b) Na^+ > Cu^+
2.8 2.8.18
Inert gas configuration Pseudolnert gas configuration
Higher lattice energy also favours ionic bond formation

LATTICE ENERGY:- (v)

The amount of energy released when the oppositely charged gaseous ions combine to form one mole of solid ionic crystal (or)

The amount of energy absorbed to separate one mole of solid ionic crystal into oppositely charged gaseous ions is called lattice energy.

$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} + 184.2$ kcal

$\rightarrow NaCl_{(s)} + 782$ KJ/mole

$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)} - 782$ KJ/mole

- In a given ionic crystal, there are attractions between opposite charges and repulsions between electron clouds of cation and anion.
- Thus, lattice energy is the sum of potential energy due to attractions and potential energy due to repulsions.

$$PE_{att}n = -\frac{NAZ^+Z^-e^2}{r}$$

$$PE_{rep}n = +\frac{NBe^2}{r^n}$$

$$\text{Lattice energy (u)} = -\frac{NAZ^+Z^-e^2}{r} + \frac{NBe^2}{r^n}$$

Where N → Avogadro's number
A → Madelung's constant
Z^+ → Positive charge
Z^- → Negative charge
e → Charge of e^-
B → Repulsive co-efficient
n → Born exponent

- Lattice energy is inversely proportional to the sum of radii of cation and anion.

$$u \propto \frac{1}{r^+ + r^-}$$

u ∝ charge,

$$u \propto \frac{1}{\text{size}}$$

- Generally, the ion, (cation or anion) with **smaller size and more charge will have greater lattice energy.**

Born-Haber's cycle:

The basis for Born-Haber's cycle is Hess's law. It states that the heat energy change will remain constant whether a chemical reaction occurs in one step or several steps.

(s - s, s - p, p - p)	
5) It can be formed by pure valence orbitals or hybrid orbitals.	It is formed by only pure valence orbitals.
6) If s orbital is involved in overlapping, the bond formed is always sigma.	If p-orbital is involved in overlapping, it may be sigma or pi
7) The first formed bond between two atoms is always sigma bond. Sigma has Independent existence	It is formed only after the formation of sigma bond. It has no Independent existence
8) It determines the geometry of molecules	It has no role in determining geometry of molecules.
9) One of the two lobes is involved in over lapping	Both the lobes of p - orbital are involved in bond formation
10) Free rotation of orbitals is possible around sigma bond.	Free rotation of orbitals is restricted

All single bonds are sigma bonds

- In double bond, one σ and and one π bonds are present.
- In triple bond, one σ and 2 π bonds are present.

Eg : CH_4 4σ and 0 π
N_2 1σ and 2π
O_2 1σ and 1π

VSEPR Theory:

(Valence shell electron pair repulsion theory)

This was proposed by Gillespe and Nyholm

- It mainly deals with repulsions in between e^-_s and shapes of molecules.

Postulates:

The electron pairs present in valence shell of central atom will be situated around it so that repulsions are minimum.

- The electron pair shared between two atom is called localised (fixed) electron pair and the bond is called localised electron pair bond.

  Order of repulsions in between various Electron pairs:

  Lone pair - lone pair > lone pair - bond pair > bond pair - bond pair
- Lone pair is attracted by one nucleus where as bond pair by two nuclei.

∴ lone pair occupies more spaces and bond pair less space

- In case of bond pairs, triple bond causes more repulsion than double bond and double bond more than single bond
- The bond pair – bond pair repulsion is influenced by EN of central atom (BP – BP repulsion ∝ EN)
- If the central atom contains only bond pairs, the molecule will have regular geometry. If one or more lone pairs are present, it will have irregular geometry

  Thus, shape of molecule depends on extent of mutual repulsions between various electron pairs.

  Eg : $CH_4 \rightarrow$ 4 bond pairs and no lone pairs.

  ∴ Its shape is regular tetrahedral

  In ammonia, there are three bond pairs and one lone pair.

(i) The molecule is stable if N_b is grater than N_a

(ii) The molecule is unstable if N_b is less than N_a.

Note : $KK = \sigma 1s^2 . \sigma^* 1s^2$

Electronic configuration /Bond order of simple diatomic molecules

The electronic configuration and the bond order in case of simple diatomic molecules can be obtained by filling the molecular orbitals by applying Aufbau principle and Hunds rule etc.

- **BOND ORDER:** The relative stability of a molecule can be determined on the basis of bond order. It is defined as the number of covalent bonds in a molecule. It is equal to **one half of the difference between the number of electrons in the bonding and antibonding molecular orbitals.**

Bond order = $\frac{1}{2}$ [Number of bonding electrons - Number of antibonding electrons]

or $= \frac{N_b - N_a}{2}$

The bond orders of 1,2 or 3 correspond to single, double or triple bond. But bond order may be fractional in some cases.

The magnetic properties of molecules can also be ascertained

- **Bonding in some diatomic molecules and ions**
- **Hydrogen molecule -**

Total number of electrons = 2, filling in molecular orbitals we have $\sigma_{1s}^2 < \sigma_{1s}^{*0}$

Bond order = $\frac{(N_b - N_a)}{2} = \frac{2-0}{2} = 1$

Hence there is a single bond between two hydrogen atoms and due to absence of unpaired electrons it is **diamagnetic**

- **Helium molecule (He_2)**

The total number of electrons =4 and filling in molecular orbitals we have $\sigma_{1s}^2 < \sigma_{1s}^{*2}$

Bond order = $\frac{(N_b - N_a)}{2} = \frac{2-2}{2} = 0$

Hence He_2 molecule **can not exist**

- **Nitrogen molecule (N_2) -**

The total number of electrons =14 and filling in molecular orbitals we have

$$\sigma_{1s}^2 \ \sigma_{1s}^{*2} \ \sigma_{2s}^2 \ \sigma_{2s}^{*2} \left\{ \begin{matrix} \pi_{2Pz}^2 \\ \pi_{2Py}^2 \end{matrix} \right\} \sigma_{2Px}^2$$

Bond order = $\frac{(N_b - N_a)}{2} = \frac{10-4}{2} = 3$

It is **diamagnetic**

- **Oxygen molecule (O_2) -**

Total number of electrons =16 and electronic configuration is

$$\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2Px}^2 \left\{\begin{matrix}\pi_{2Pz}^2 \\ \pi_{2Py}^2\end{matrix}\right\}\left\{\begin{matrix}\pi_{2Pz}^{*1} \\ \pi_{2Py}^{*1}\end{matrix}\right\}\sigma_{2Px}^*$$

Bond order = $\frac{(N_b - N_a)}{2} = \frac{10-6}{2} = 2$

As shown by electronic configuration the O_2 molecule contains two unpaired electrons, hence it is **paramagnetic** in nature

- **O_2^+ ion -**

  Total number of electrons (16 - 1) = 15,

  Electronic configuration $\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2Px}^2 \left\{\begin{matrix}\pi_{2Pz}^2 \\ \pi_{2Py}^2\end{matrix}\right\}\left\{\begin{matrix}\pi_{2Pz}^{*1} \\ \pi_{2Py}^{*}\end{matrix}\right\}\sigma_{2Px}^*$

Bond order= $\frac{10-5}{2} = 2.5$

It is paramagnetic

- **O_2^- (Super oxide ion):**

  Total number of electrons (16 +1) = 17. Electronic fonguration

$$\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2Px}^2 \left\{\begin{matrix}\pi_{2Pz}^2 \\ \pi_{2Py}^2\end{matrix}\right\}\left\{\begin{matrix}\pi_{2Pz}^{*2} \\ \pi_{2Py}^{*1}\end{matrix}\right\}\sigma_{2Px}^*$$

  Bond order = $\frac{(Nb - Na)}{2} = \frac{10-7}{2} = 1.5$

  It is **paramagnetic**

- **Peroxide ion (O_2^{2-})** - Total number of electrons (16 + 2) =18. The electronic configuration is $\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2Px}^2 \left\{\begin{matrix}\pi_{2Pz}^2 \\ \pi_{2Py}^2\end{matrix}\right\}\left\{\begin{matrix}\pi_{2Pz}^{*2} \\ \pi_{2Py}^{*2}\end{matrix}\right\}\sigma_{2Px}^*$

  Bond order = $\frac{10-8}{2} = 1$

  It is **diamagnetic**

- $[B_2]$ *no of electrons* $= 10$

  The electronic configuration is $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p^1{}_y = \pi 2p^1{}_z$

  it has 2 paired electrons . Hence **paramagnetic**

- **FORMAL CHARGE.**

Formal charge is a factor based on a pure covalent bond formed by the sharing of electron pairs equally by neighbouring atoms . Formal charge may be regarded as the charge that an atom in a molecule would have if all the atoms had the same electronegativity. It may or may not approximate the real ionic charge. In case of a polyatomic ions, the net charge is possessed the real ion as a whole and not by an particular atom. It is, however, feasible to assign a formal charge on an atom in a polyatomic molecule or ion.

Where $Q_f = [N_A - N_M] = [N_A - N_{LP} - 1/2N_{BP}]$

N_A= number of electrons in the valence shell in the free atom

N_M= number of electrons belonging to the atom in the molecule