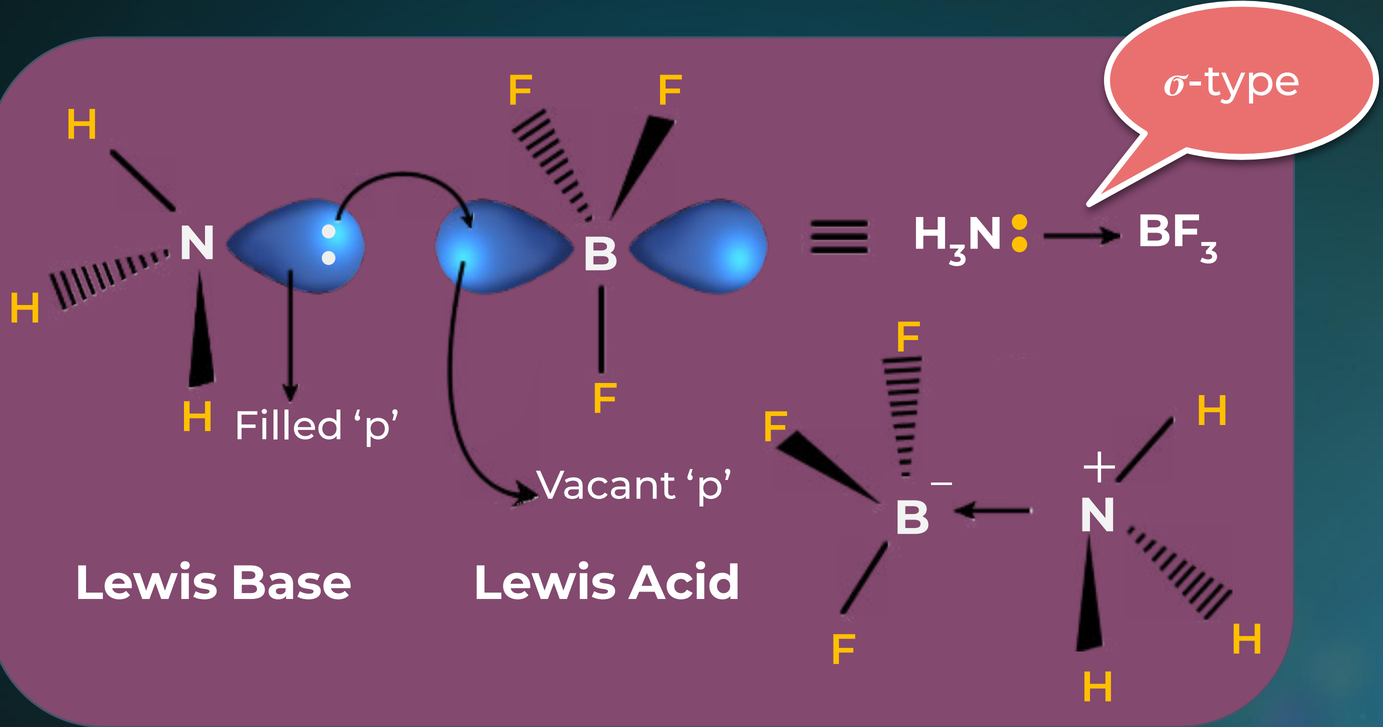
σ - type

π - type

$H_3N\!: \longrightarrow BF_3$



σ - Coordinate Bond



Lewis Base

Lewis Acid

π - Coordinate Bond

Back bonding

Kind of **coordinate π bonding**

Partial double bond character

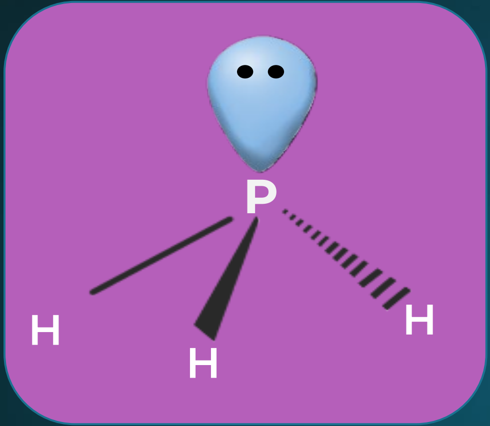
Back bond forms between

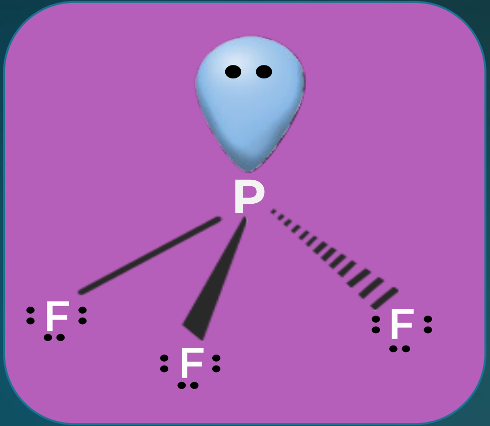
Atom having non bonded electron pair

&

Atom having vacant orbital

π - Coordinate Bond





Back Bonding ✗

Because Hydrogen has no lone pairs

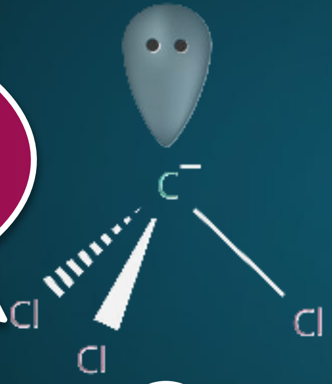
Back Bonding ✓

Because F has lone pairs and can donate to one empty p-orbital of P

$$CHCl_3 \rightleftharpoons H^+ + \bar{C}Cl_3$$

$$CHF_3 \rightleftharpoons H^+ + \bar{C}F_3$$

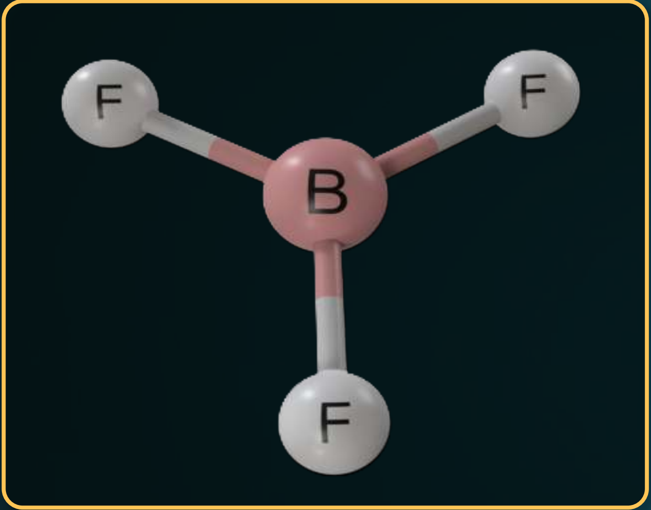
Cl atom have vacant d -orbital to accommodate electron pair



F atom does not have vacant d -orbital

Vacant orbital	✓	✗
Back bonding	2pπ-3dπ	-

BF_3



Species	Bond Length (pm)
BF_4^-	130.7
BF_3	139.6

B-F bond in **BF_3** is found to be **shorter** and **stronger** than expected due to back bonding.

Order of Accepting Tendency

Lone pairs are present already

Si > P > S > Cl

When lone pairs are absent

Si < P < S < Cl

Factors for Coordinate π-Bonding

Stability of π-bond

$$\text{Stability} \propto \frac{1}{\text{Size of orbitals}}$$

Size of orbital increases → Weak π bond

Size of orbital decreases → Strong π bond

Relative Stability of π-Bond

$2p\pi\text{-}2p\pi > 2p\pi\text{-}3p\pi > 2p\pi\text{-}3d\pi > 3p\pi\text{-}3p\pi$

$BF_3(2p\pi\text{-}2p\pi) > PF_3(3d\pi\text{-}2p\pi)$

No. of lone pairs on the atom having vacant orbital ↑

Extent of back bonding ↓

Backbonding

Lewis acidic strength **decreases.**

Lewis basic strength **decreases.**

Bond length **decreases.**

Bond angle may or may not change.

Hybridisation may or may not change.

Point to Remember!!

One atom involved
in back bonding
must be of **2nd period**

Electron Deficient Compounds

Insufficient no. of electrons to complete **octet.**

Examples: BH_3, $BeCl_2$, BF_3

Case 1: Electron Deficiency in BH_3

- Those bonds which has **insufficient number of electrons** and makes them stable are known as **electron deficient bonds.**
- **BH_3** is electron deficient compound. That's why it undergoes **dimerisation** by means **of 3c-2e⁻** bonds also known as **banana bonds.**

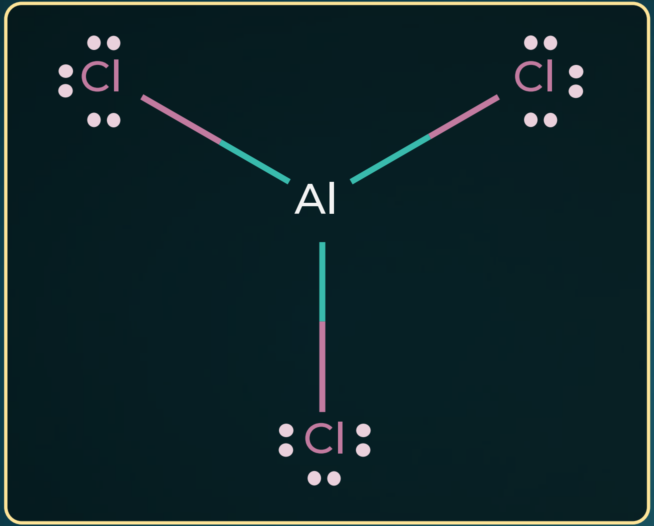
- Diborane (B_2H_6) is a **dimer** of BH_3.
- In B_2H_6 there are two **3c-2e⁻** bond which are known as **banana bonds.** In B_2H_6 there are four **2c-2e⁻** bond which are known as **terminal bonds.**
- The hybridization of boron in B_2H_6 is **sp^3.**

Electron Deficient Bonds

Those bonds which has **insufficient number of electrons** and makes them stable are known as **electron deficient bonds.**

BH_3 is electron deficient compound. That's why it undergoes **dimerisation** by means of **$3c\text{-}2e^-$** bonds also known as **banana bonds.**

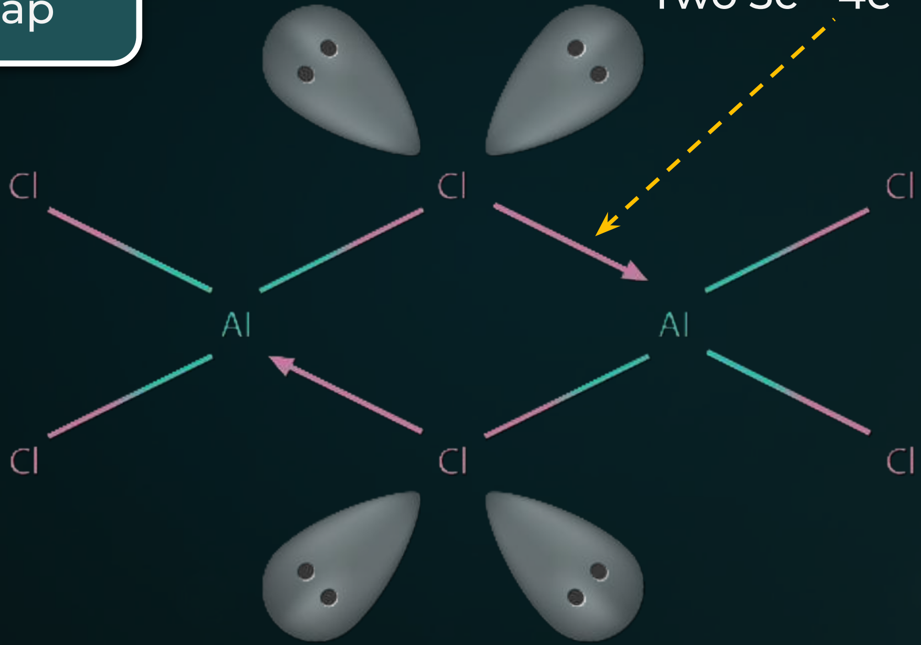
Case 2: Electron Deficiency in $AlCl_3$



Incomplete octet of Al → Tendency to form **dimer**

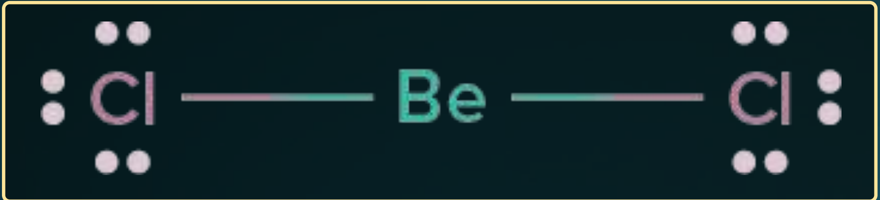
In Vapour Phase - Dimer of $AlCl_3$ (Al_2Cl_6)

sp^3 - sp^3 - sp^3 overlap



Two 3c - 4e$^-$ bonds

Case 3: Electron Deficiency in $BeCl_2$



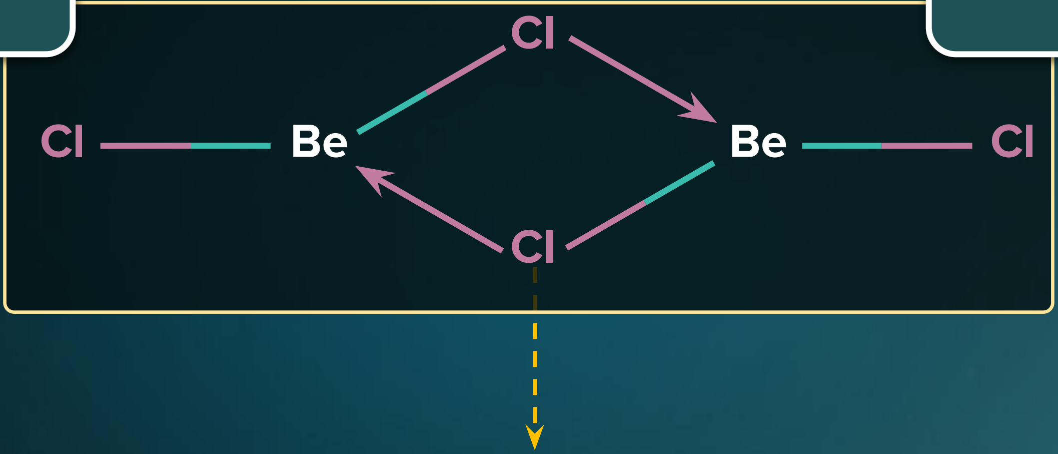
Incomplete octet of Be

Forms dimer & polymer to get stabilized

In Vapour Phase - Dimer of $BeCl_2$ (Be_2Cl_4)

sp^2 - sp^3 - sp^2 overlap

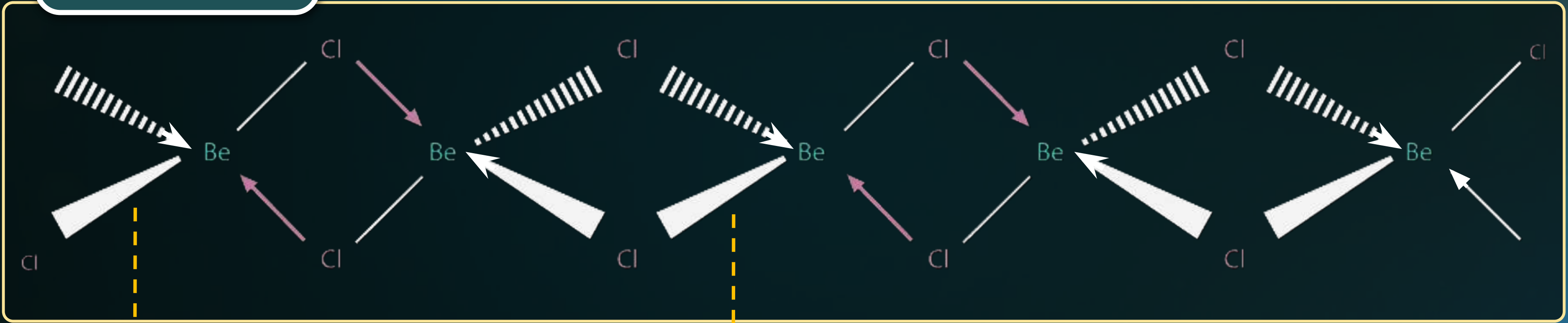
Planar



3c - 4e$^-$ bond

In Solid Phase -
Polymer of $BeCl_2$ $(BeCl_2)_n$

sp^3 - sp^3 - sp^3 overlap



Non planar

3c - $4e^-$ bond

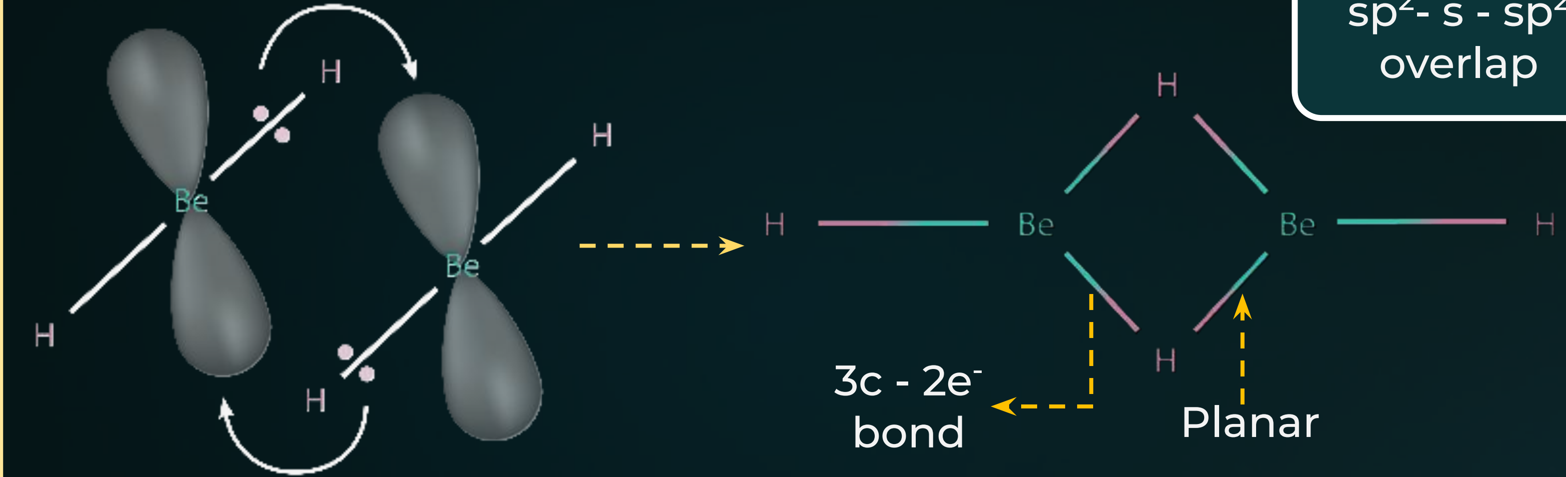
Case 4: Electron Deficiency in BeH_2

$H - Be - H$

Incomplete octet of Be

Forms dimer & polymer to get stabilized

In Vapour Phase - Dimer of BeH$_2$(Be$_2$H$_4$)

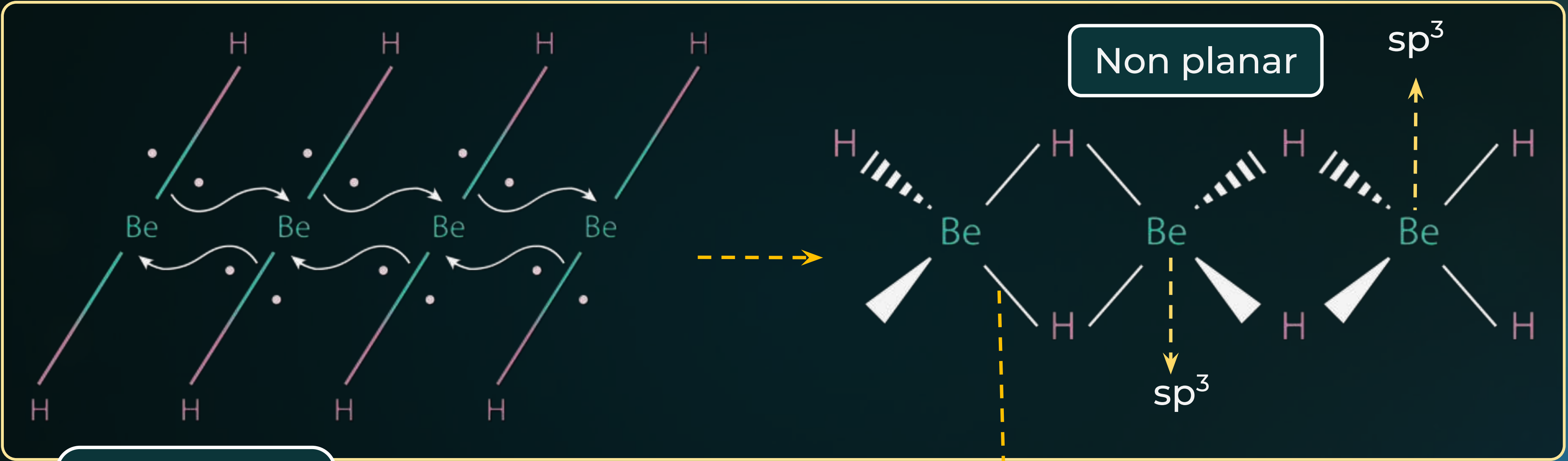


sp^2- s - sp^2 overlap

3c - 2e$^-$ bond

Planar

In Solid Phase - Polymer of BeH_2 $(BeH_2)_n$



Non planar

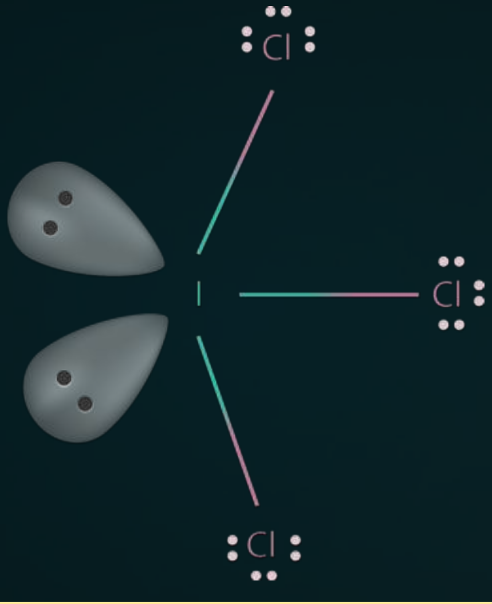
sp^3

sp^3

sp^3 - s - sp^3 overlap

3c - $2e^-$ bond

Case 5: Electron Deficiency in ICl_3



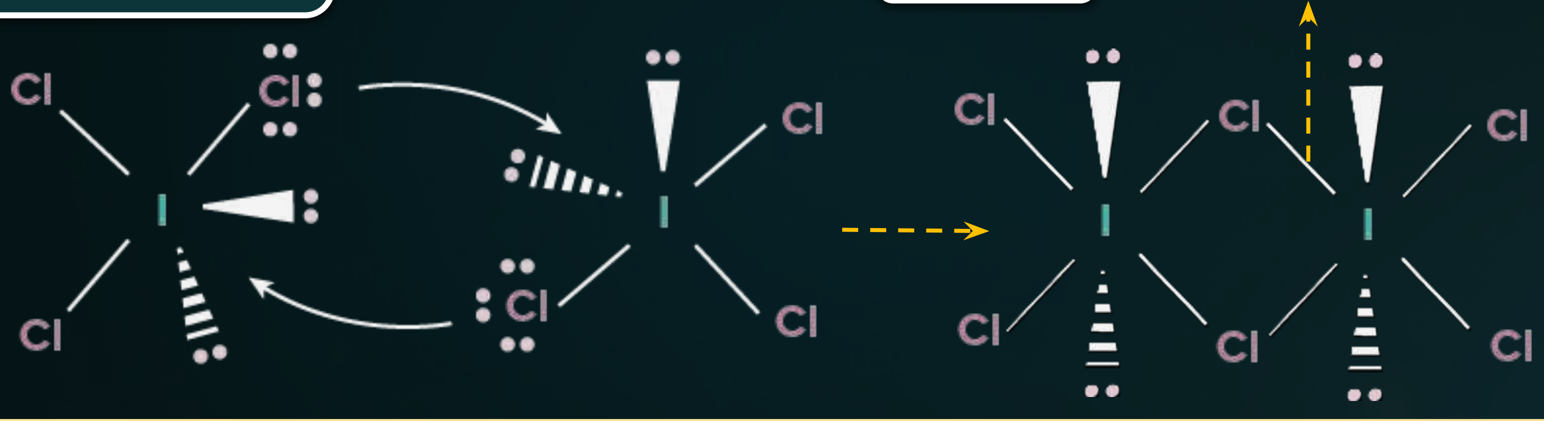
Forms dimer to minimize repulsion between lone pairs

In Solid Phase - Dimer of ICl_3 (I_2Cl_6)

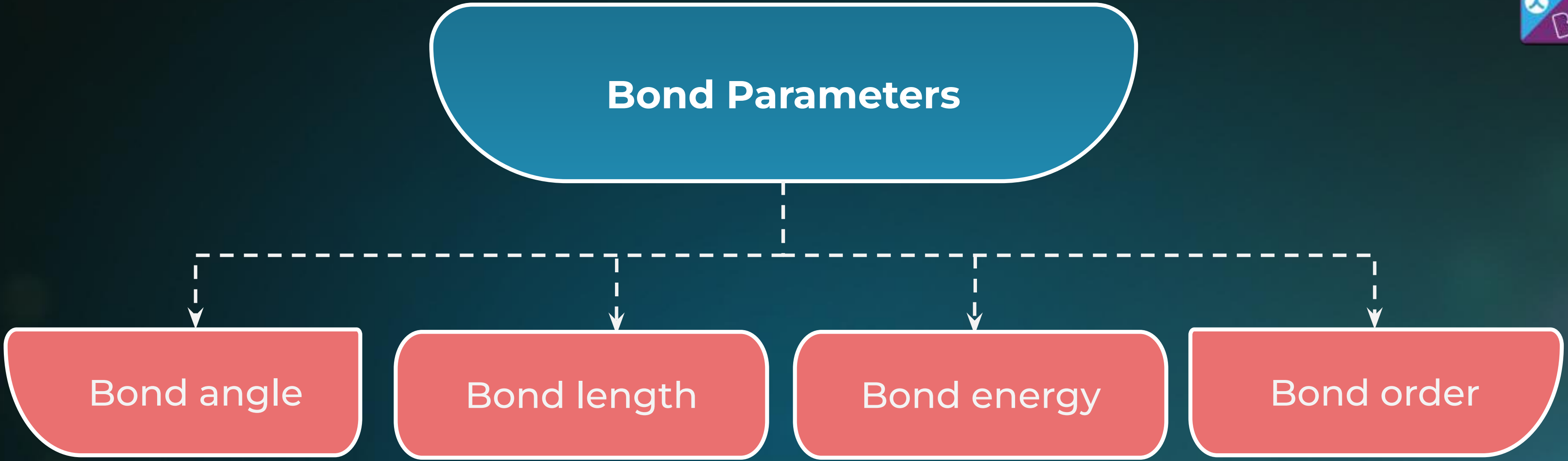
sp^3d^2 - sp^3 - sp^3d^2 overlap

Planar

3c - 4e⁻ bond



Bond Parameters

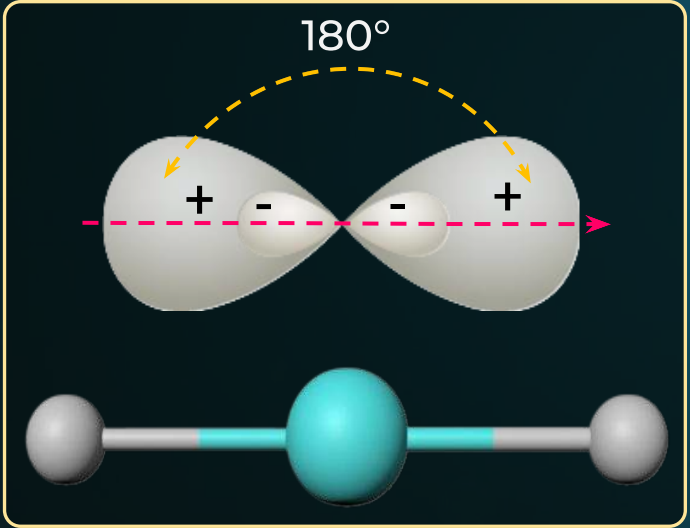


Bond Parameters

- Bond angle
- Bond length
- Bond energy
- Bond order

Bond Angle

Angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion



Expressed in degrees & is spectroscopically determined

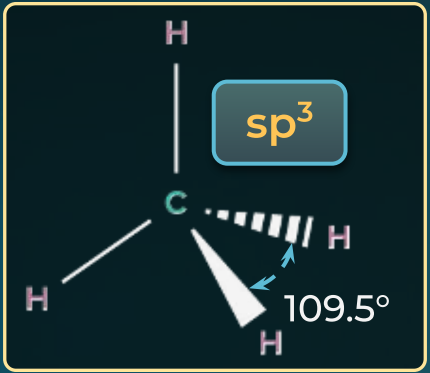
Gives ideas about distribution of orbitals around the central atom which helps in determination of shape.

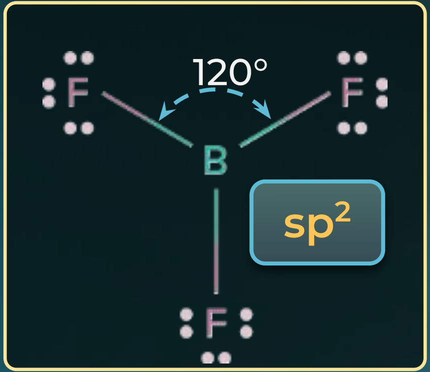
Factors Affecting Bond Angle

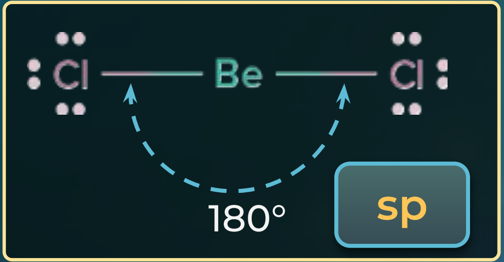
(1) Hybridization

As % s character ↑

Bond angle ↑





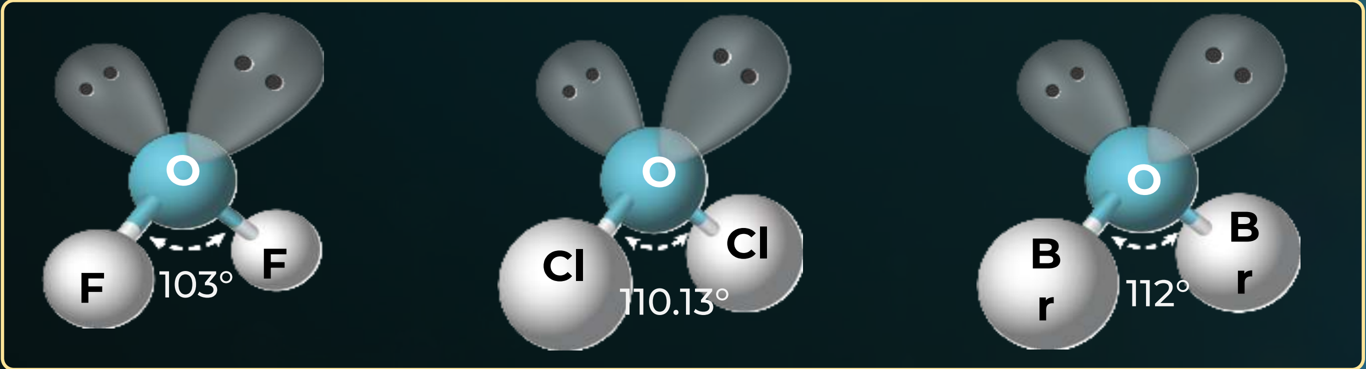


Factors Affecting Bond Angle

(2) Steric Repulsions

Steric Repulsions ↑ Bond angle ↑

Same central atom (2^{nd} period), same hybridisation (sp^3) & side atoms are of 3^{rd} period & onwards



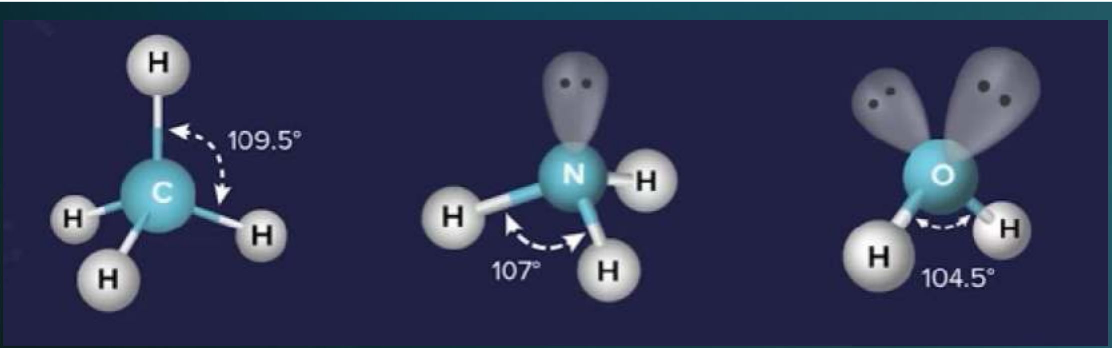
Factors Affecting Bond Angle

(3) Number of lone pairs on the central atom

As number of lone pairs ↑

Bond angle ↓

Same hybridisation of the central atom



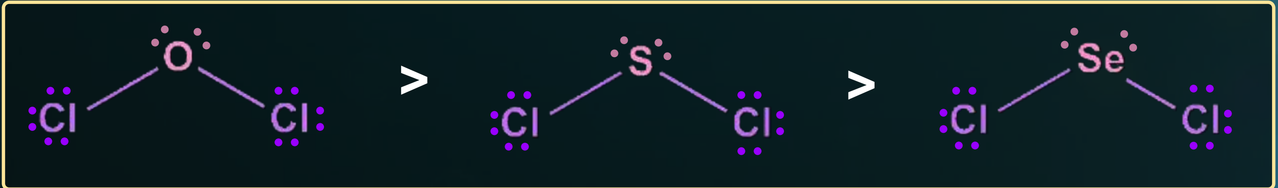
Factors Affecting Bond Angle

(4) Electronegativity of the central atom

E.N. of central atom ↑

Bond angle ↑

Same **hybridization** and number of **lone pairs** on central atom

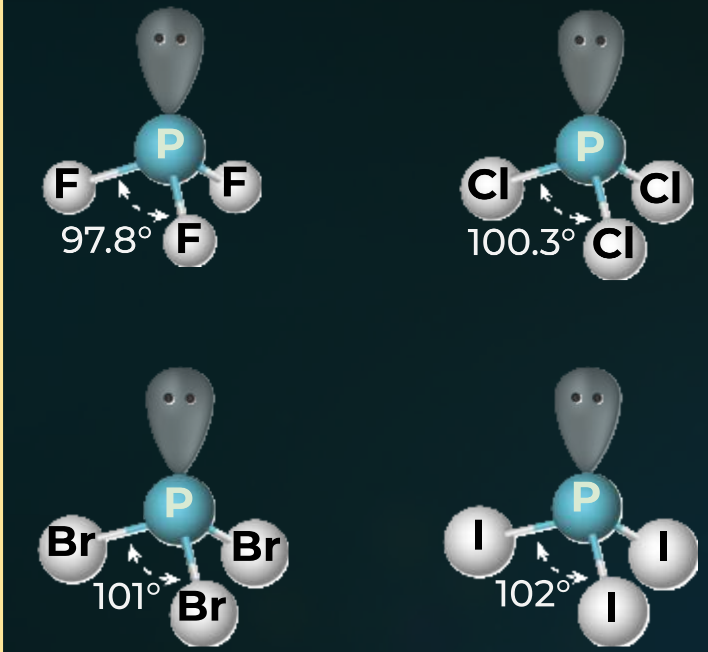


Factors Affecting Bond Angle

(5) Electronegativity of the side atoms

E.N. of side atom	↑
Bond angle	↓

Same central atom, same hybridization & same number of lone pairs



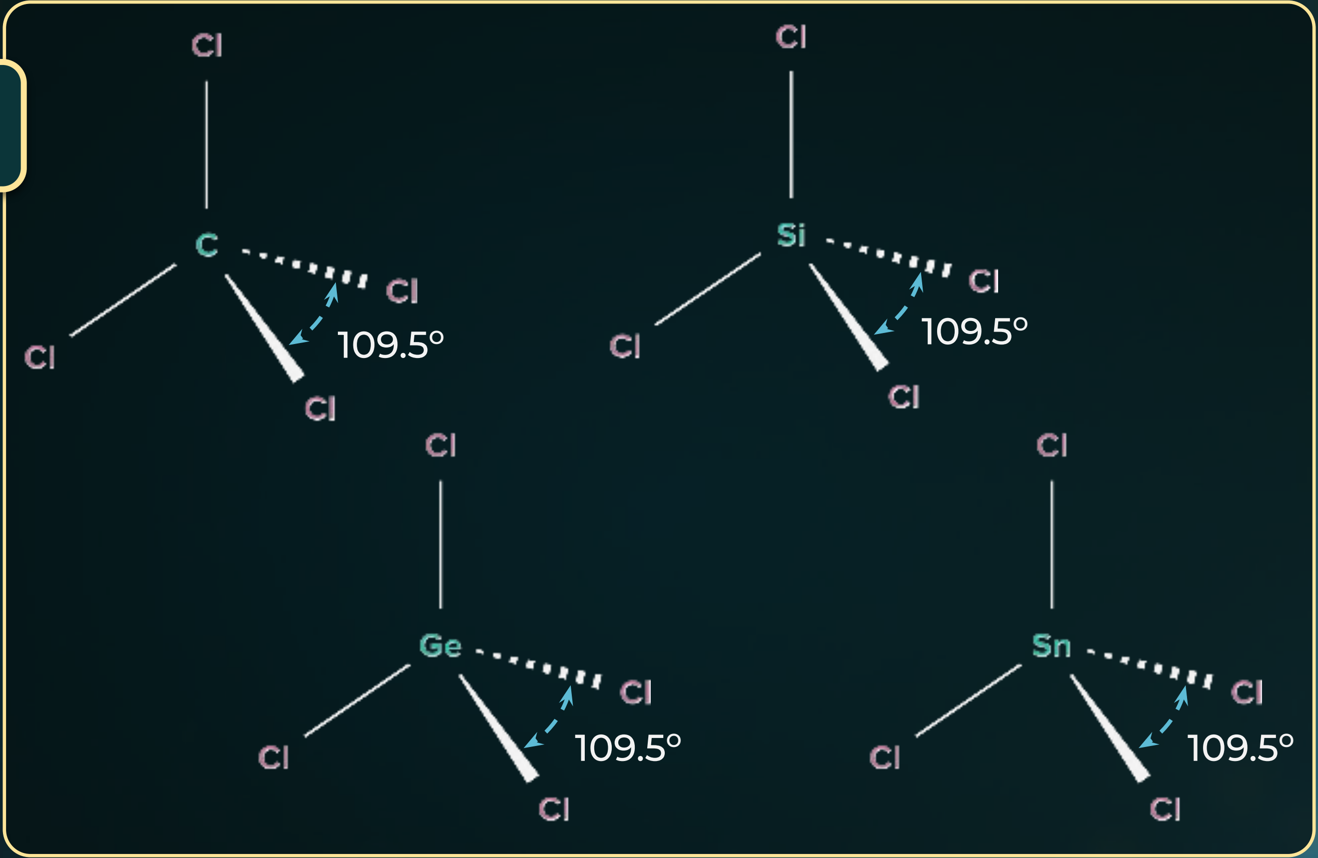
Point to Remember!!

Regular geometry

All the **side atoms** are **identical** and **no lone pair** on central atom

Bond angle **not affected** by **electronegativity**

Example



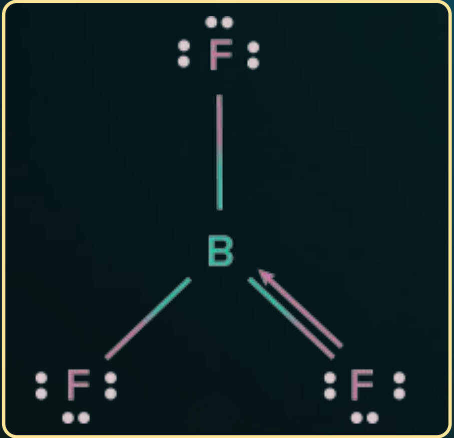
CCl_4 = $SiCl_4$ = $GeCl_4$ = $SnCl_4$

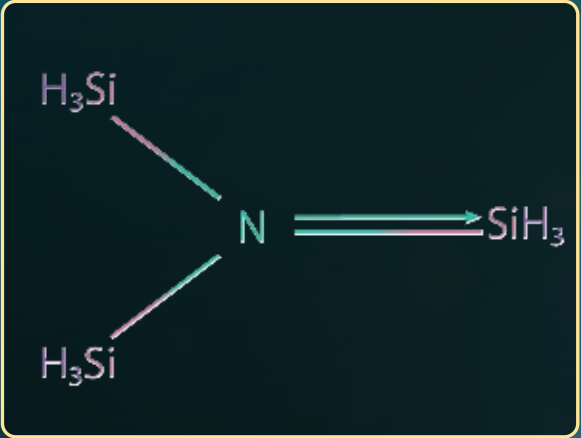
Factors Affecting Bond Angle

(6) Back Bonding

Side atom → Central atom

Central atom → Side atom





Factors Affecting Bond Angle

BF_3

Due to back bonding

Bond order ↑

But net effect in repulsion is zero

Bond angle = 120°

$N(SiH_3)_3$

Due to back bonding

Hybridization changes from sp^3 to sp^2

Bond angle ↑

Bond Length

Equilibrium distance **between** the nuclei of two bonded atoms in a molecule

Factors Affecting Bond Length

- Size of the bonded atom
- Multiplicity of Bonds
- % s-character
- Number of lone pairs on bonded atoms
- Electronegativity difference

Bond Energy

Amount of **energy** required to **break 1 mole** of **particular** type of **bonds** between two atoms in **gaseous state.**

Unit : **kJ mol^{-1}**

Multiplicity of bond ↑	**Magnitude** of Bond energy ↑

Bond	Energy (kJ mol^{-1})
C — C	347
C = C	611
C ≡ C	837

Bond Energy

Bond length (for same bonded atom) ↓ | Bond energy ↑

Bond	Bond length (pm)	Energy (kJ mol^{-1})
Cl — Cl	199	243
Br — Br	228	192
I — I	267	151

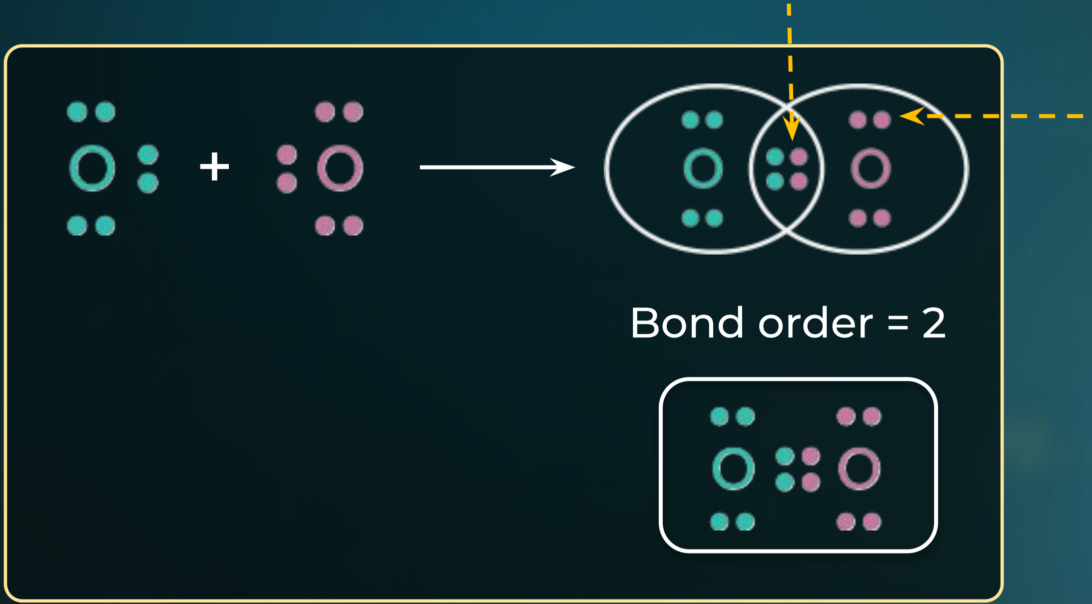
In group **15, 16** and **17 single bonds** between **2nd period** elements are exceptionally weaker due to **l.p - l.p. repulsions**

Example :

Cl — Cl > Br — Br > F — F > I — I

Bond Order

The **number of bonds** between the two atoms in a molecule.

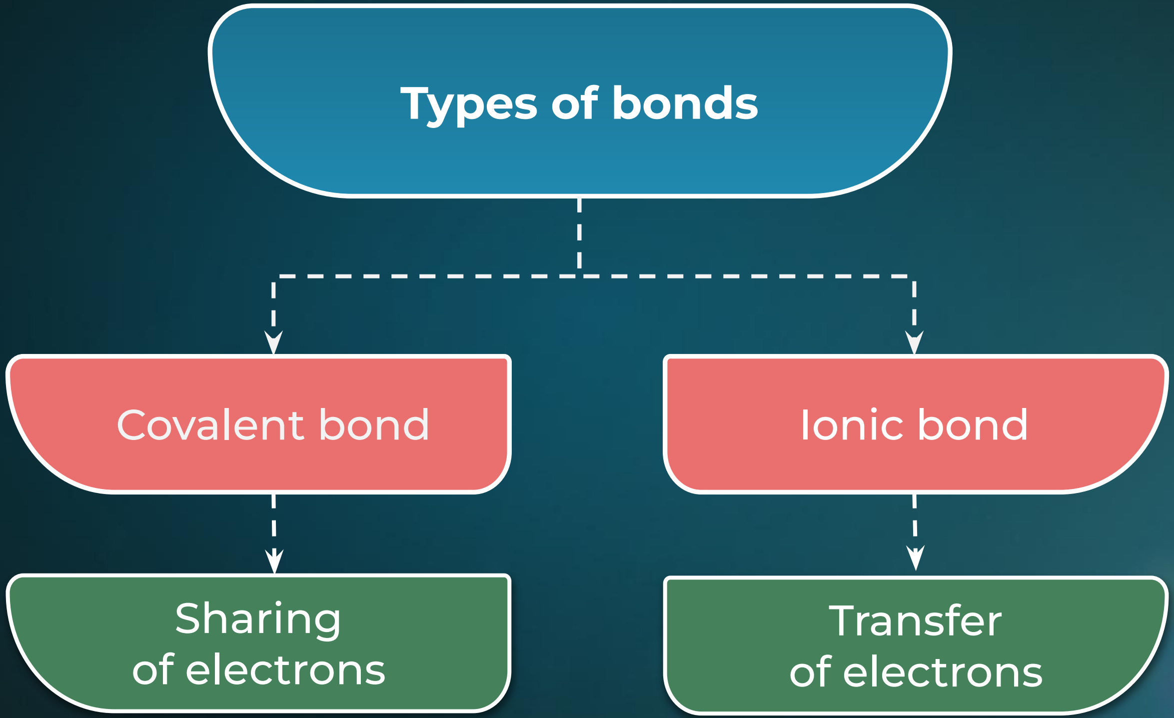


Shared pairs of electrons

Lone pair of electrons

Bond order = 2

What We Know?



Types of bonds

Covalent bond

Ionic bond

Sharing of electrons

Transfer of electrons

What Exists in Reality?

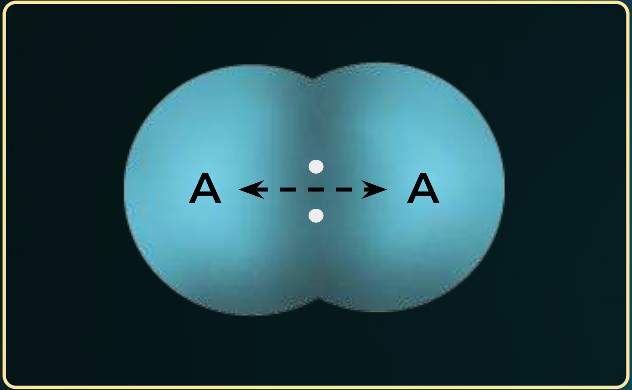
There exists some covalent character
in an ionic bond
and some ionic character
in a covalent bond!

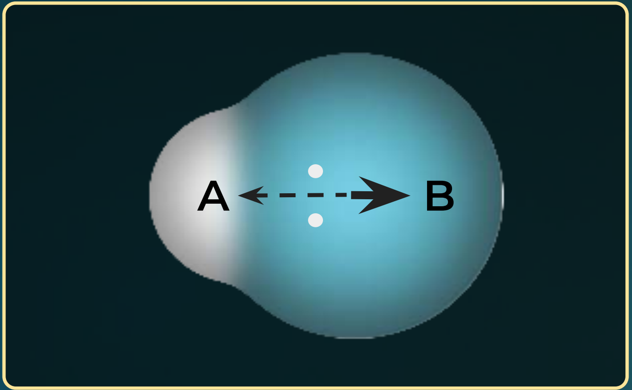
Covalent Bond

Covalent Bond

- Non-polar Covalent: When ΔE.N. $\leq$ 0.4 between the bonded atoms
- Polar Covalent: When ΔE.N. $>$ 0.4 between the bonded atoms

Non-polar & Polar Covalent Bond





E.N. of A < B

Symmetrical electron cloud

Asymmetrical electron cloud

H_2, Cl_2, N_2, F_2...

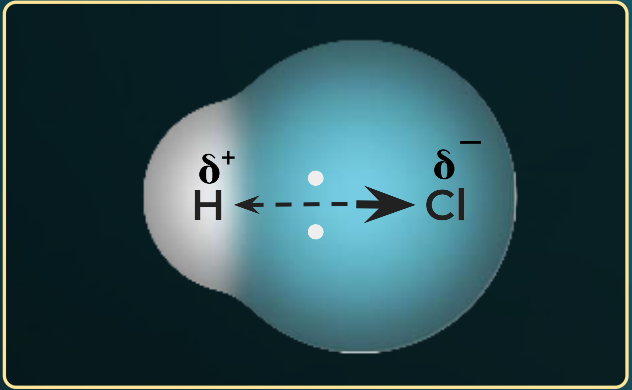
HF, HCl, HBr, HI ...

Polarisation

Due to polarisation

Charged ends develop

Act as an electric dipole



Dipole Moment

1. Dipole moment is a **measure** of the **separation of charges**(polarity) between the **two ends** of a dipole.
2. It's **magnitude** is equal to the **product** of **charge** and the **distance** of separation.
3. It a **vector** quantity.
4. It is denoted by **μ.**

Dipole Moment

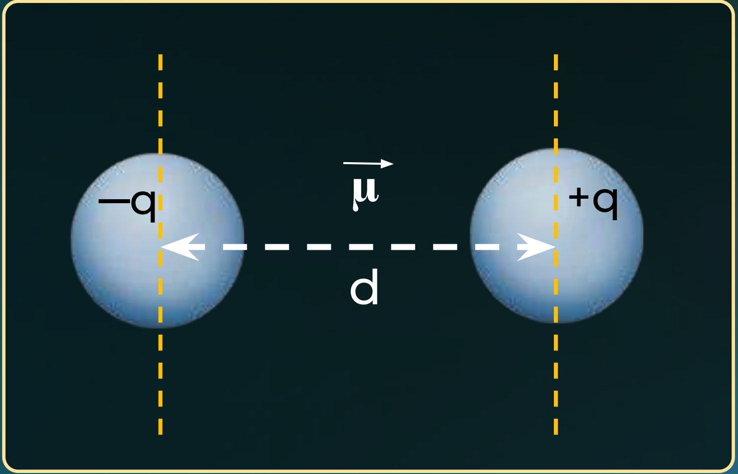
Formula of dipole moment is given as:

$$\mu = q \times d$$

Unit = Debye

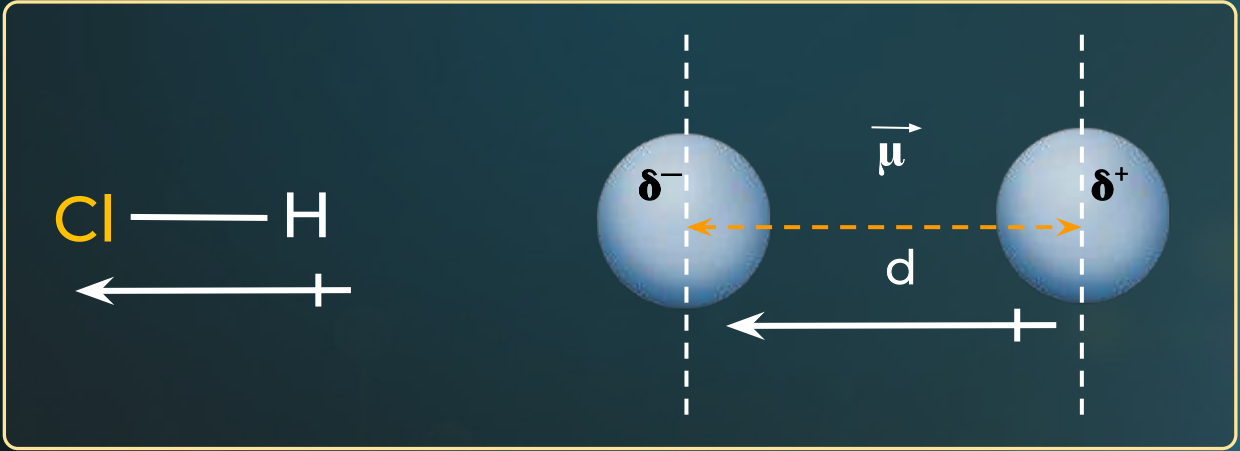
d = Distance of separation (Å)

q = Magnitude of charge (e.s.u.)

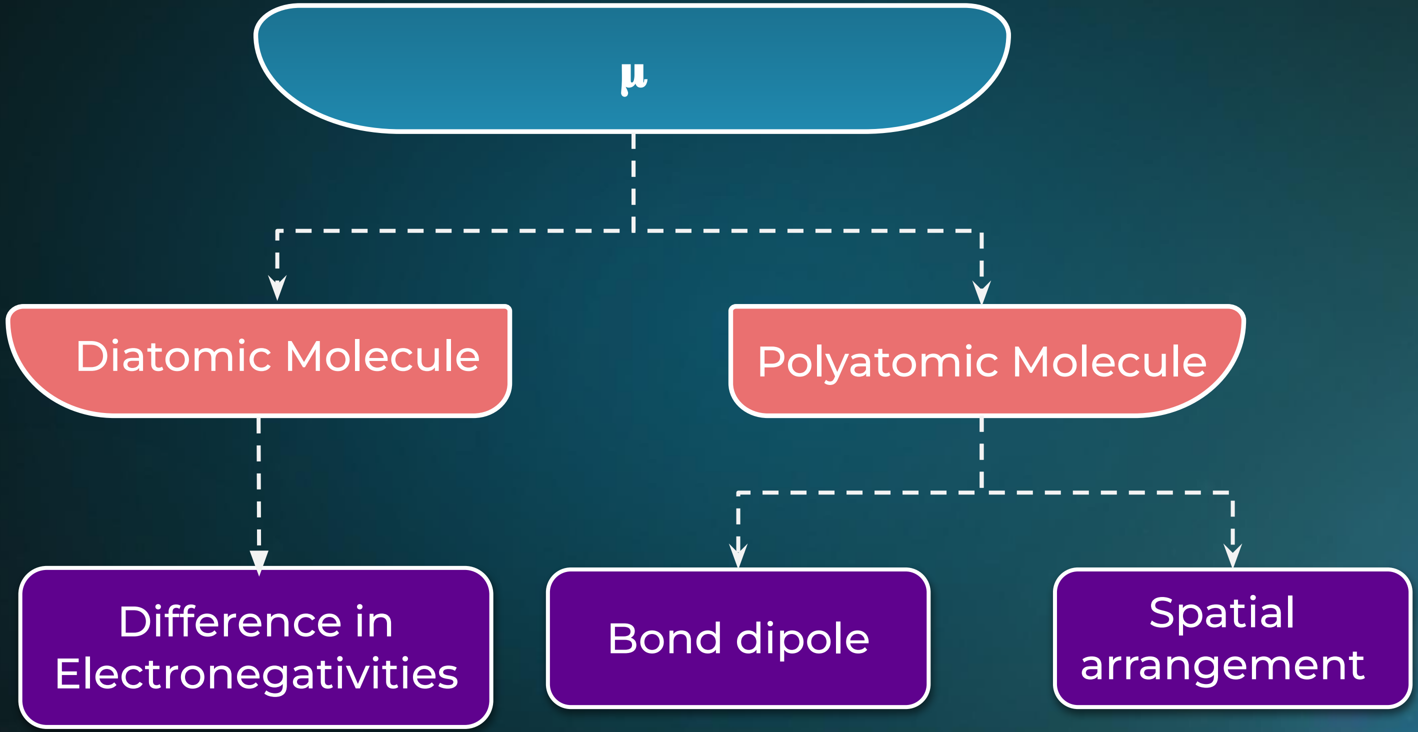


Direction and Representation

Represented by a small arrow with **tail** on the positive centre and **head** pointing towards the negative centre.



Value of Dipole Moment (μ)



μ

Diatomic Molecule

Polyatomic Molecule

Difference in Electronegativities

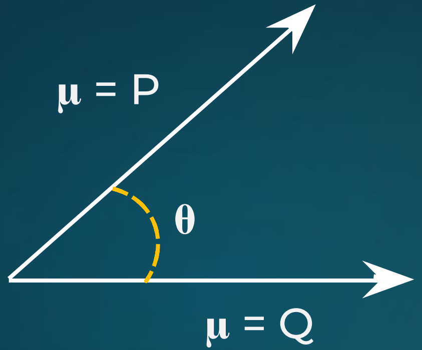
Bond dipole

Spatial arrangement

Dipole Moment (μ)

In **diatomic molecules,** μ depends upon	**Difference** in **electronegativities** & **bond length**
In **polyatomic molecules,** μ depends upon	**Bond dipole** and **spatial arrangement**

Resultant Dipole Moment (R)



$$R = \sqrt{(P^2 + Q^2 + 2PQ\cos\theta)}$$

Dipole Moment

Generally, out of ‘q’ and ‘d’, **‘q’** is the **dominant factor.**

q depends on **Δ.E.N.**

Δ.E.N. ↑ q ↑ μ ↑

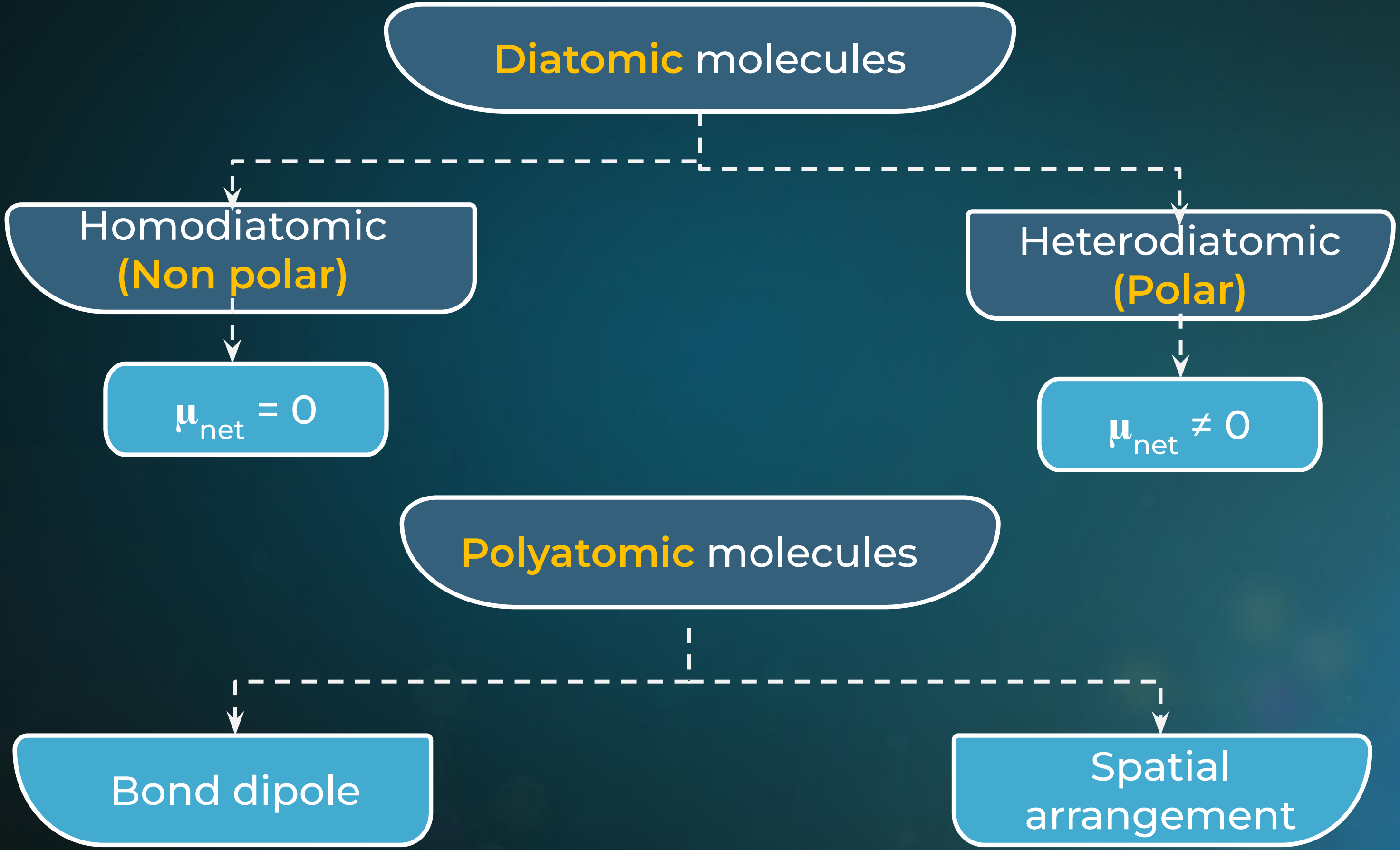
For a **non-polar molecule,**

$\mu_{net} = 0$

For a **polar molecule,**

$\mu_{net} \neq 0$

Dipole Moment



Diatomic molecules

Homodiatomic
(Non polar)

$\mu_{net} = 0$

Heterodiatomic
(Polar)

$\mu_{net} \neq 0$

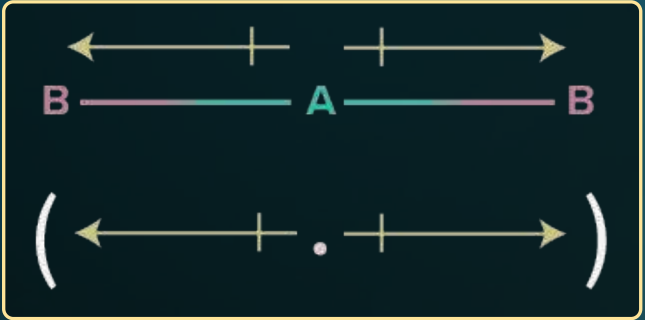
Polyatomic molecules

Bond dipole

Spatial arrangement

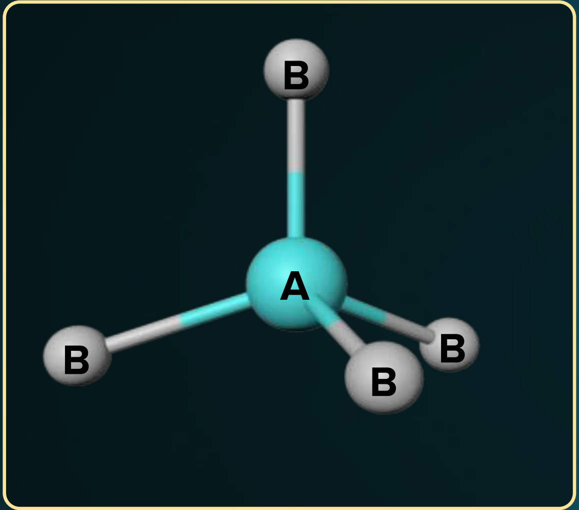
Dipole Moment

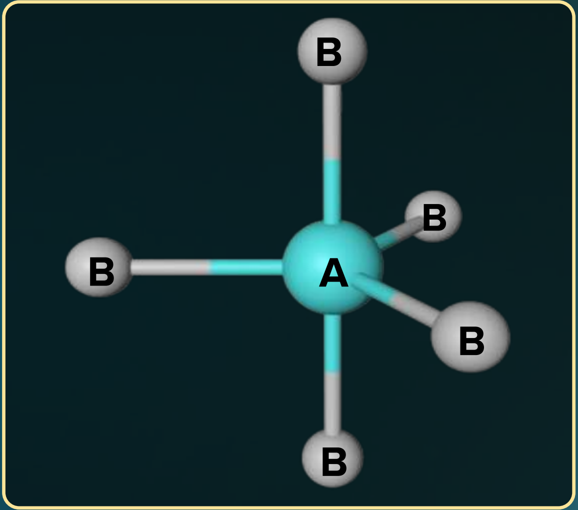
It can be zero as the two oppositely acting bond dipoles can cancel each other



Net dipole moment(μ_{net}) = 0

Regular Geometries





$\mu_{net} = 0$

$\mu_{net} = 0$

Dipole Moment

Lone pair contributes in dipole moment, but its contribution can’t be quantified as size of lone pair is not known.

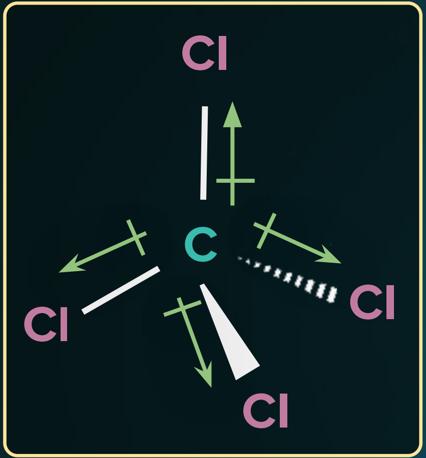
Dipole Moment = 0

Symmetrical Molecule

Dipole Moment ≠ 0

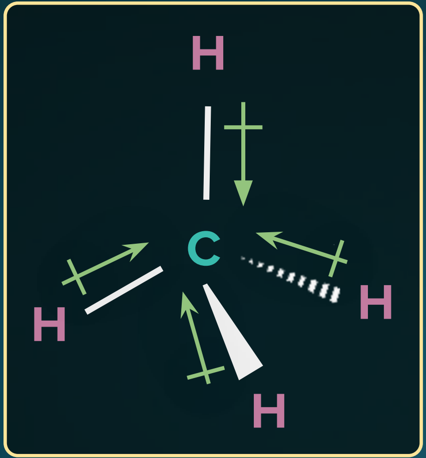
Asymmetrical Molecule

Predicting Geometry Using Dipole Moment



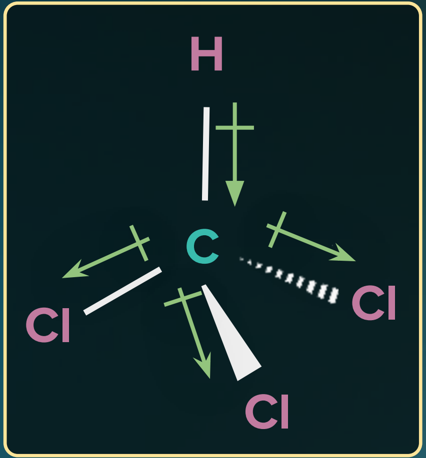
CCl_4

$\mu = 0$



CH_4

$\mu = 0$

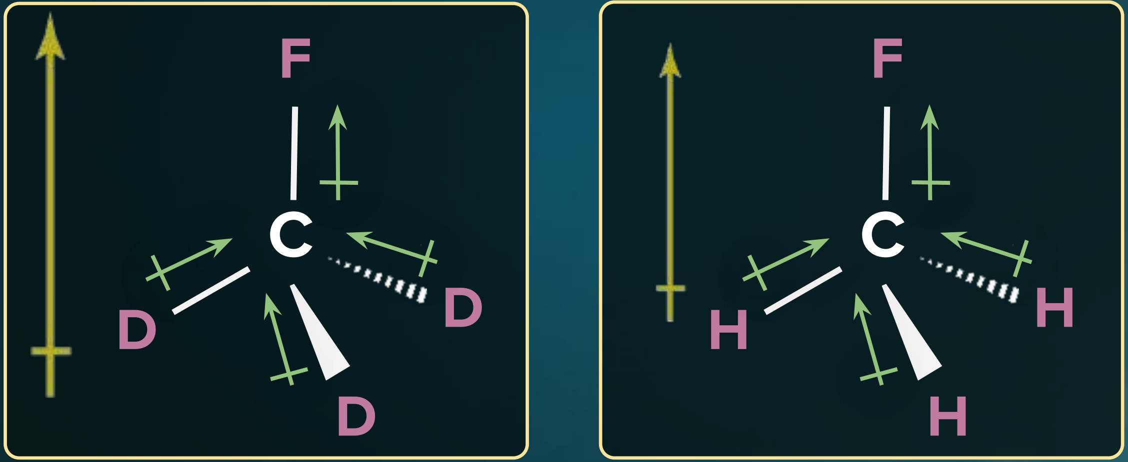


$CHCl_3$

$\mu = 1.04$ D

Some Important Order of Dipole Moment

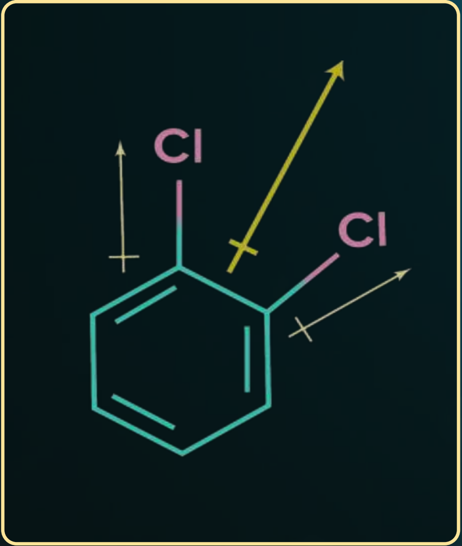
CD_3F > CH_3F

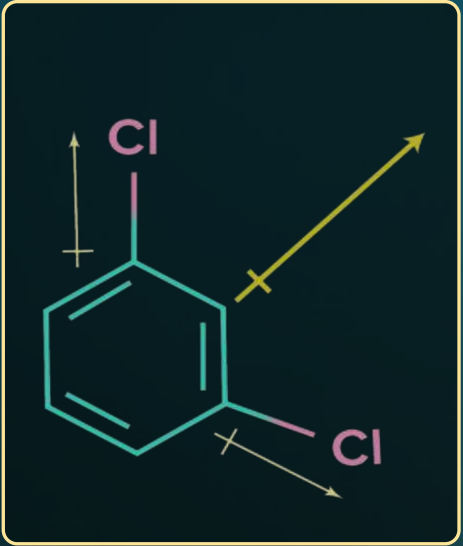


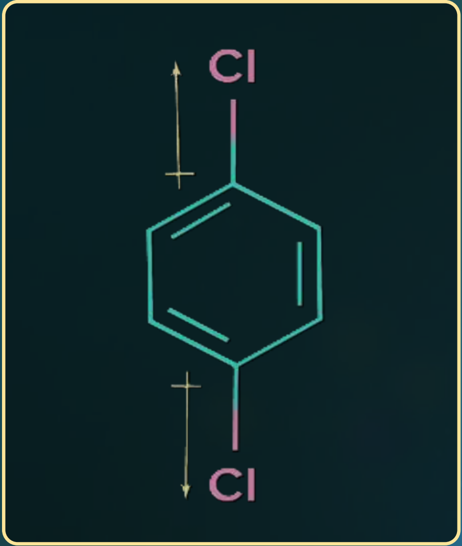
Δ E.N. in C - D > Δ E.N. in C - H

Dipole Moment of Dichlorobenzene

Ortho-dichlorobenzene > Meta-dichlorobenzene > Para-dichlorobenzene



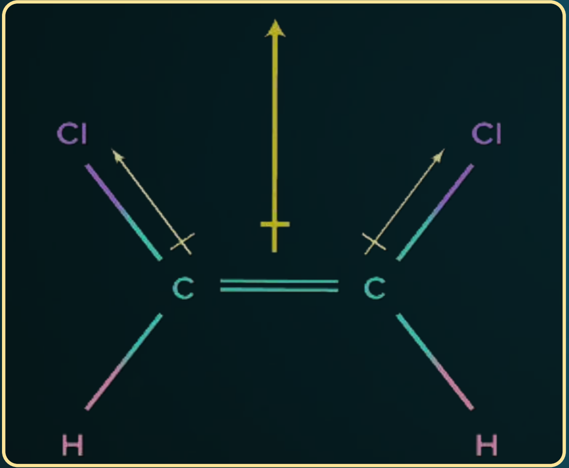


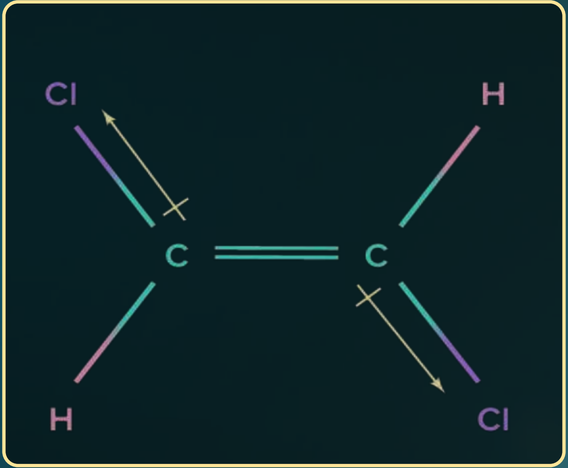


What are Cis and Trans?

Cis: Similar groups on same side

Trans: Similar groups on opposite sides





$\mu_{net} \neq 0$

$\mu_{net} = 0$

Effect of Dipole Moment on Boiling Point

Generally,

Dipole moment ↑ → Boiling point ↑

B.P. of cis is **greater than** trans

Dipole Moment and Percentage Ionic Character

$$\%\ \text{Ionic character} = \frac{\mu_{\text{Observed}}}{\mu_{\text{Theoretical}}} \times 100$$

μ_{Observed}	Experimental value of μ
$\mu_{\text{Theoretical}}$	Assuming 100% ionic compound

Covalent Character in Ionic Compounds

When an anion and a cation approach each other

Valence shell of the anion is pulled towards the nucleus of the cation

The shape of the anion is deformed

Polarisation	Phenomenon of deformation of an anion by a cation
Polarising power of the cation	The ability of a cation to polarise a nearby anion
Polarisability of the anion	Ability of an anion to get polarised

Fajan’s Rule

Greater is the polarisation of an anion in a molecule, more is the covalent character in the molecule.

Polarization ∝

Charge on Cation

$\frac{1}{\text{Size of Cation}}$

Charge on Anion

Size on Anion

Covalent character

Example: $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

(As size of cation increases from left to right, Polarisation decreases)

Factors affecting polarisation

For the cations of nearly the same size and charge,

Order of polarizing power:

Pseudo inert gas configuration > Inert gas configuration

Eg: CuCl > NaCl (Covalent character)

Cu^+	$[Ne]\ 3s^2\ 3p^6\ 3d^{10}$	Pseudo inert gas configuration
Na^+	$1s^2\ 2s^2\ 2p^6$	Inert gas configuration

Fajan's Rule

Cations with pseudo inert gas configuration: **$(n-1)d^{10}\ ns^0$**

01

More Z_{eff} due to poor shielding effect of d and f electrons.

02

Polarising power **increases**

Polarisability of Anion

Polarisability ∝ Charge on the anion

Oxyanions are generally less polarisable because charge is present on O atom which is very small and we need to consider only the element which acquires the charge (and not the complete anion)

$S^{2-} > SO_3^{2-} > SO_4^{2-}$

$Cl^- < ClO_2^- < ClO_3^- < ClO_4^-$

Applications of Fajans’ Rule

Determination of Covalent Character in an Ionic Compound

Extent of polarisation ↑

Covalent character ↑

$\mathrm{LiF} < \mathrm{LiCl} < \mathrm{LiBr} < \mathrm{LiI}$

$\mathrm{NaF} < \mathrm{Na_2O} < \mathrm{Na_3N}$

Variation in Melting Point

Melting point of ionic solids depends upon

01 Lattice energy

02 Extent of polarisation

Fluorides (F^-) of s-block metals (except BeF_2) & Al^{3+} and Cl^-, Br^-, I^- of alkali metals (except Li^+) are **dominantly ionic.**

Melting point $\propto$ **Lattice Energy**

Variation in Melting Point

For Cl^-, Br^-, I^- of Li^+, all alkaline earth metals & Al^{3+}, **extent of polarisation** is **high.**

$$\text{Melting point} \propto \frac{1}{\text{Extent of polarisation}}$$

As **covalent character** in an ionic compound, the melting point decreases.

M.P. of **covalent compound** **<** M.P. of **ionic compound**

Variation in Melting Point

LiF > LiCl > LiBr > LiI

NaCl > $MgCl_2$ > $AlCl_3$ > $SiCl_4$

Intensity of Colour

Colour of some compounds can be explained by

Polarisation of their bigger negative ions.

Bigger anions are **more polarised** & hence their electrons get excited by

Partial absorption of visible light.


$SnCl_2$


SnI_2


$PbCl_2$


$PbBr_2$


PbI_2

Solubility in Water

Solubility of p-block/d-block salts & halides of Be is low

Extent of polarisation is high

$$\text{Solubility in Water} \propto \frac{1}{\text{Extent of polarisation}}$$

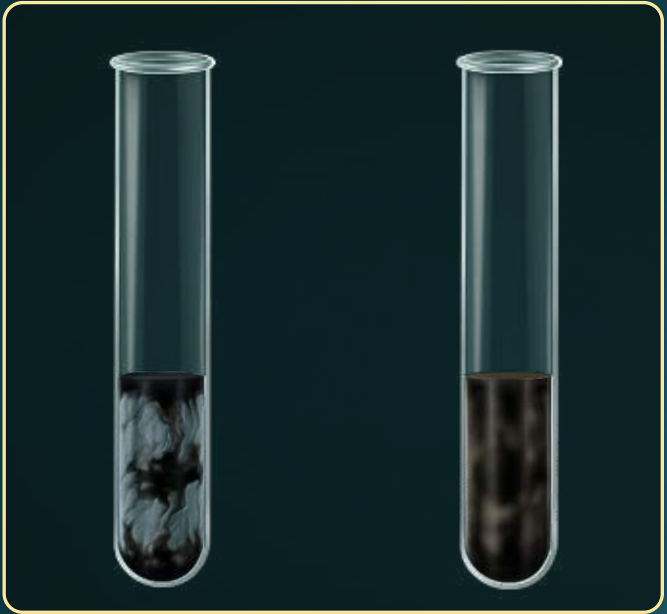
Covalent character ↑

Solubility in water ↓

$AgCl > AgBr > AgI$

$Fe(OH)_2 > Fe(OH)_3$

Solubility in Water



Ag_2O > Ag_2S

Thermal Stability of Ionic Compounds

- For **uniatomic anion**, as interionic distance increases, lattice energy decreases, hence **thermal stability decreases.**
- $Be_2N_2 > MgN_2 > CaN_2 > Sr_2N_2 > Be_3N_2$
- For **multiatomic anion** (for compounds having the same anion) **thermal stability increases down** the **group.**

Molecular Orbital Theory

Features of MOT

01 **Electrons** in a molecule are **present** in the molecular orbitals **(MO's)**

02 **Atomic orbitals** (AO's) of comparable **energies** & **proper symmetry** combine to form **MO's**

03 **AO** is **monocentric** whereas a **MO** is **polycentric**

04 Number of **MO's** formed is equal to the number of **combining AO's**

Features of MOT

05

There are two types of molecular orbitals: **Bonding** Molecular Orbitals **(BMO)** and **antibonding** Molecular Orbitals **(ABMO).**

06

BMO has **lower energy** and hence **greater stability** than the corresponding **ABMO**

07

Electron probability distribution around a group of **nuclei in a molecule** is given by a **MO**

08

MO's are filled according to **Aufbau principle**, **Pauli's exclusion principle** & **Hund's rule**

Linear Combination of Atomic Orbitals (LCAO)

BMO (Bonding Molecular Orbitals)

Constructive interference

ABMO (Anti Bonding Molecular Orbitals)

Destructive interference

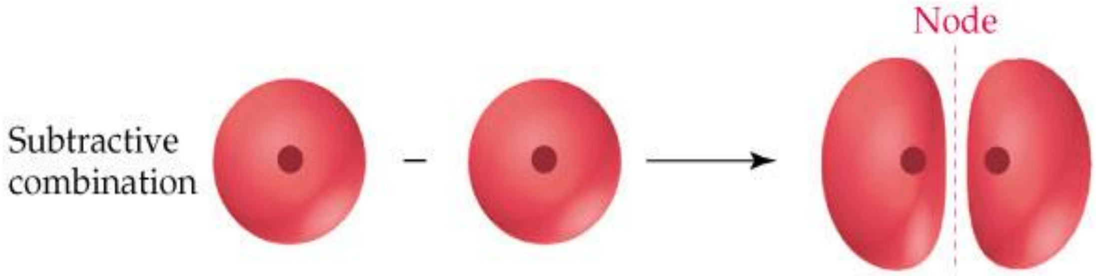
$$\Psi_{BMO} = \Psi_A + \Psi_B$$

$$\Psi_{ABMO} = \Psi_A - \Psi_B$$

Where, A and B are atoms

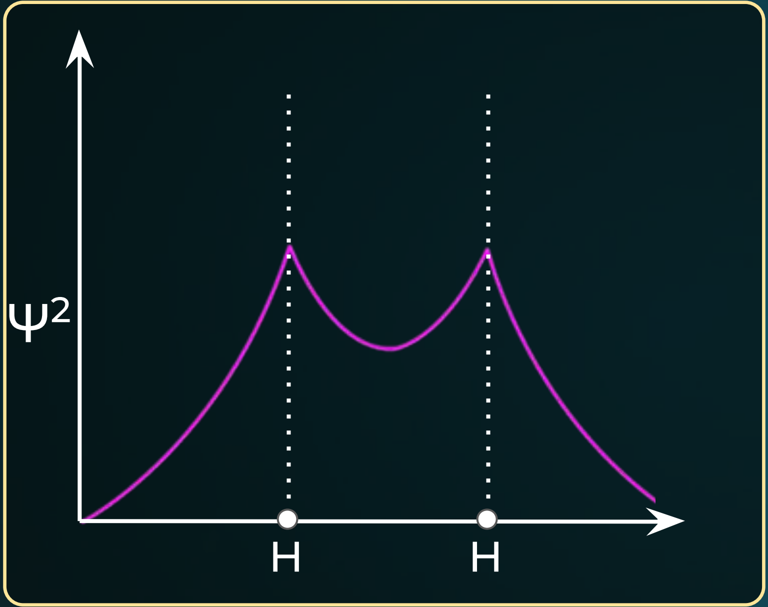
Molecular Orbitals

Bonding Molecular Orbital



AntiBonding Molecular Orbital

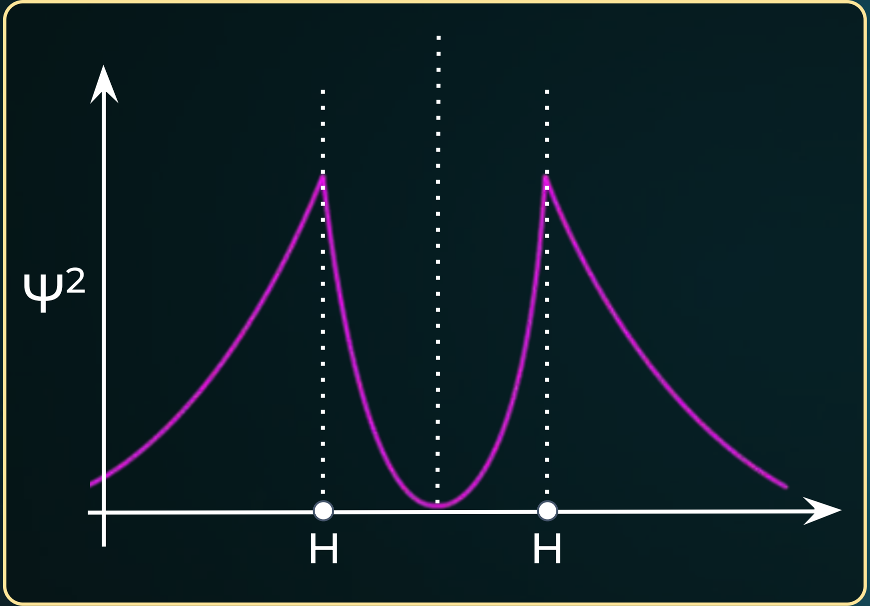
Electron Density in BMO



BMO

Electron density increases in the internuclear region.

Electron Density in ABMO



ABMO

Electron density decreases in the internuclear region.

Linear Combination of Atomic Orbitals

Types of MO's

01 **Bonding** Molecular Orbital (BMO)

02 **Antibonding** Molecular Orbital (ABMO)

Difference between BMO and ABMO

Bonding Molecular Orbital (BMO)	Antibonding Molecular Orbital (ABMO)
MO formed by the addition of Atomic orbitals	MO formed by the subtraction of atomic orbitals
$\Psi_{BMO} = \Psi_A + \Psi_B$	$\Psi_{ABMO} = \Psi_A - \Psi_B$
Formed by constructive interference (Stabilized MO)	Formed by destructive interference (Destabilized MO)

Bonding Molecular Orbital (BMO)	Antibonding Molecular Orbital (ABMO)
Lower in energy as compared to atomic orbital	Higher in energy as compared to atomic orbital
Electron density increases in the internuclear region	Electron density decreases in the internuclear region
May or may not have a nodal plane	Always has a nodal plane
Represented by $\sigma 1s, \sigma 2p_z, \pi 2p_x, \pi 2p_y$	Represented by $\sigma^* 1s, \sigma^* 2p_z, \pi^* 2p_x, \pi^* 2p_y$

σ and π Molecular Orbitals

σ Head on

Symmetrical around the bond axis

π Sideways

Asymmetrical around the bond axis

Shapes of MOs Formed by s-orbitals

When two orbitals combine in same phase then **constructive interference** take place.

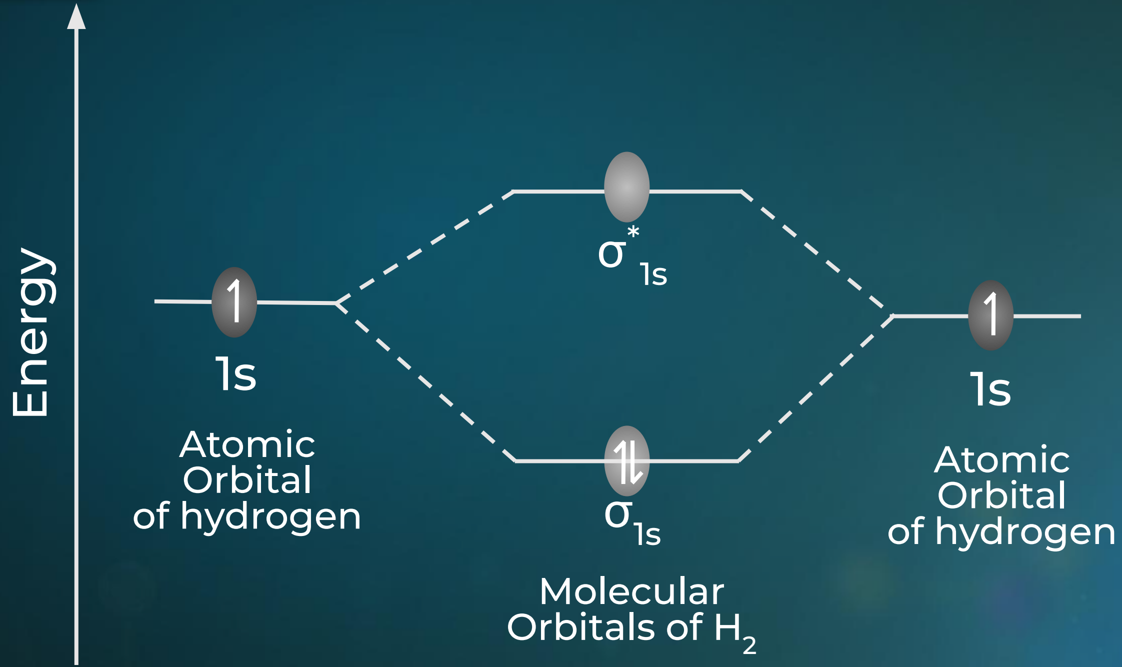
When two orbitals combine out of the phase then **destructive interference** take place.

$s + s \xrightarrow{\text{(Constructive Interference)}} \sigma_s$

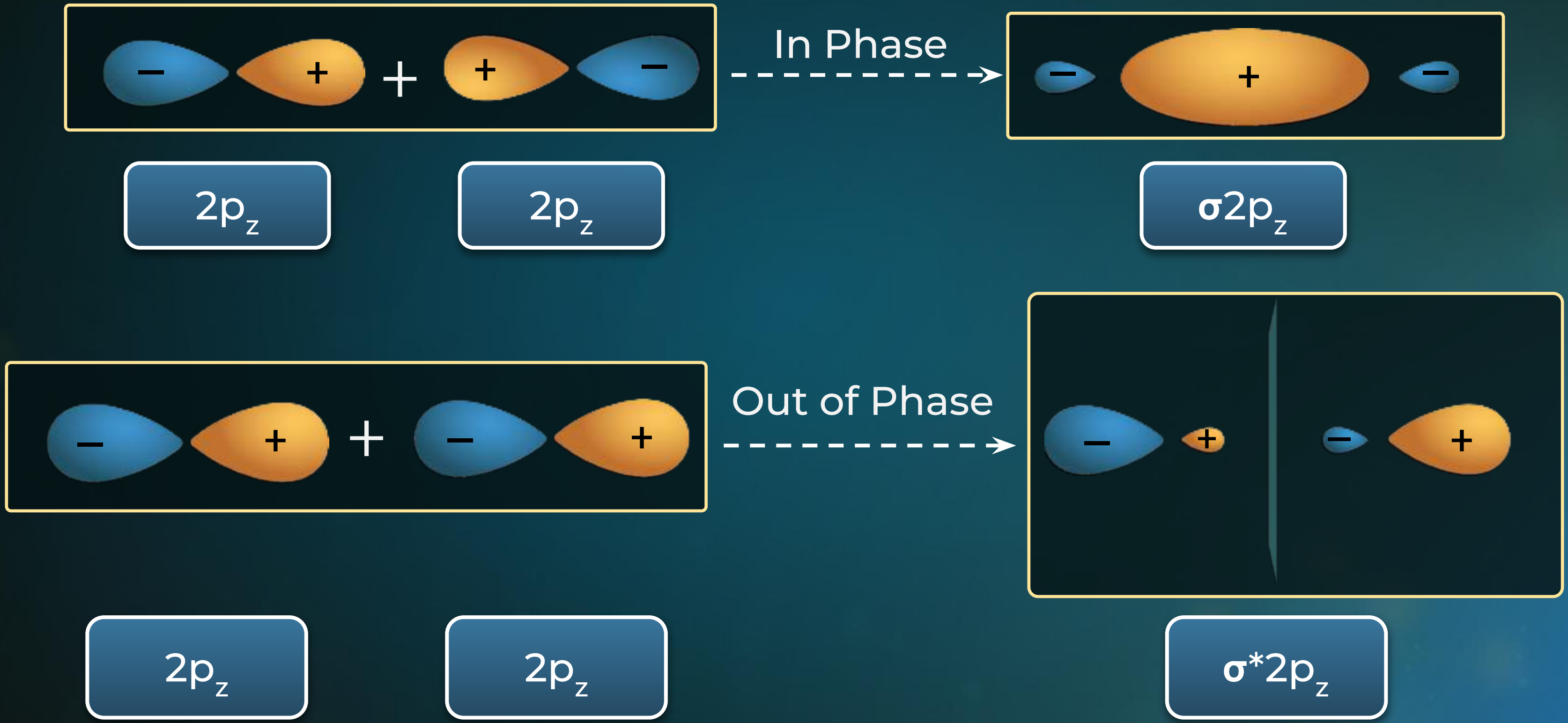
$s - s \xrightarrow{\text{(Destructive Interference)}} \sigma^*_s$

Molecular Orbital Energy Diagram

H_2 molecule



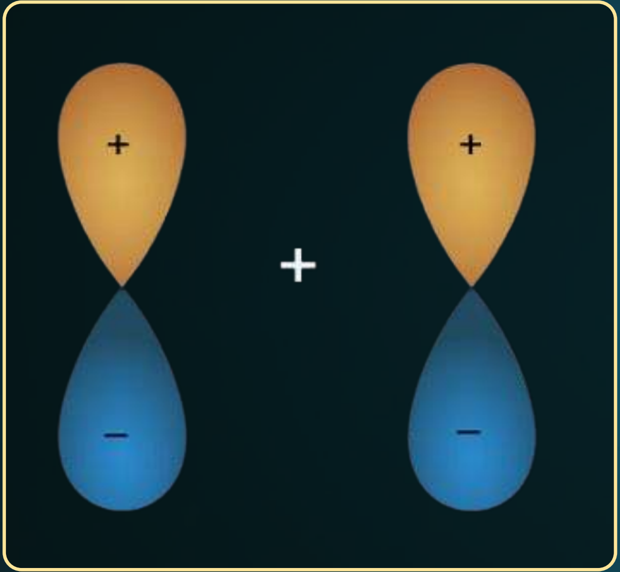
Shapes of MO's: $\sigma 2p_z$

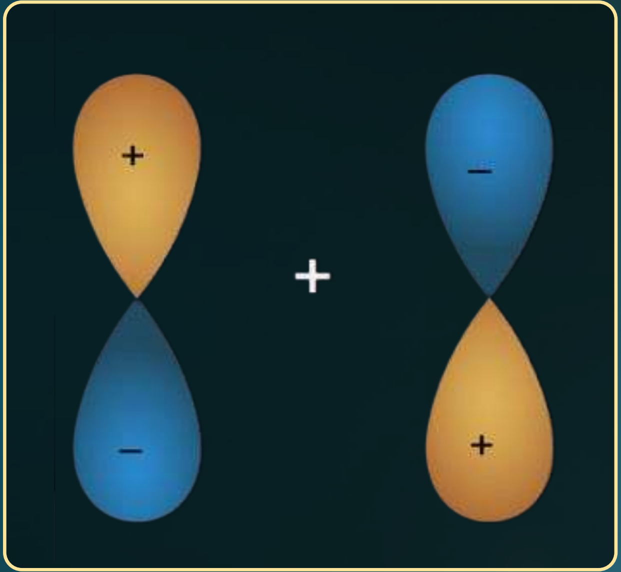


$2p_z$ + $2p_z$ In Phase → $\sigma 2p_z$

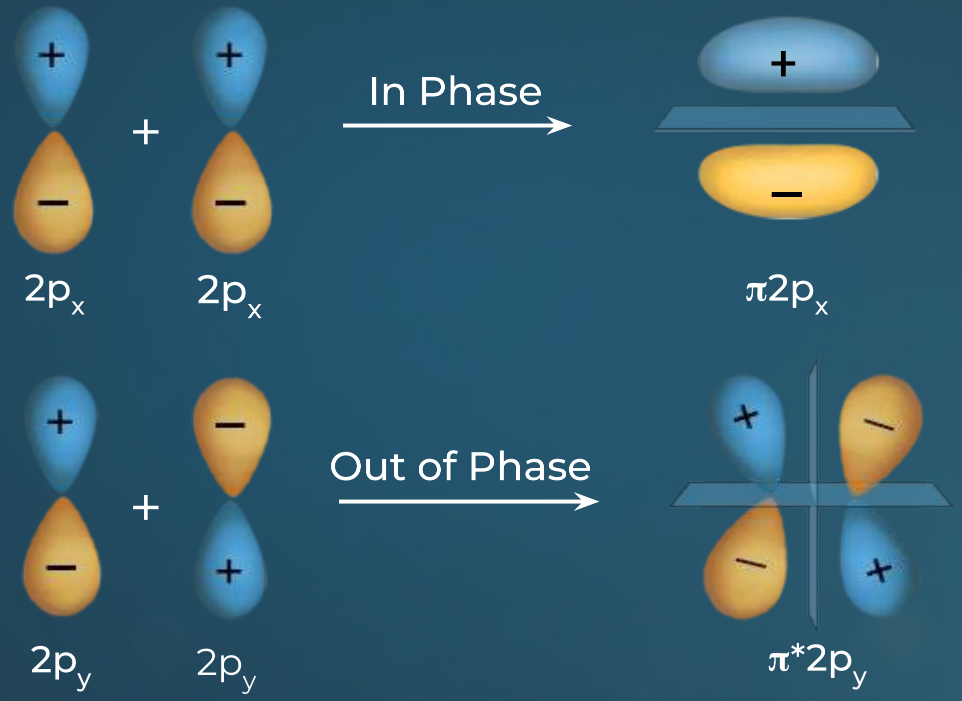
$2p_z$ + $2p_z$ Out of Phase → $\sigma^* 2p_z$

Shapes of MO’s





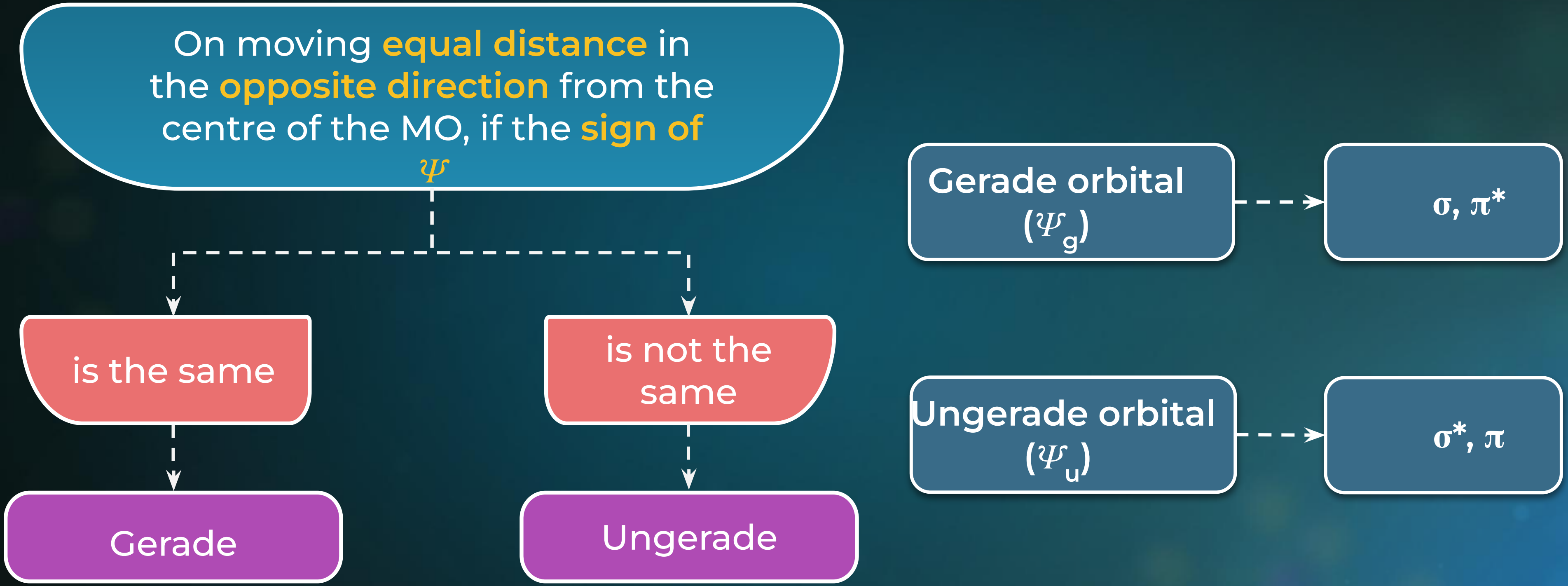
Shapes of MO's



$2p_x + 2p_x \xrightarrow{\text{In Phase}} \pi 2p_x$

$2p_y + 2p_y \xrightarrow{\text{Out of Phase}} \pi^* 2p_y$

Gerade & Ungerade Molecular Orbitals



On moving **equal distance** in the **opposite direction** from the centre of the MO, if the **sign of Ψ**

is the same → Gerade

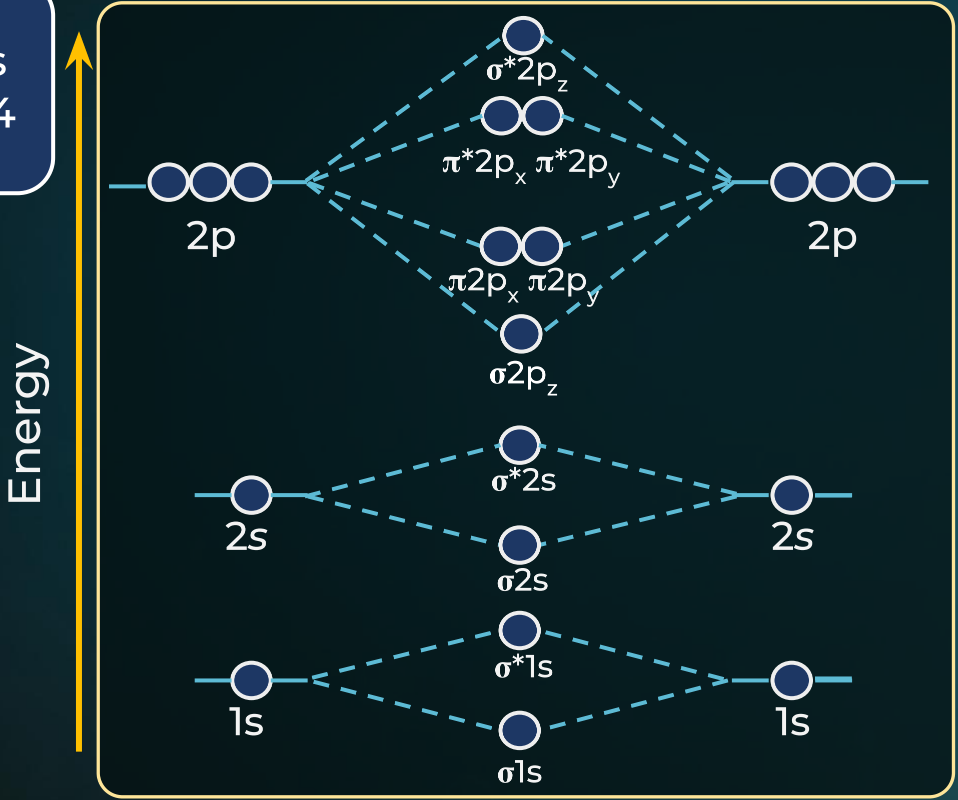
is not the same → Ungerade

Gerade orbital (Ψ_g) → σ, π^*

Ungerade orbital (Ψ_u) → σ^*, π

Molecular Orbital Diagram for > 14 Electron System

For molecules having > 14 electrons



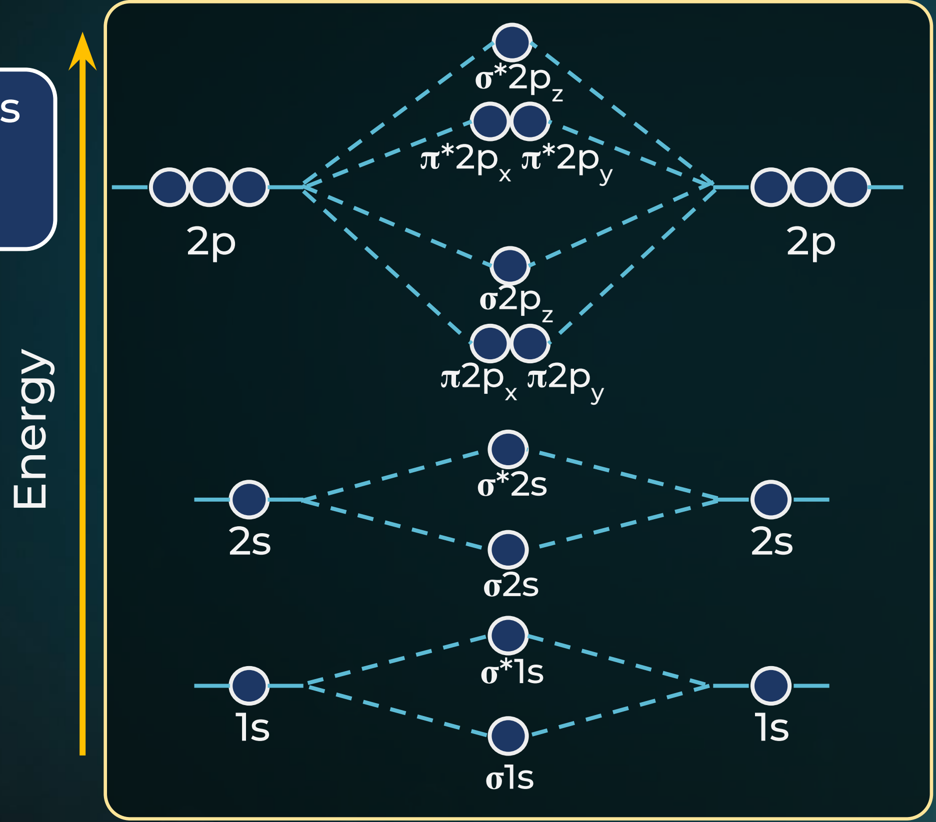
$(\sigma1s) < (\sigma^*1s) < (\sigma2s) < (\sigma^*2s)$

$< (\sigma2p_z) < [\pi2p_x = \pi2p_y] <$

$[\pi^*2p_x = \pi^*2p_y] < (\sigma^*2p_z)$

Molecular Orbital Diagram for ≤ 14 Electron System

For molecules having ≤ 14 electrons



$(\sigma1s) < (\sigma^*1s) < (\sigma2s) < (\sigma^*2s)$

$< [\pi2p_x = \pi2p_y] < (\sigma2p_z)$

$< [\pi^*2p_x = \pi^*2p_y] < (\sigma^*2p_z)$

s & p-Mixing

Modifications in the energies of MO’s due to s and p - mixing.

Also known as symmetry contribution.

Electronic Configuration (E.C.)

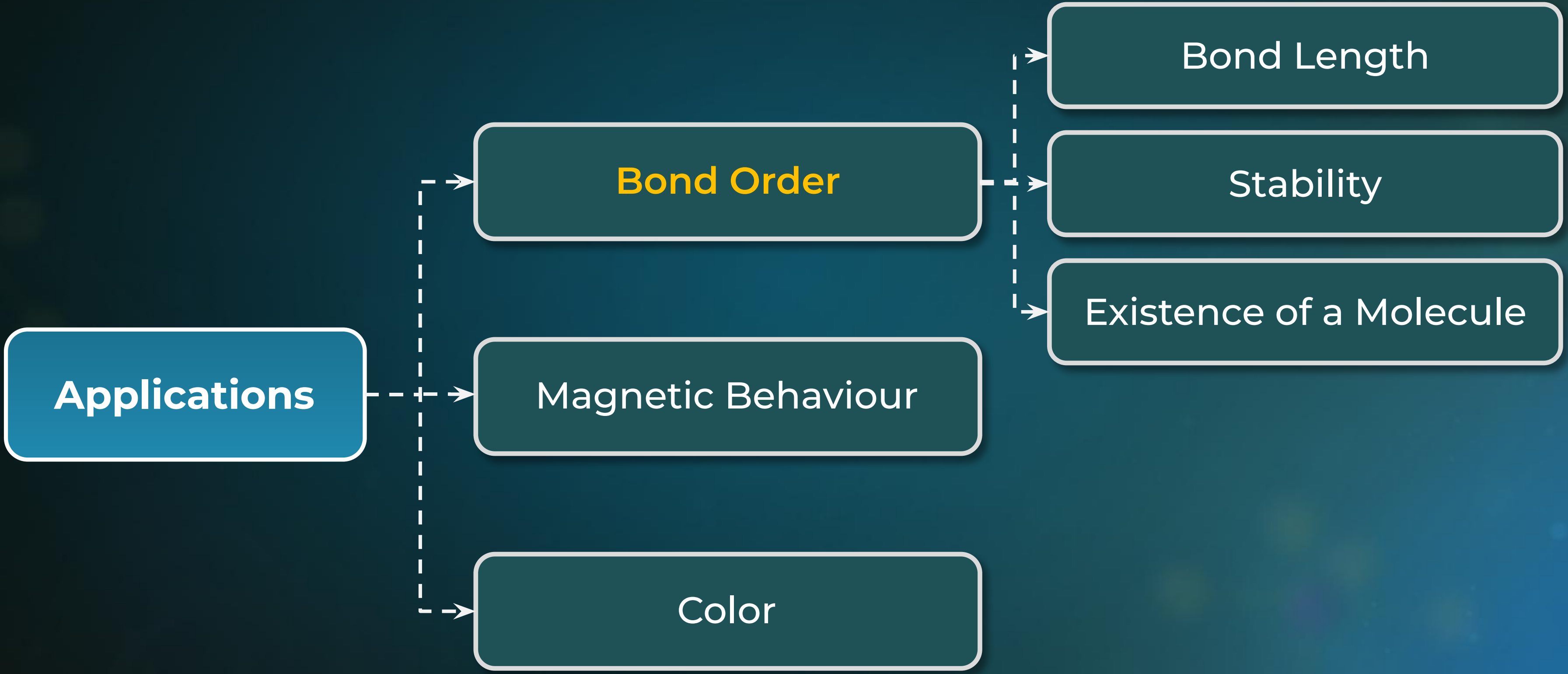
B - $1s^2\ 2s^2\ 2p^1$ (5 electrons)

For B_2 molecule, 10 electrons (< 14 electrons)

E.C. of B_2

$(\sigma 1s)^2\ (\sigma^*1s)^2\ (\sigma 2s)^2\ (\sigma^*2s)^2\ [(\pi 2p_x)^1 = (\pi 2p_y)^1]$

What Does MOT Tell?



Applications

- Bond Order
  - Bond Length
  - Stability
  - Existence of a Molecule
- Magnetic Behaviour
- Color

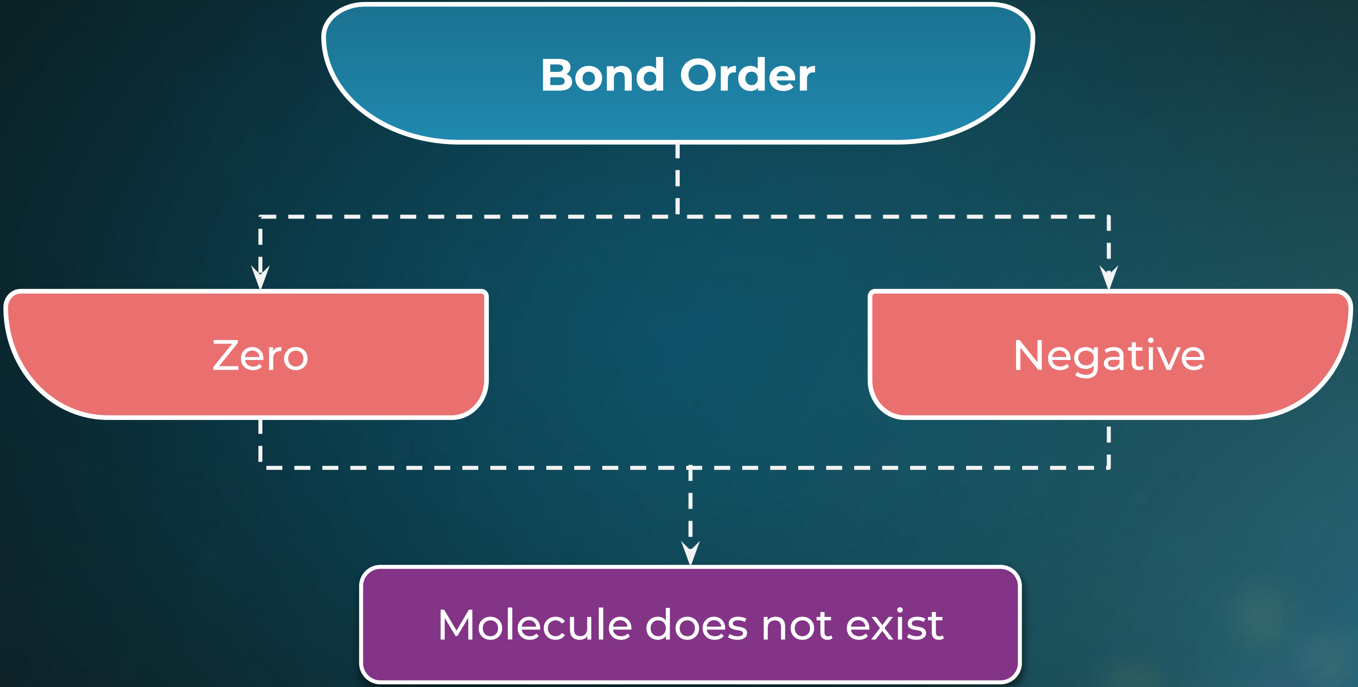
Bond Order

One half the difference between the number of electrons present in the BMO & the ABMO

$$\text{Bond Order (B.O.)} = \frac{1}{2}(N_b) - \frac{1}{2}(N_a)$$

N_a	Number of electrons in ABMO
N_b	Number of electrons in BMO

Existence of Molecules



Bond Order

Zero

Negative

Molecule does not exist

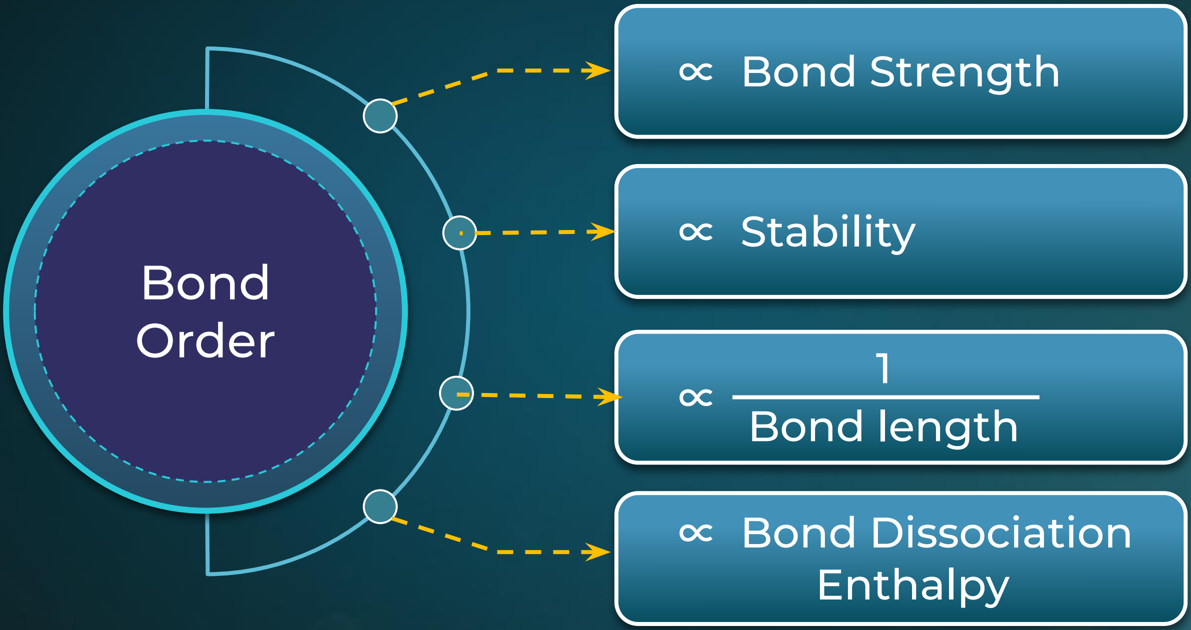
Thus, He_2 does not exist!!!

Calculation of Bond Order

Shortcut to find the bond order of homonuclear diatomic molecules

Number of electrons	10	11	12	13	14	15	16	17	18
Bond order	1	1.5	2	2.5	3	2.5	2	1.5	1

Bond Order and Stability of Molecules



Bond Order

$\propto$ Bond Strength

$\propto$ Stability

$$\propto \frac{1}{\text{Bond length}}$$

$\propto$ Bond Dissociation Enthalpy

Species with the Same Bond Order

01 If the bond order is same for two species

02 The one with higher number of electrons in ABMO is less stable.

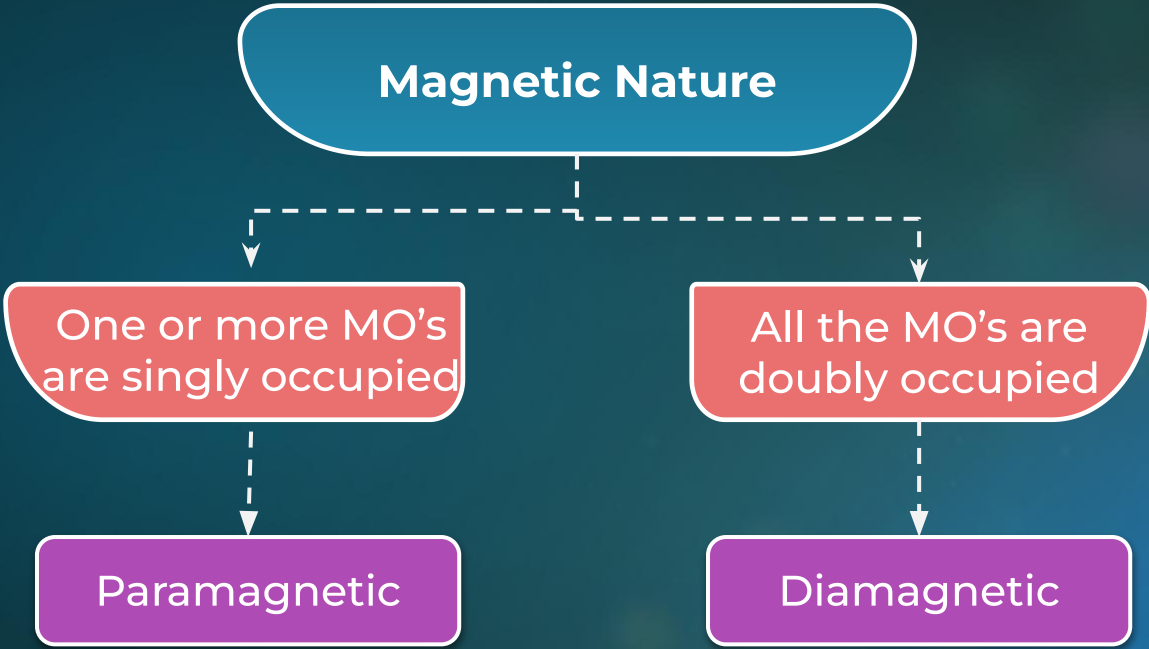
03 And the one with higher number of electrons in BMOs is more stable.

Magnetic Behaviour

Generally,

If the total number of electrons present in the species is odd, the species is paramagnetic

Examples : O_3^- , NO_2, NO, ClO_2



Magnetic Nature

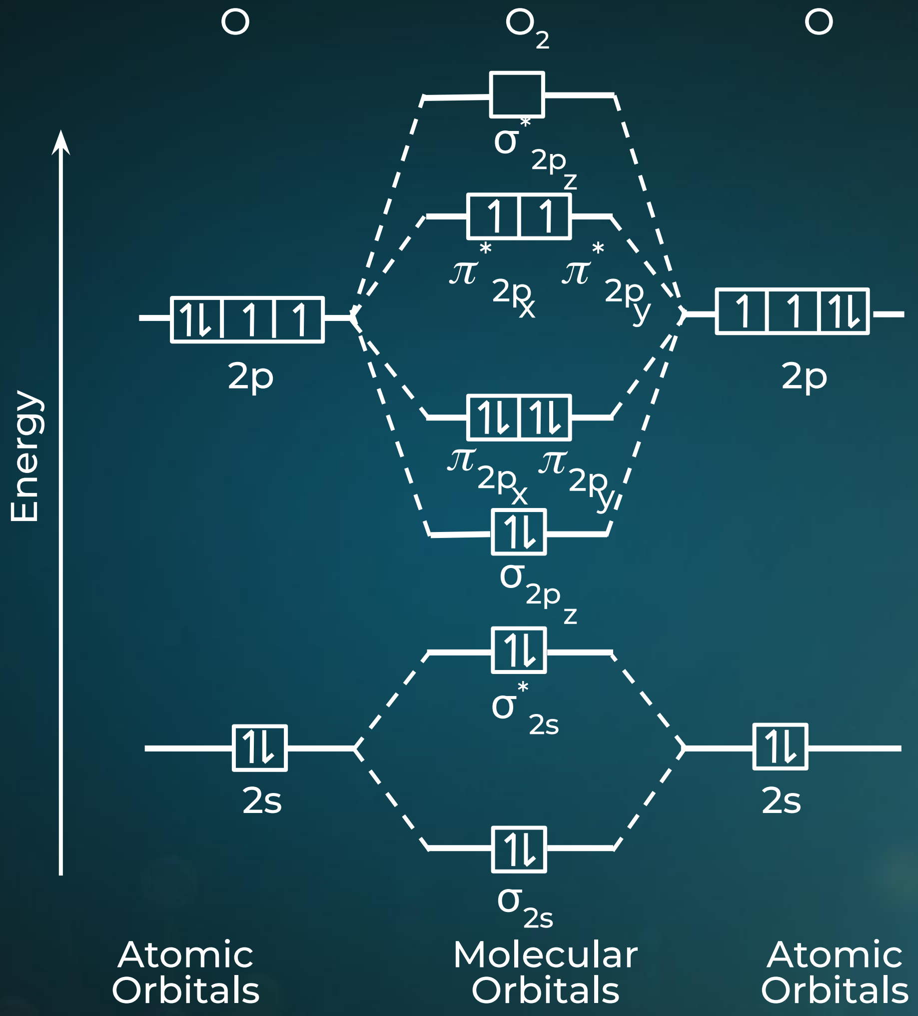
One or more MO's are singly occupied

Paramagnetic

All the MO's are doubly occupied

Diagmagnetic

O_2 molecule


O
O_2
O
$\sigma^*_{2p_z}$
$\pi^*_{2p_x}$
$\pi^*_{2p_y}$
Energy
2p
2p
π_{2p_x}
π_{2p_y}
σ_{2p_z}
σ^*_{2s}
2s
2s
σ_{2s}
Atomic Orbitals
Molecular Orbitals
Atomic Orbitals

Point to Remember!!

An unpaired electron acts as a magnetic dipole

Magnetic Moment (μ) = $\sqrt{n(n+2)}$ B.M.

n = Number of unpaired electrons

B.M. = Bohr Magneton

HOMO and LUMO

Highest Occupied Molecular Orbital

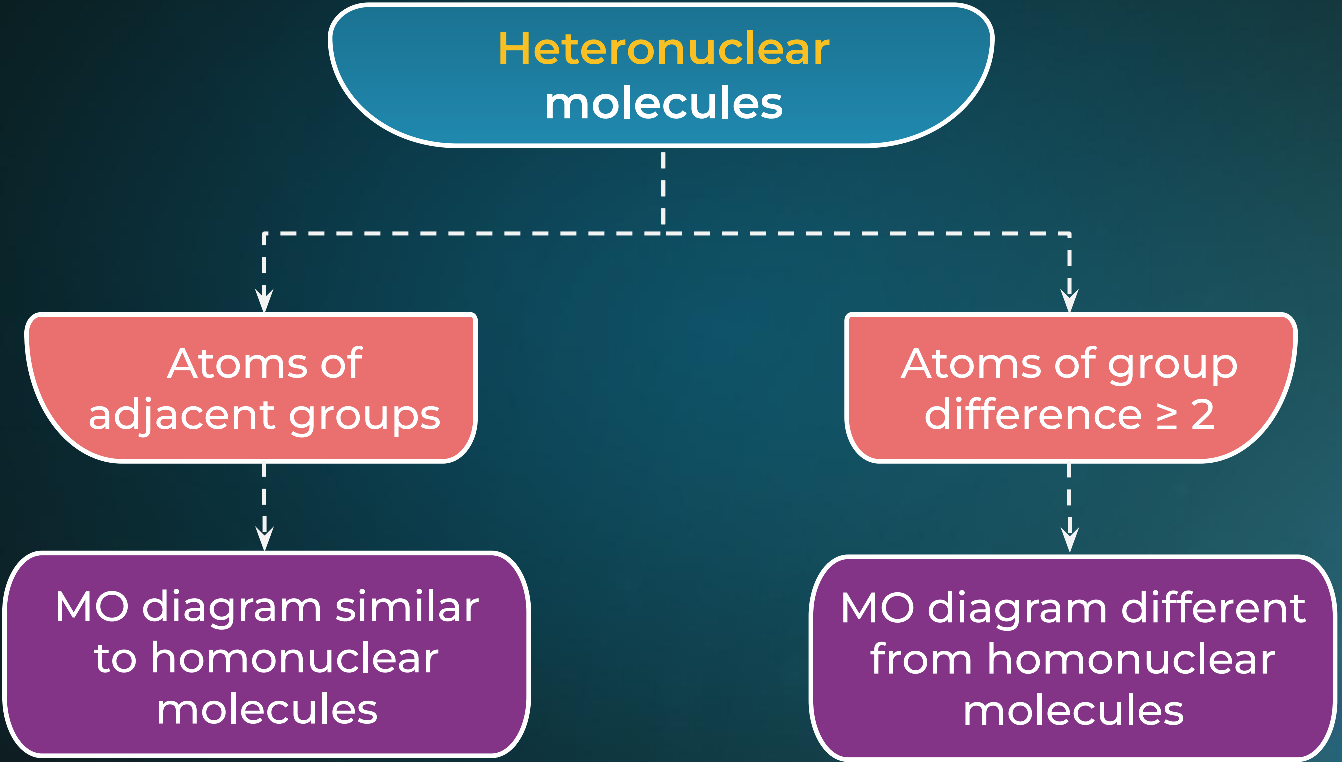
HOMO

Lowest Unoccupied Molecular Orbital

LUMO

MO Diagram of Heteronuclear Diatomic Molecules

MO Diagram of Heteronuclear Diatomic Molecules



Heteronuclear molecules

Atoms of adjacent groups

MO diagram similar to homonuclear molecules

Atoms of group difference ≥ 2

MO diagram different from homonuclear molecules

Heteronuclear Diatomic Molecules

Experimentally the bond orders of **NO and O_2^+** are the same.

Bond Order = 2.5

Paramagnetic

Experimentally the bond orders of **CN^- and N_2** are the same.

Bond Order = 3

Diamagnetic

Heteronuclear Diatomic Molecules

Experimentally the bond orders of **CO** and N_2 are the same.

Bond Order = 3

$1\sigma + 2\pi$ bonds

Diamagnetic

Bond Order

Isoelectronic molecules and ions have **identical** bond order.

Examples:

N_2 & CO: Bond order = 3

Metallic Bonding

Metallic Bonding

Formed between metal (electropositive element) and metal (electropositive element).

Electron sea model : Metal kernels occupy lattice positions in the crystal structure of a metal and are embedded is a gas of free valence electrons.

Point to Remember!!

Many mechanical properties of metals can be related to the strength of metallic bond

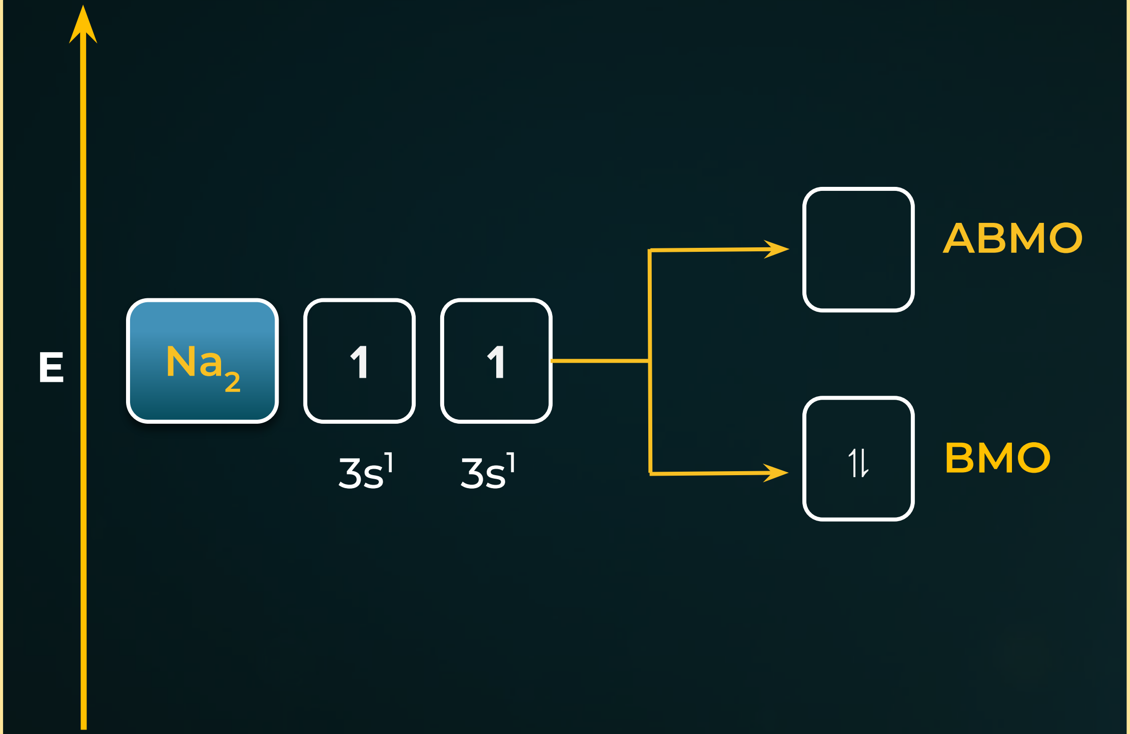
Melting point (M.P.) & hardness

M.P. & hardness of metals $\propto$ Strength of metallic bond

Band Theory

Overlap of atomic orbitals in solids gives rise to **bands of energy levels**

Band Theory



E

Na_2

1 1

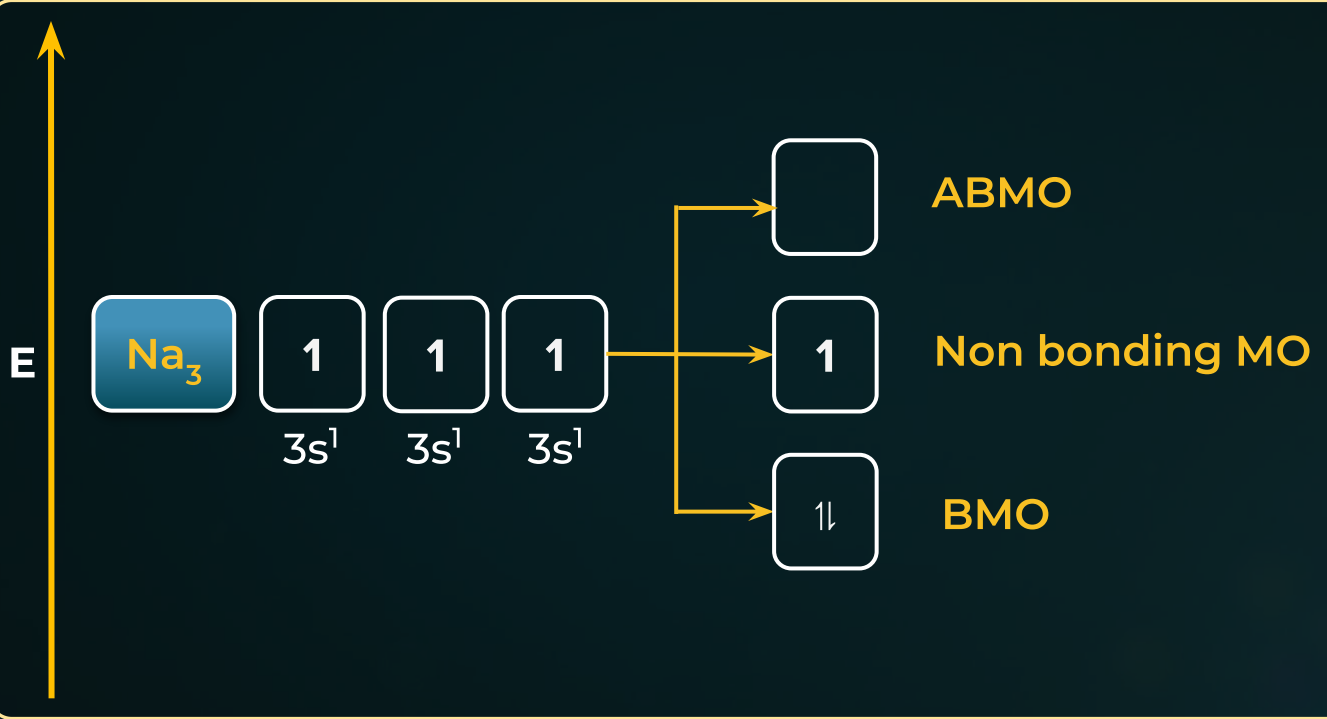
$3s^1$ $3s^1$

ABMO

⇅

BMO

Band Theory



E

Na_3

1 1 1

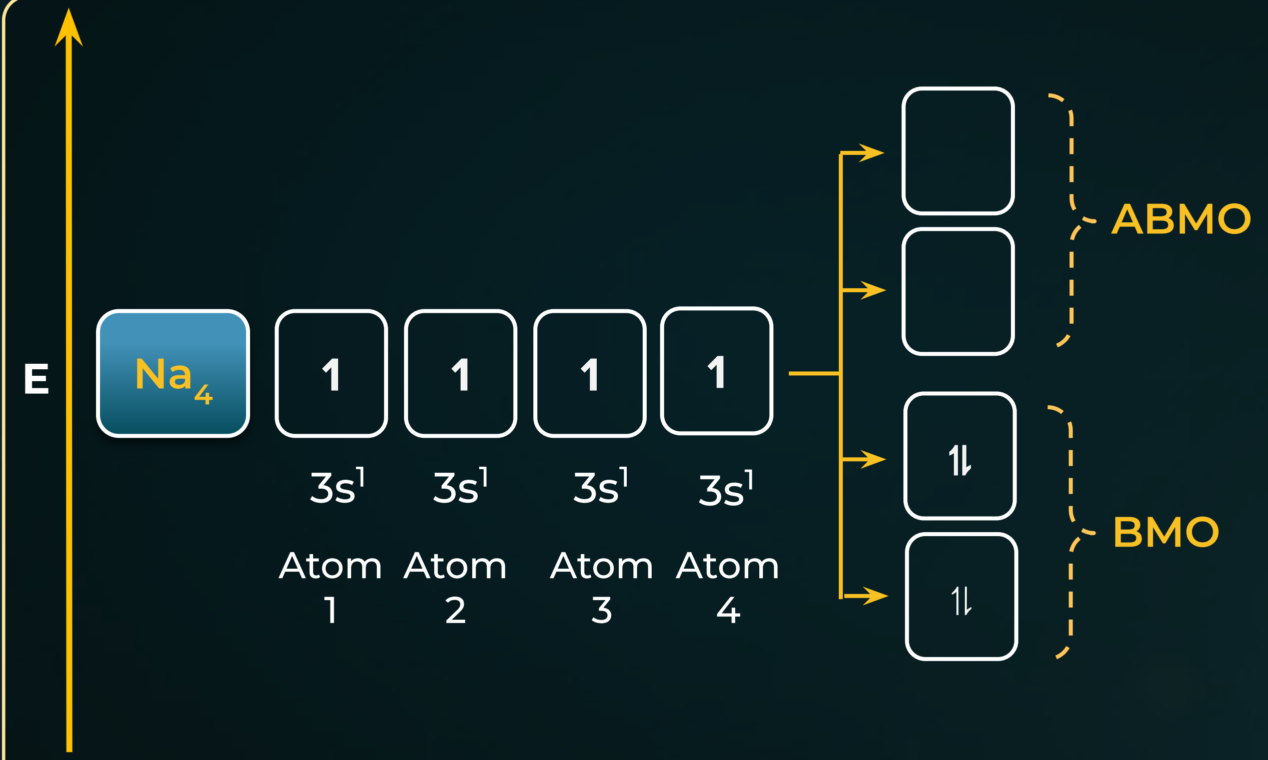
$3s^1$ $3s^1$ $3s^1$

ABMO

1 Non bonding MO

⇅ BMO

Band Theory



E

Na_4

1 1 1 1

$3s^1$ $3s^1$ $3s^1$ $3s^1$

Atom 1 Atom 2 Atom 3 Atom 4

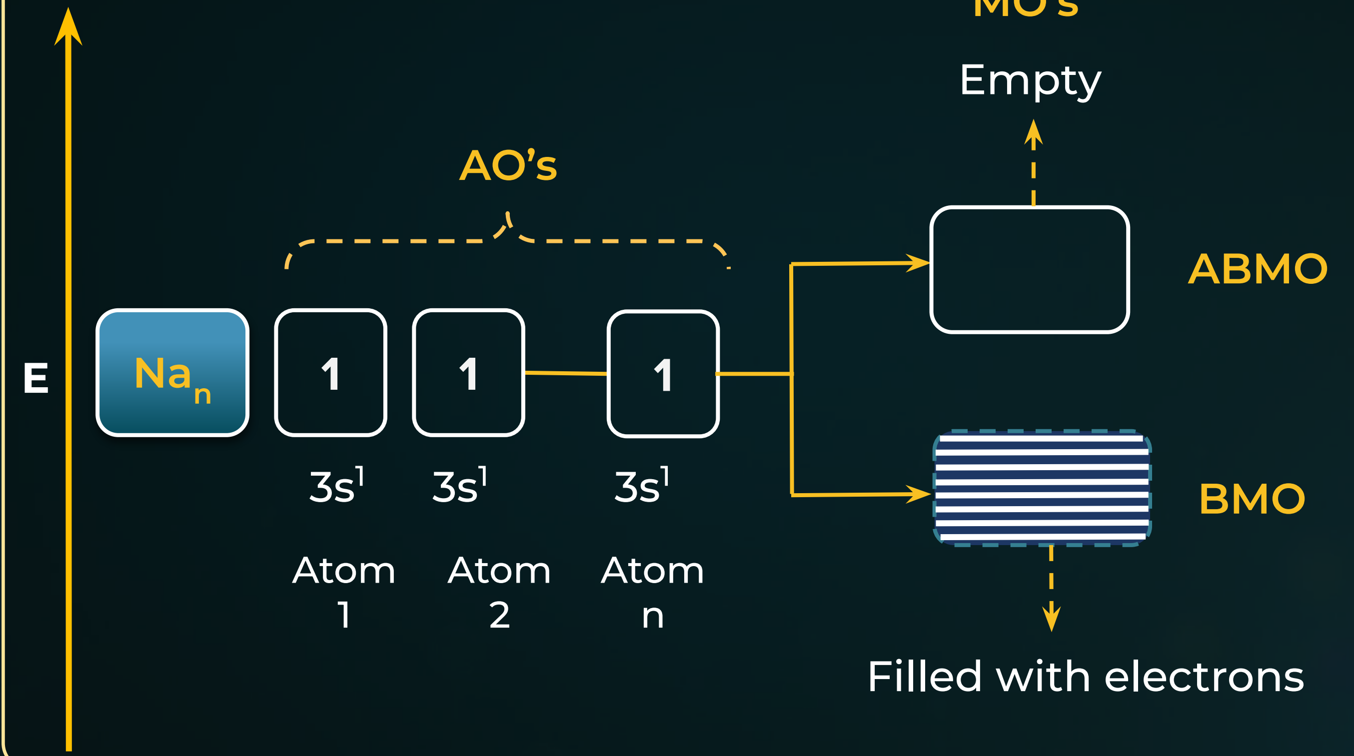
ABMO

⇅

⇅

BMO

Band Theory



E

Na_n

AO's

1 1 1

$3s^1$ $3s^1$ $3s^1$

Atom 1

Atom 2

Atom n

MO's

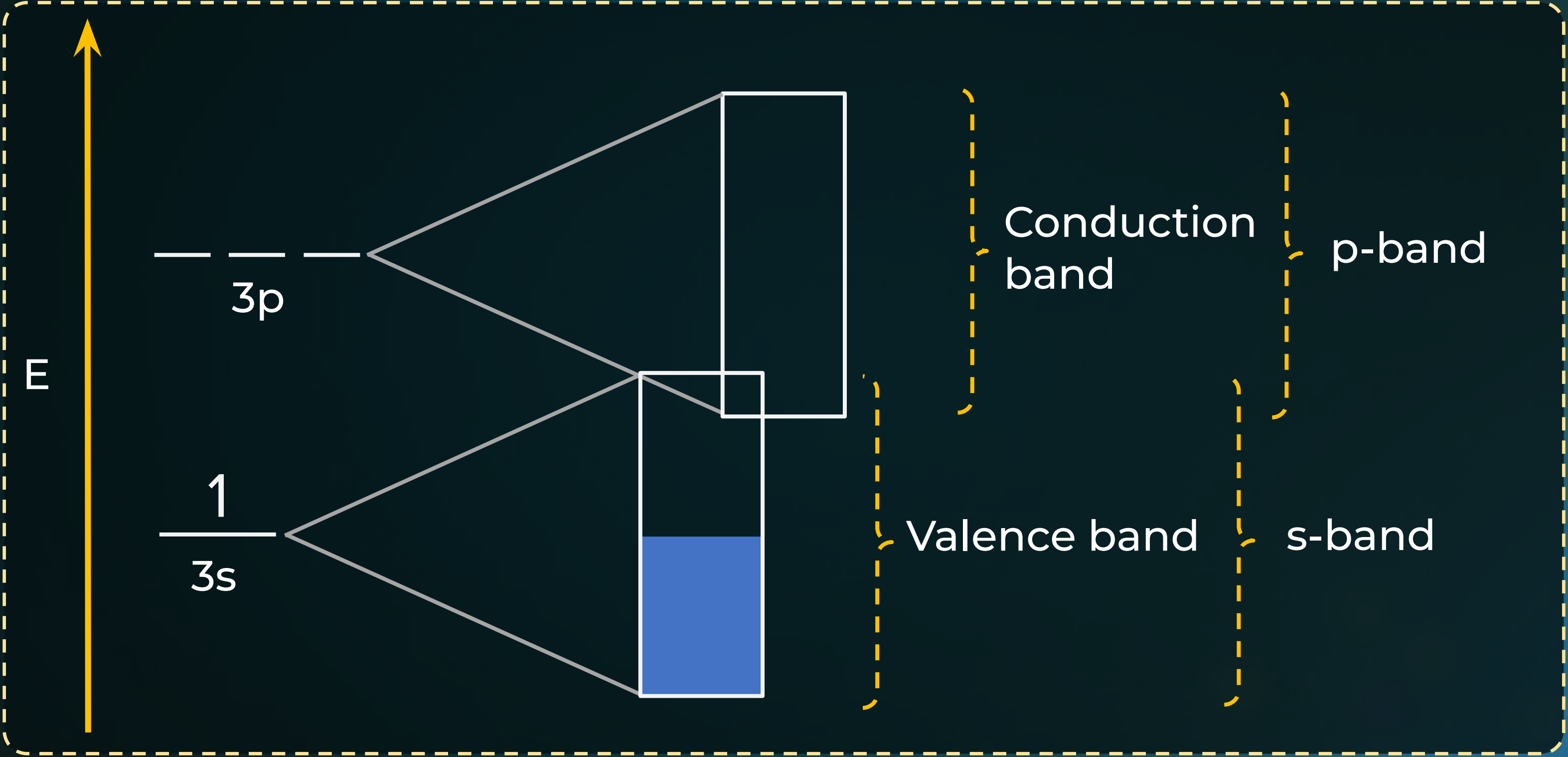
Empty

ABMO

BMO

Filled with electrons

Band of Orbital In Crystal of Sodium



Band Theory

Highest energy electrons of the metallic crystals occupy either a **partially filled band** or a **filled band that overlaps with an empty band**.

These **filled/ partially filled** bands and **empty** bands are known as **valence band** and **conduction band** respectively.

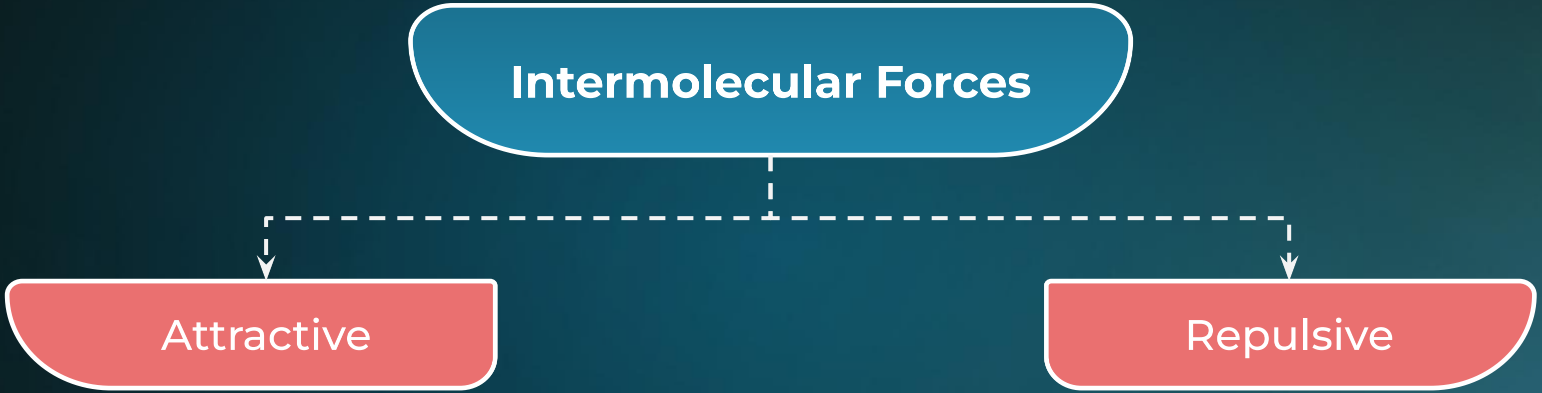
Band Gap

Energy difference between the **valence band** and the **conduction band**.

For **conductors**: No energy gap

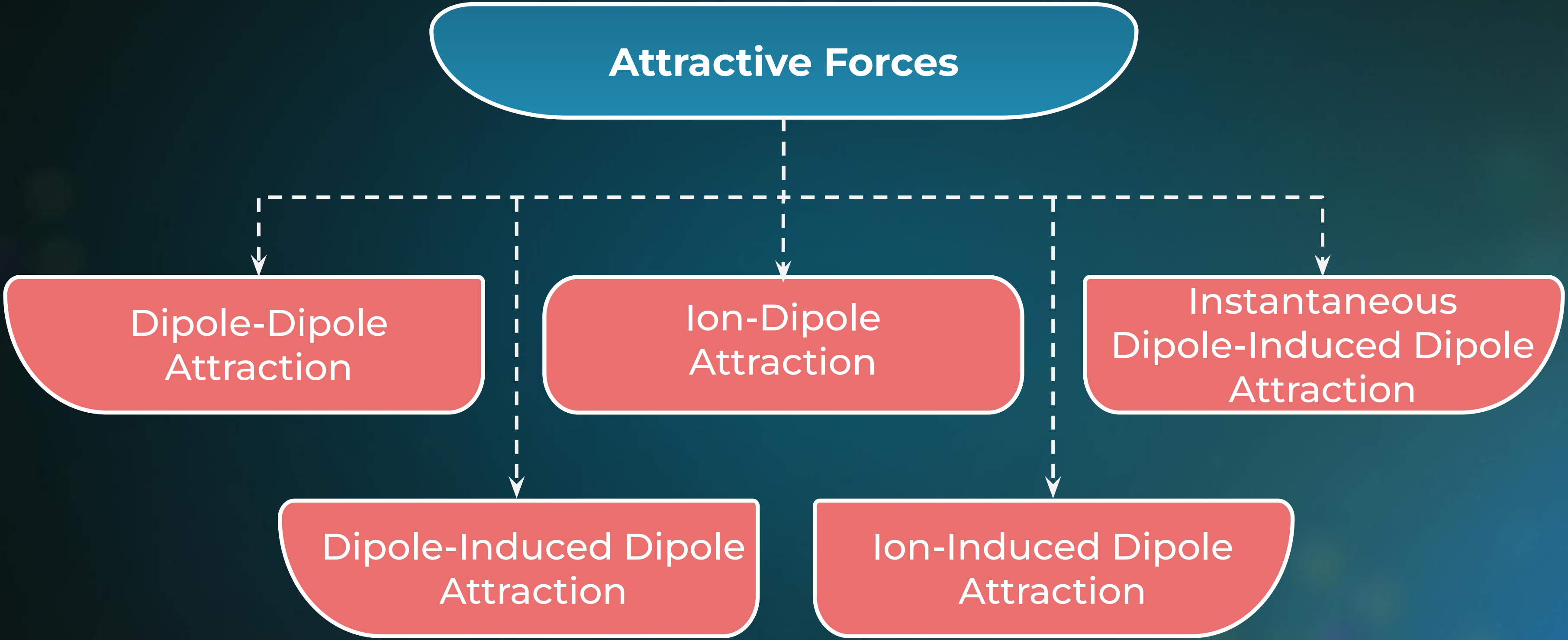
For **insulators**: Large energy gap

For **semiconductors**: Small energy gap



Intermolecular Forces

- Attractive
- Repulsive



Attractive Forces

- Dipole-Dipole Attraction
- Ion-Dipole Attraction
- Instantaneous Dipole-Induced Dipole Attraction
- Dipole-Induced Dipole Attraction
- Ion-Induced Dipole Attraction

van Der Waals Forces

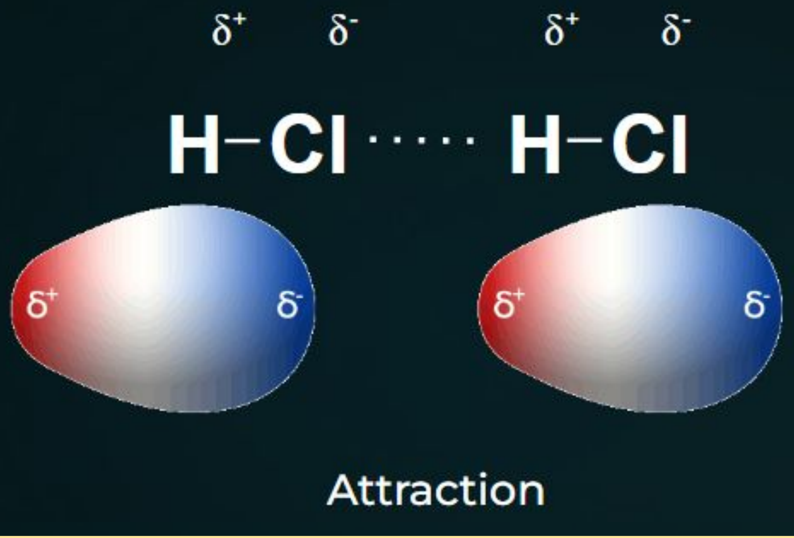
Weak chemical forces

Forces holding **two or more molecules together**

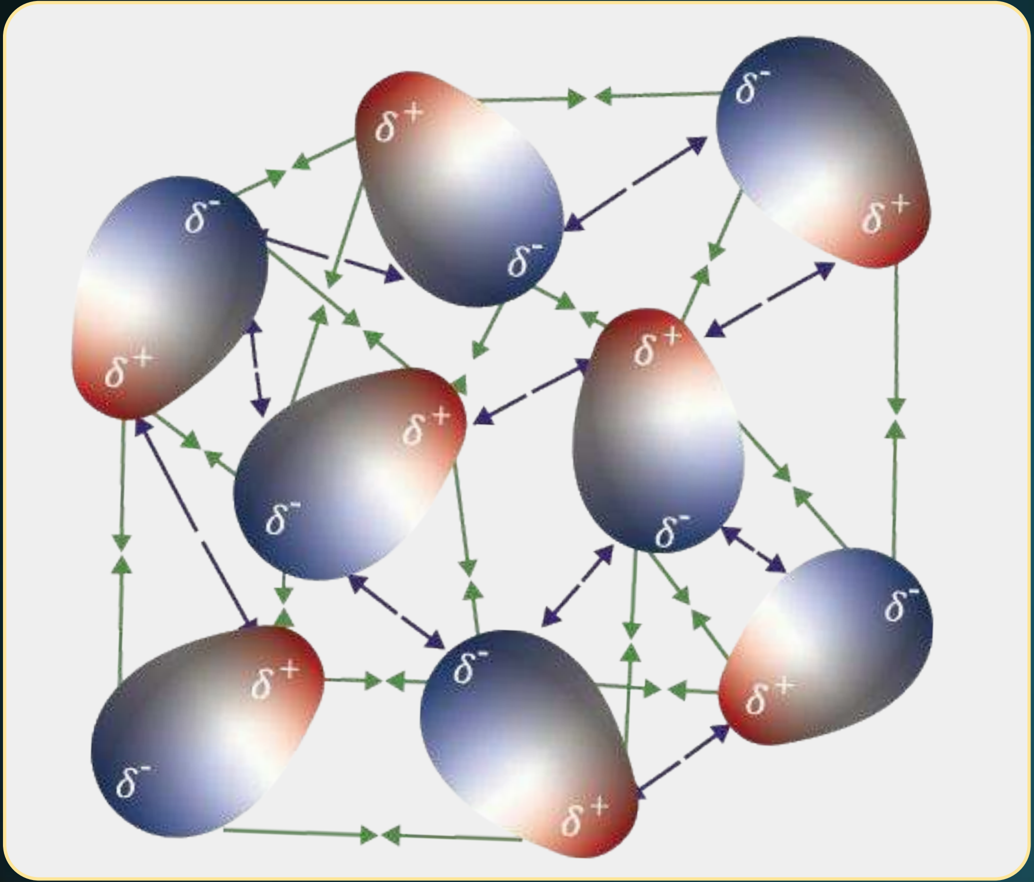
van der Waals forces

- Dipole-dipole forces
  - **Keesom forces**
- Dipole-induced dipole forces
  - **Debye forces**
- Dispersion forces
  - **London forces**

Dipole-Dipole Attraction



Exists between oppositely charged ends of permanent dipoles



Attraction → ←

Repulsion ← →

Dipole -Induced Dipole Attraction

It is a **weak attraction**, when a **polar molecule** induces a dipole in an **atom** or in a nonpolar molecule by disturbing the arrangement of electrons in the non-polar species.

Factors Affecting Boiling Point

Boiling Point $\propto$ **van der Waals forces**

Boiling Point $\propto$ **Molecular mass**

If **molecular mass is same**, then factor responsible is **molecular surface area**.

van der Waals Force $\propto$ Surface area.

Note!!

Polar molecules can interact via **London Forces** also.

Ion-Dipole Attraction

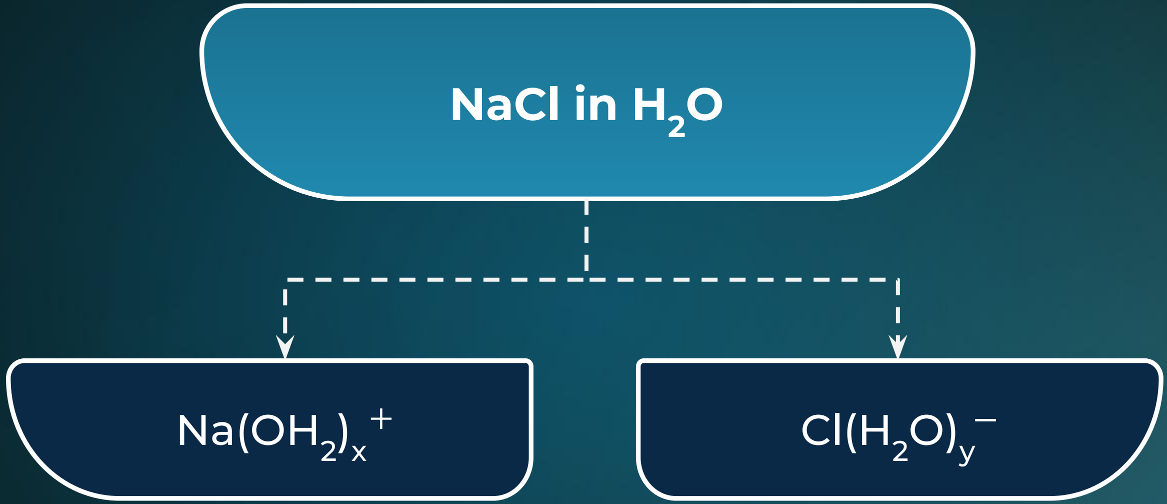
Ion ← Electrostatic Force → **Polar Molecule (Dipole)**

Strength of attraction is **directly proportional** to

(1) **Charge density** on the ion

(2) **Dipole moment** of the polar molecule

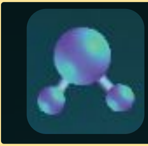
Ionic Compounds in Polar Solvents



NaCl in H_2O

$Na(OH_2)_x^{\ +}$

$Cl(H_2O)_y^{\ -}$



- - → H_2O

Ion-Induced Dipole Attraction

Ion

Electrostatic Force

Non-Polar Molecule (Induced Dipole)

Formation of Polyhalide Ions (X_3^-)

Interaction Energy v/s Distance

Type of interaction	Interaction energy $\propto \frac{1}{r^x}$
Ionic bond	$\frac{1}{r}$
Ion-dipole	$\frac{1}{r^2}$
Dipole-dipole	$\frac{1}{r^3}$

Type of interaction	Interaction energy $\propto \frac{1}{r^x}$
Ionic-Induced Dipole	$\frac{1}{r^4}$
Dipole-Induced dipole	$\frac{1}{r^6}$
London Forces	$\frac{1}{r^6}$

Strength of Intermolecular Forces

Ion-dipole attraction

Dipole-dipole attraction

Ion-induced dipole attraction

Dipole-induced dipole attraction

Instantaneous dipole - induced dipole attraction

Strength ↓

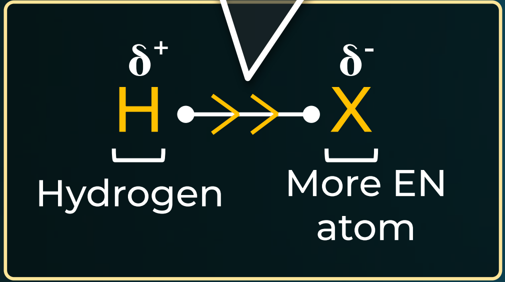
Strongest Dipole-Dipole interaction

↓

Hydrogen Bonding

Hydrogen Bond

Displacement of electrons towards X



Polar molecule having electrostatic force of attraction

Represented by a dotted line

$$---H^{\delta+}\text{—}X^{\delta-}---H^{\delta+}\text{—}X^{\delta-}---H^{\delta+}\text{—}X^{\delta-}---$$

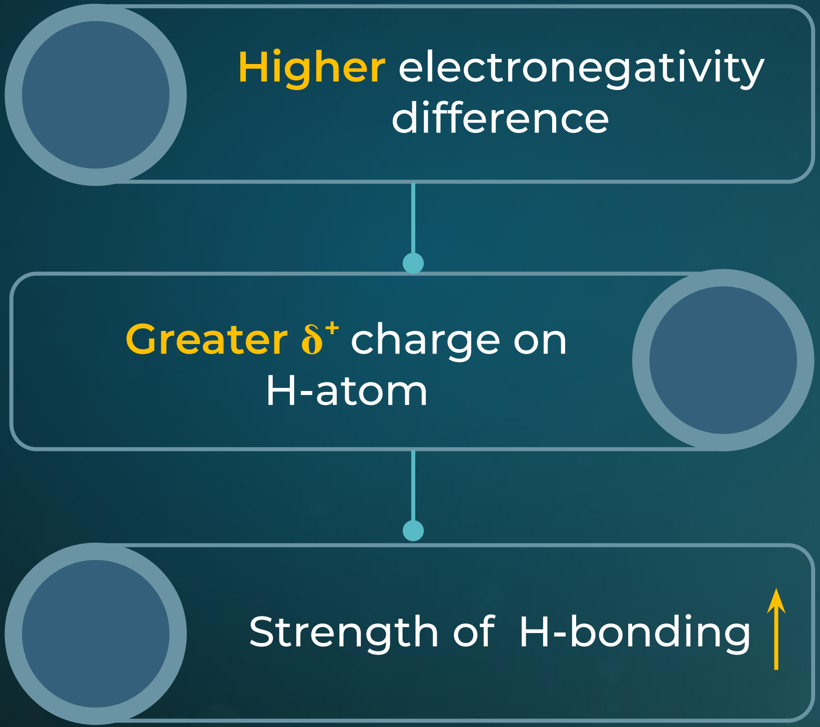
Hydrogen Bond

(1) Special case of dipole-dipole attraction

(2) Molecules with H atom attached to a highly electronegative atom

Strength of the H bond is determined by the coulombic interaction b/w the **lone pair of the E.N. atom** & **H atom.**

Factors Affecting Strength of H - bonding

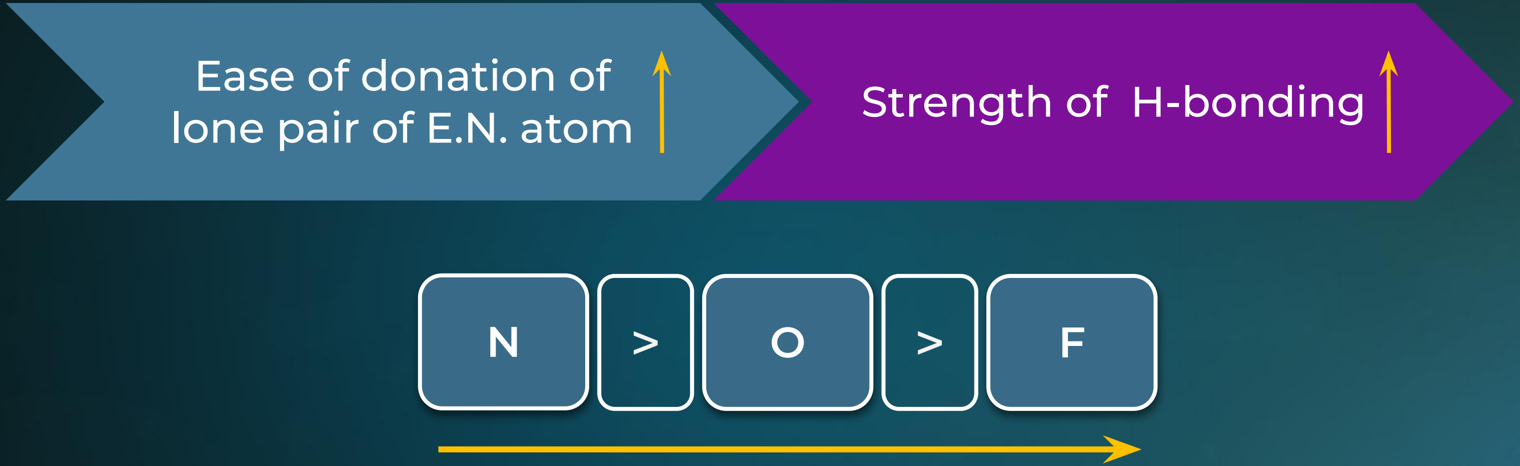


Higher electronegativity difference

Greater δ^{+} charge on H-atom

Strength of H-bonding ↑

Factors Affecting Strength of H - bonding



Ease of donation of lone pair of E.N. atom ↑

Strength of H-bonding ↑

N > O > F

Decreasing tendency to donate lone pair

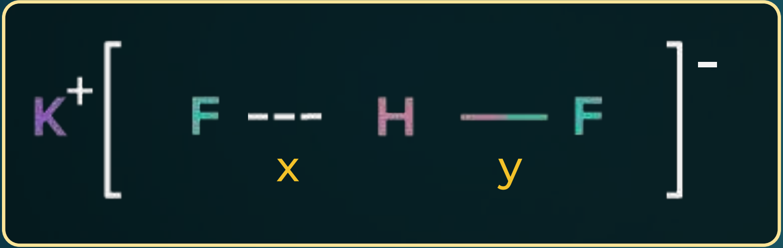
Point to Remember!!

To compare strength of H-bond

First check **Δ E.N.** and then **tendency to donate lone pair**

Symmetrical Hydrogen Bonding

Very strong H-bonding occurs in the **alkali metal hydrogen fluorides** of formula $M[HF_2]$

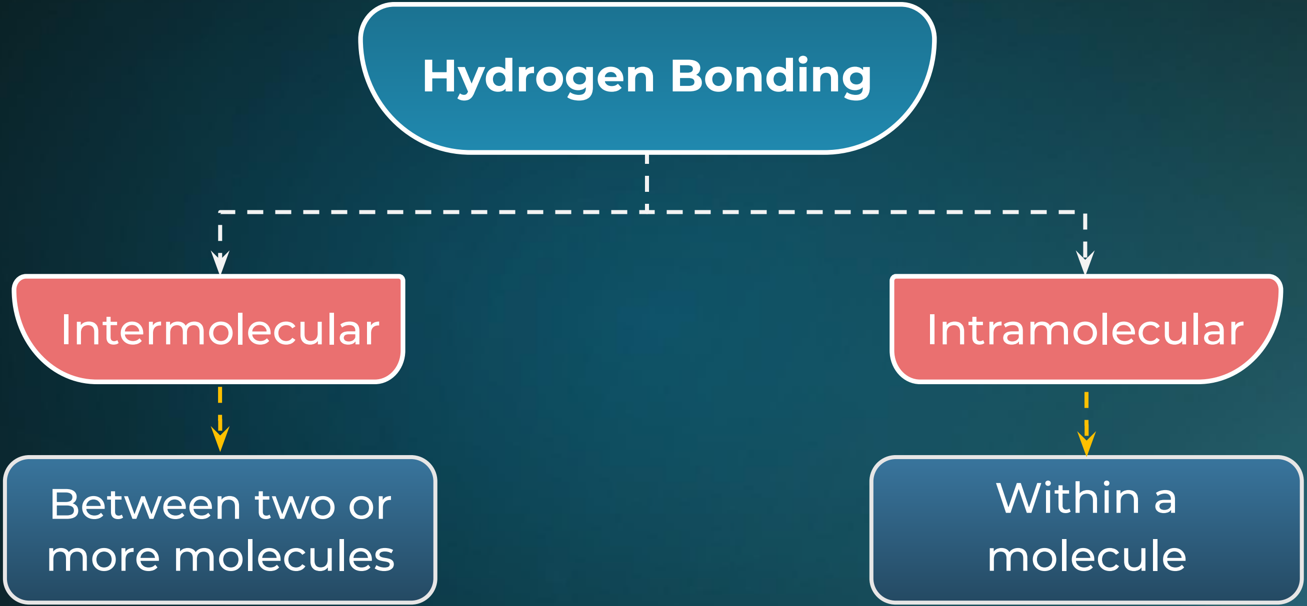


$$K^+\left[\, F \underset{x}{---} H \underset{y}{\text{—}} F \,\right]^-$$

Bond lengths: $x = y = 113$ pm

Bond energy of both H-F = 163 kJ/mol

Types of Hydrogen Bonding



Hydrogen Bonding

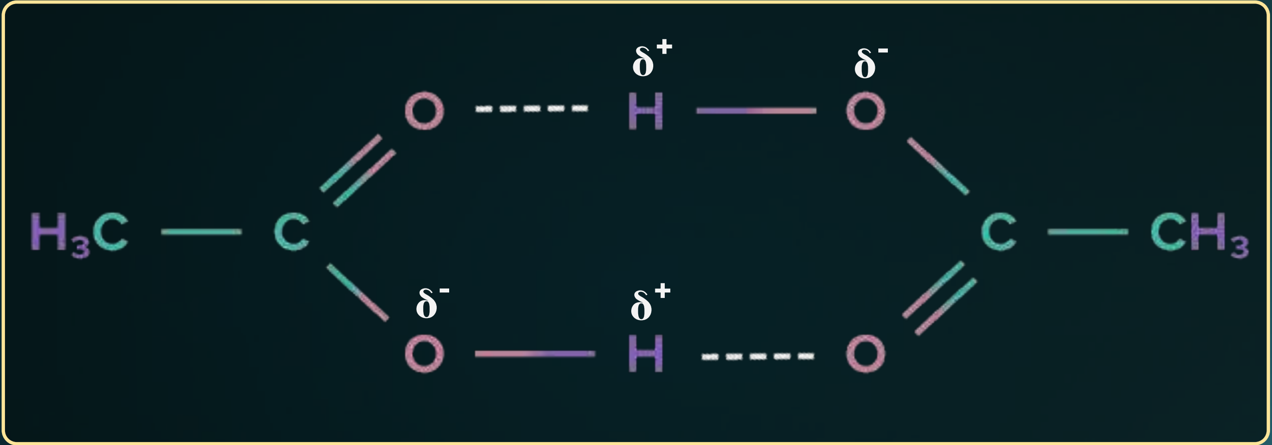
Intermolecular

Between two or more molecules

Intramolecular

Within a molecule

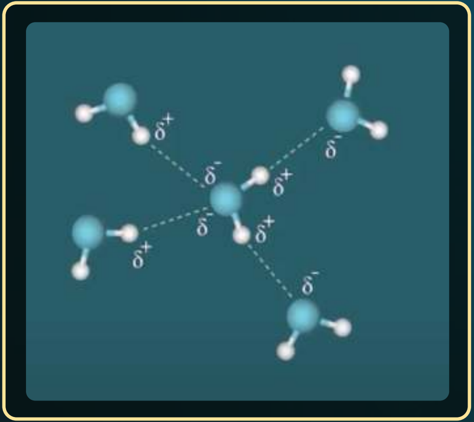
Examples of Intermolecular Hydrogen Bonding



Acetic Acid

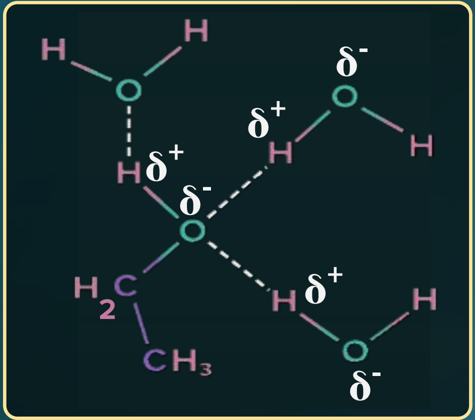
Intermolecular H - Bonding

Homo Intermolecular



Water

Hetero Intermolecular



Alcohol in Water

Conditions for the Formation of Intramolecular Hydrogen Bond

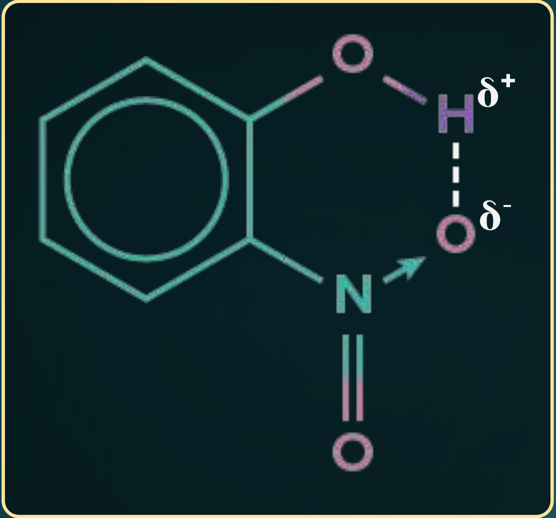
(1) Ring formed as a result of H bonding should be planar

(2) 5 or 6 membered ring should be formed

(3) Minimum strain should be there during ring closure

Intramolecular H-Bonding

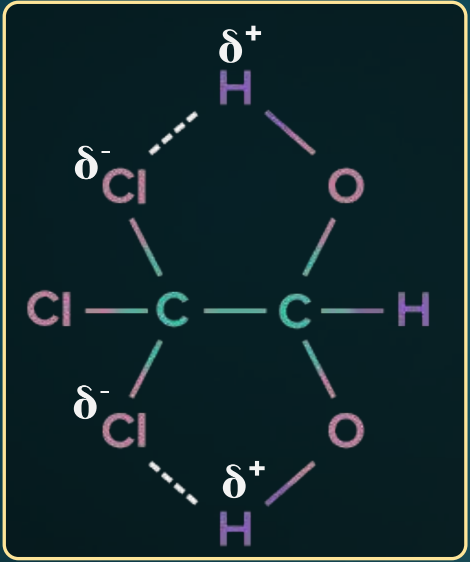
Examples



o-Nitrophenol

Point to Remember!!

Cl usually doesn't form H - bond due to their low charge density



Chloral hydrate ($CCl_3CH(OH)_2$)

H-Bonding Dependency on Physical State of Compounds

Extent of H–bonding depends on the **physical state** of the compound.

Gaseous state < Liquid state < Solid state

Effect of H-Bonding on Physical Properties

- Solubility
- Viscosity
- Boiling Point
- Physical State
- Acidic and Basic Strength

Solubility

01

Few organic compounds (Non-polar) are soluble in water (Polar solvent) due to H-bonding.
Example: Alcohol in water.

02

C_2H_2 is **highly soluble** in **acetone** due to H-bonding but not in water.

03

Intramolecular hydrogen bonding leads to chelate formation, so the **solubility** of that species involved in intramolecular H-bonding in water **decreases.**

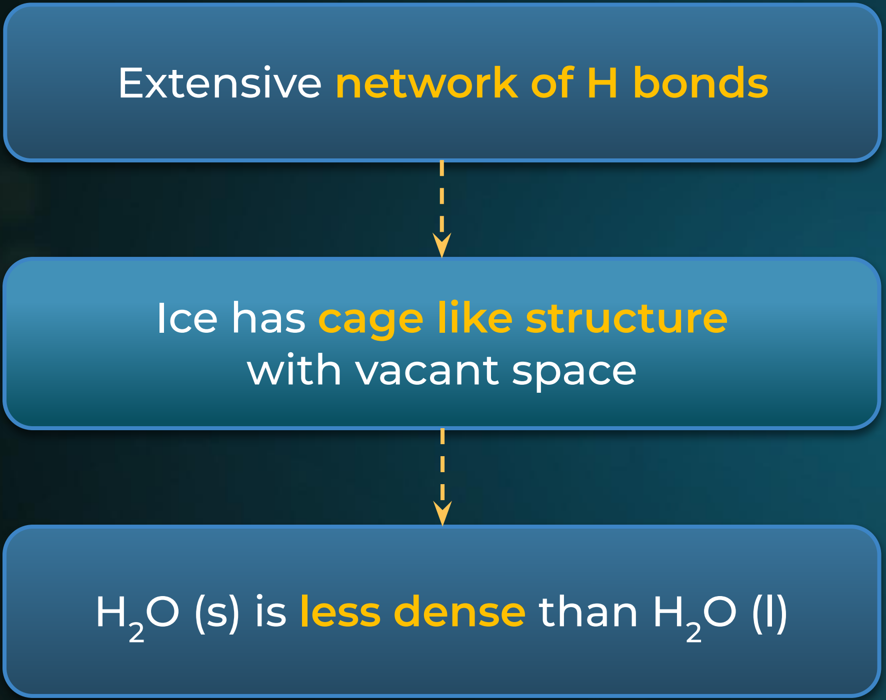
Order of Boiling Point

$SbH_3 > NH_3 > AsH_3 > PH_3$

$H_2O > H_2Te > H_2Se > H_2S$

$HF > HI > HBr > HCl$

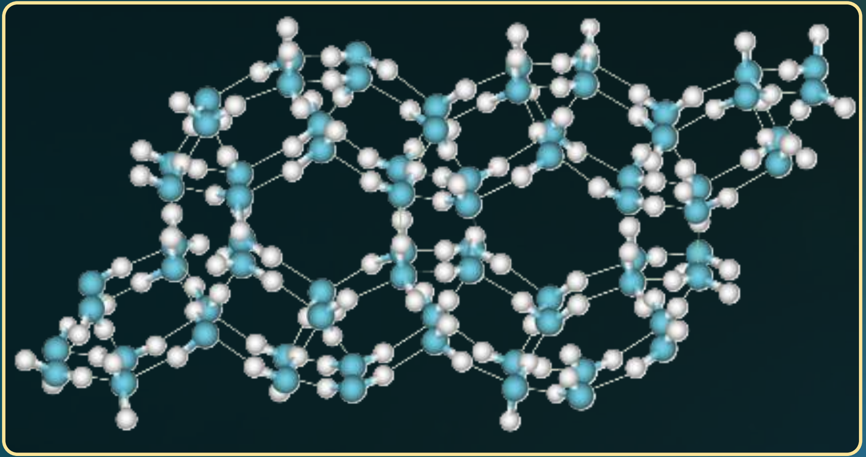
Why does Ice Floats over Water?



Extensive **network of H bonds**

Ice has **cage like structure**
with vacant space

H_2O (s) is **less dense** than H_2O (l)



Did You Know?

D_2O (s) sinks in H_2O (l)

E.N. of **D** is **less** than **H**

D forms **stronger** H-bond

Density: D_2O (s) > H_2O (l)

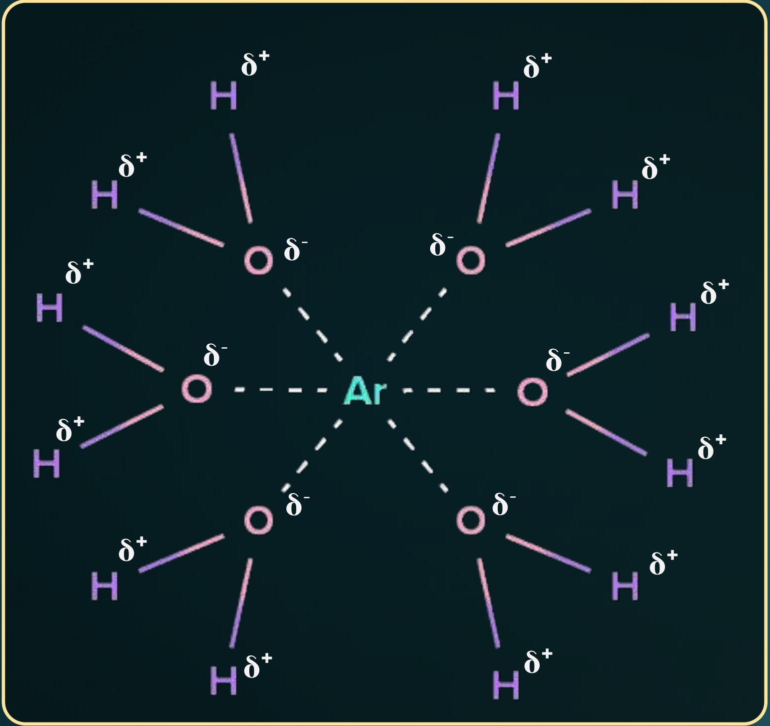
Clathrates

Species formed by **entrapment** of appropriately sized **gas molecules** (e.g.: Xe, Kr etc.) into the **voids of ice**

Noble Gas Clathrates

- $Ar.6H_2O$
- $Kr.6H_2O$
- $Xe.6H_2O$

Clathrates



$Ar.6H_2O$