

Welcome to

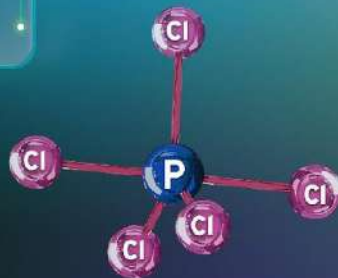
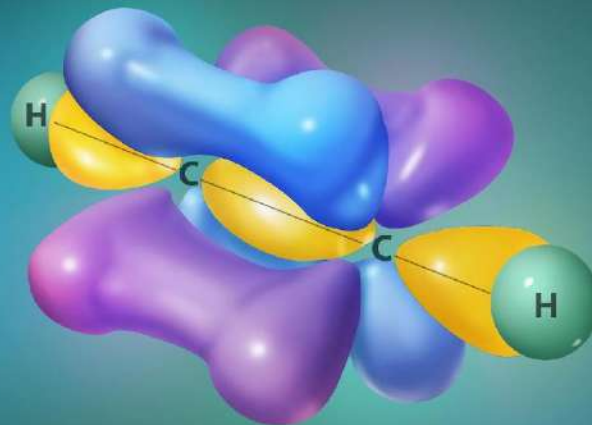


Aakash



BYJU'S LIVE

Chemical Bonding and
Molecular Structure

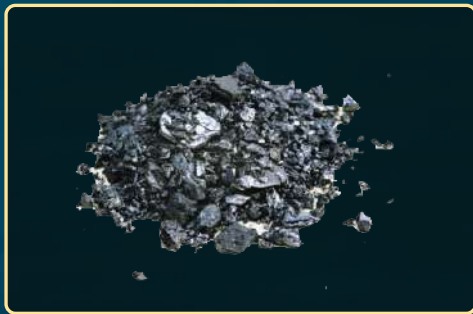




NaCl



CaCO₃



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?

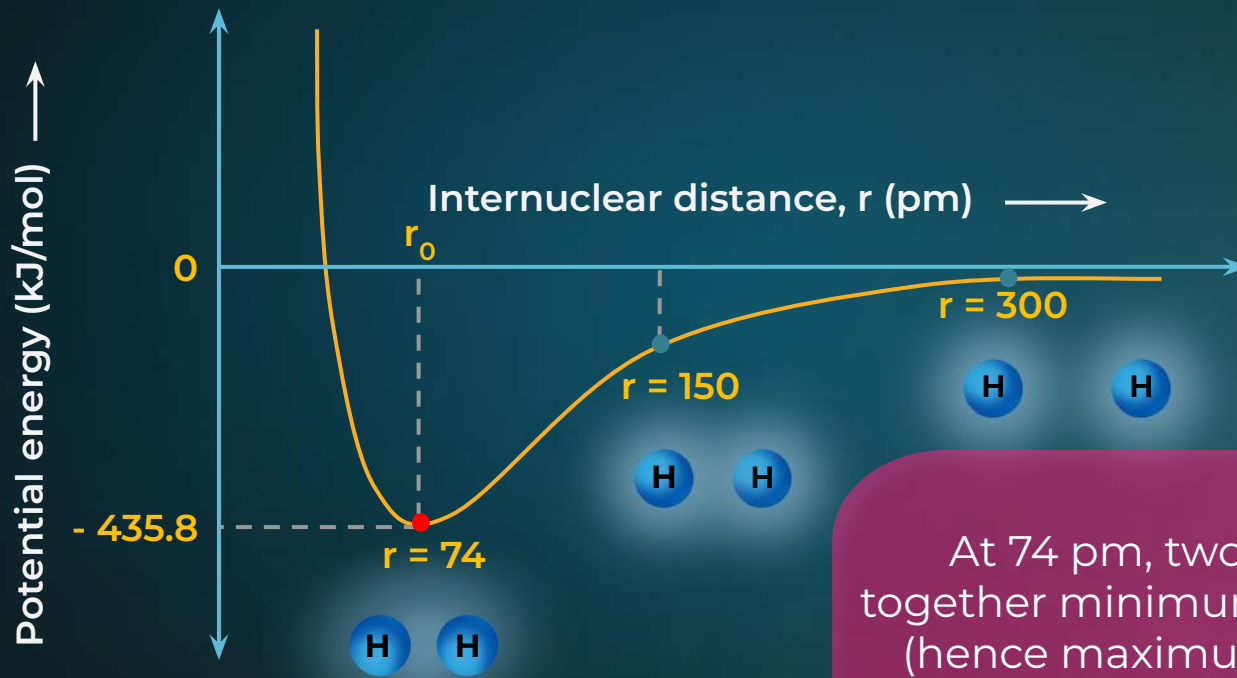


Chemical Bond

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

Electropositive &
Electronegative
atoms

Covalent Bond

Two
electronegative
atoms

Metallic Bond

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**.

(3)

Large difference in **electronegativity** of two elements

(2)

The element accepting electron should have **HIGH electron gain enthalpy**.

(4)

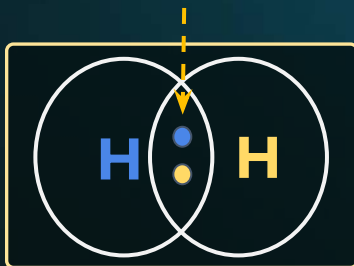
High Lattice enthalpy

Covalent Bond and Coordinate Bond

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

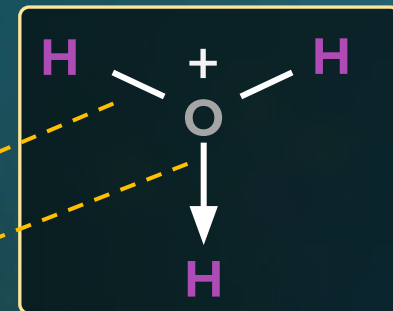
A bond in which the shared pair of electrons **originate from one atom** and none from the other is called coordinate bond.

Shared pair of electrons



Covalent Bond

Coordinate Bond



Metallic Bonds

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



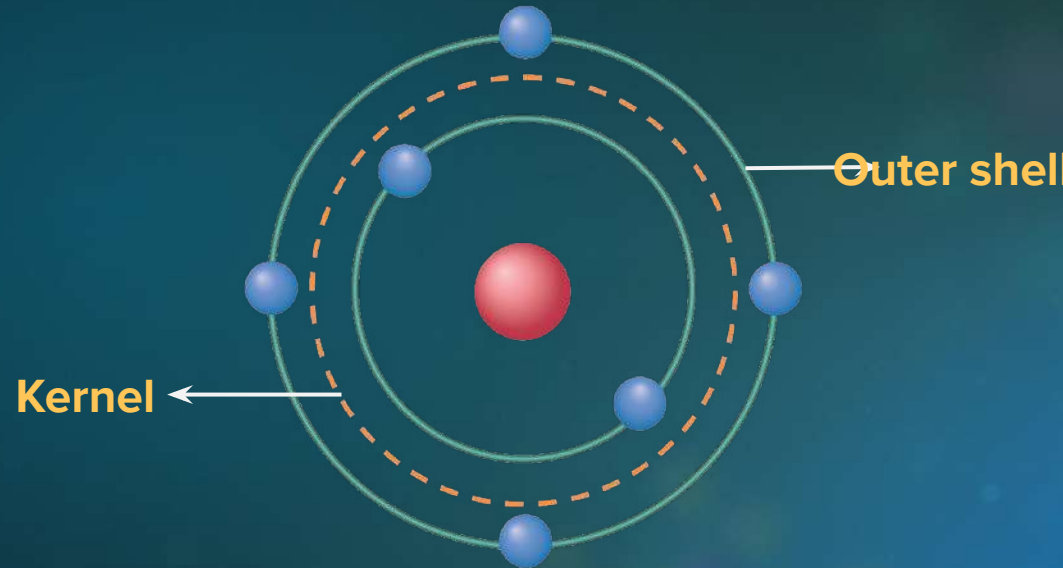
Metallic Bonds

Kernel

Nucleus plus
the inner electrons

Valence electrons

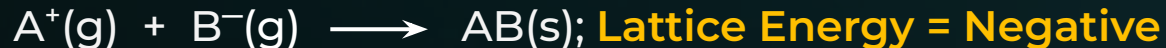
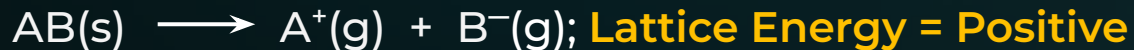
Mobile or free electrons





Lattice Energy

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





Factors Affecting Lattice Energy

Lattice Energy (L.E.)

\propto

$$\frac{1}{r}$$

$$r^+ + r^-$$

=

r

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

<

MgF₂

<

AlF₃



Properties of Ionic Compounds

01

Soluble in polar solvent

High Melting point and Boiling point

02

03

Conduct Electricity in aqueous & molten state

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

04

05

Forms **crystal** in Solid state

Highly **Polar**

06



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**.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Green vitriol

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Epsom salt

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
White vitriol



Polymorphism



Occurrence 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**.

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

Size of ion ↑

Hydration energy ↓

Charge of ion ↑

Hydration energy ↑



Solvation



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

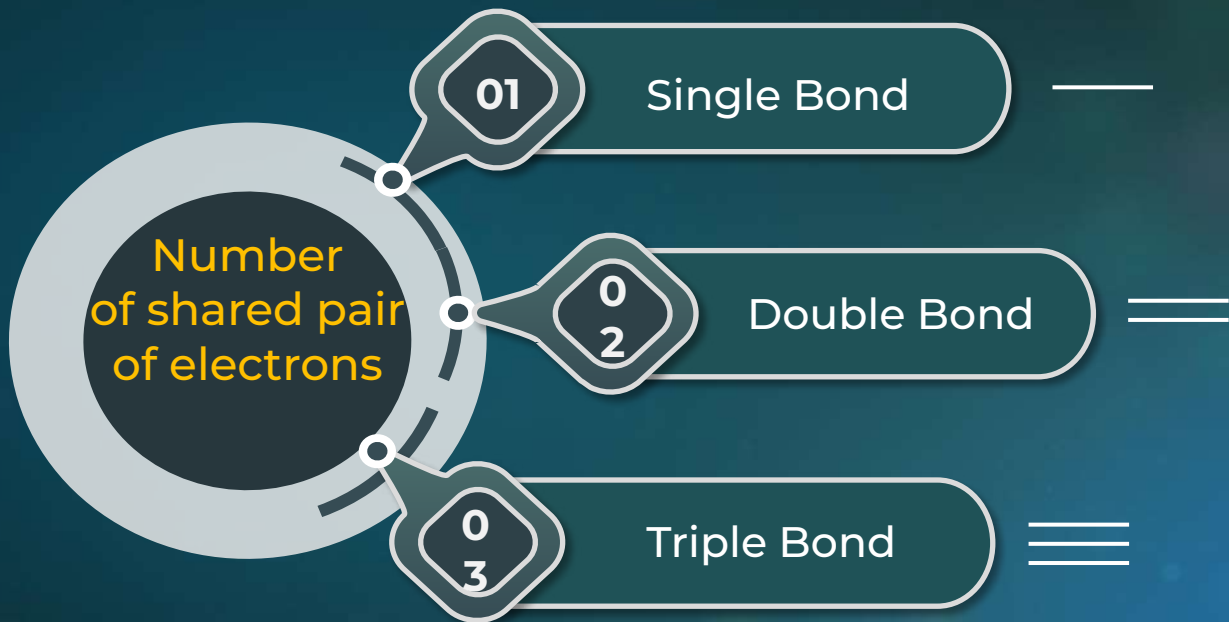
If the solvent is water, then it is known as Hydration

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.



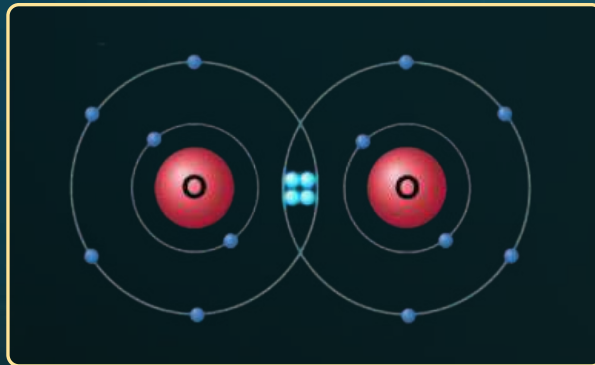
Types of Covalent Bond

(1) One pair of electrons is shared



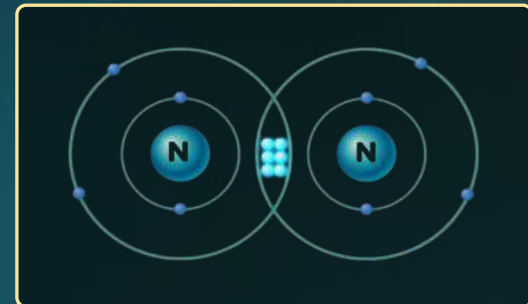
Single Covalent bond

(2) Two pairs of electrons are shared



Double Covalent bond

(3) Three pairs of electrons are shared



Triple Covalent bond

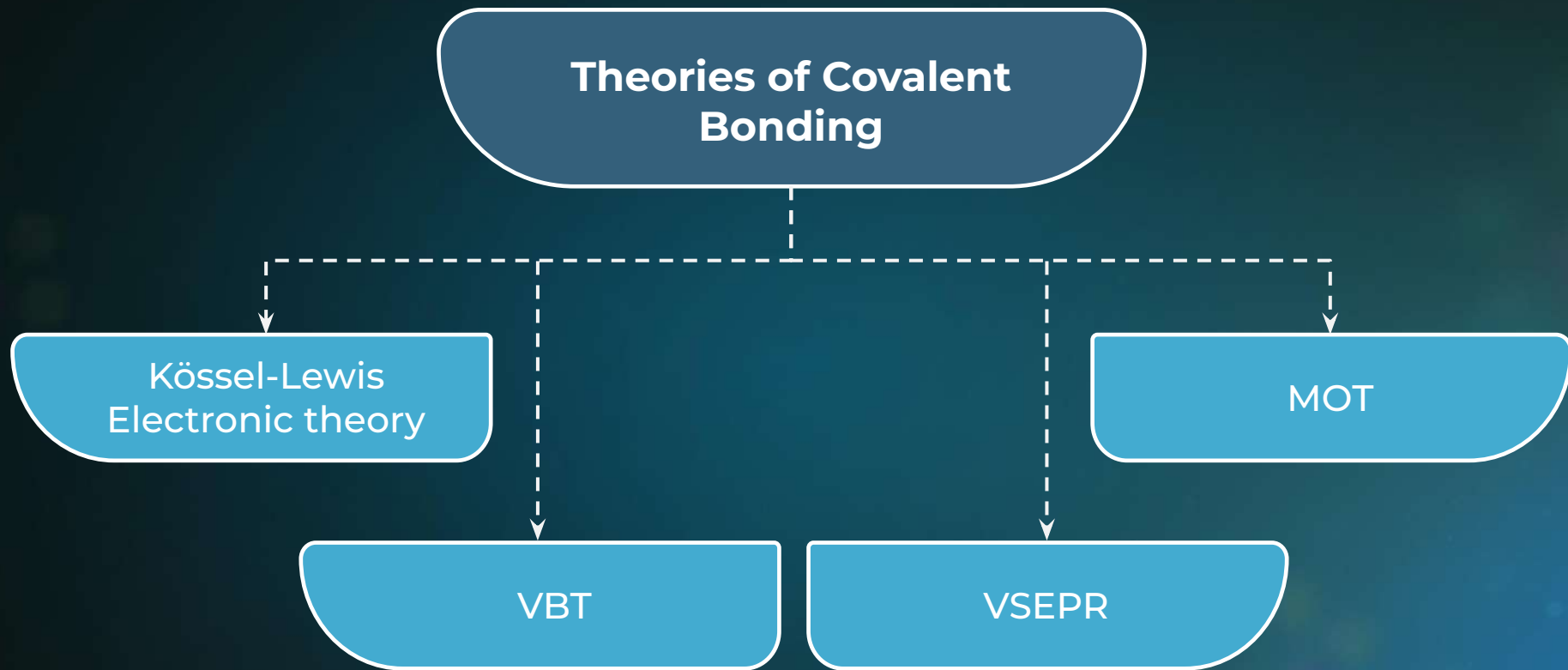
Theories of Covalent Bonding

Kössel-Lewis
Electronic theory

MOT

VBT

VSEPR





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

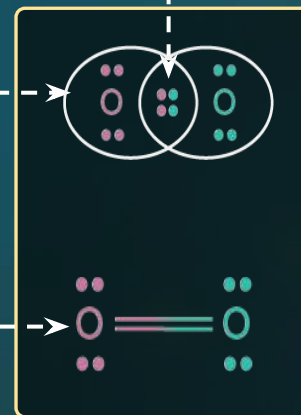
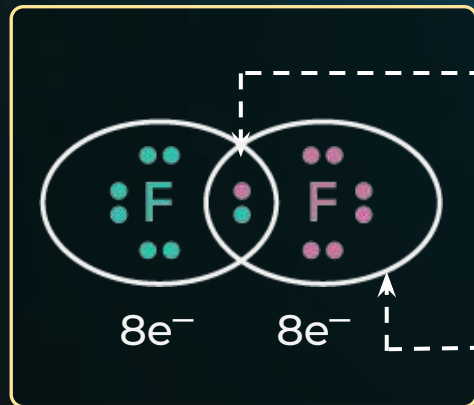
Covalent Bond

Attains **noble**
gas
configuration

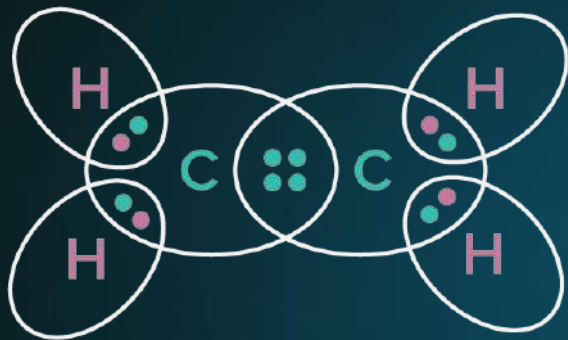
Shared pair of
electrons (e^-)

Octet complete

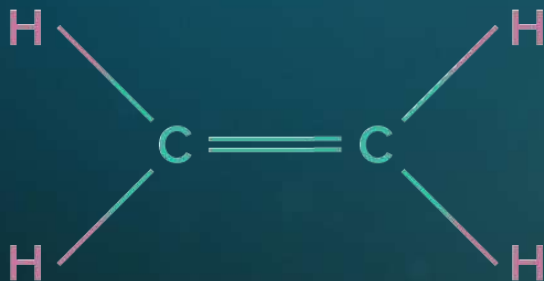
Shared pair
of electrons

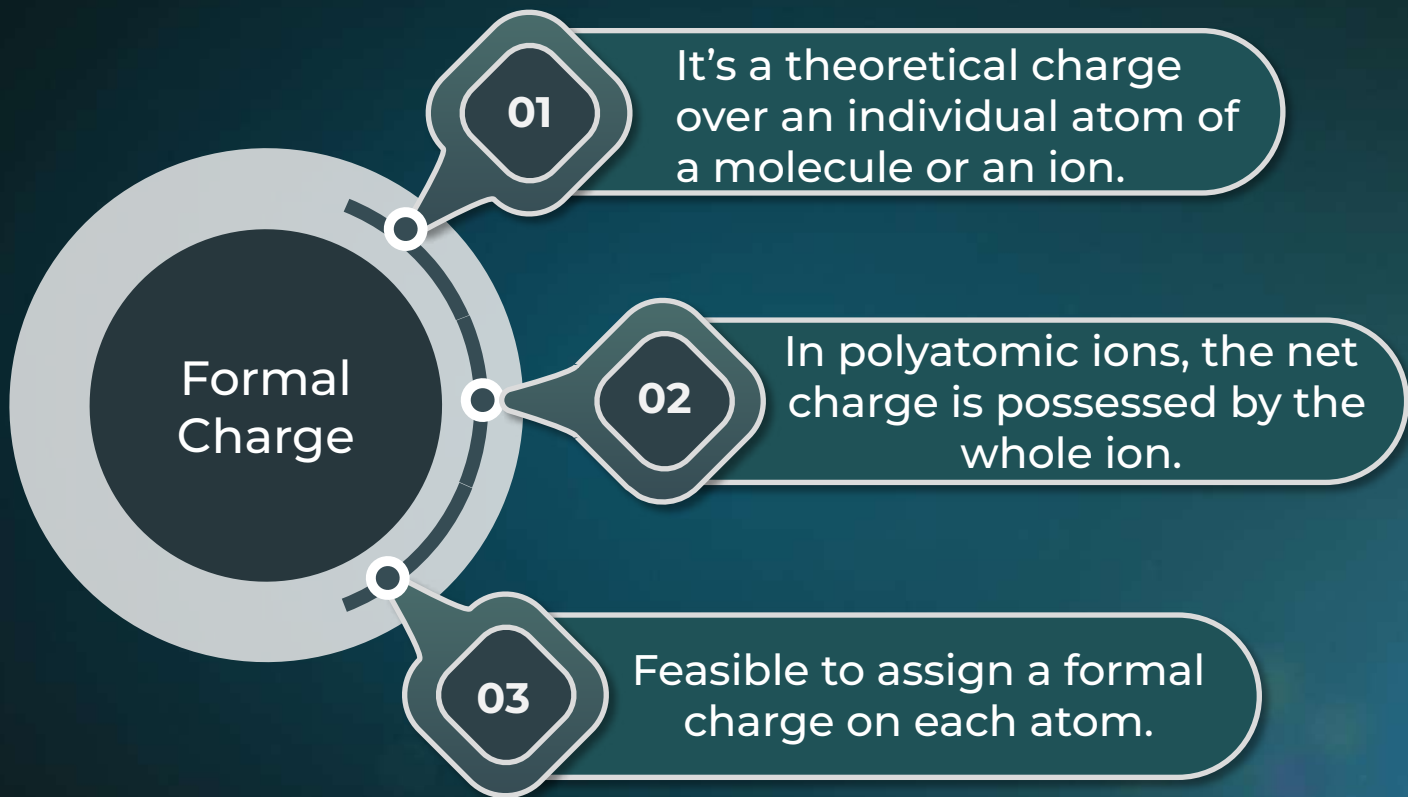


Lewis Dot Structures



Ethene





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

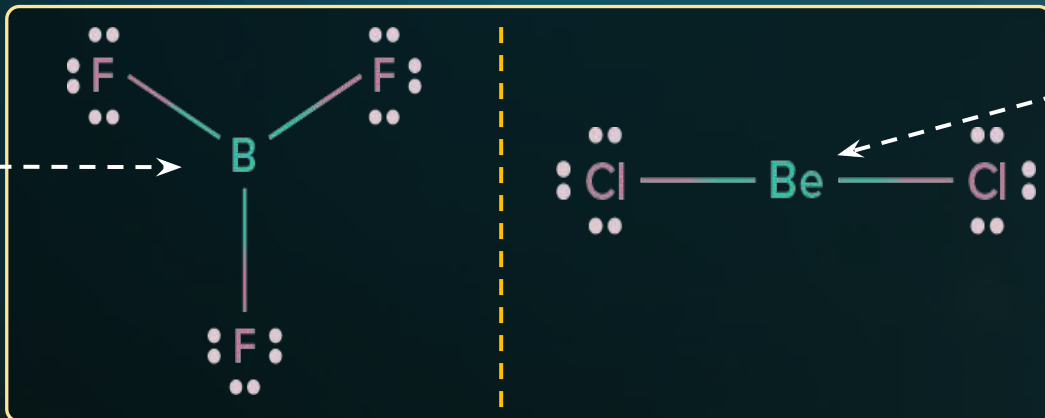
1

Molecules with **incomplete octet** of the central atom

Hypovalent compound

Electrons around central atom < 8

6 valence electrons



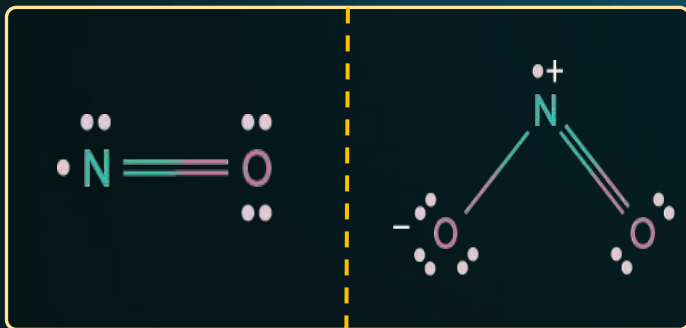
4 valence electrons

Limitations of Octet Rule

2

Molecules with odd electrons

NO , NO_2 , ClO_2 , ClO_3



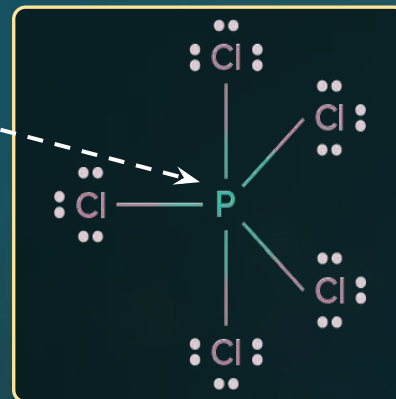
3

Molecules with expanded octet

Hypervalent compound

Electrons around central atom > 8

10 valence electrons



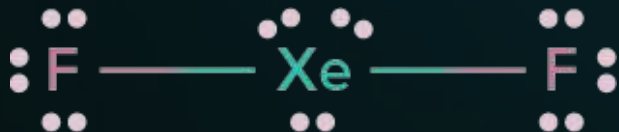


Limitations of Octet Rule

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

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

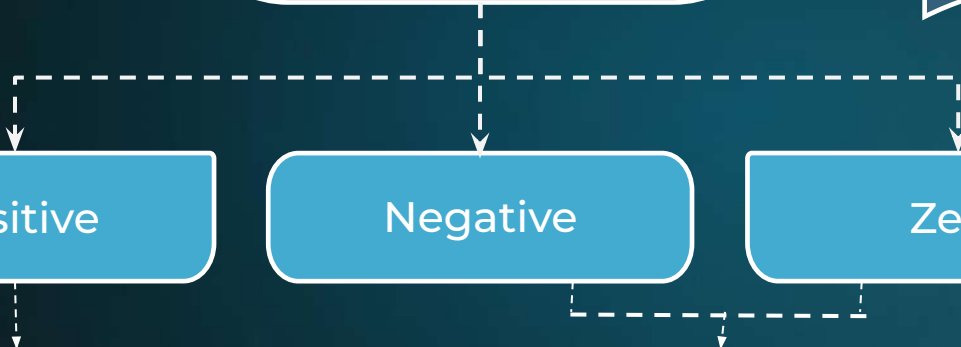
Positive

Bond will be formed

Negative

Bond will not be formed

Zero



Directional Properties of Bonds





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**.

Coordinate 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?

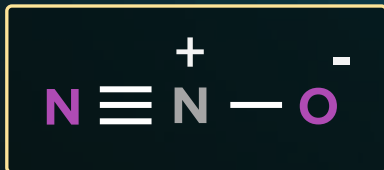
Different covalency
than usual



Presence of
coordinate bond

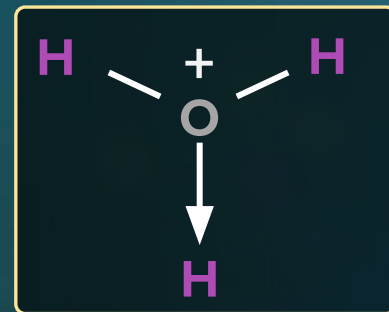
Fourth bond formed by **N** is always
coordinate

Example: N_2O



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

Example: $[\text{H}_3\text{O}^+]$



Lewis Acid and Lewis Base

Lone pair donors are called **Lewis bases**

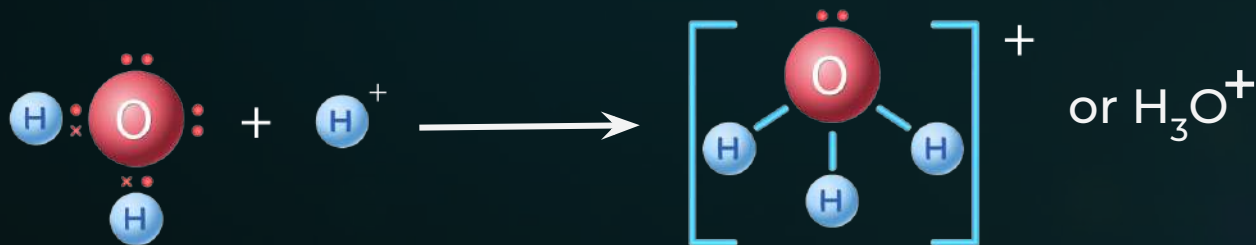
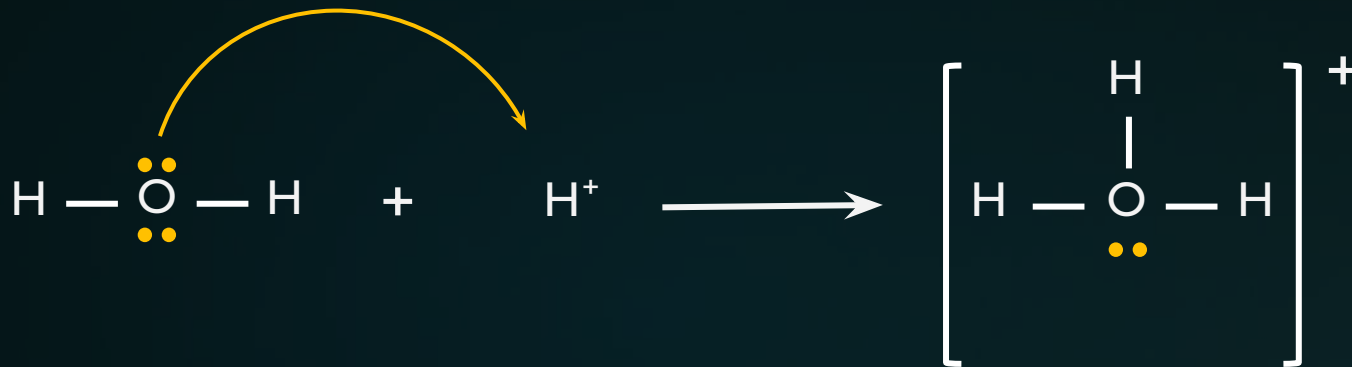
Lone pair acceptors are called **Lewis acids**



Donor

Acceptor

Co-ordinate Bond or Dative Bond





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**

Axial or Head-on Overlapping

Sigma (σ) bond

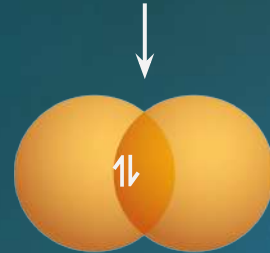


s orbital

+



s orbital



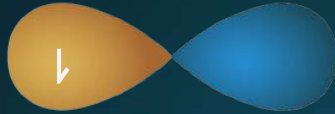
s - s overlap

Axial or Head-on Overlapping

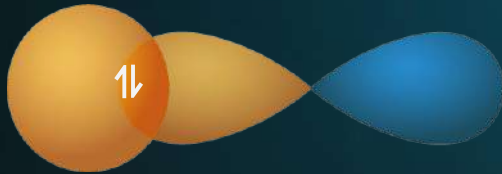


s orbital

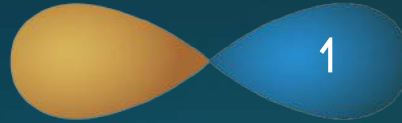
+



p orbital

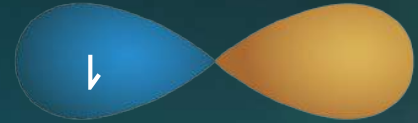


s - p overlap



p orbital

+



p orbital



p - p overlap

Types of π bond

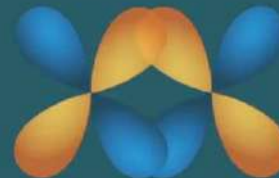
$p\pi$ - $p\pi$ overlap



$p\pi$ - $d\pi$ overlap



$d\pi$ - $d\pi$ 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

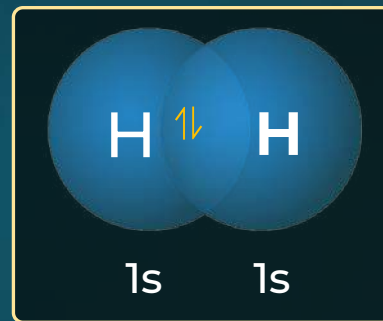


$1s^1$

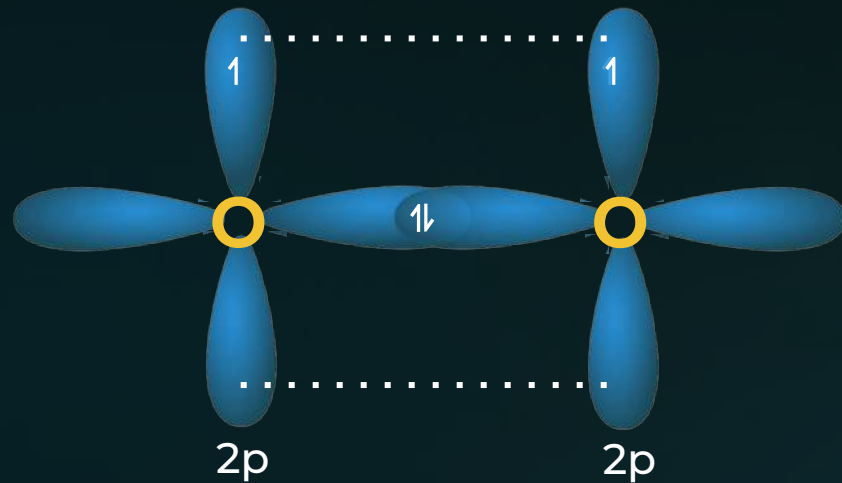
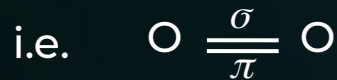
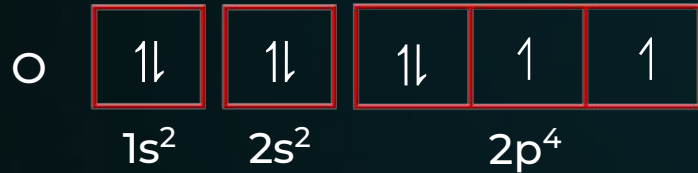
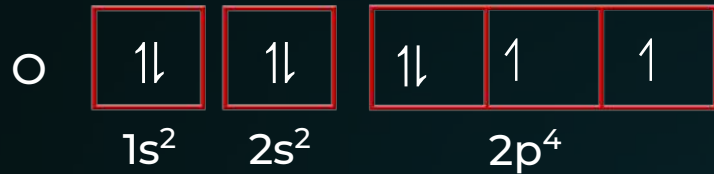


$1s^1$

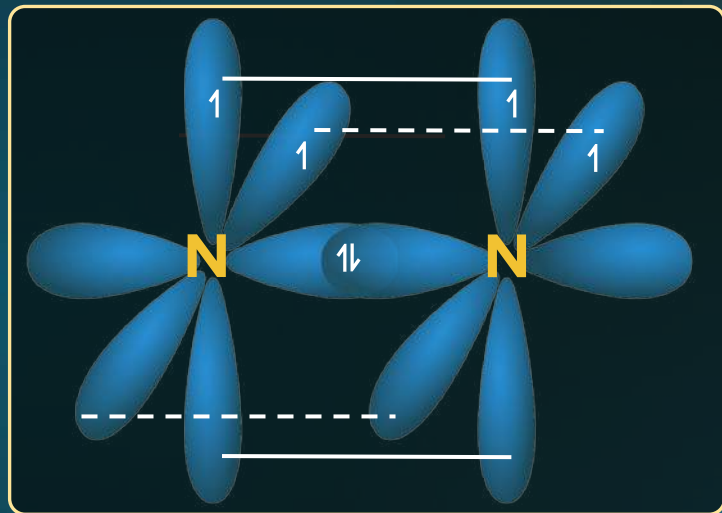
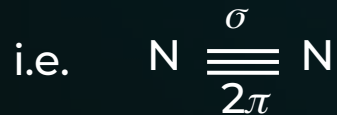
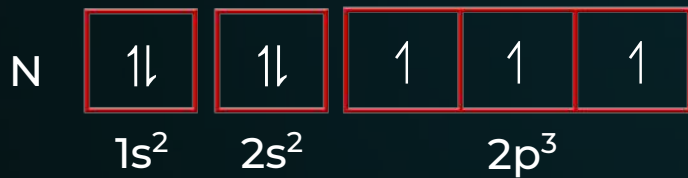
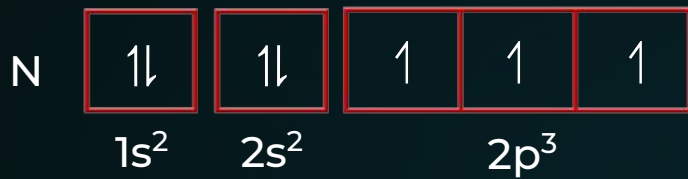
i.e. $H \overset{\sigma}{-} H$



Bonding in O₂ Molecule



Bonding in N₂ Molecule





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

SO₃ - Sulphur

Central
atom

Largest size

Least
electronegative

Less in number

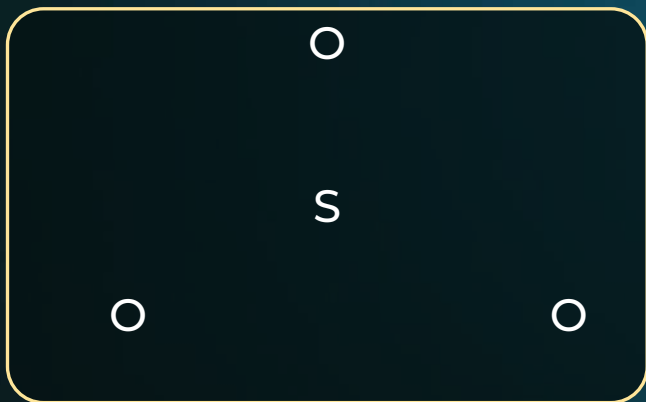
Can form
maximum bonds



Steps to Draw Structures

02

Draw a symmetrical skeleton of atoms.



03

Calculate the total number of valence electrons

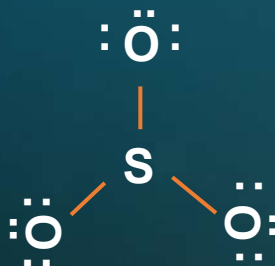
$$\text{Valence electrons in } \text{SO}_3 = 6 + (3 \times 6) = 24$$

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

Steps to Draw Structures

04

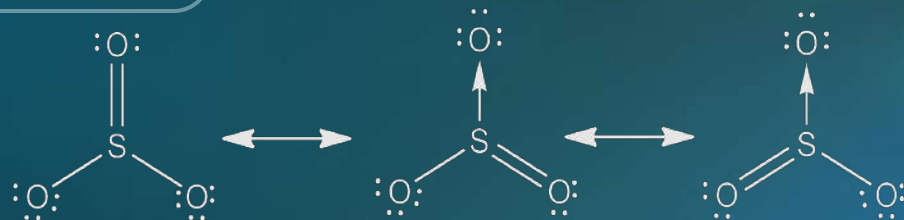
Make a single bond using the electron pairs. Then complete the octet of the side atoms. If any electron pair is left, assign it to the central atom.



Steps to Draw Structures

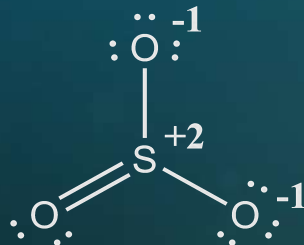
05

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 |
| $\text{O} = \overset{+}{\text{C}} - \text{H}$ | Linear | 1 |
| $\text{O} = \text{C} = \text{O}$ | Linear | 2 |
| $\text{H} - \text{C} \equiv \text{N}$ | Linear | 2 |



Point to Remember!!

For **electronic geometry**

Both **bond pairs** and **lone pairs** are considered

For **shape**

Only **bond pairs** are considered

Lone pairs are not a **part of the shape**

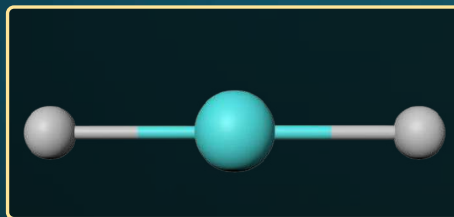
but they can **alter the shape**

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

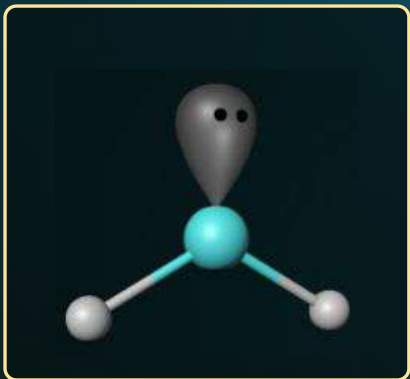


VSEPR Theory

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

<

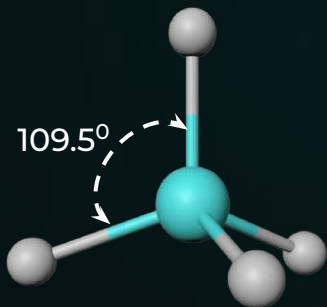
120°

Example: SO_2 , $SnCl_2$

VSEPR Theory

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

| Electron Pairs | Bonding Pairs | Lone Pairs | Electronic Geometry | Shape |
|----------------|---------------|------------|---------------------|-------------|
| 4 | 4 | 0 | Tetrahedral | Tetrahedral |



Bond Angle

=

109.5°

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

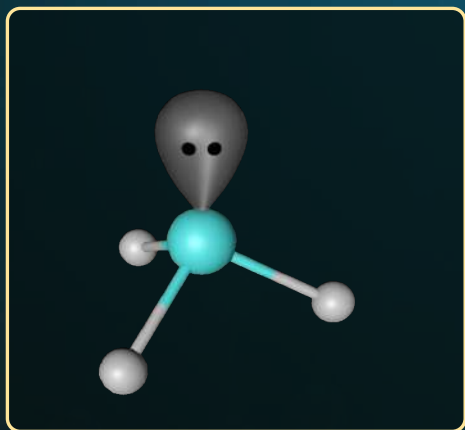


VSEPR Theory

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

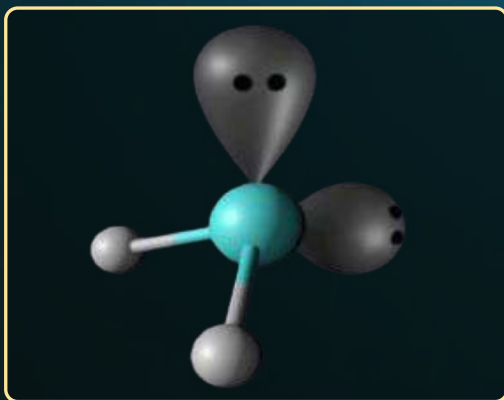


VSEPR Theory

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

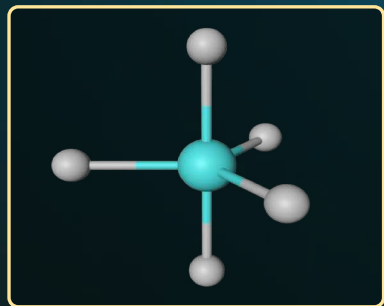


VSEPR Theory

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

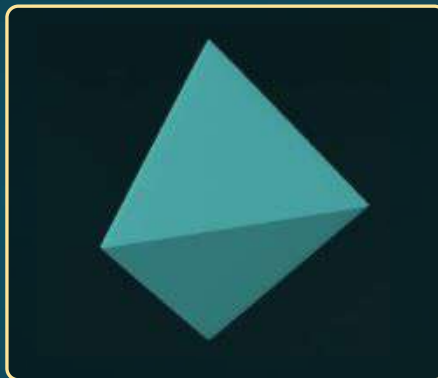
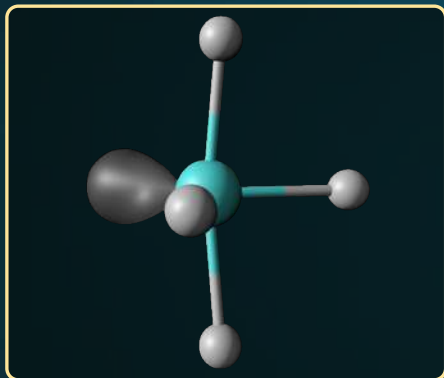
=

$90^\circ, 120^\circ, 180^\circ$

Example: PCl_5 , SOF_4

Valence Shell Electron Pair Repulsion Theory (VSEPR)

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



Bond Angle

<

$90^\circ, 120^\circ$

Example: SF_4 , XeO_2F_2



VSEPR Theory

General Formula:



(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

<

$90^\circ, 180^\circ$

Example: ClF_3

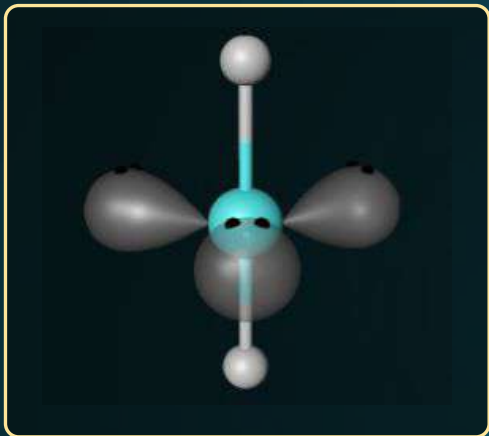


VSEPR Theory

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 |



Bond Angle

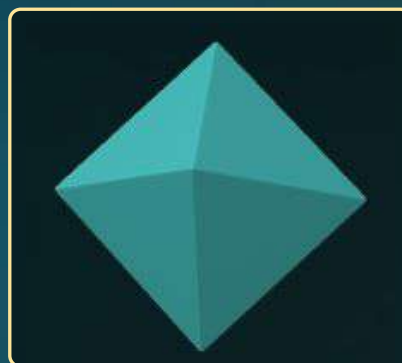
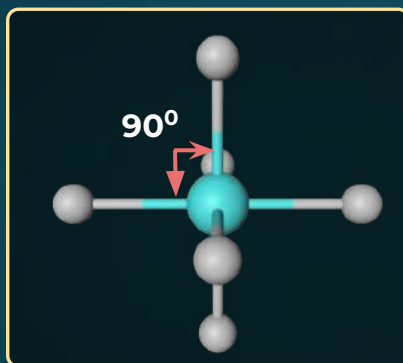
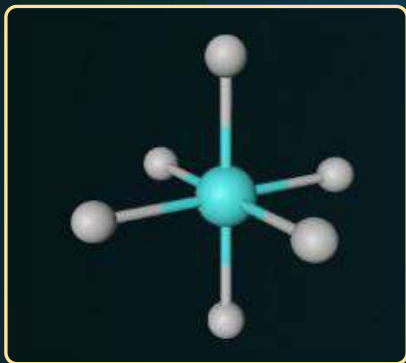
=

180°

Example: XeF_2 , I_3^-

VSEPR Theory

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



Bond Angle

=

90°

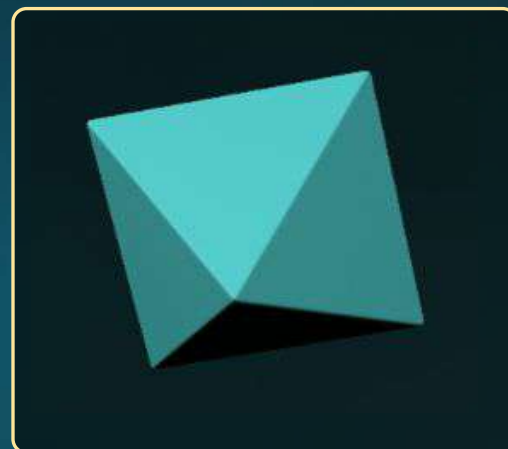
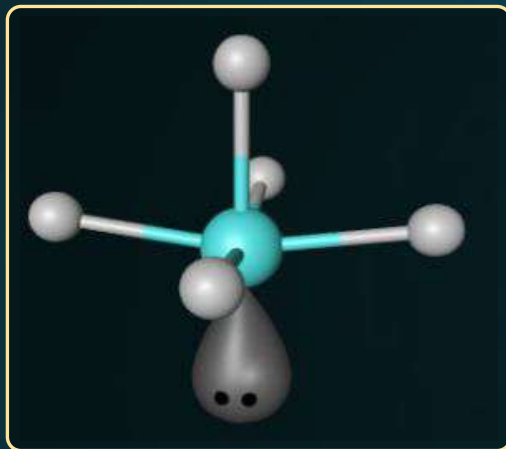
Example: SF_6



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)

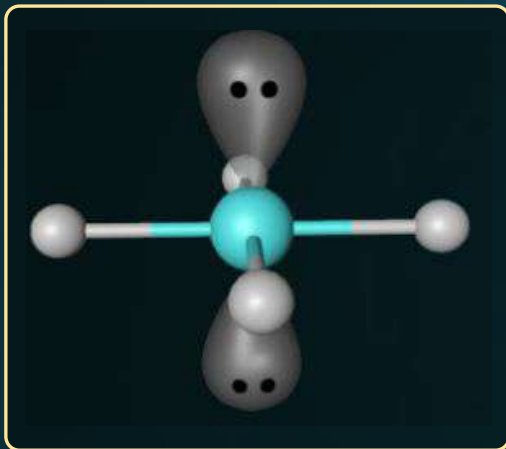


Bond Angle

<

$90^\circ, 180^\circ$

Example: BrF_5 , $XeOF_4$



Bond Angle

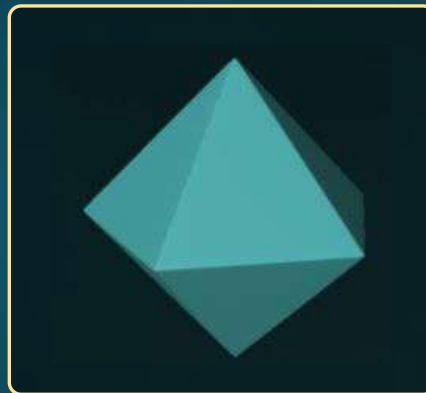
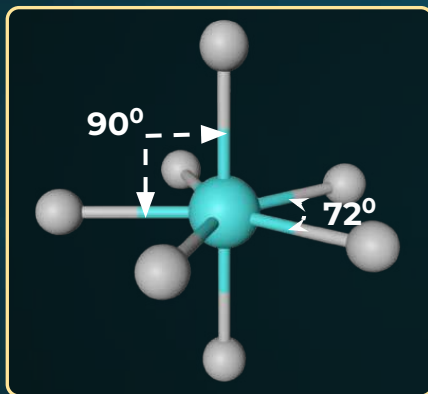
=

$90^\circ, 180^\circ$

Example: XeF_4

VSEPR Theory

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



Bond Angle

=

$72^\circ, 90^\circ$

Example: IF_7

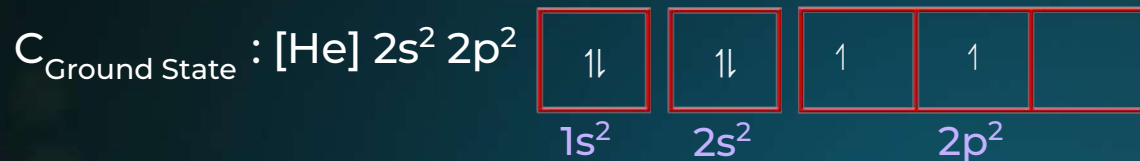


Need for Hybridisation

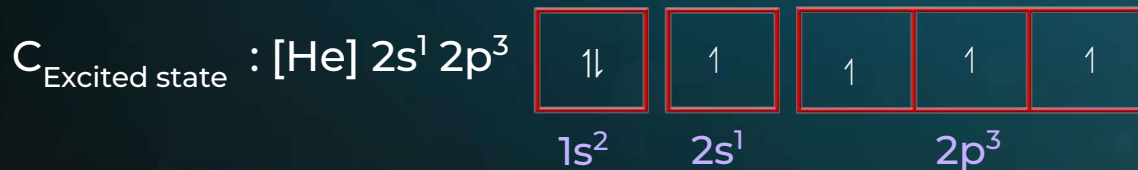
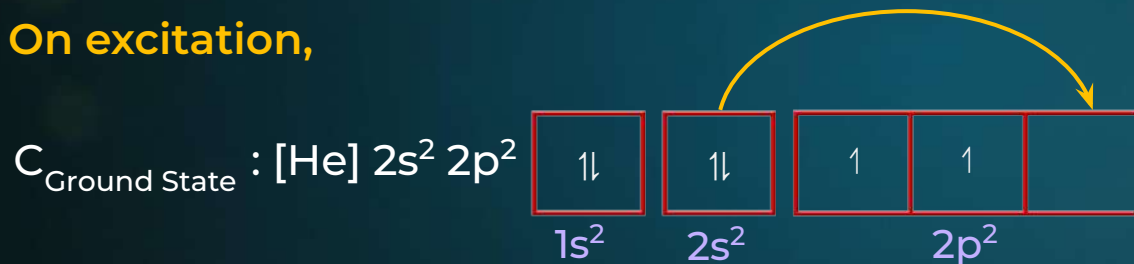


Shape of CH₄ Molecule

Electronic configuration of carbon is:

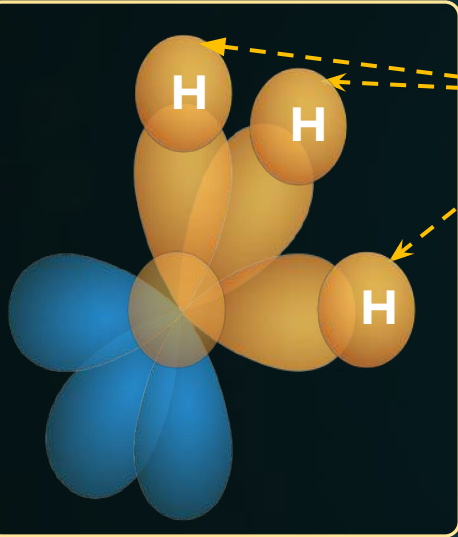


On excitation,



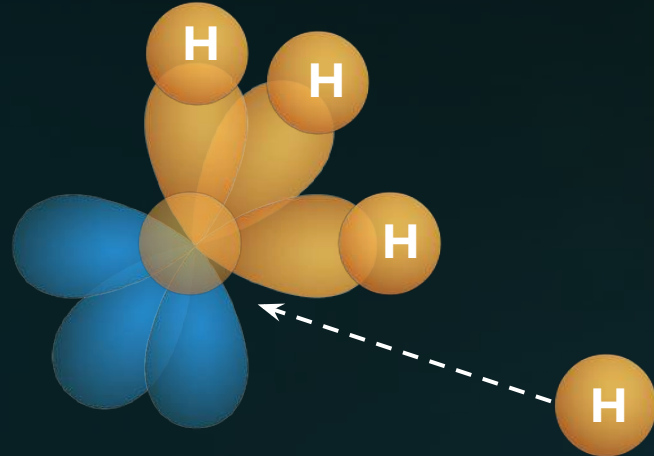
Release of energy due to overlap between the orbitals of C and H

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 CH₄ Molecule

s-orbital overlap can
be in any direction

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



Shape of CH₄ 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)

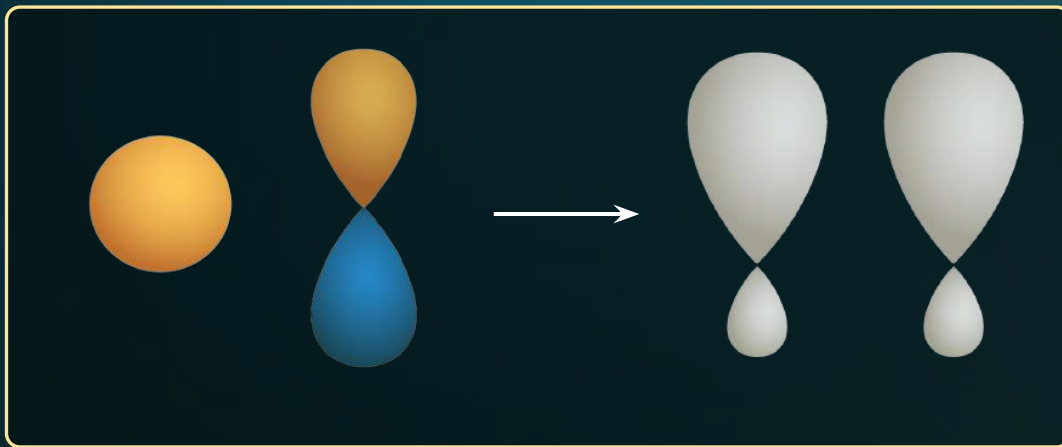
The **orbitals** present in the **valence shell** (and sometimes **penultimate shell** also) of the atom can hybridise.

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)

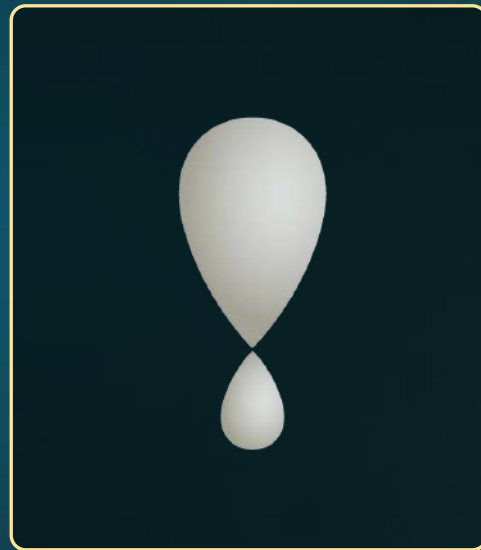


Did you Know?

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

$sp^n d^m$ hybrid orbital

Types of Hybridisation

sp

sp^2

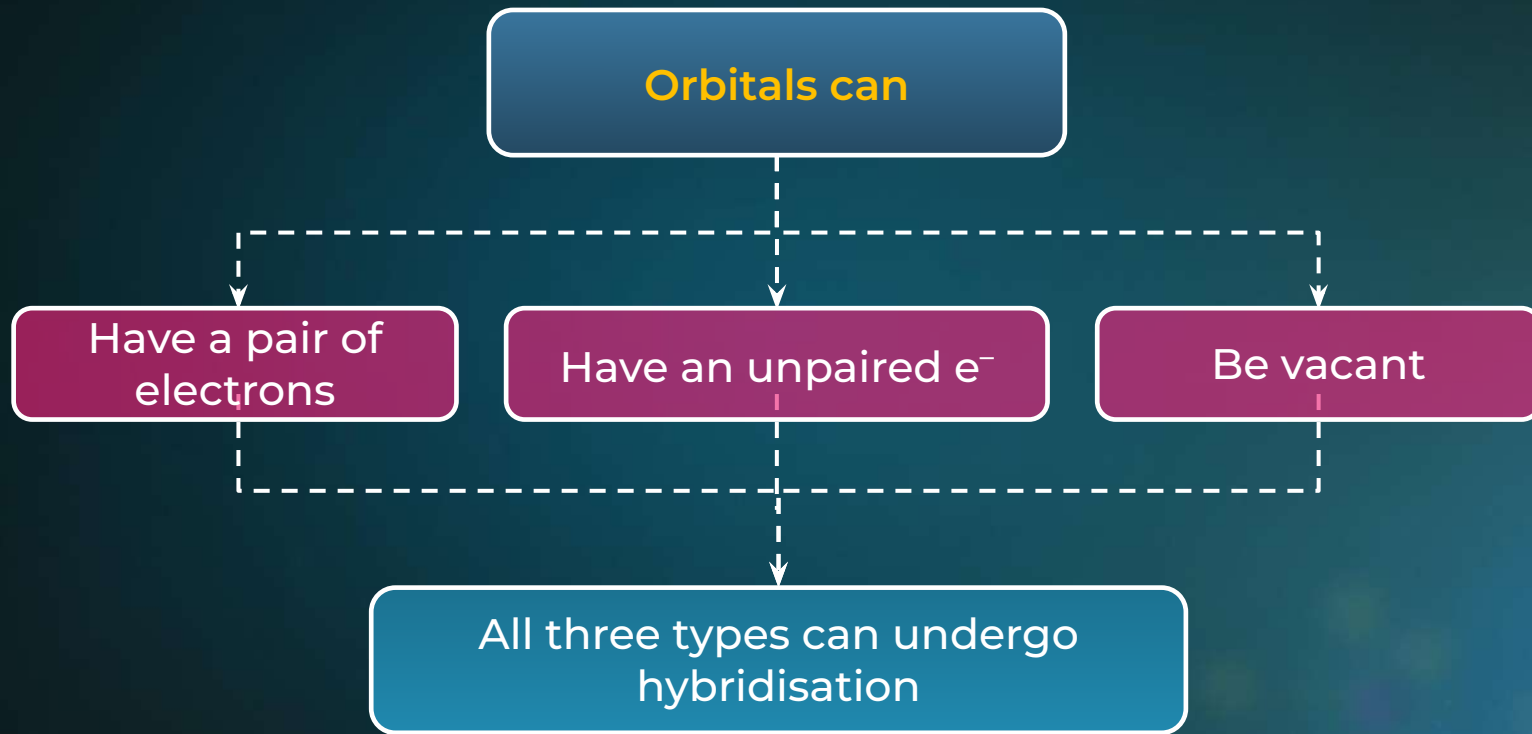
sp^3

sp^3d

sp^3d^2

sp^3d^3

Important Conditions for 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**.

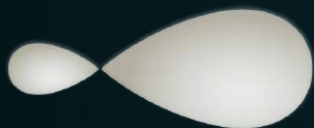
| Participating atomic orbitals | Number of hybridised orbitals | Hybridisation |
|---|-------------------------------|---------------|
| One s + One p  | 2 | sp |

% s Character

% s
character

=

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



sp

>



sp²

>

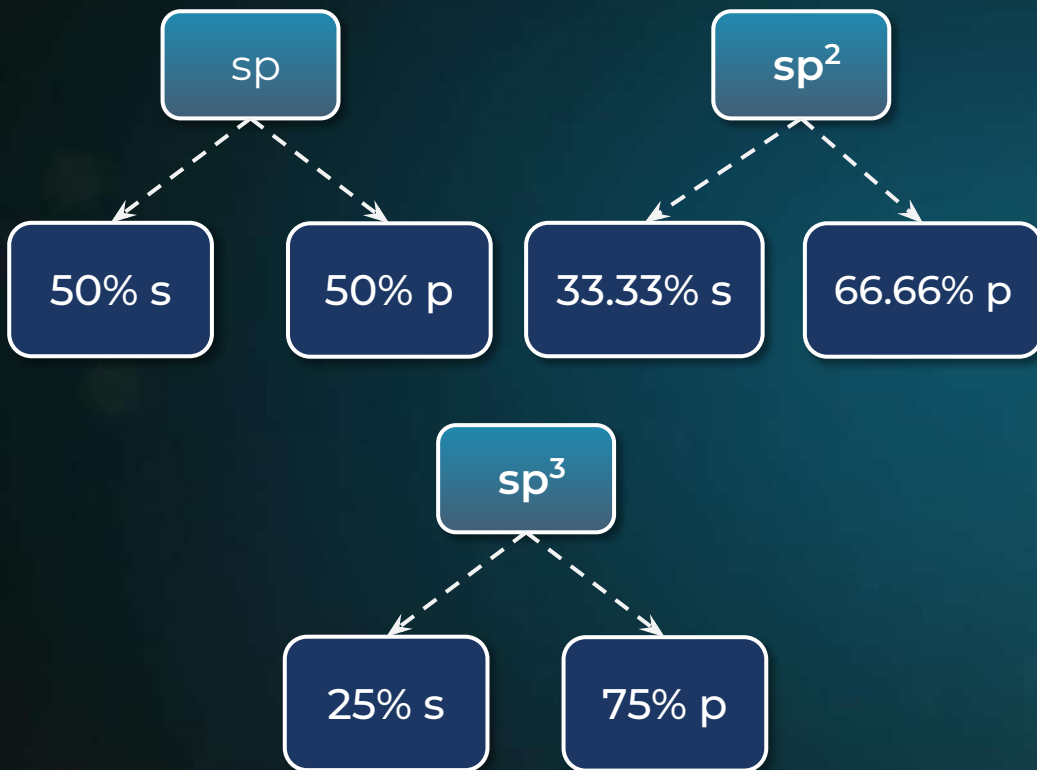


sp³

Decreasing order of s character



Percentage Character of Orbitals



| % 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

Steric
Number

=

$$\frac{V + M - q}{2}$$

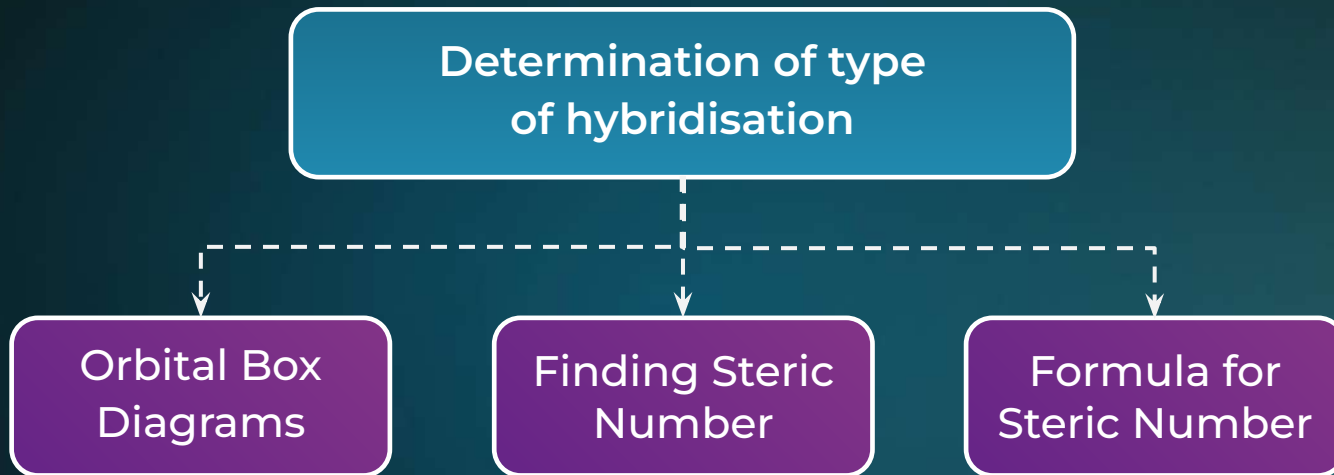
Type of **hybridization** indicates
the **geometry** of the molecule

Steric Number, Hybridization and Geometry




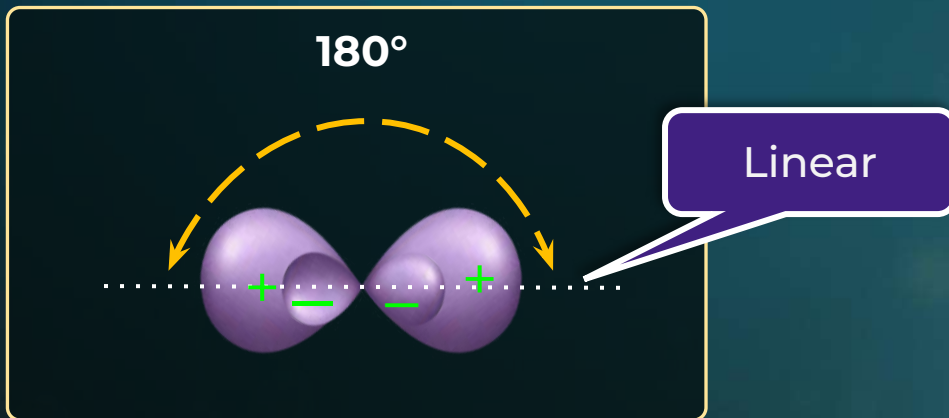
| Steric number | Hybridization | Geometry | Involving Orbitals |
|---------------|---------------|------------------------|--|
| 2 | sp | Linear | $s, p_x / p_z / p_y$ |
| 3 | sp^2 | Trigonal Planar | $s, p_x, p_z / p_y, p_z / p_x, p_y$ |
| 4 | sp^3 | Tetrahedral | s, p_x, p_z, p_y |
| 5 | sp^3d | Trigonal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

Methods for Finding Hybridisation

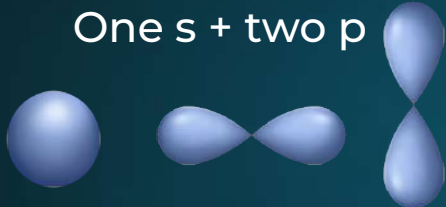


sp Hybridisation

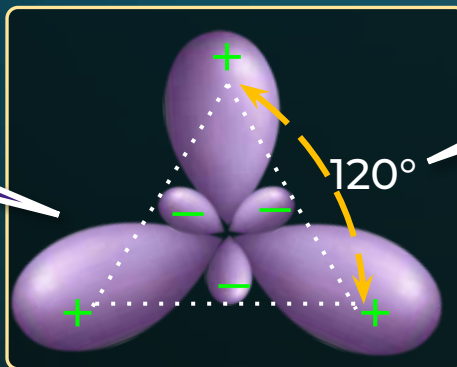
| Participating atomic orbitals | Number of hybridised orbitals | Hybridisation |
|--|-------------------------------|---------------|
| One s + One p  | 2 | sp |



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

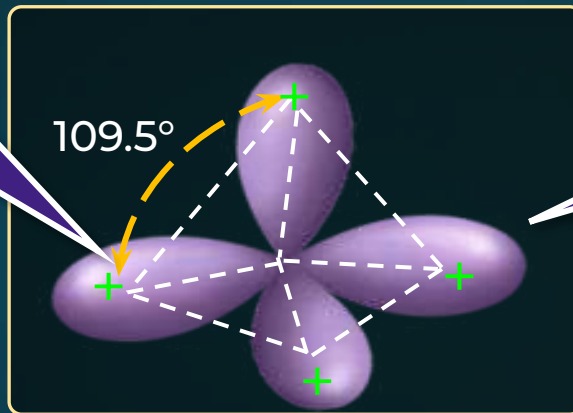
sp^2 Hybridisation

sp^3 Hybridisation

| Atomic orbitals participating in hybridisation | Number of hybridised orbitals | Hybridisation |
|--|-------------------------------|---------------|
| <p data-bbox="434 500 763 540">One s + three p</p>  | 4 | sp^3 |

sp^3 Hybridisation

4 new sp^3
hybridised
orbitals

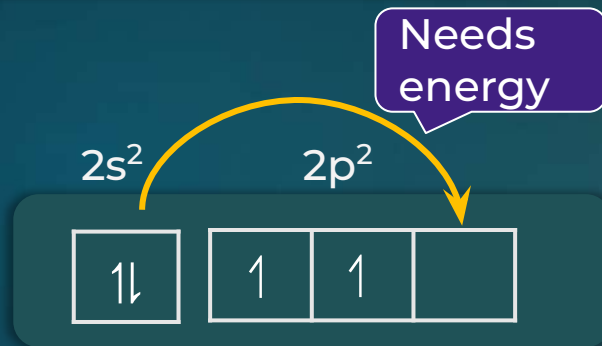


Tetrahedral

Bonding of CH₄ Molecule

Here, electronic configuration of carbon is

C_{Ground State} : [He] 2s² 2p²



C_{Excited state} : [He] 2s¹ 2p_x¹ 2p_y¹ 2p_z¹





Bent's Rule

In T.B.P. geometry,





Berry Pseudorotation

Fluxional behaviour
of **PF₅** due to fast
exchange between axial
and equatorial F atoms

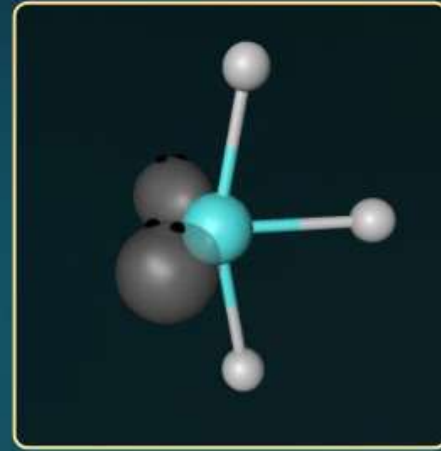
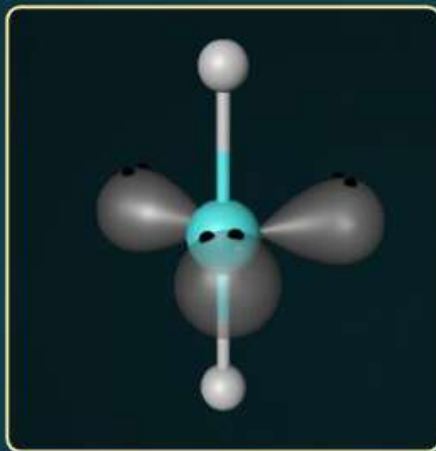
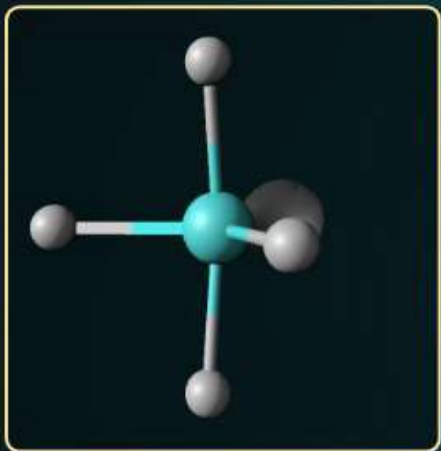
All P-F bonds are
observed to be equivalent

Energy difference
b/w **T.B.P.** and
square pyramidal
geometry

<

Thermal energy
at room
temperature

Examples of sp^3d Hybridisation

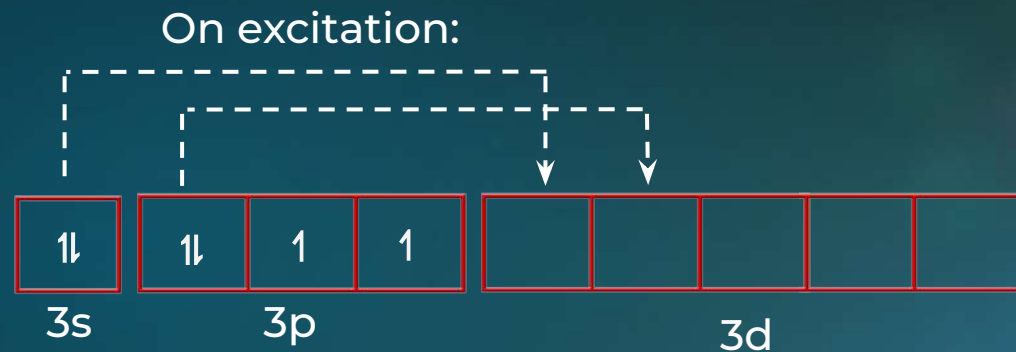




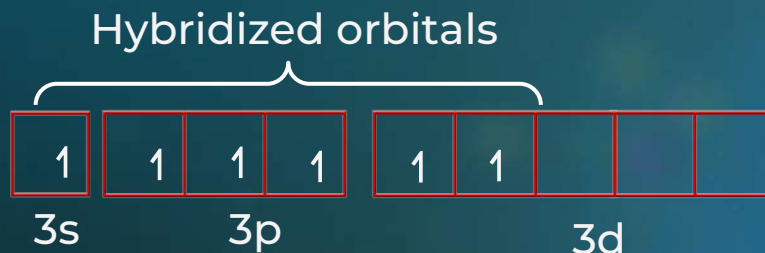
sp^3d^2 Hybridisation



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



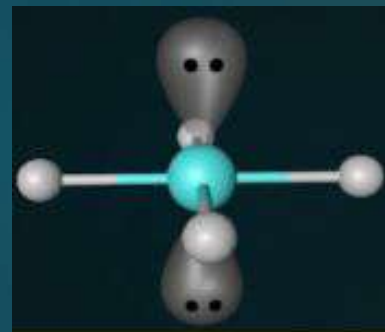
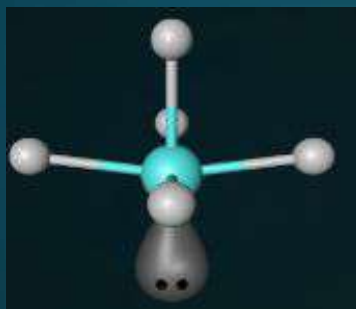
$S_{\text{Excited state}} : [Ne] 3s^1 3p^3 3d^2$



sp^3d^2 Hybridisation

No equatorial & no axial bonds

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

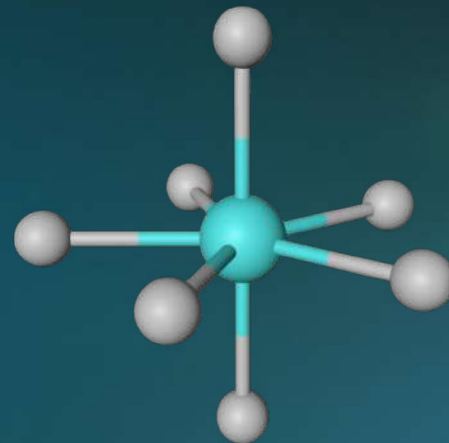
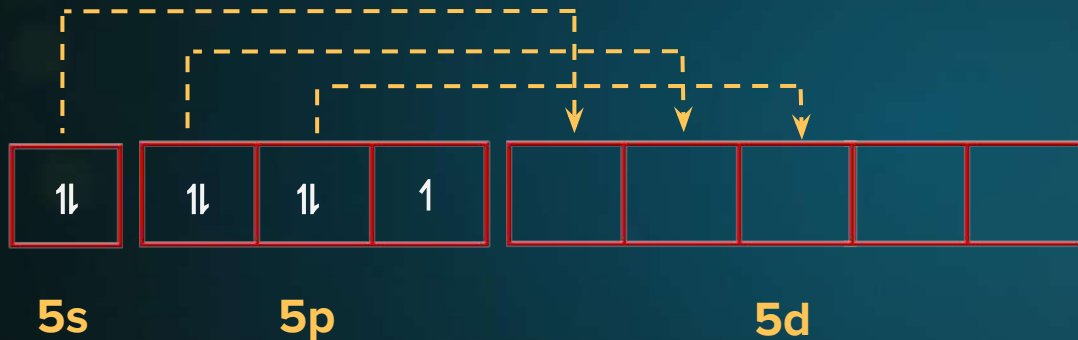


sp^3d^3 Hybridisation

IF_7

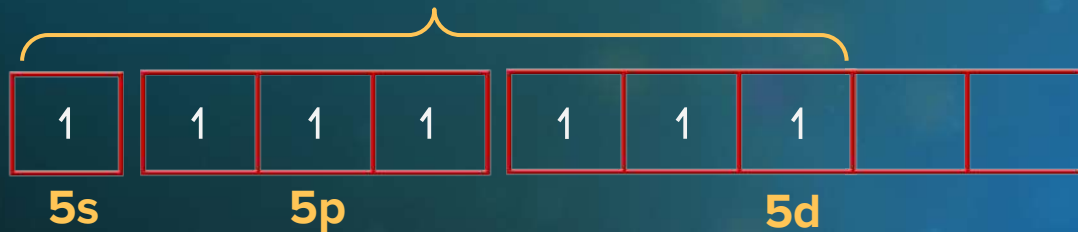
$I_{\text{Ground state}} : [Kr] 4d^{10} 5s^2 5p^5$

On excitation

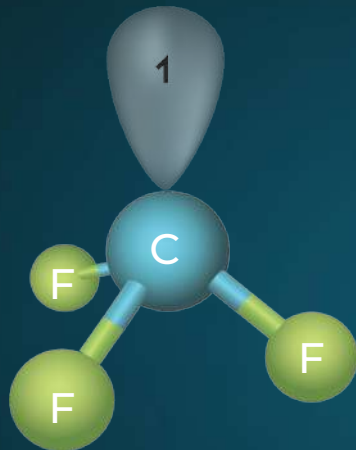


7 sp^3d^3 Hybridized orbitals

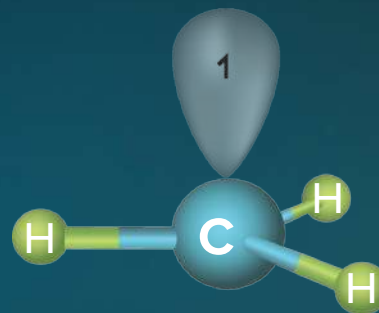
$I_{\text{Ground state}} : [Kr] 4d^{10} 5s^2 5p^5$



Hybridisation in Odd Electron Species



Hybridisation:
 sp^3



Hybridisation:
 sp^2



Did you Know?



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

Resonance

Localised electrons



Restricted
between 2
atoms

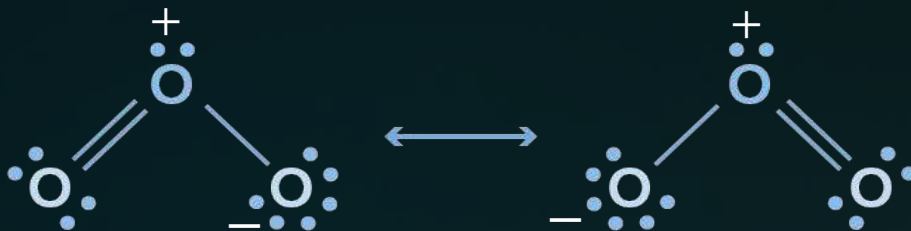
Delocalised electrons



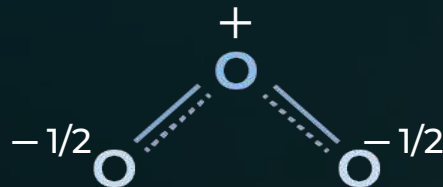
Spread
across several
adjacent atoms

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

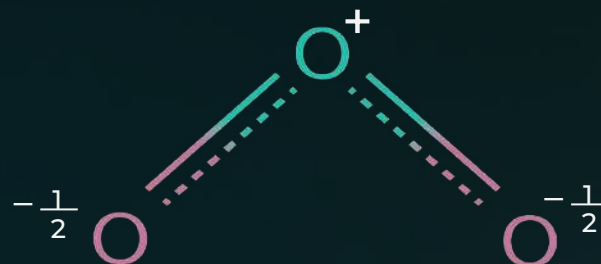
Does not violate the rules of **covalence maxima**

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**

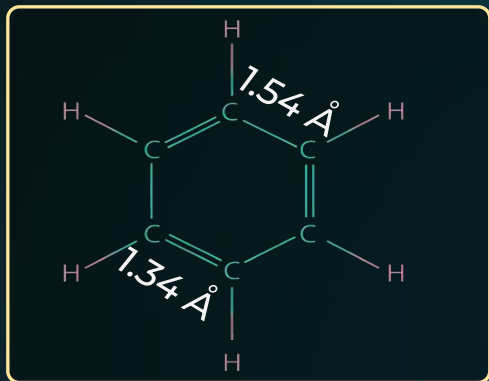
B Only **π electrons** or **lone pairs** can be moved

C Overall **charge** of the system must **remain the same**

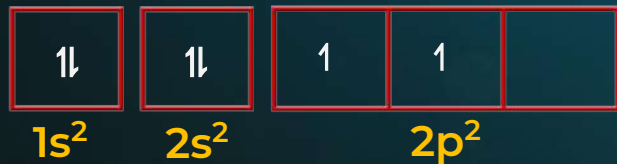
D **Bonding framework** of a molecule must **remain intact**



Benzene

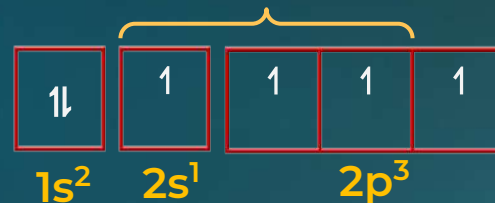


C Ground state : $1s^2 2s^2 2p^2$

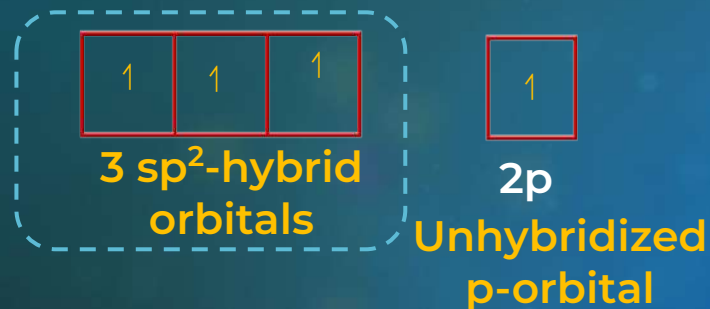


C Excited state : $1s^2 2s^1 2p^3$

Hybridize



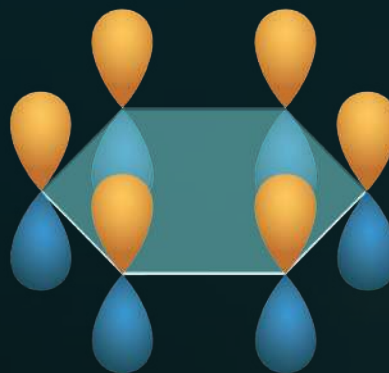
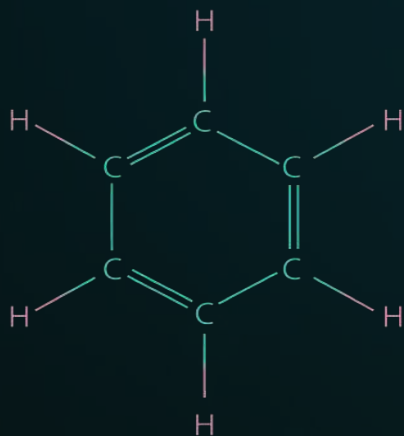
C (Excited and hybrid state)



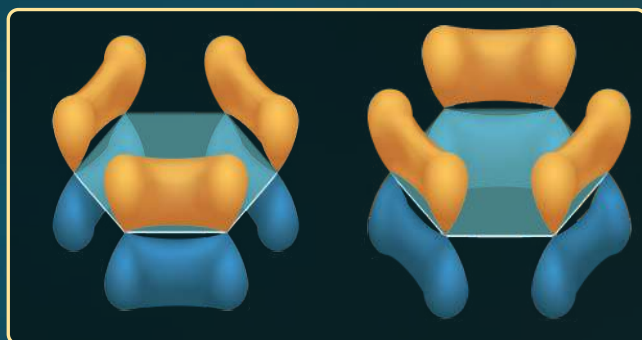
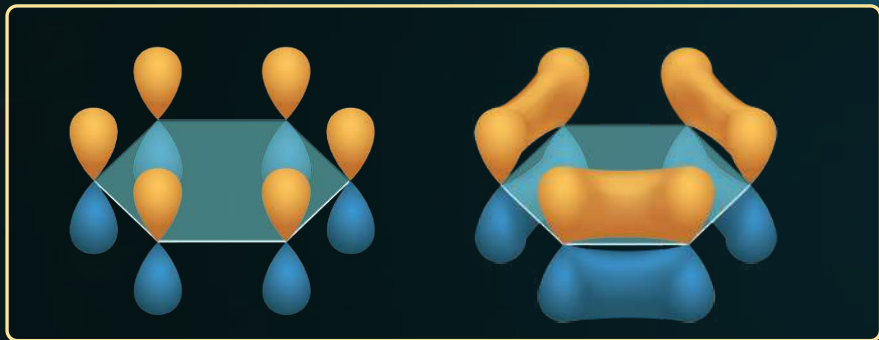
Benzene

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

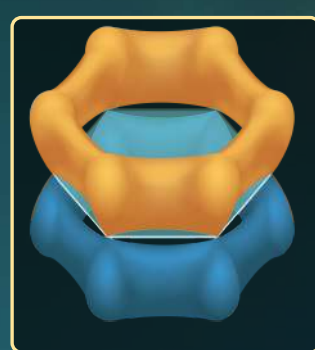
Unhybridised p-orbitals of each carbon are **parallel to each other**



Benzene

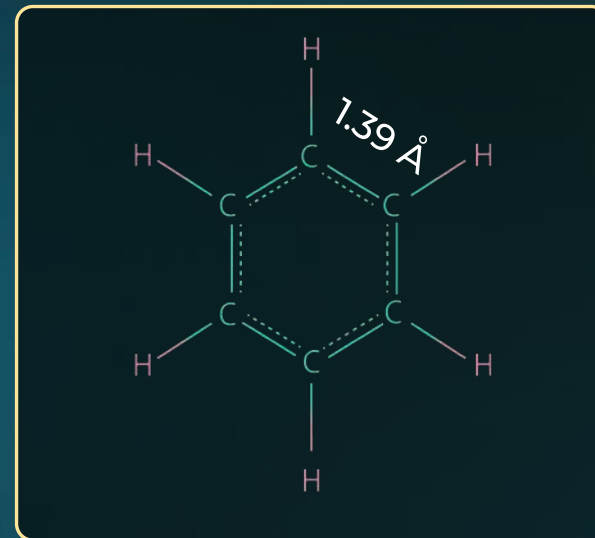
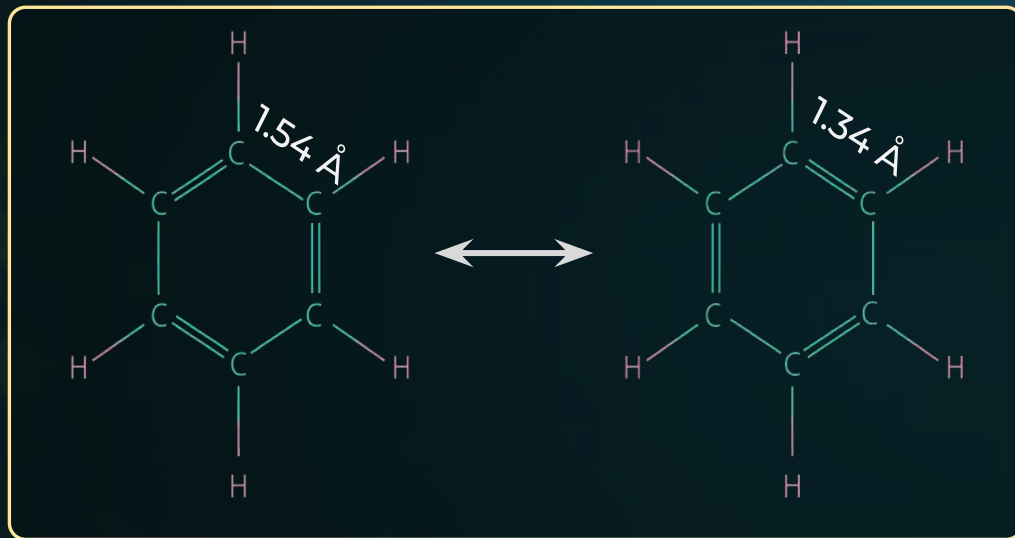


Localised π
bonds



Delocalised
 π bonds

Resonance Structures and Resonance Hybrid of Benzene





Bond order of Resonance Structures

For degenerate resonating structures:

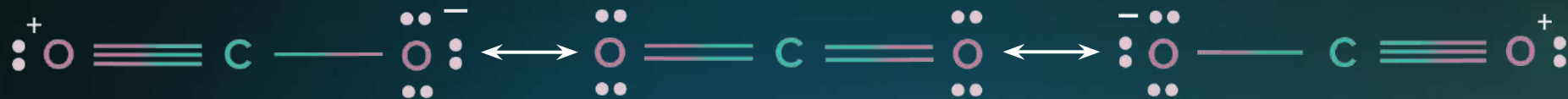
Bond Order
between
two atoms

=

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.

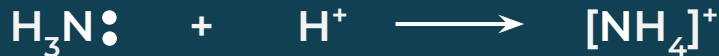
Lewis Acid and Lewis Base

01

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

02

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



Donor

Acceptor



Lewis Acids



Incomplete octet



Central atom has
vacant d-orbitals



Metal cations



Central atom is
attached to a more **E.N.**
atom with multiple
bonds



Lewis Bases



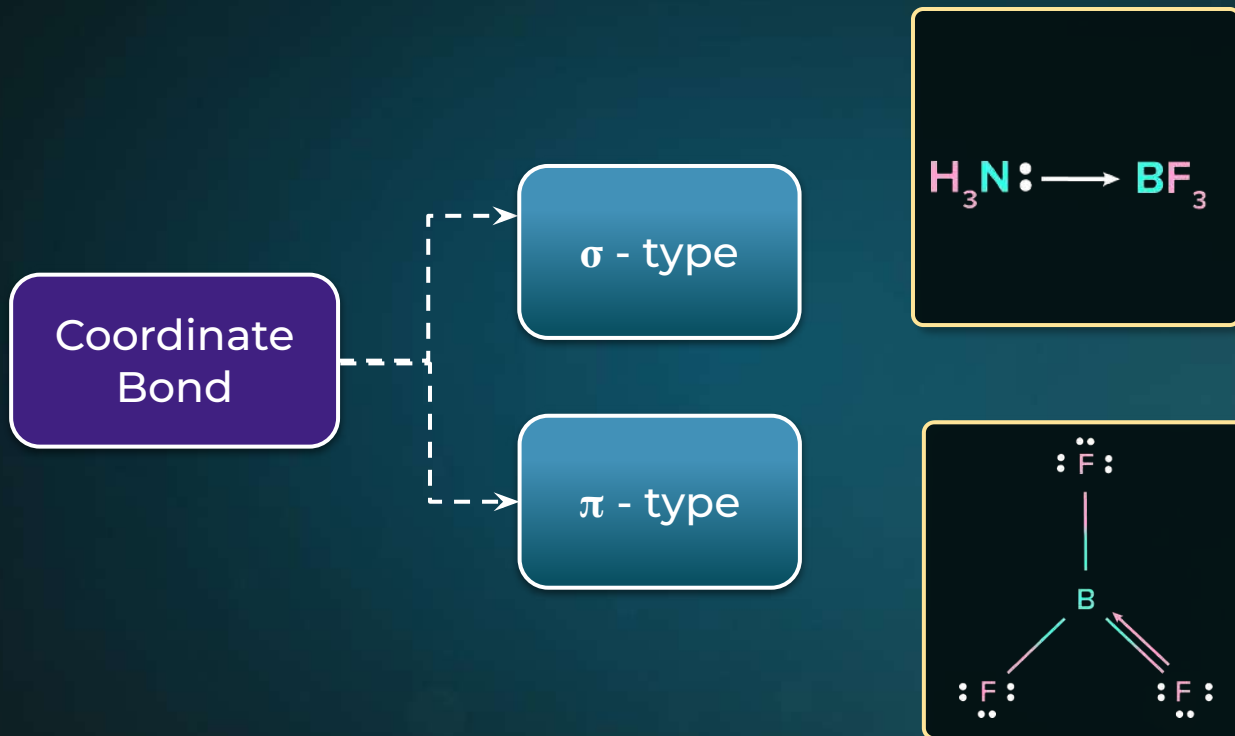
Central atom has at least **one lone pair** and is surrounded by **less E.N. atom**



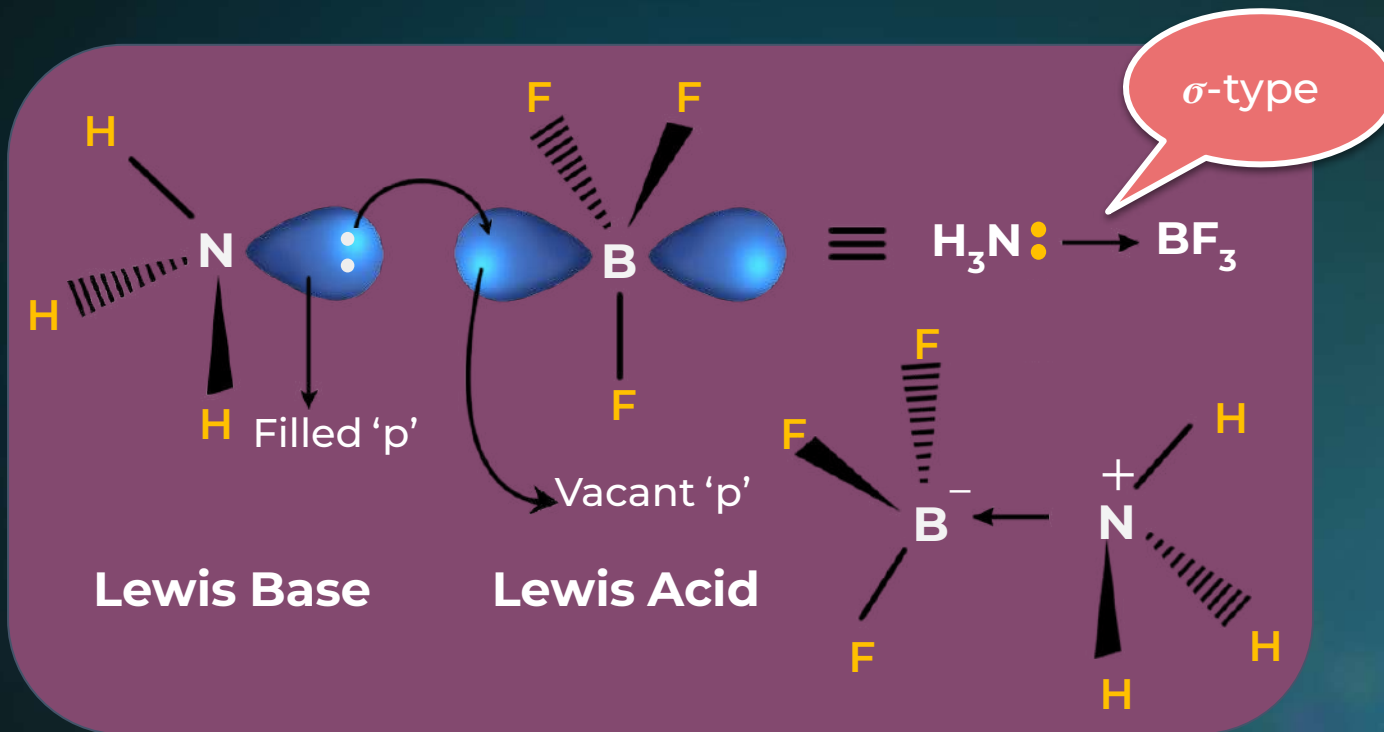
Anions

Back Bonding

Coordinate Bond



σ - Coordinate Bond





π - Coordinate Bond

Back bonding

Kind of **coordinate π bonding**



Partial double bond character

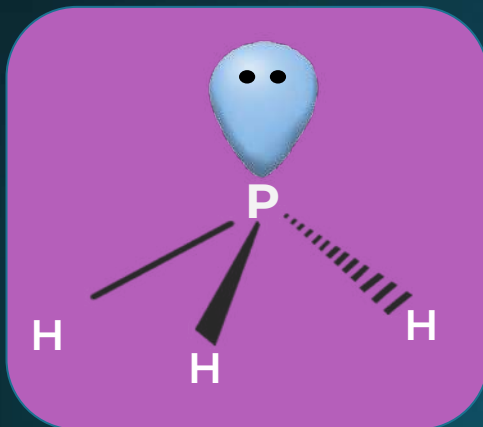
Back bond forms
between

Atom having non bonded electron
pair

&

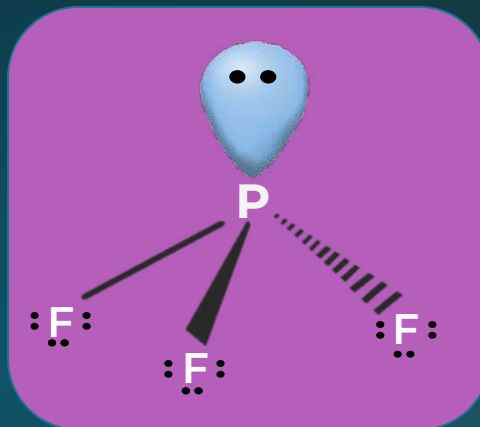
Atom having vacant orbital

π - Coordinate Bond



Back Bonding

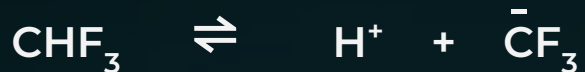
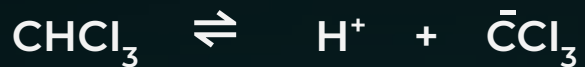
Because
Hydrogen
has no
lone pairs



Back Bonding

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





Cl atom have
vacant d -orbital
to accommodate
electron pair

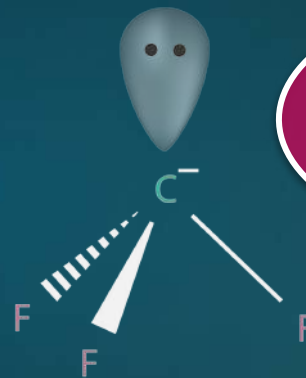


Vacant orbital

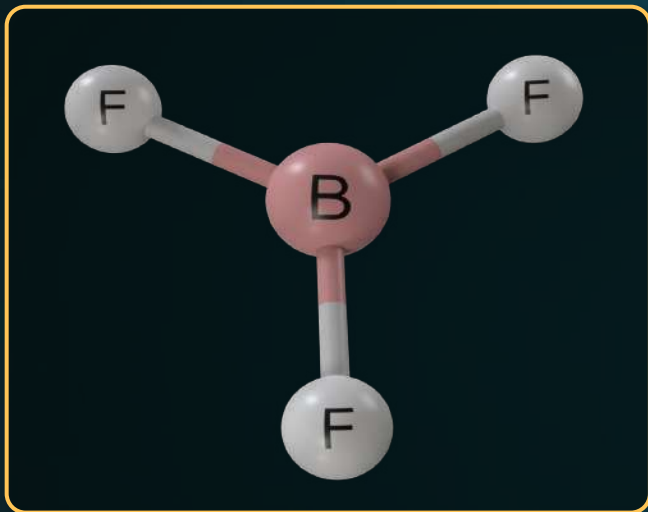
Back bonding

$2p\pi-3d\pi$

F atom does
not have
vacant
d -orbital



-



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

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

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

$2p\pi-2p\pi$

>

$2p\pi-3p\pi$

>

$2p\pi-3d\pi$

>

$3p\pi-3p\pi$

$\text{BF}_3(2p\pi-2p\pi)$

>

$\text{PF}_3(3d\pi-2p\pi)$

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

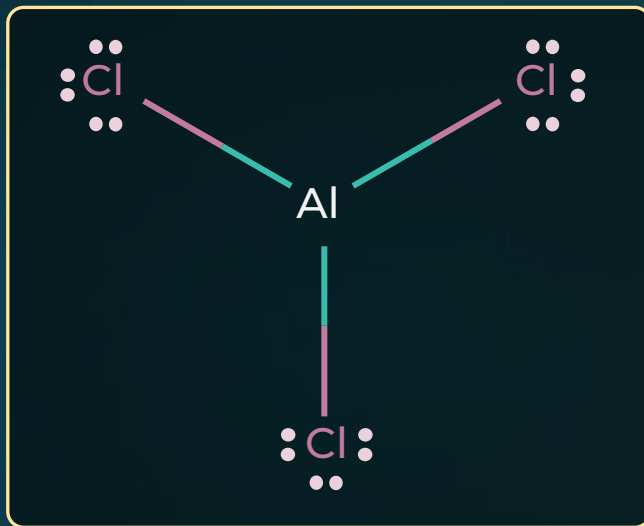


Electron Deficient Bonds

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

BH₃ is electron deficient compound. That's why it undergoes **dimerisation** by means of **3c-2e⁻** bonds also known as **banana bonds**.

Case 2: Electron Deficiency in AlCl_3

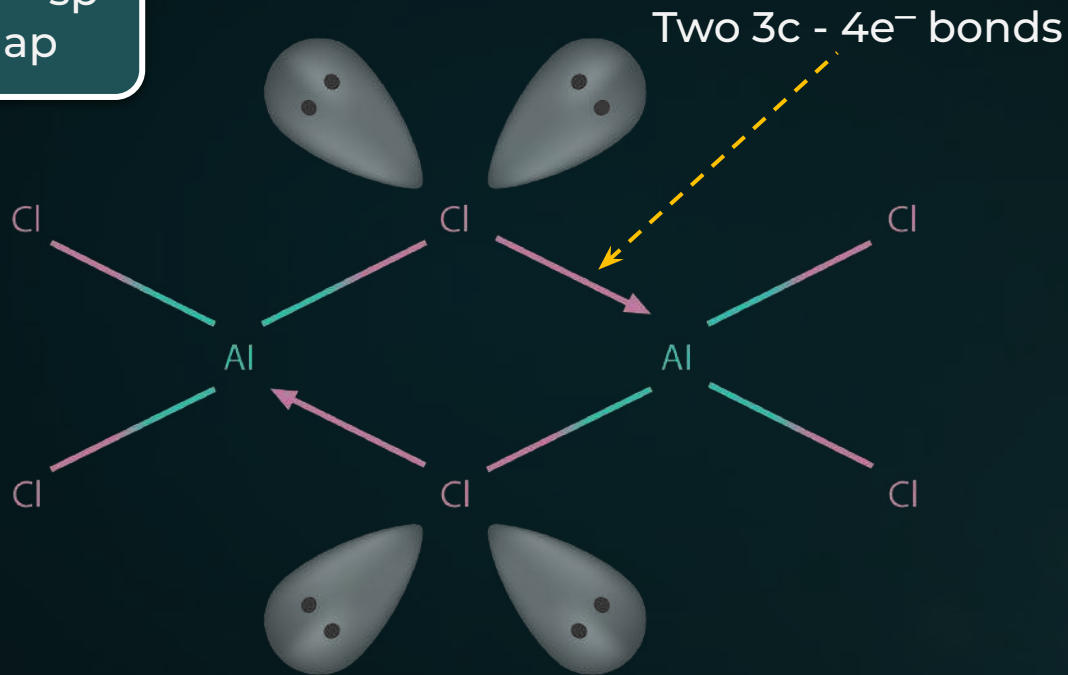


Incomplete
octet of Al

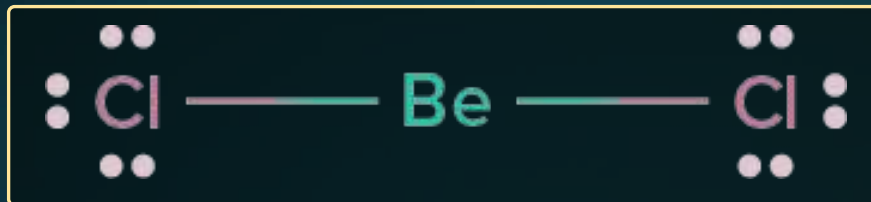
Tendency to
form **dimer**

In Vapour Phase - Dimer of AlCl_3 (Al_2Cl_6)

$\text{sp}^3 - \text{sp}^3 - \text{sp}^3$
overlap



Case 3: Electron Deficiency in BeCl_2



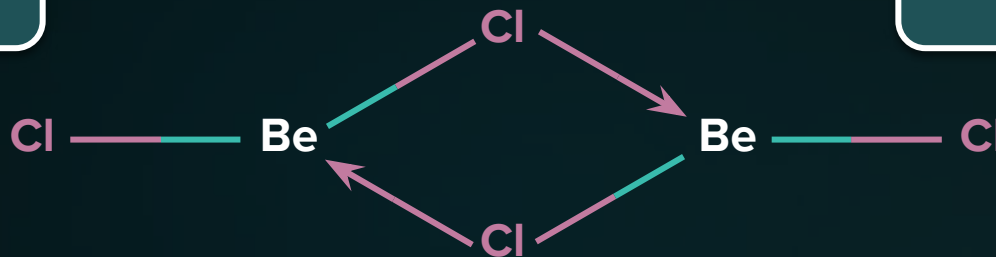
Incomplete
octet of Be

Forms dimer &
polymer
to get stabilized

In Vapour Phase - Dimer of BeCl_2 (Be_2Cl_4)

$\text{sp}^2 - \text{sp}^3 - \text{sp}^2$
overlap

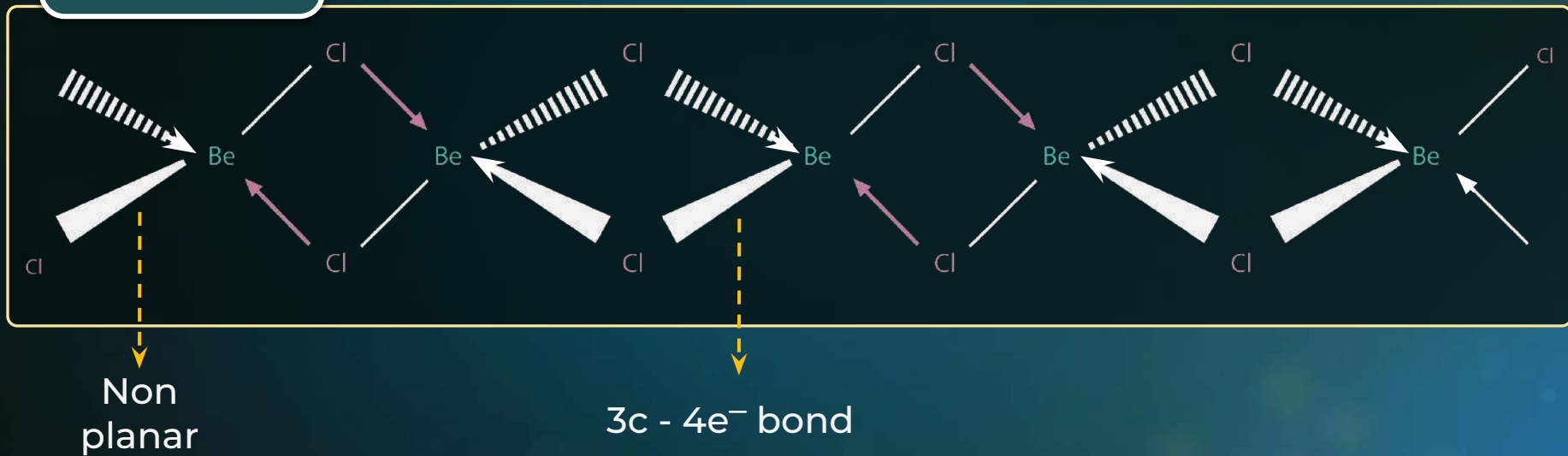
Planar



$3\text{c} - 4\text{e}^-$ bond

In Solid Phase - Polymer of BeCl_2 (BeCl_2)_n

$\text{sp}^3 - \text{sp}^3 - \text{sp}^3$
overlap



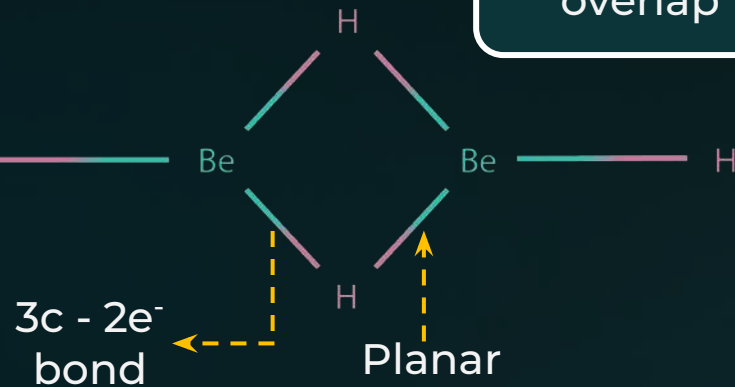
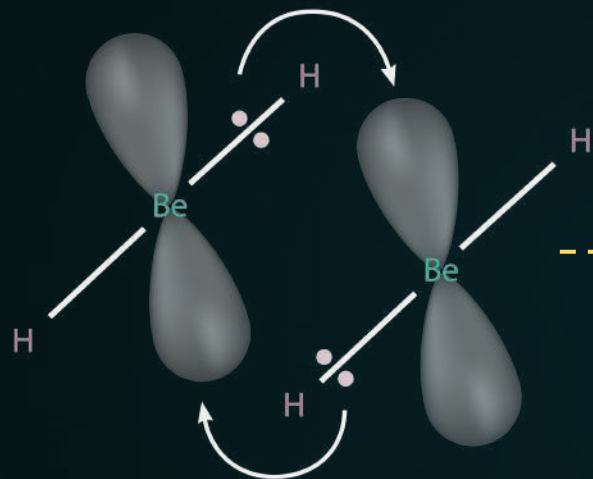
Case 4: Electron Deficiency in BeH_2



Incomplete
octet of Be

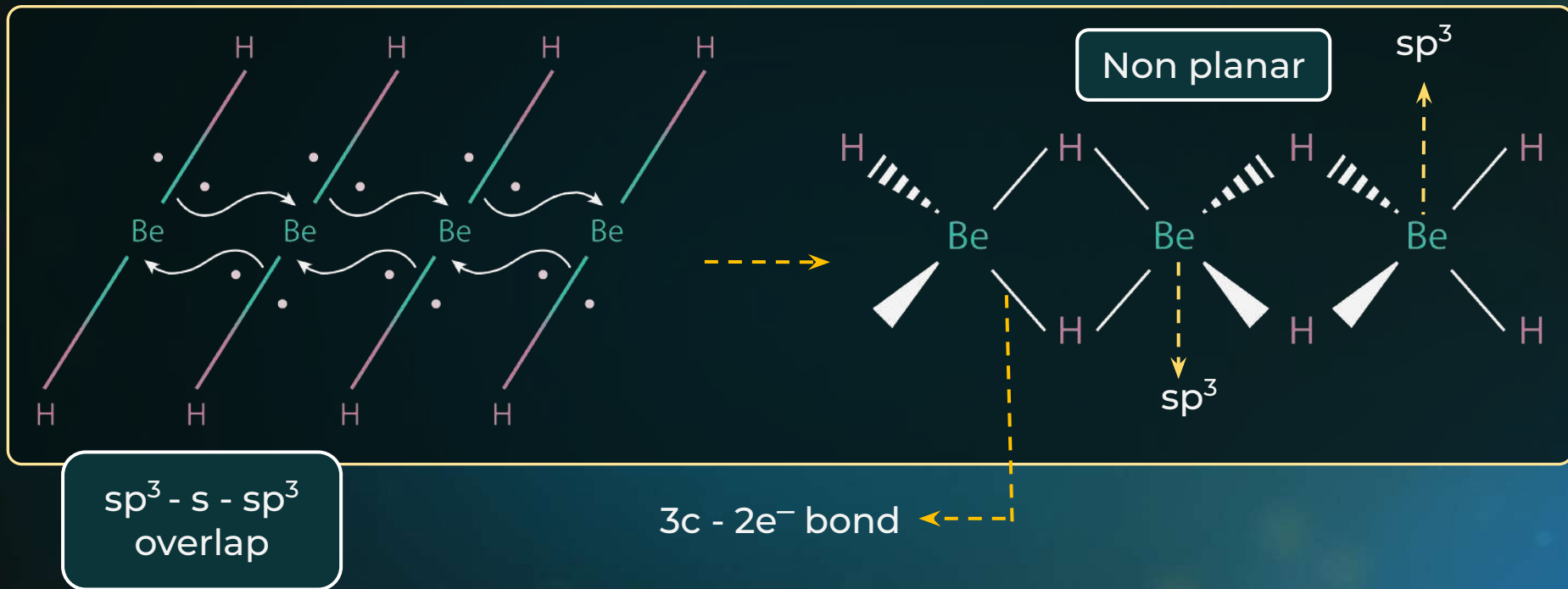
Forms dimer
& polymer
to get stabilized

In Vapour Phase - Dimer of $\text{BeH}_2(\text{Be}_2\text{H}_4)$

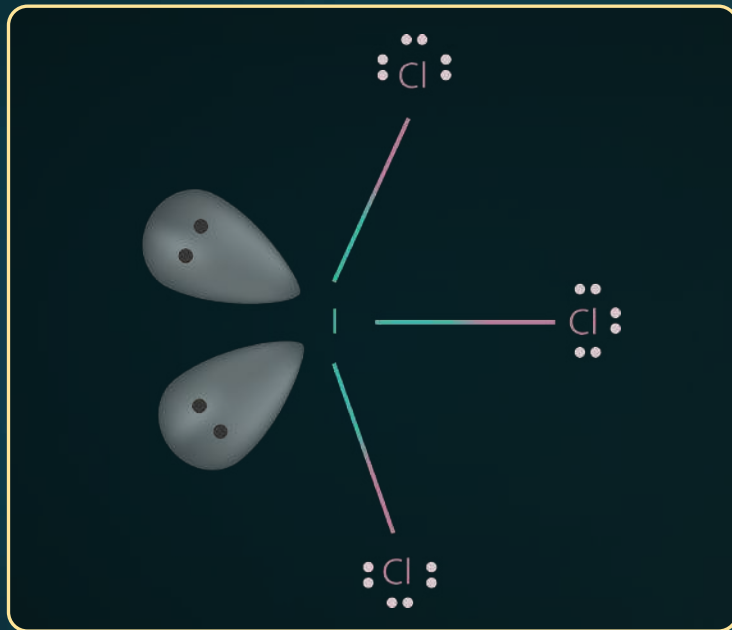


sp^2 - s - sp^2
overlap

In Solid Phase - Polymer of BeH_2 (BeH_2)_n



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)

$\text{sp}^3\text{d}^2 - \text{sp}^3 - \text{sp}^3\text{d}^2$
overlap

Planar

$3\text{c} - 4\text{e}^-$ bond



Bond Parameters



Bond Parameters

Bond angle

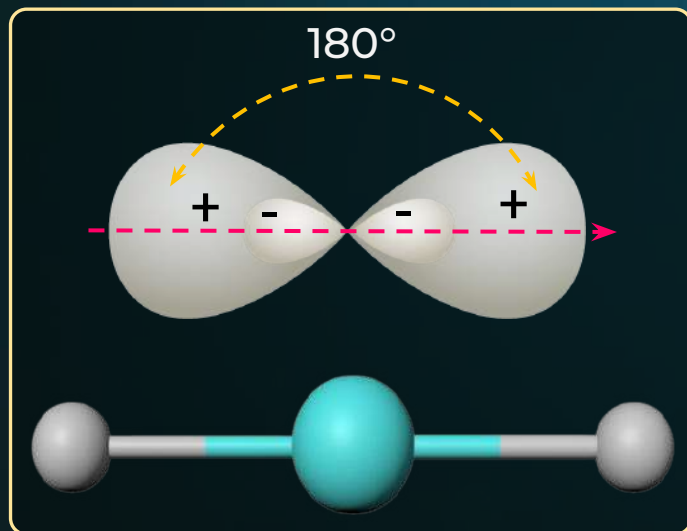
Bond length

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

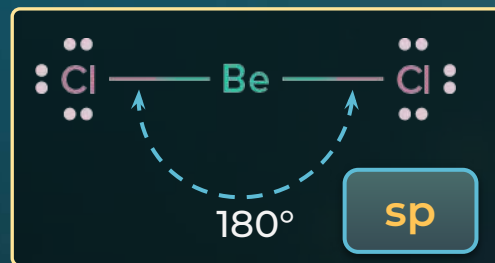
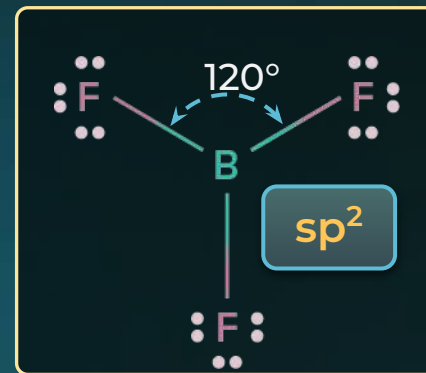
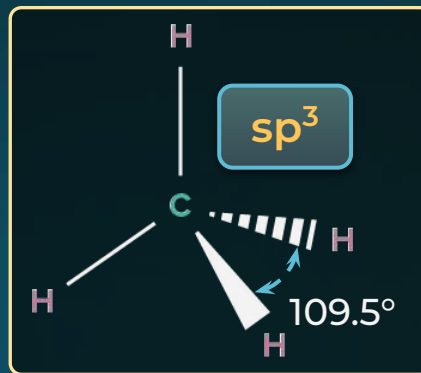
(1)

Hybridization

As % s
character



Bond angle



Factors Affecting Bond Angle

(2)

Steric Repulsions

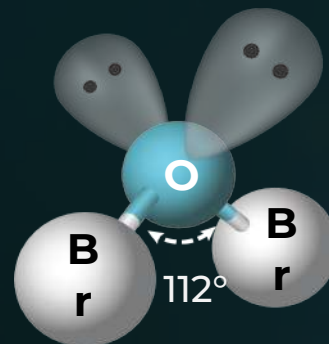
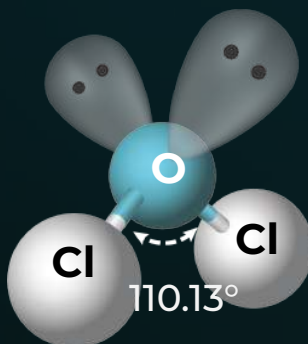
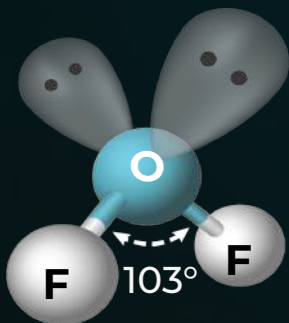
Steric Repulsions



Bond angle



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



Factors Affecting Bond Angle

(3)

Number of lone pairs on the central atom

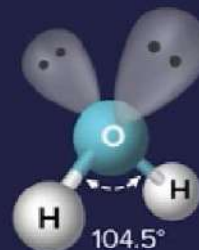
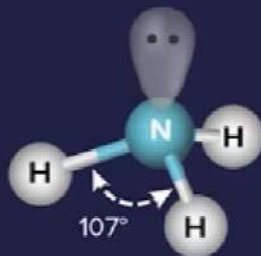
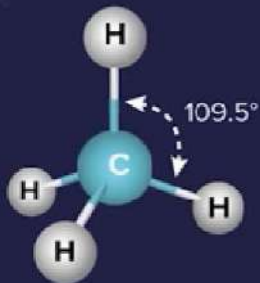
As number of lone
pairs



Bond angle



Same hybridisation of the central atom



Factors Affecting Bond Angle

(4)

Electronegativity of the central atom

E.N. of
central atom



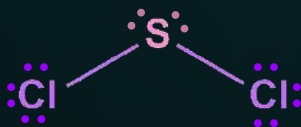
Bond angle



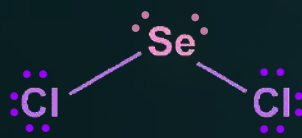
Same **hybridization** and number
of **lone pairs** on central atom



>



>



Factors Affecting Bond Angle

(5)

Electronegativity of
the side atoms

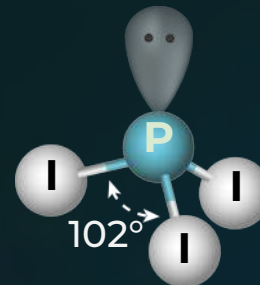
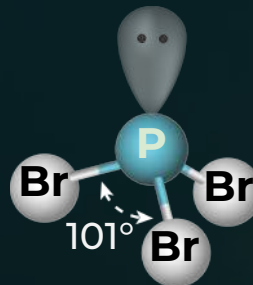
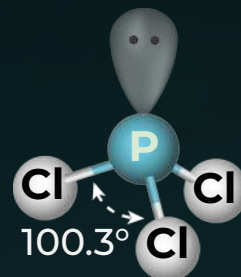
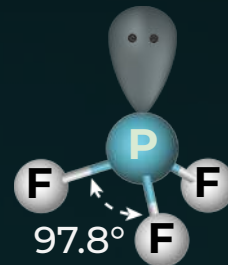
E.N. of
side atom



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

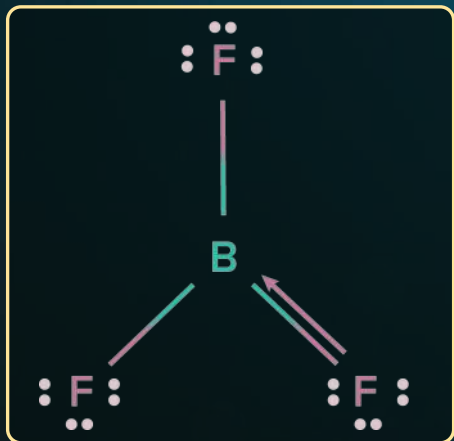
(6)

Back Bonding

Side
atom



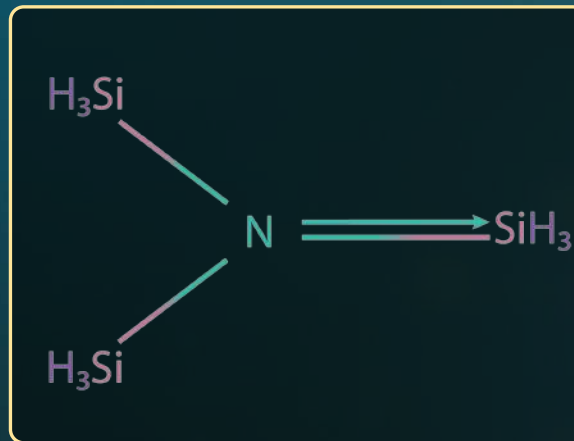
Central
atom



Central
atom



Side
atom





Factors Affecting Bond Angle



Due to back bonding

Bond order ↑

But net effect in
repulsion is zero

Bond angle = 120°



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 \uparrow

Magnitude of Bond energy \uparrow

| Bond | Energy (kJ mol^{-1}) |
|----------------------------|---------------------------------|
| $\text{C} - \text{C}$ | 347 |
| $\text{C} = \text{C}$ | 611 |
| $\text{C} \equiv \text{C}$ | 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

>

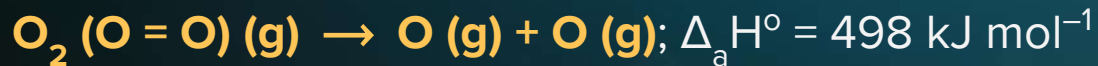
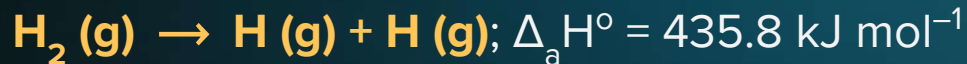
I — I



Bond Energy

Larger bond
enthalpy

Stronger bond



For **polyatomic molecules**,
Enthalpy needed to
break each bond
between the same
atoms is **different**.



Average Bond Enthalpy

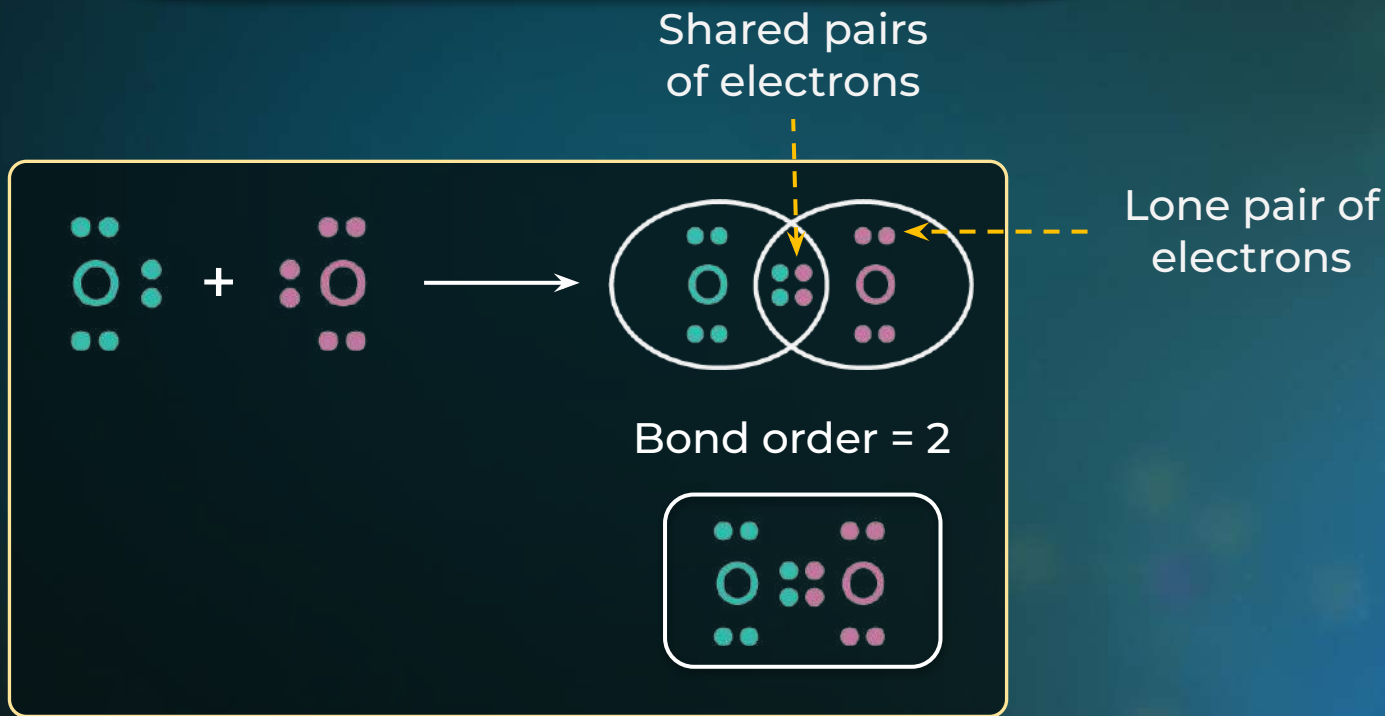
$$\text{Average bond enthalpy} = \frac{\text{Total bond dissociation enthalpy}}{\text{Number of bonds broken}}$$

For H_2O :

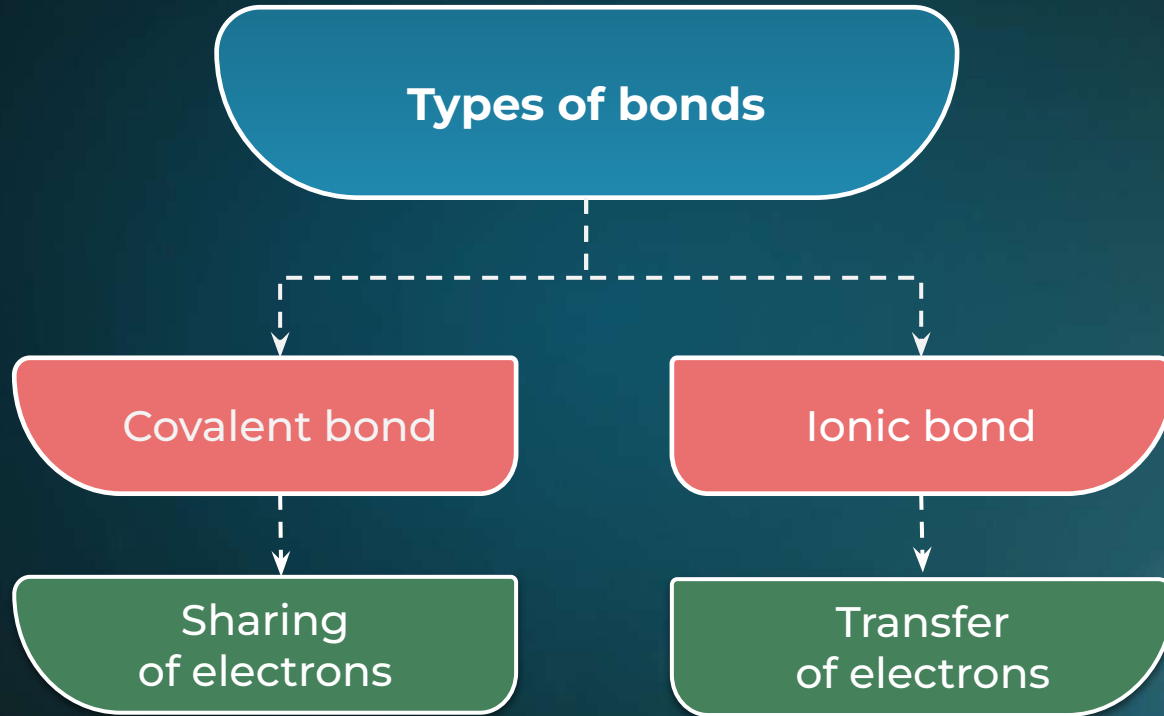
$$\begin{aligned}\text{Average bond enthalpy} &= \frac{502 + 427}{2} \\ &= 464.5 \text{ kJ mol}^{-1}\end{aligned}$$

Bond Order

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



What We Know?



What Exists in Reality?



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

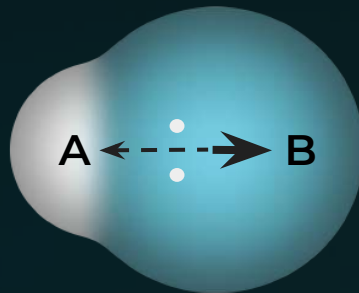
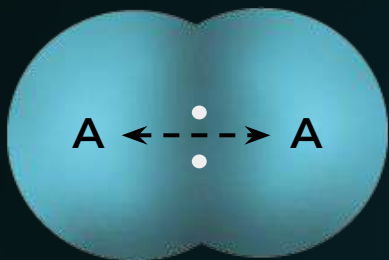


Covalent Bond





Non-polar & Polar Covalent Bond



E.N. of A < B

Symmetrical electron cloud

Asymmetrical electron cloud

$\text{H}_2, \text{Cl}_2, \text{N}_2, \text{F}_2 \dots$

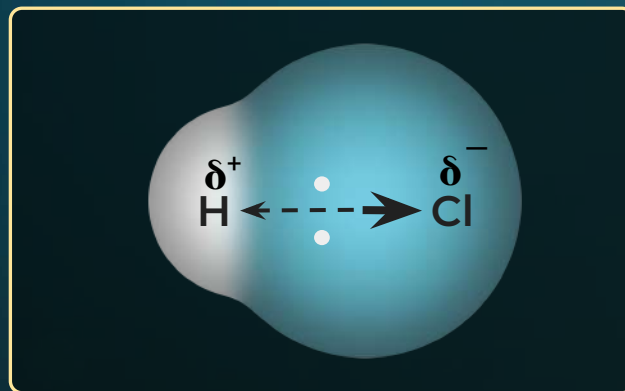
$\text{HF}, \text{HCl}, \text{HBr}, \text{HI} \dots$

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

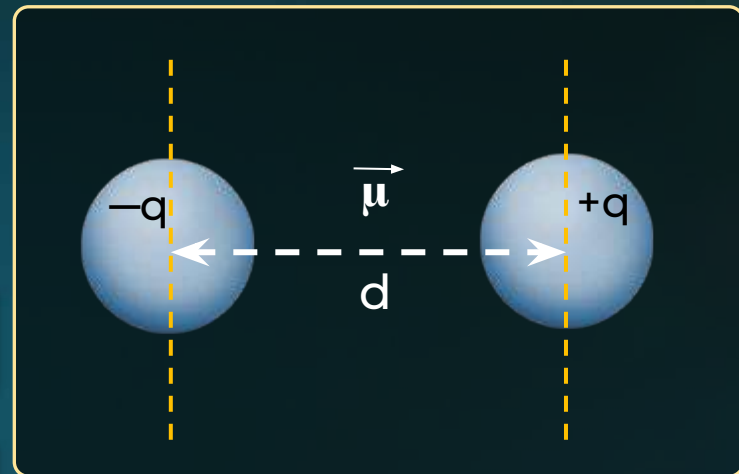
Formula of dipole moment is given as:

$$\mu = q \times d$$

Unit = Debye

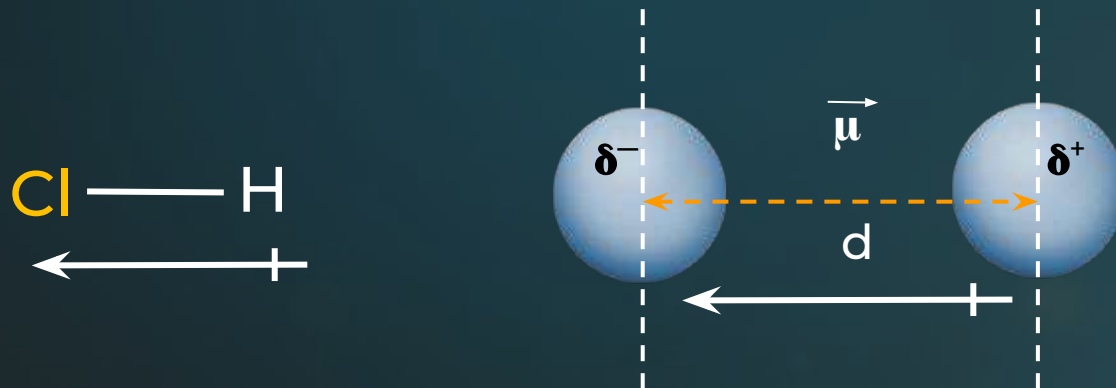
d = Distance of separation (\AA)

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

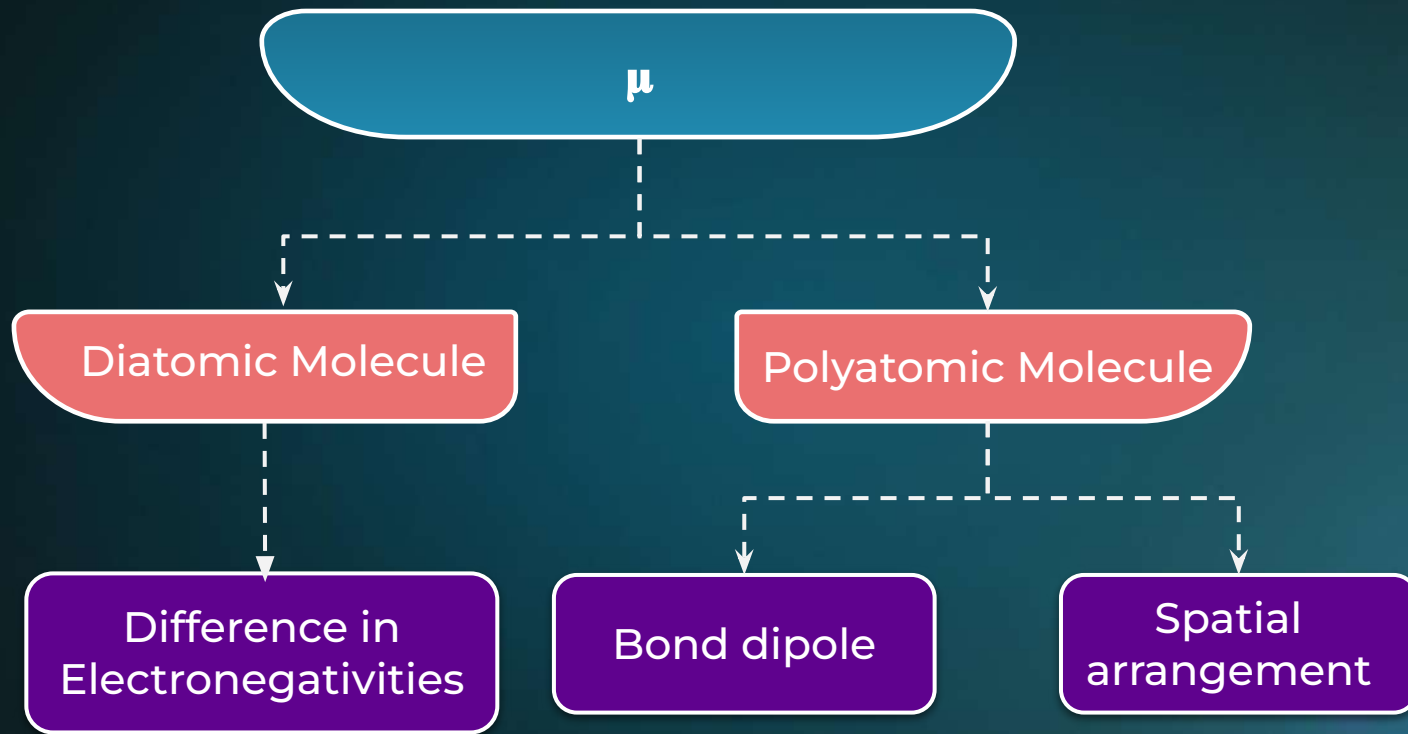


Direction and Representation

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



Value of Dipole Moment (μ)





Dipole Moment (μ)

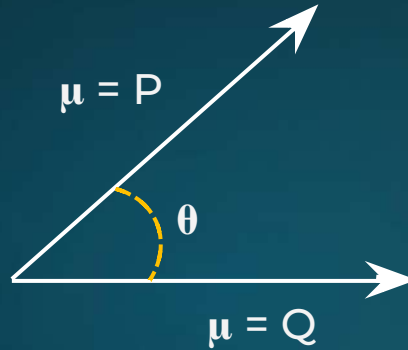
In **diatomic molecules**,
 μ depends upon

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 $\Delta\text{E.N.}$

$\Delta\text{E.N.} \uparrow$

$q \uparrow$

$\mu \uparrow$

For a **non-polar molecule**,

μ_{net}

=

0

For a **polar molecule**,

μ_{net}

\neq

0



Dipole Moment

Diatomic molecules

Homodiatomic
(**Non polar**)

$$\mu_{\text{net}} = 0$$

Heterodiatomic
(**Polar**)

$$\mu_{\text{net}} \neq 0$$

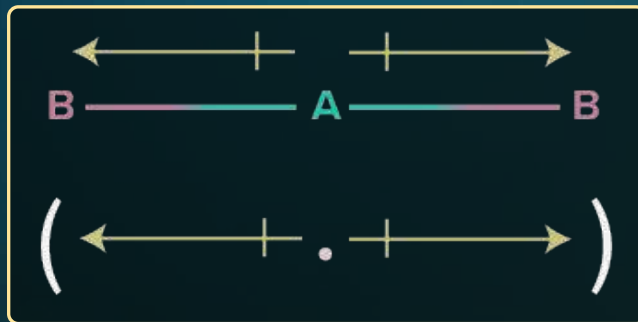
Polyatomic molecules

Bond dipole

Spatial
arrangement

Dipole Moment

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

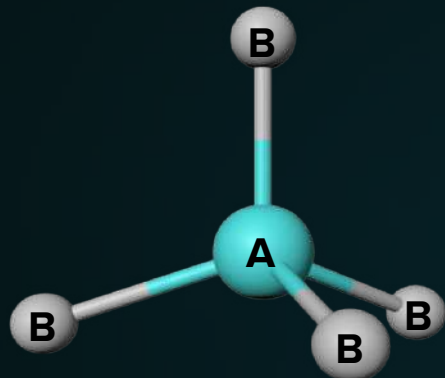
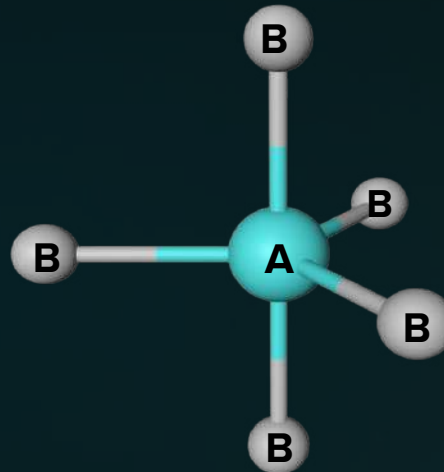


Net dipole moment (μ_{net})

=

0

Regular Geometries


 μ_{net}
 $=$
 0

 μ_{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 \neq 0

Asymmetrical
Molecule



Dipole Moment

Magnitude
of charge on
an electron

$$4.8 \times 10^{-10} \text{ e.s.u.}$$

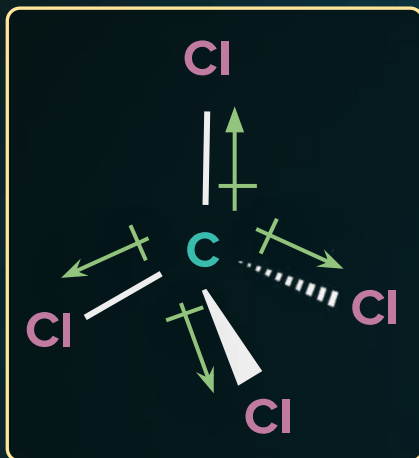
$$1.6 \times 10^{-19} \text{ C}$$

1 Debye

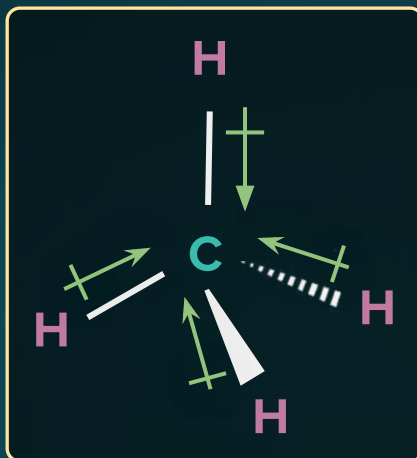
$$3.33564 \times 10^{-30} \text{ C m}$$

$$10^{-18} \text{ e.s.u. cm.}$$

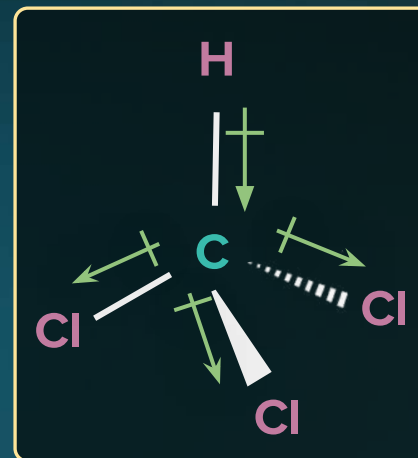
Predicting Geometry Using Dipole Moment



$\mu = 0$



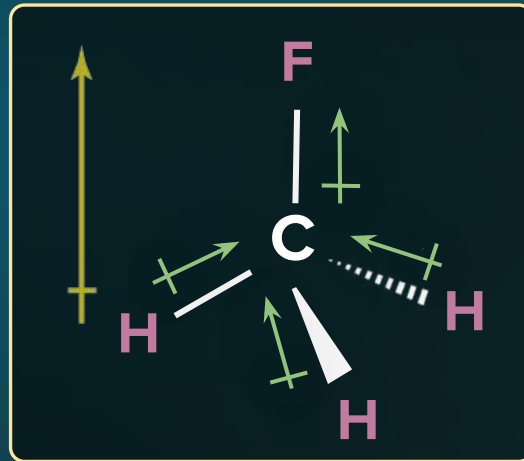
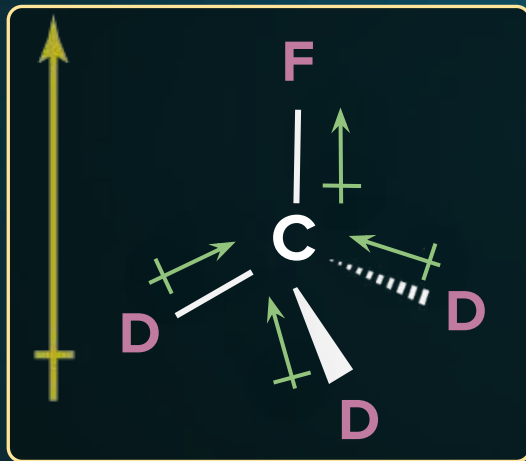
$\mu = 0$



$\mu = 1.04 \text{ D}$

Some Important Order of Dipole Moment



$$>$$


$$\Delta \text{E.N. in C - D}$$

$$>$$

$$\Delta \text{E.N. in C - H}$$

Dipole Moment of Dichlorobenzene

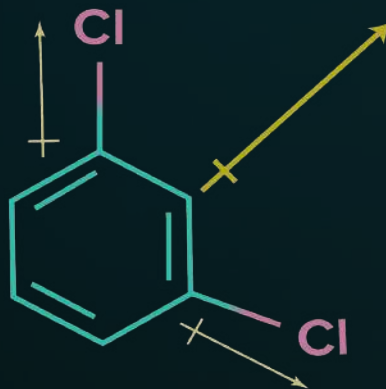
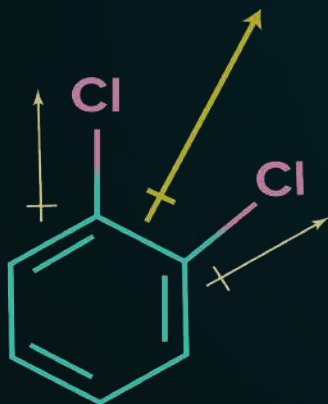
Ortho-
dichlorobenzene

>

Meta-
dichlorobenzene

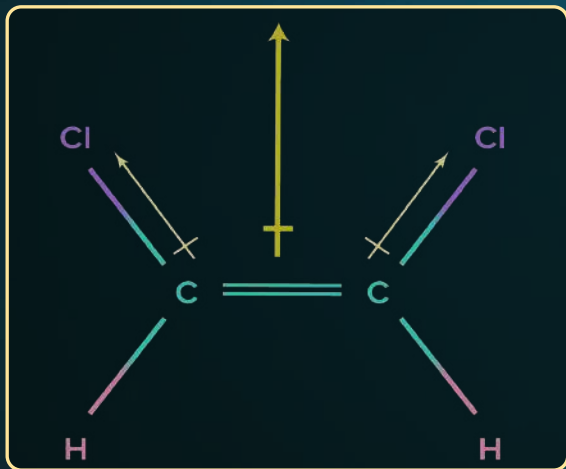
>

Para-
dichlorobenzene



What are Cis and Trans?

Cis: Similar groups
on same side



μ_{net}

\neq

0

Trans: Similar groups
on opposite sides



μ_{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

% 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 \propto

Charge on Cation

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

Charge on Anion

Size on Anion

Covalent character

Example: $\text{BeCl}_2 > \text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2 > \text{BaCl}_2$

(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: $\text{CuCl} > \text{NaCl}$ (Covalent character)

Cu^+

$[\text{Ne}] 3s^2 3p^6 3d^{10}$

Pseudo inert gas configuration

Na^+

$1s^2 2s^2 2p^6$

Inert gas configuration

Fajan's Rule

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

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

01

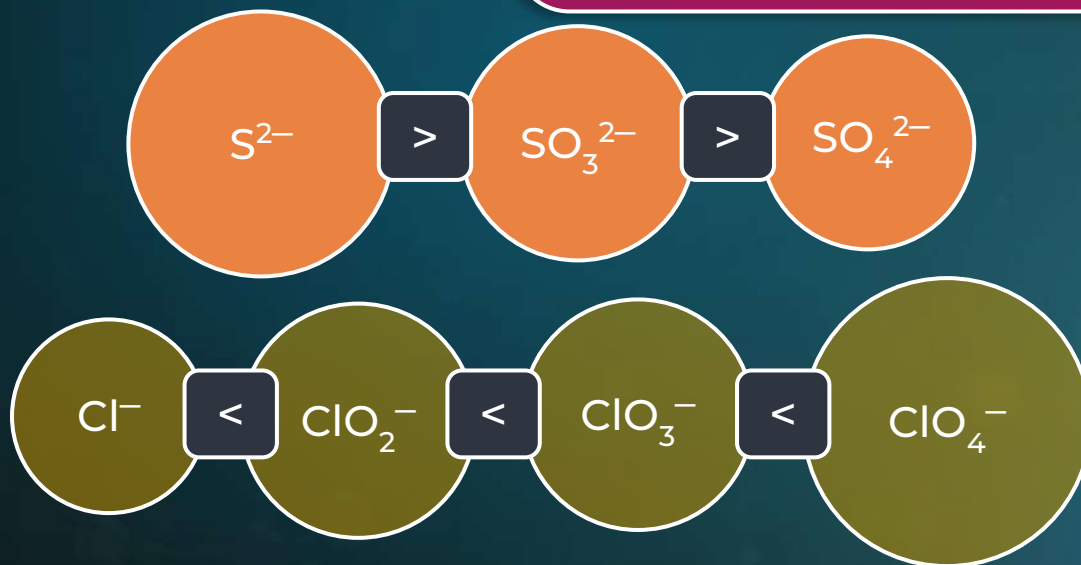
02

Polarising power
increases

Polarisability of Anion

Polarisability \propto 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 other elements)



Applications of Fajans' Rule

Determination of Covalent Character in an Ionic Compound

Extent of polarisation



Covalent character



LiF

<

LiCl

<

LiBr

<

LiI

NaF

<

Na₂O

<

Na₃N

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.**

Melting
point

\propto

$\frac{1}{\text{Extent of polarisation}}$

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

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

Variation in Melting Point

LiF

>

LiCl

>

LiBr

>

LiI

NaCl

>

MgCl₂

>

AlCl₃

>

SiCl₄

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

Solubility in Water

∞

$\frac{1}{\text{Extent of polarisation}}$

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**.
- ❖ $\text{Be}_2\text{N}_2 > \text{MgN}_2 > \text{CaN}_2 > \text{Sr}_2\text{N}_2 > \text{Be}_3\text{N}_2$
- ❖ 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**).

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

06

07

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

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

08



Linear Combination of Atomic Orbitals (LCAO)

BMO (Bonding Molecular Orbitals)

Constructive interference

ψ_{BMO}

=

$\psi_A + \psi_B$

ABMO (Anti Bonding Molecular Orbitals)

Destructive interference

ψ_{ABMO}

=

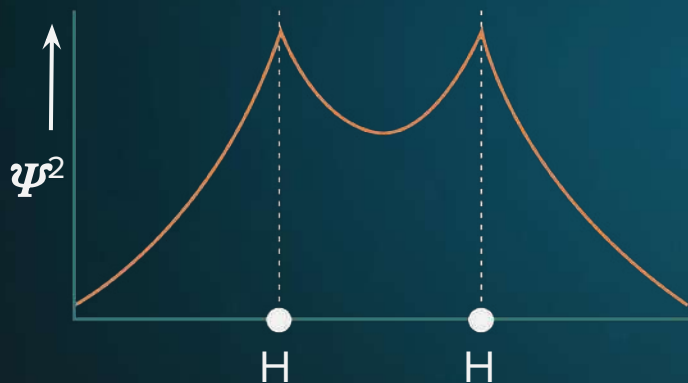
$\psi_A - \psi_B$

Where, A and B are atoms

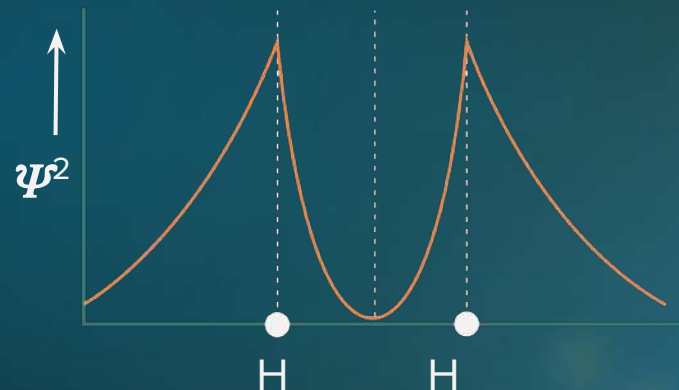
Linear Combination of Atomic Orbitals (LCAO)

Electron density **increases** in the **internuclear** region

Electron density **decreases** in the **internuclear** region



BMO



ABMO

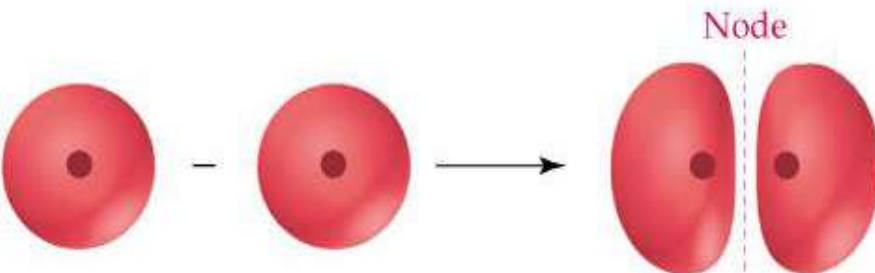
Molecular Orbitals

Additive
combination



Bonding
Molecular
Orbital

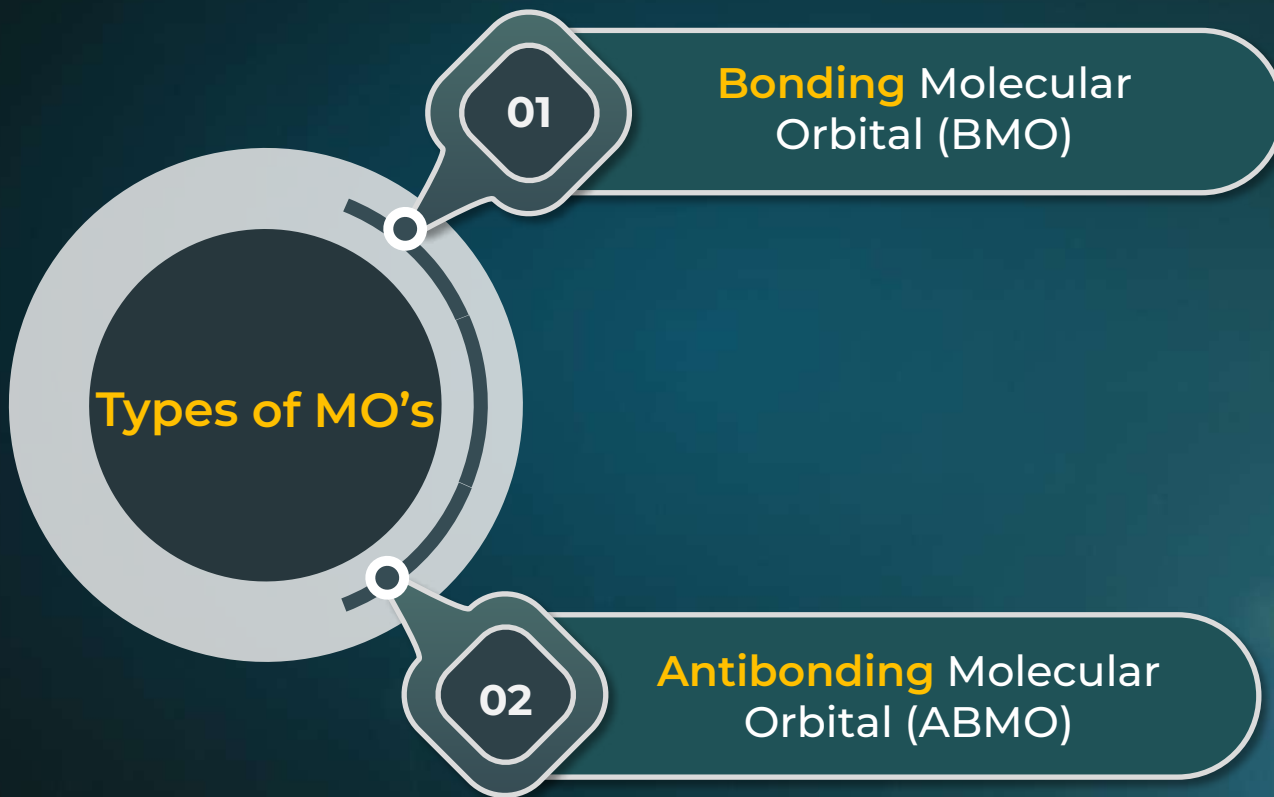
Subtractive
combination



AntiBonding
Molecular
Orbital



Linear Combination of Atomic Orbitals



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 |
| $\psi_{\text{BMO}} = \psi_{\text{A}} + \psi_{\text{B}}$ | $\psi_{\text{ABMO}} = \psi_{\text{A}} - \psi_{\text{B}}$ |
| Formed by constructive interference (Stabilized MO) | Formed by destructive interference (Destabilized MO) |



Difference between BMO and ABMO

| 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

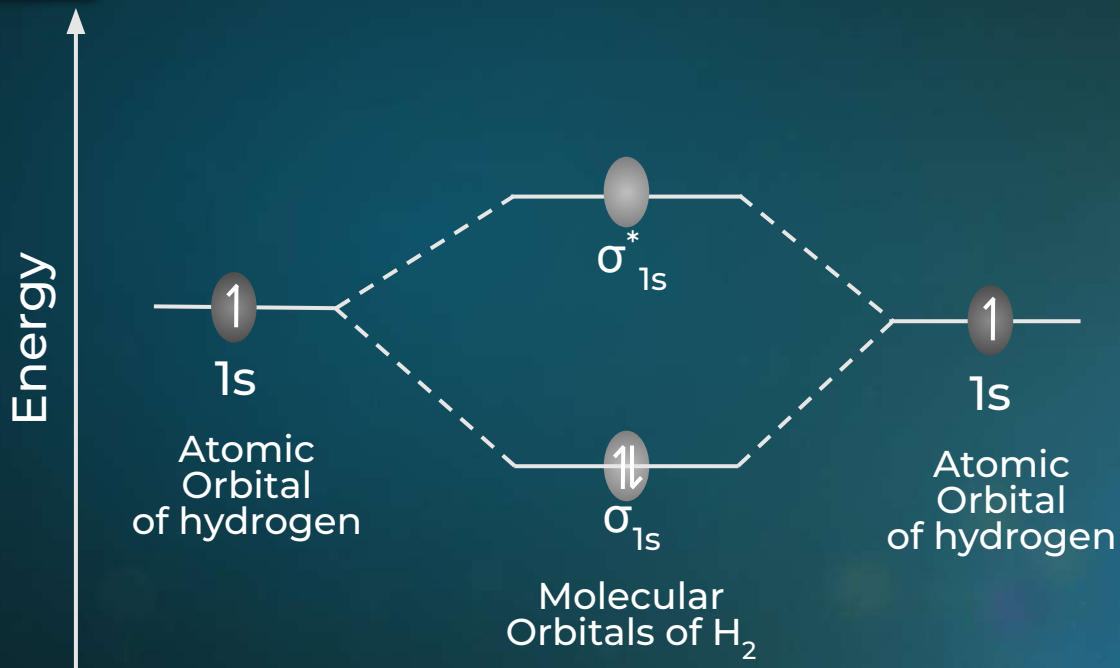
When two orbitals combine in same phase then **constructive interference** take place.

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

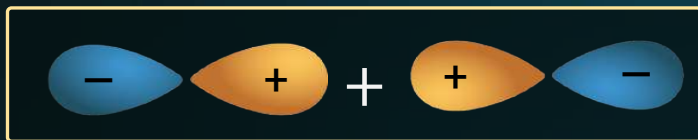


Molecular Orbital Energy Diagram

H₂ molecule



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



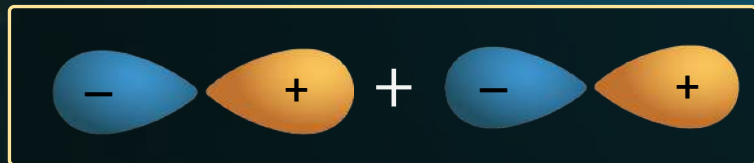
In Phase



$2p_z$

$2p_z$

$\sigma 2p_z$



Out of Phase

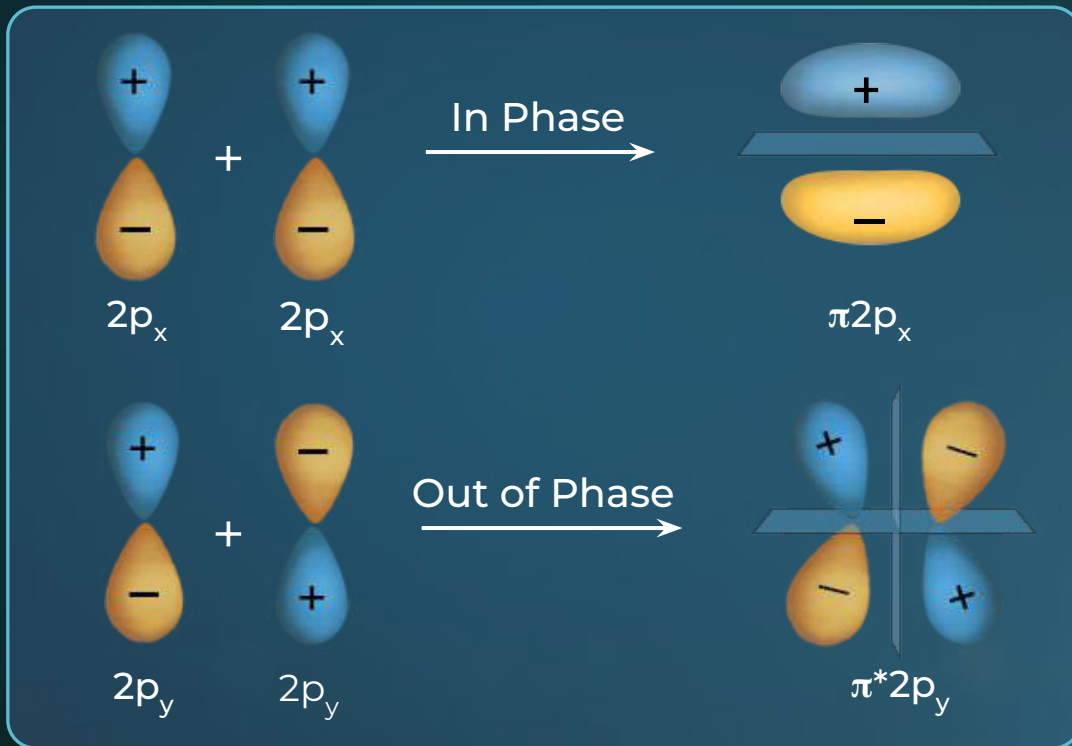


$2p_z$

$2p_z$

$\sigma^* 2p_z$

Shapes of MO's





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)

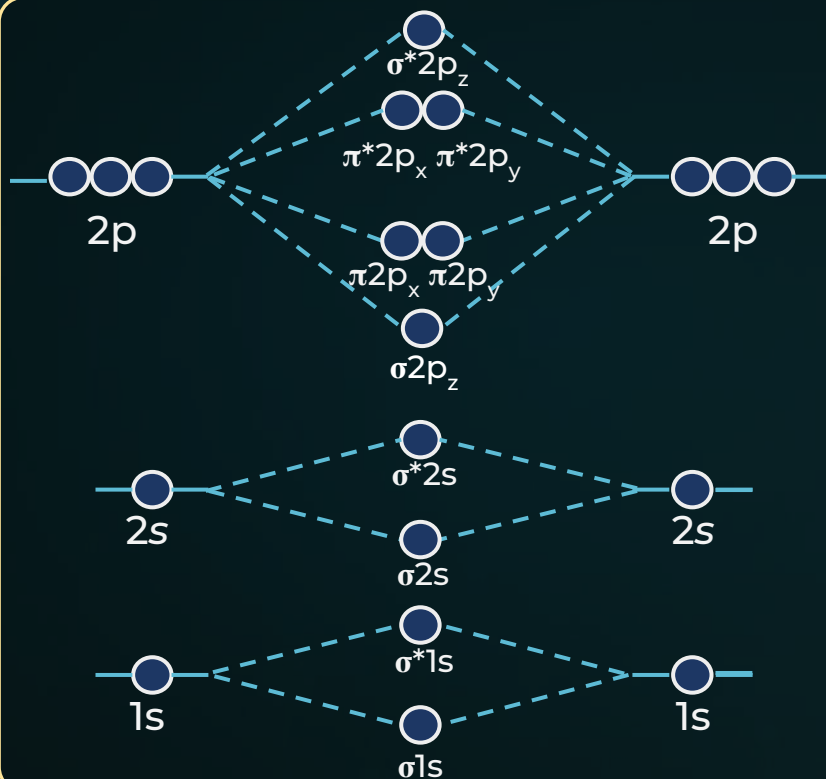
σ^*, π



Molecular Orbital Diagram for > 14 Electron System

For
molecules
having > 14
electrons

Energy



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

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

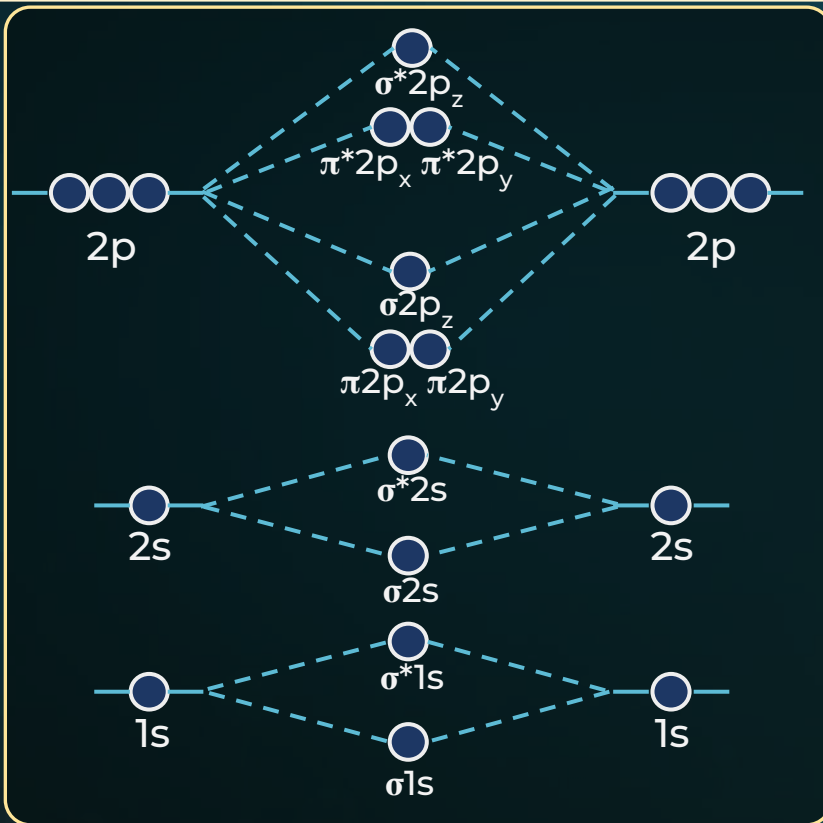
$$[\pi^* 2p_x = \pi^* 2p_y] < (\sigma^* 2p_z)$$



Molecular Orbital Diagram for ≤ 14 Electron System

For molecules having ≤ 14 electrons

Energy ↑



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

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

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



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)



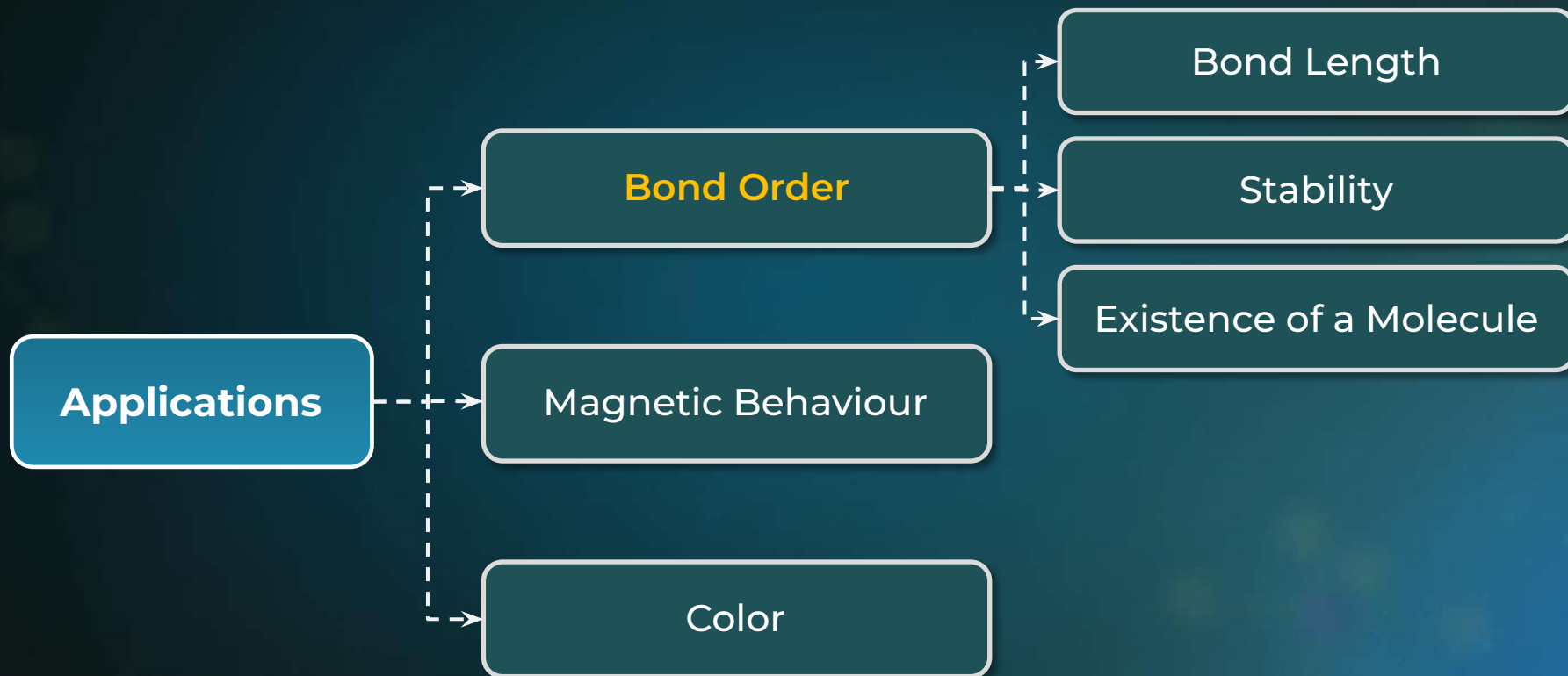
For B_2 molecule, 10 electrons (< 14 electrons)

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?



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

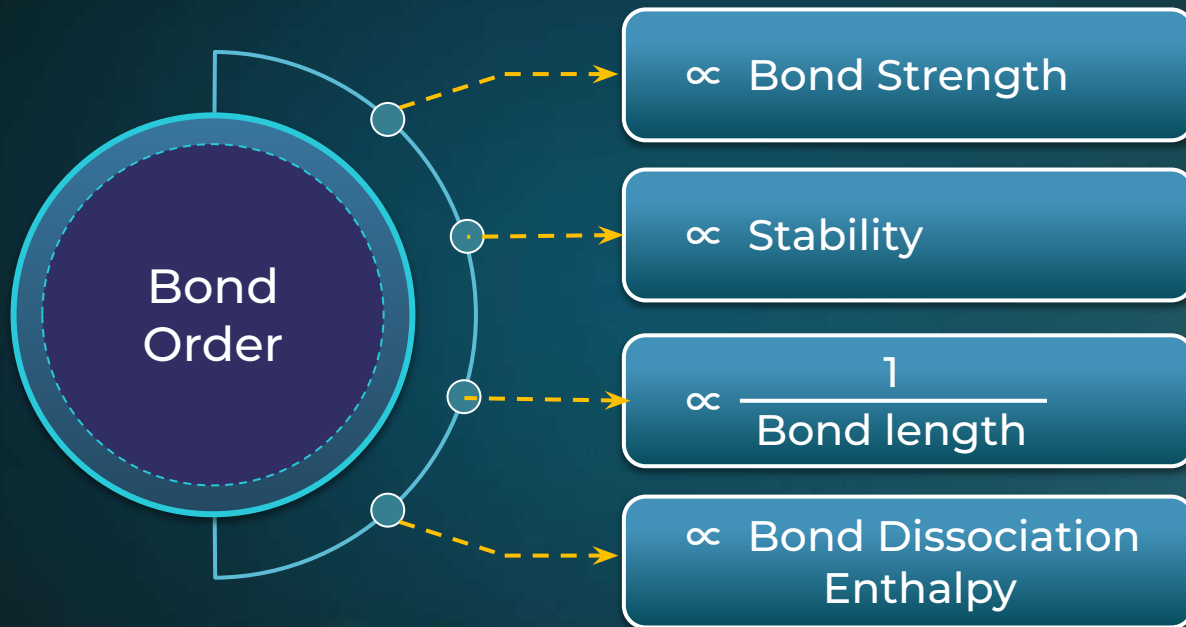
Shortcut to find the bond order of homonuclear diatomic molecules

| | | | | | | | | | |
|---------------------|----|-----|----|-----|----|-----|----|-----|----|
| 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 |

Diagram illustrating the shortcut to find the bond order of homonuclear diatomic molecules. The table shows the relationship between the number of electrons and the resulting bond order. Dashed arrows indicate the change in bond order for each additional electron:

- From 10 to 11 electrons: +0.5
- From 11 to 12 electrons: +0.5
- From 12 to 13 electrons: +0.5
- From 13 to 14 electrons: +0.5
- From 14 to 15 electrons: -0.5
- From 15 to 16 electrons: -0.5
- From 16 to 17 electrons: -0.5
- From 17 to 18 electrons: -0.5

Bond Order and Stability of Molecules



Species with the Same Bond Order

01

If the **bond order** is **same** for two species

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

02

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

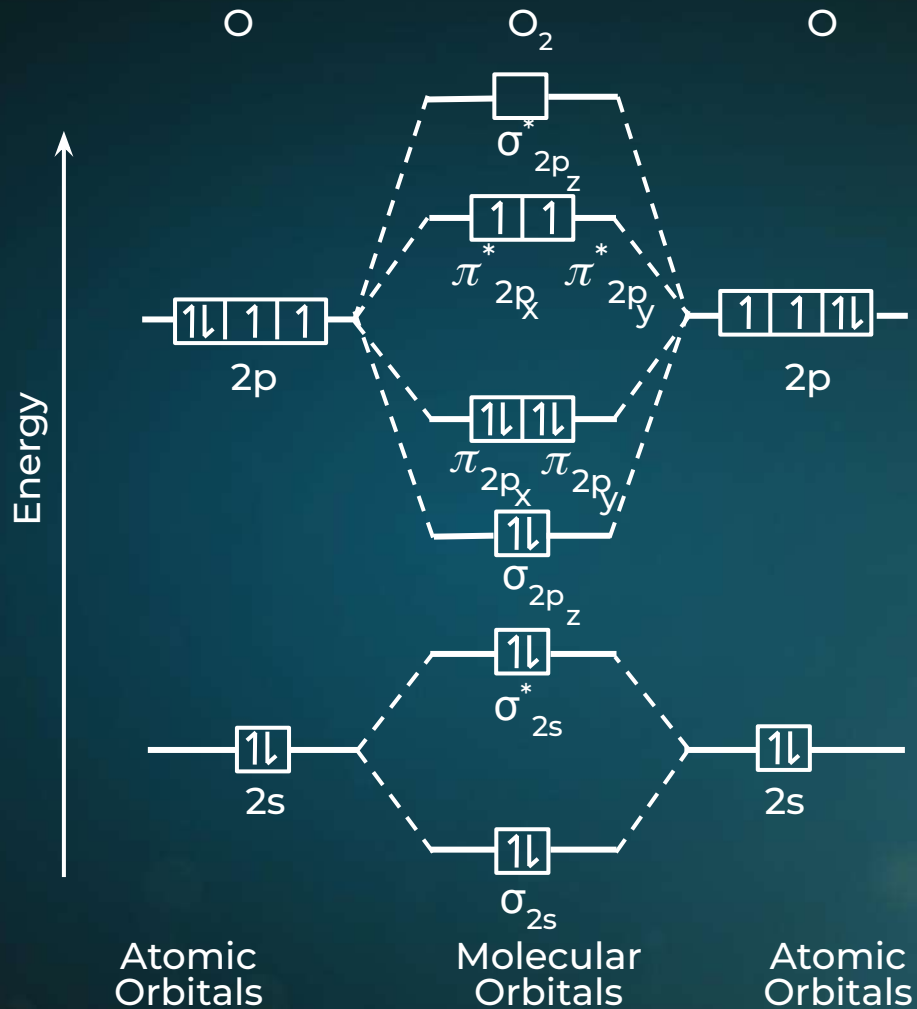
One or more MO's are singly occupied

Paramagnetic

All the MO's are doubly occupied

Diamagnetic

O₂ molecule





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 **O₂⁺** are the same.

Bond
Order

=

2.5

Paramagnetic

Experimentally the bond orders of **CN⁻** and **N₂** are the same.

Bond Order

=

3

Diamagnetic



Heteronuclear Diatomic Molecules

Experimentally the bond orders of **CO** and **N₂** are the same.

Bond Order

=

3

$1\sigma + 2\pi$
bonds

Diamagnetic



Bond Order

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

Examples:

N₂ & 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 in 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



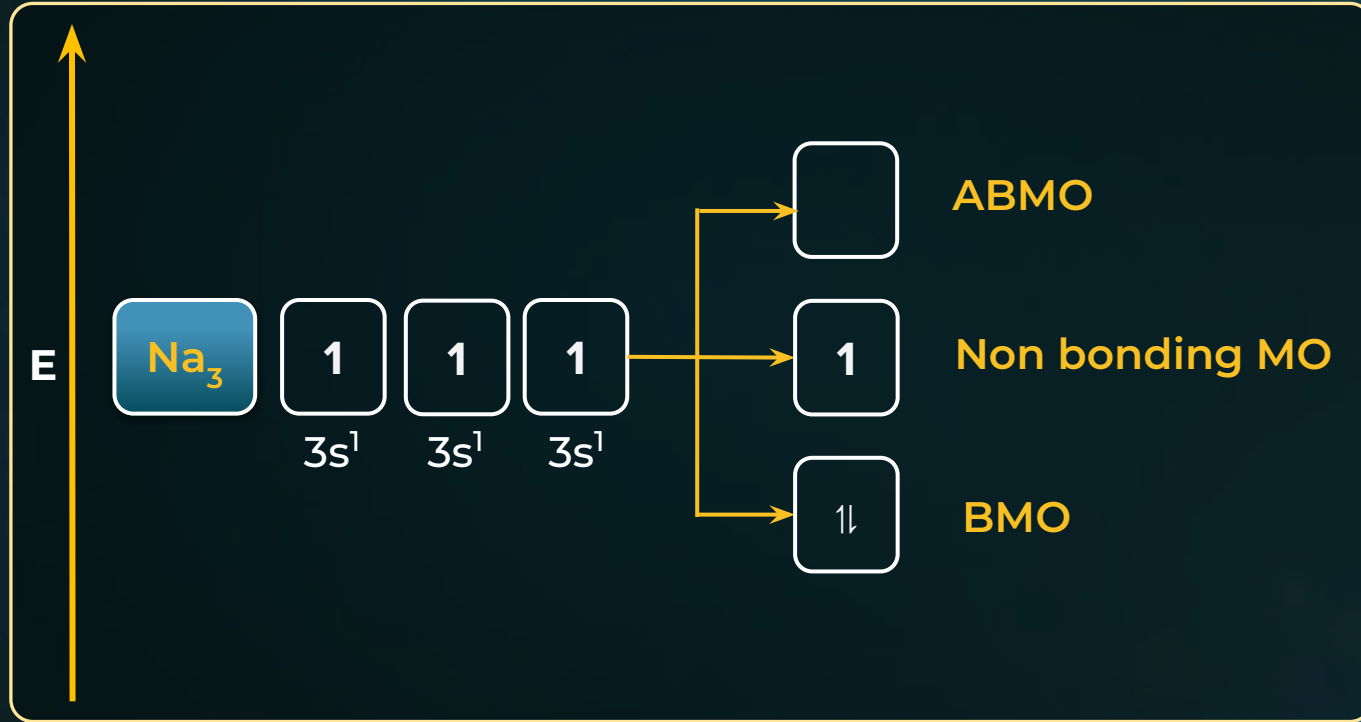
Band Theory

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

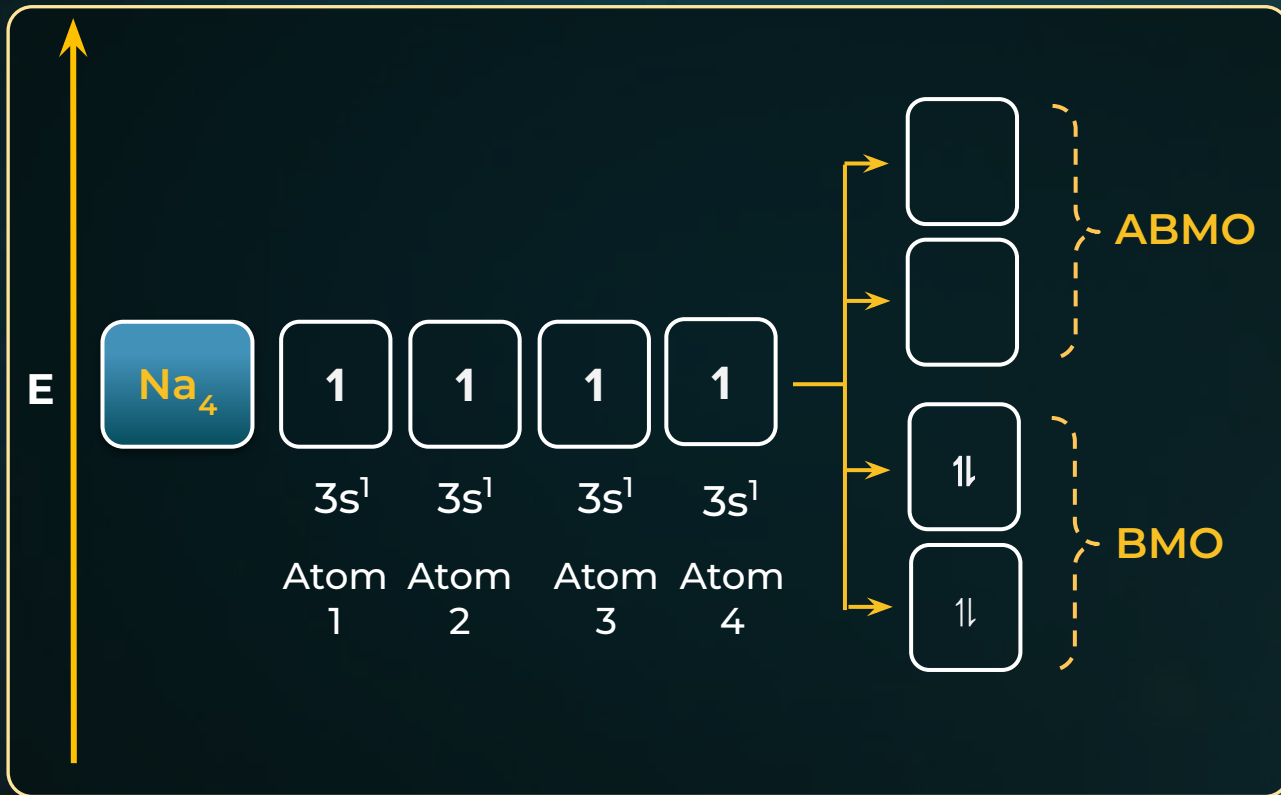
Band Theory



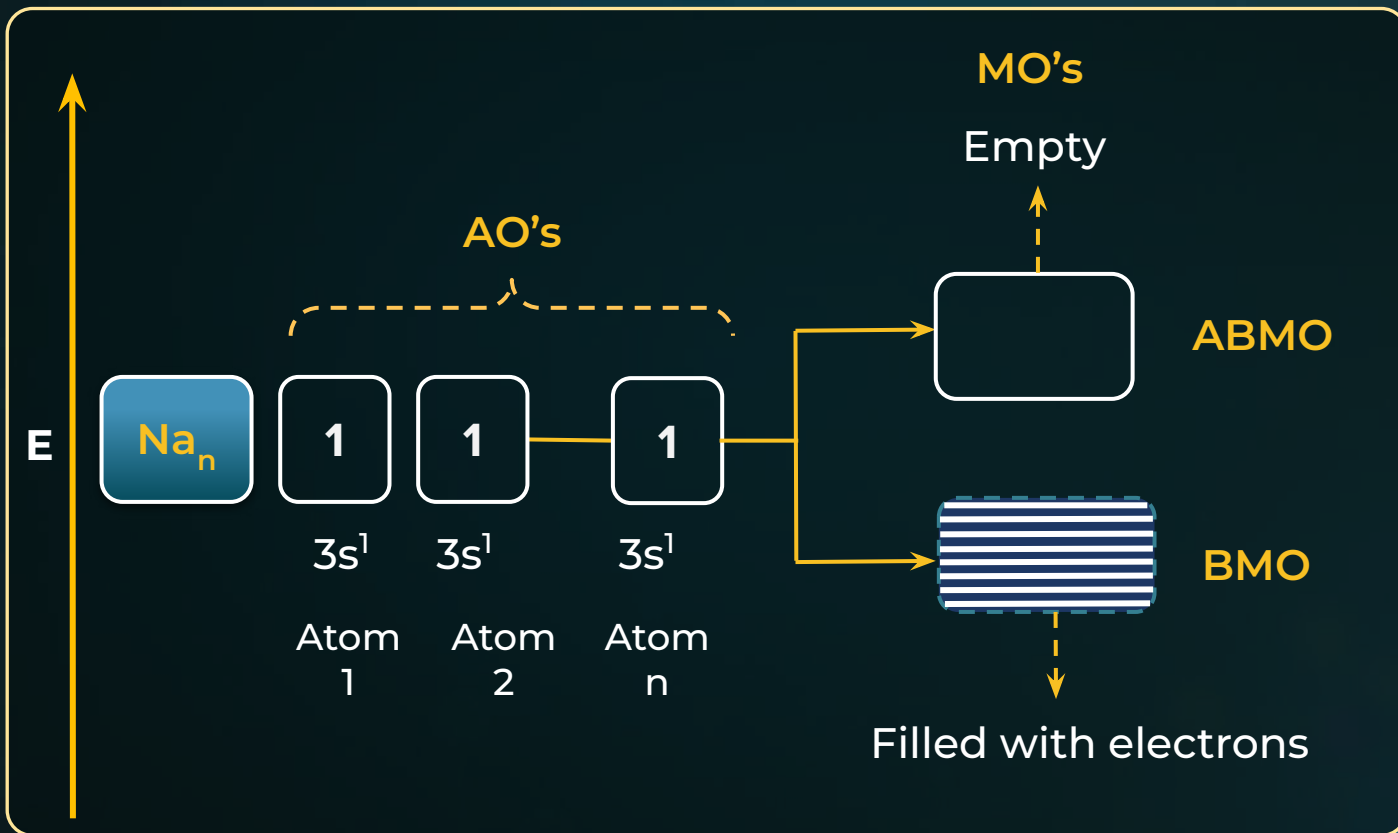
Band Theory



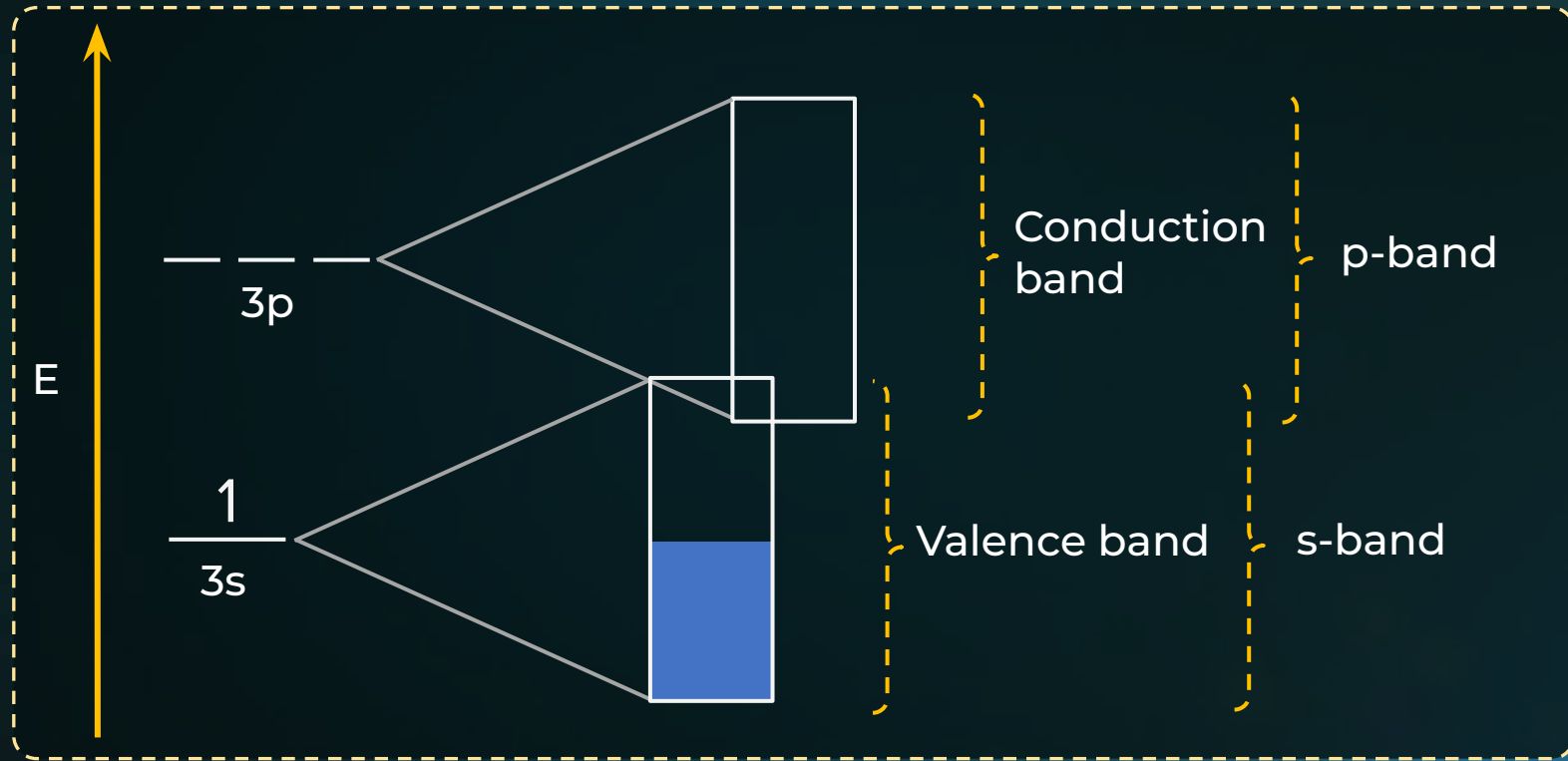
Band Theory



Band Theory



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

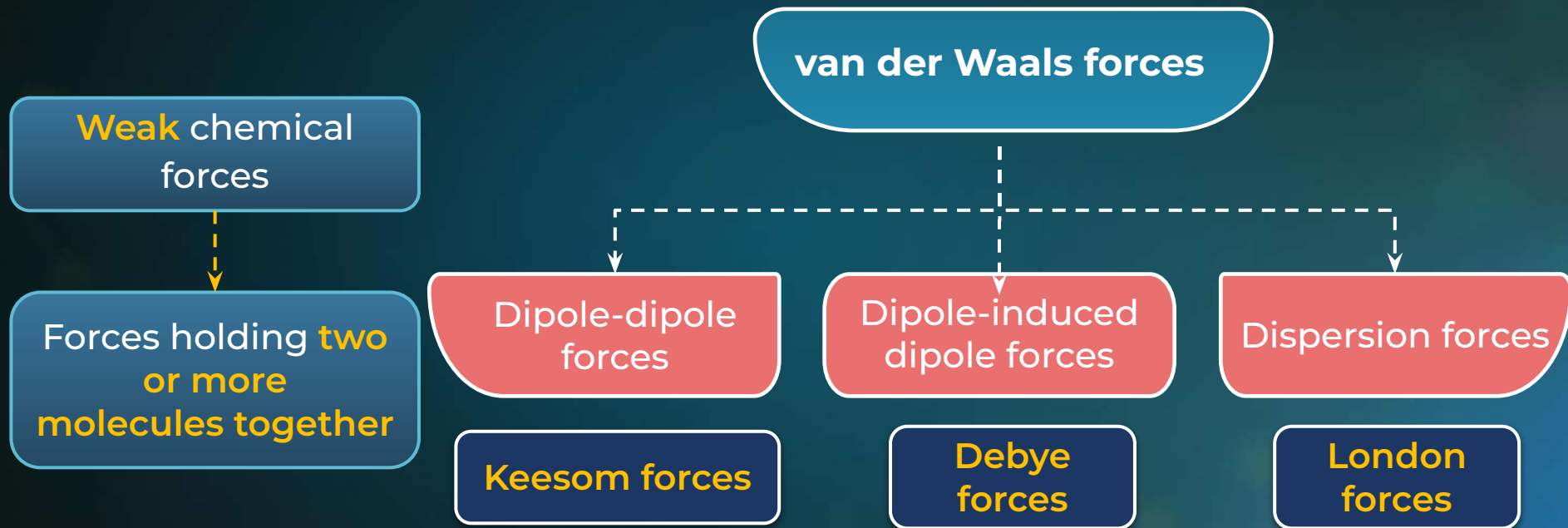
Ion-Dipole
Attraction

Instantaneous
Dipole-Induced Dipole
Attraction

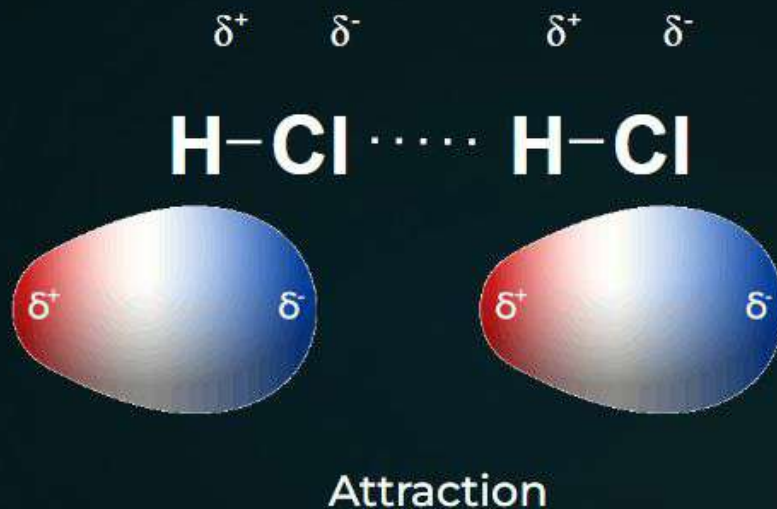
Dipole-Induced Dipole
Attraction

Ion-Induced Dipole
Attraction

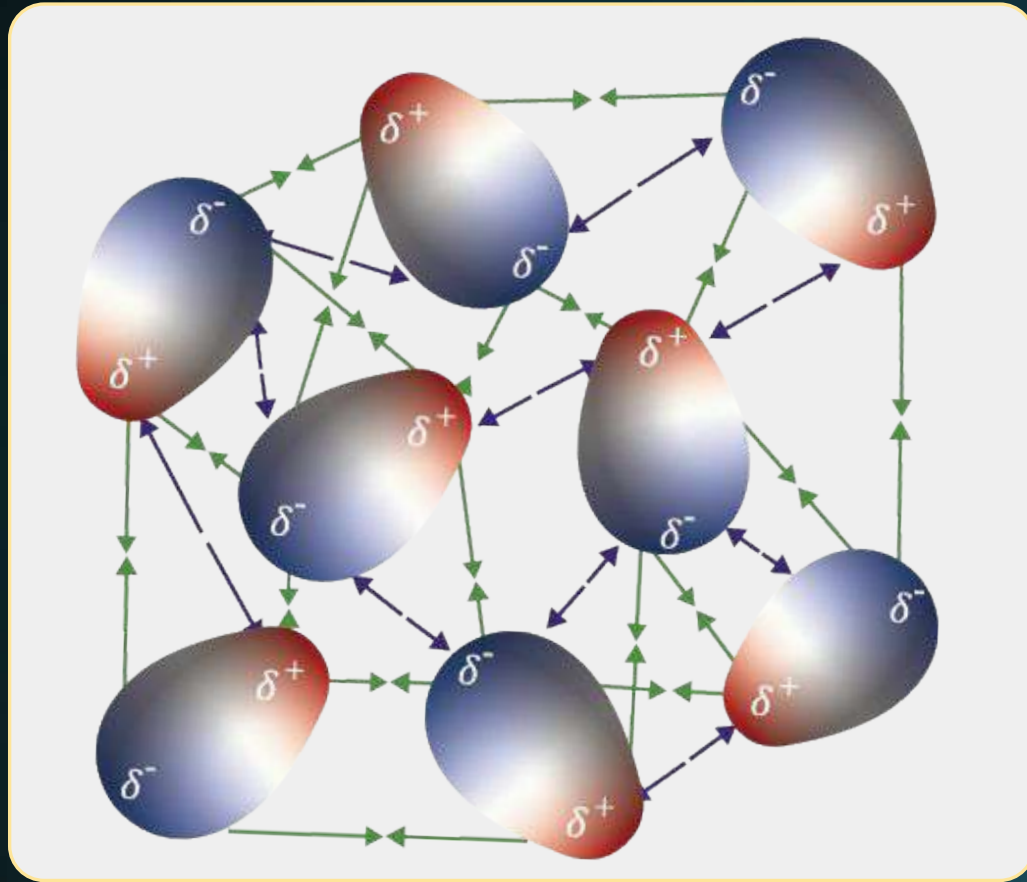
van Der Waals Forces



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



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 H₂O

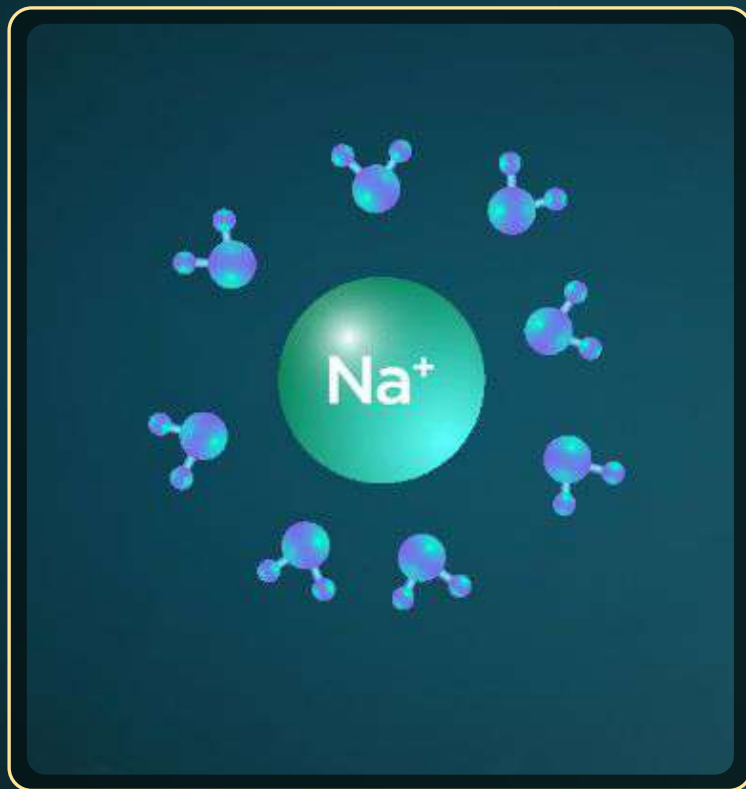
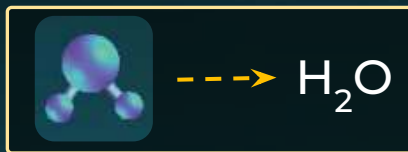


```
graph TD; A[NaCl in H2O] -.-> B[Na(OH2)x+]; A -.-> C[Cl(H2O)y-];
```

The diagram illustrates the dissociation of sodium chloride (NaCl) in water (H₂O). A central blue rounded rectangle labeled "NaCl in H₂O" has two dashed arrows pointing downwards to two dark blue rounded rectangles. The left rectangle contains the formula $\text{Na}(\text{OH}_2)_x^+$ and the right rectangle contains the formula $\text{Cl}(\text{H}_2\text{O})_y^-$.

$\text{Na}(\text{OH}_2)_x^+$

$\text{Cl}(\text{H}_2\text{O})_y^-$



Ion-Induced Dipole Attraction



Formation of Polyhalide Ions (X_3^-)





Dispersion Forces

Exists in **atoms & non-polar molecules** like H_2 , O_2 , Cl_2 , etc., in **solid or liquid states**



Which are **electrically symmetrical** & have **no permanent dipole**

Momentary imbalance in the electronic **charge distribution** in the molecule

polarization in adjacent species

Called **instantaneous dipole-induced dipole interactions**

Dispersion Forces

Magnitude of
London forces

\propto

Polarizability
of the particle

Interaction energy

\propto

$\frac{1}{r^6}$

r

Distance between
two molecules



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 ↓



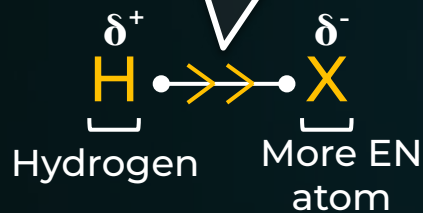
Strongest Dipole-Dipole
interaction



Hydrogen Bonding

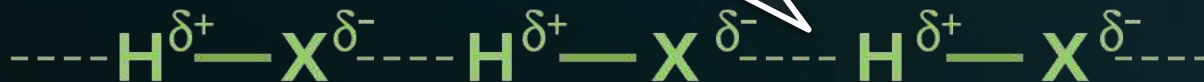
Hydrogen Bond

Displacement
of electrons
towards X



Polar molecule having electrostatic force of attraction

Represented
by a dotted line



Hydrogen Bond

(1)

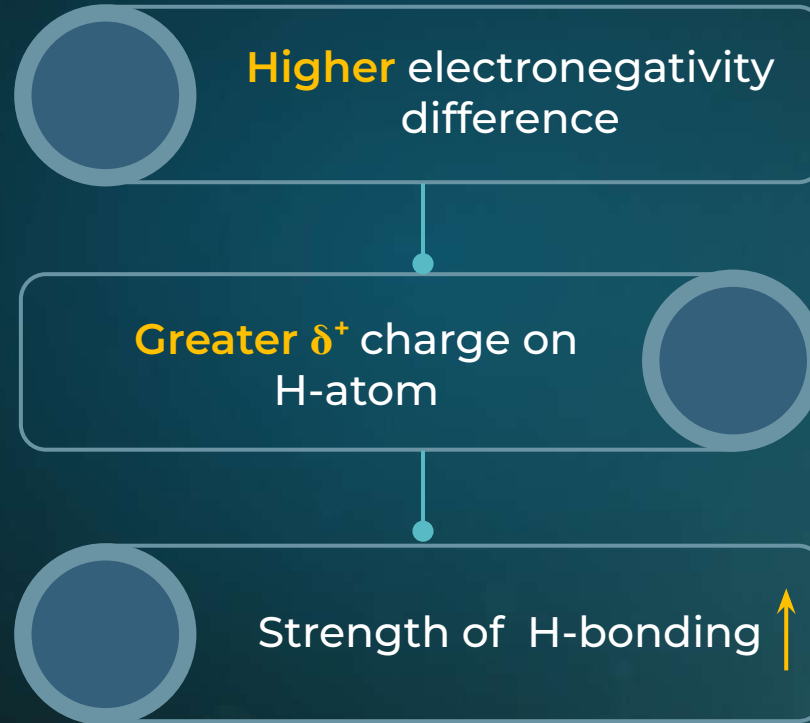
Special case of dipole-dipole attraction

(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





Factors Affecting Strength of H - bonding

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

Strength of H-bonding ↑



Decreasing tendency
to donate lone pair



Point to Remember!!

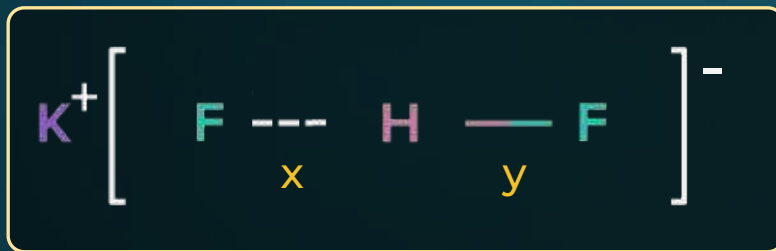


To compare strength of H-bond

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 $M[HF_2]$



Bond lengths: $x = y = 113 \text{ pm}$

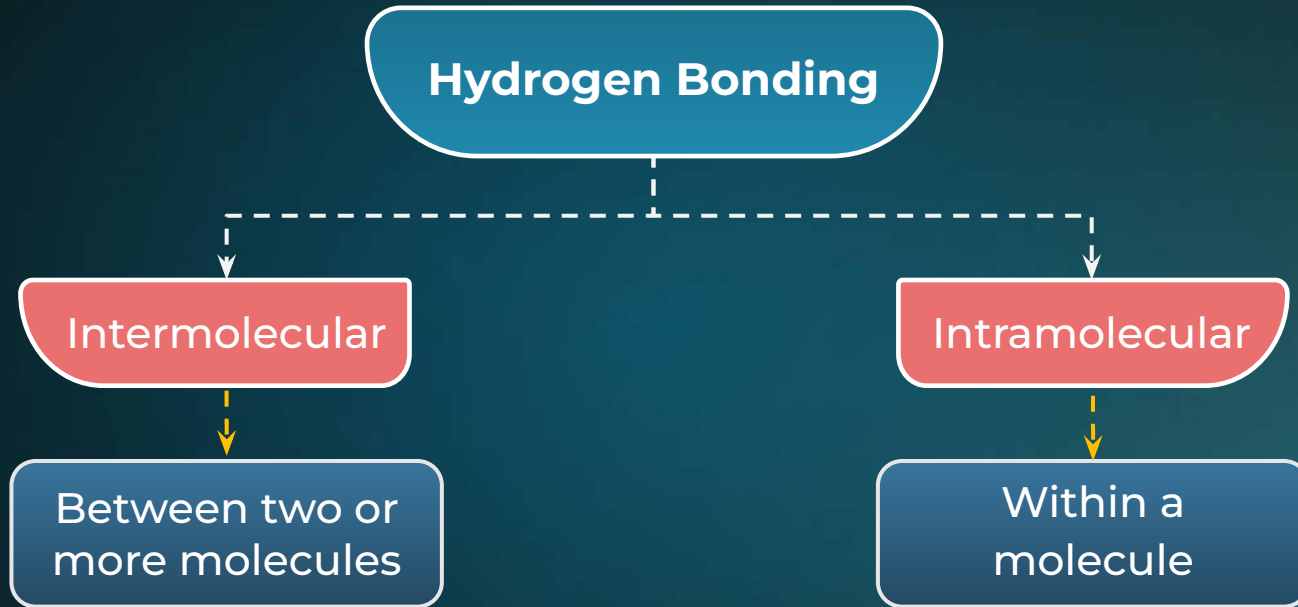
Bond energy
of both H-F

=

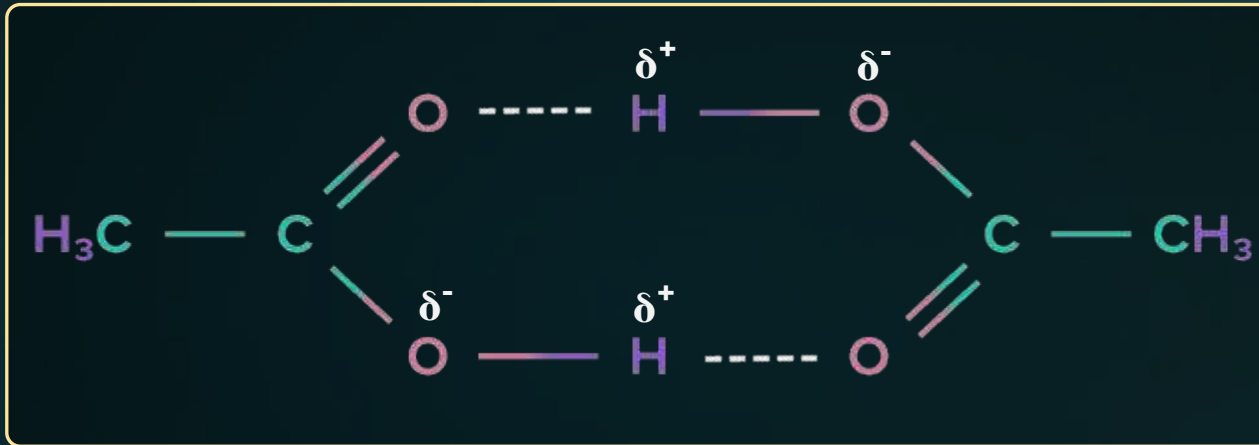
163 kJ/mol



Types of Hydrogen Bonding



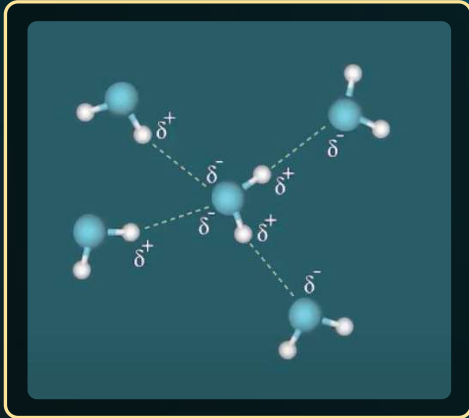
Examples of Intermolecular Hydrogen Bonding



Acetic Acid

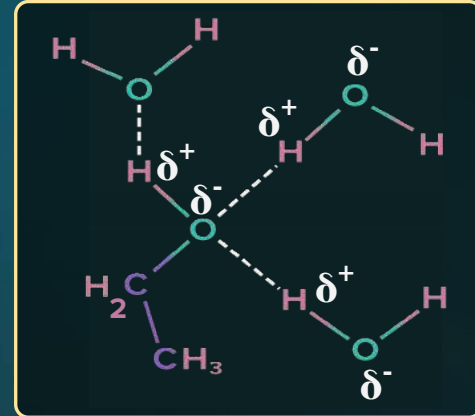
Intermolecular H - Bonding

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)

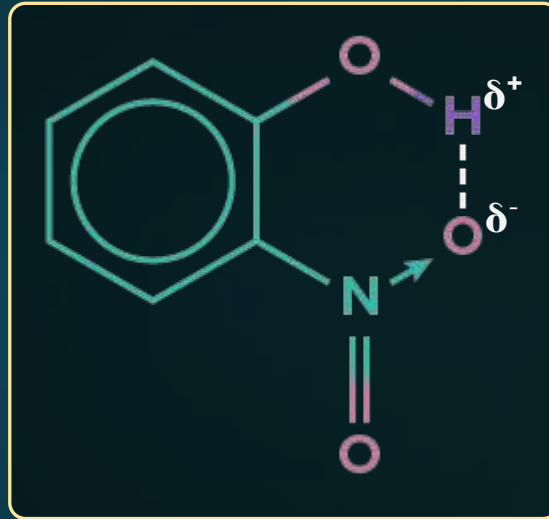
5 or 6 membered ring should be formed

(3)

Minimum strain should be there during ring closure

Intramolecular H-Bonding

Examples

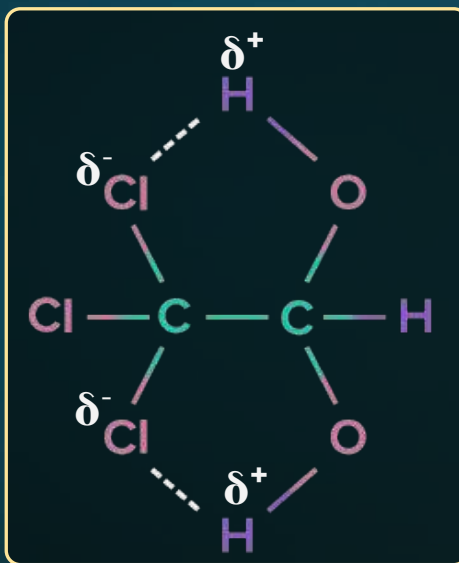


o-Nitrophenol



Point to Remember!!

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



Chloral hydrate ($\text{CCl}_3\text{CH}(\text{OH})_2$)

H-Bonding Dependency on Physical State of Compounds

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

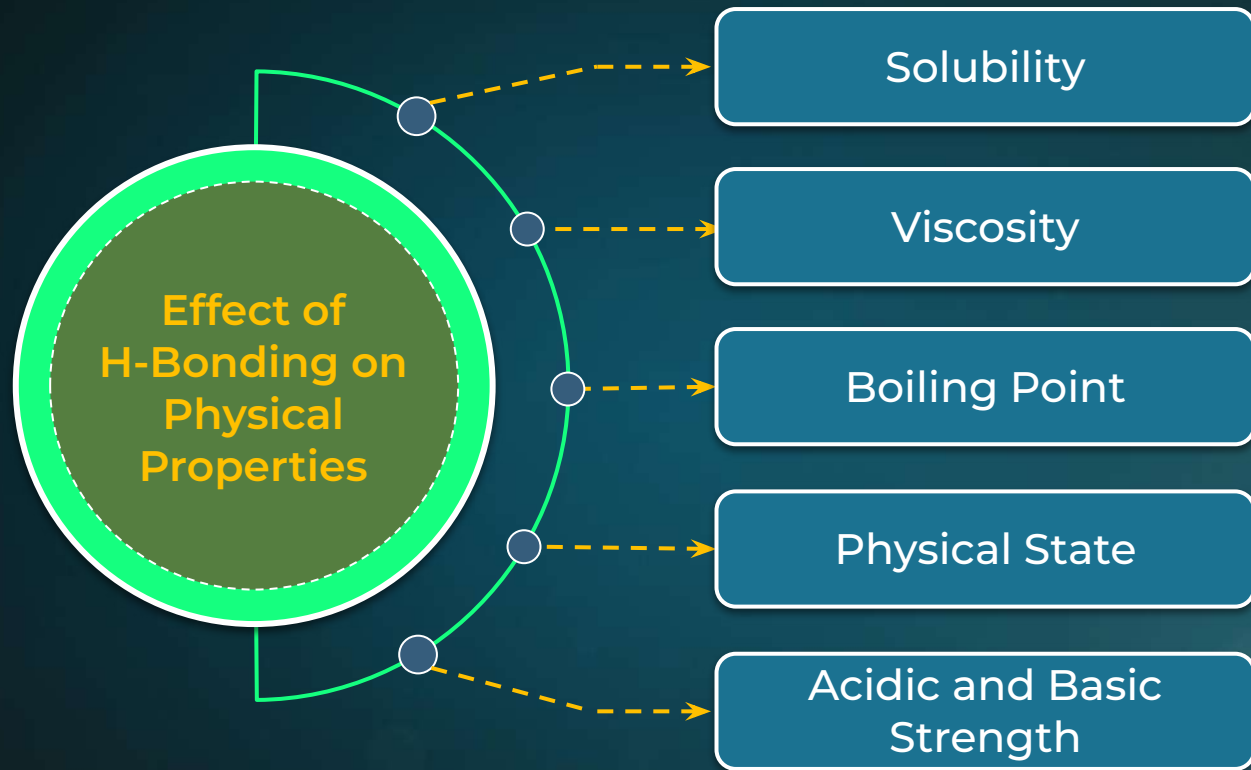
Gaseous state

<

Liquid state

<

Solid state



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



>



>



>



>



>



>



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>



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Why does Ice Floats over Water?

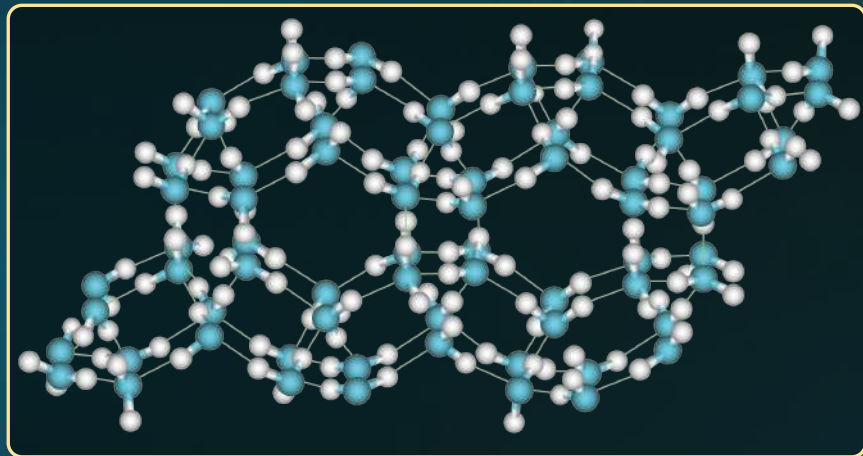
Extensive **network of H bonds**



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)

>

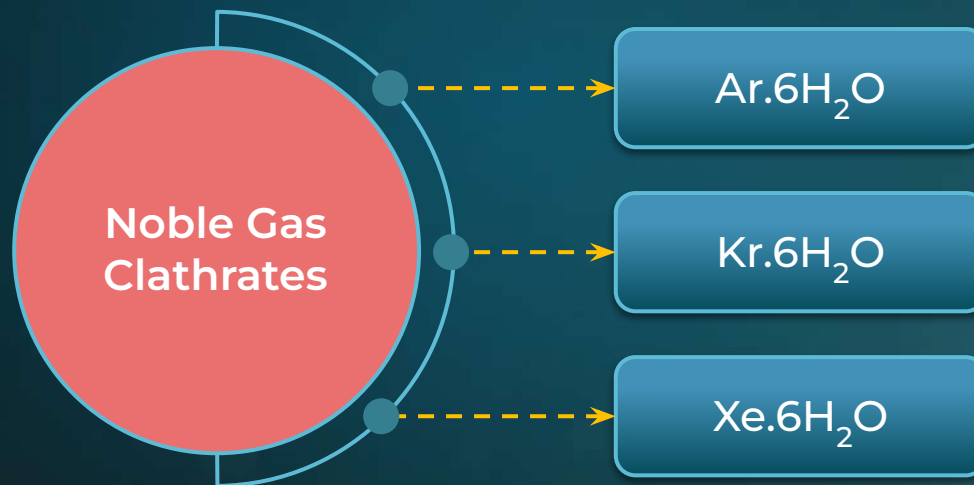
H_2O (l)

Clathrates

Species formed by
entrapment of

appropriately sized
gas molecules
(e.g.: Xe, Kr etc.)

into the **voids**
of ice



Clathrates

