

# Bonds in Solids

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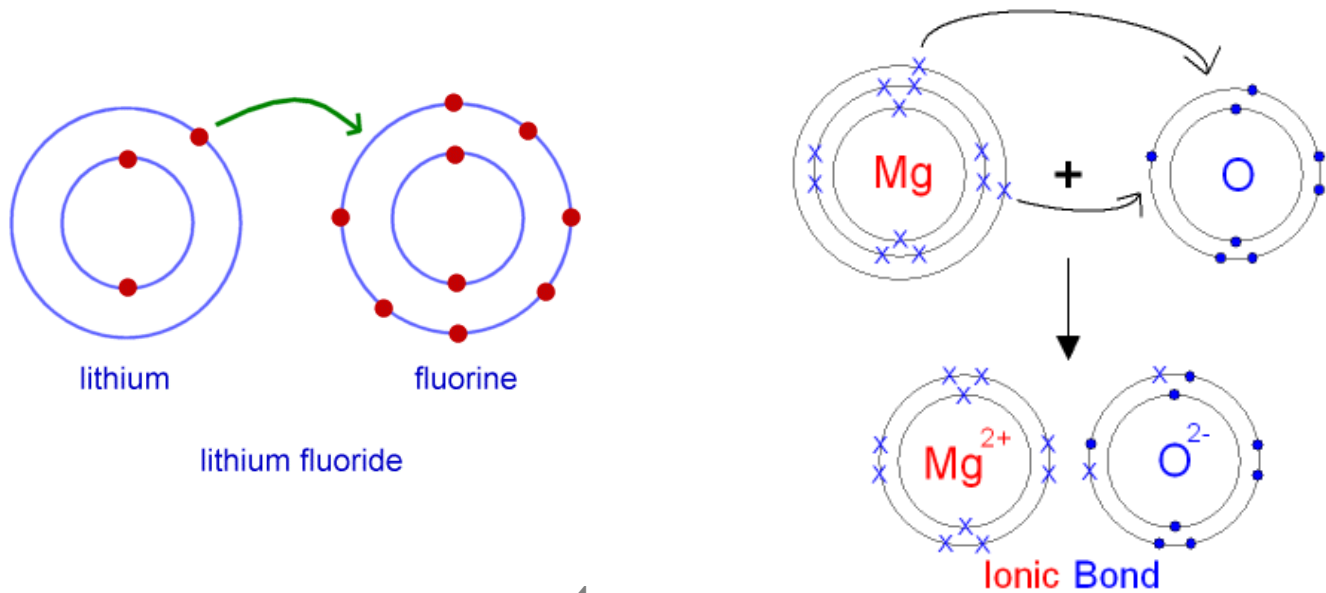
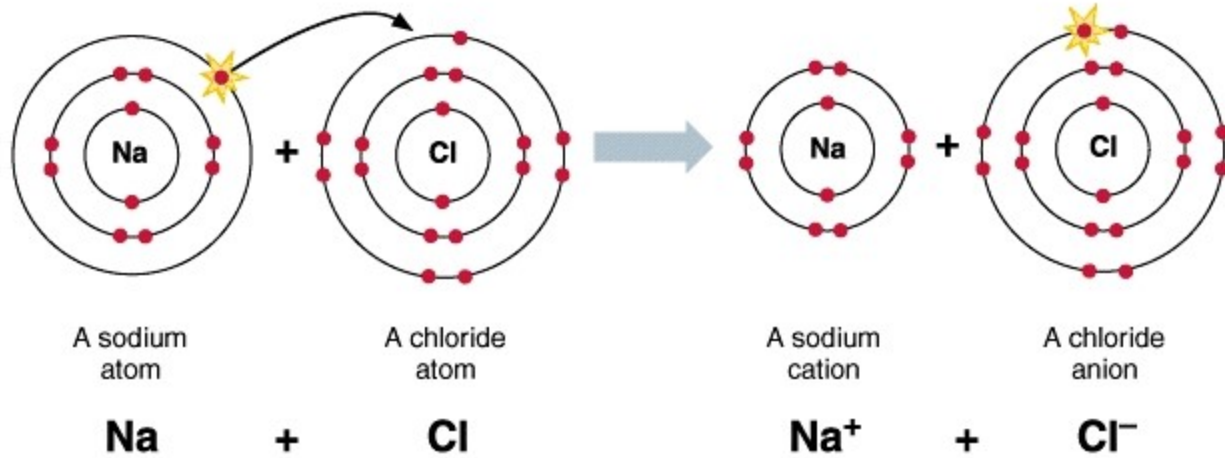
# Formation of Bond

- Solid is formed and remain stable in structure due to the existence of attractive interatomic force which hold them together. The force is known to be the **Cohesive force**.
- Cohesion in solid actually occurs due to the attractive electrostatic force between +ve and -ve charges. Usually magnetic and gravitational forces have negligible contribution to cohesion.
- **Cohesive energy= Free atom energy - crystal energy**
- A crystal is only stable if the total energy of it is lower than that of the free atom and molecules.

# Types of Bonds in Solid

Primary Bonds	Secondary Bonds
<ul style="list-style-type: none"><li>• Electrons are either transferred or shared</li><li>• Primary bonding forces are short range and strong forces.</li><li>• Relatively strong; Energy range: 100-1000 kJ/mole or 1 -10 ev/atom</li><li>• Types of primary bonds-<ol style="list-style-type: none"><li>1. Ionic bonds</li><li>2. Covalent bonds</li><li>3. Metallic bonds</li></ol></li></ul>	<ul style="list-style-type: none"><li>• No electron is shared or transferred. Formed due to dipolar interactions of molecules or atoms</li><li>• Secondary bonding forces are long range and weak forces.</li><li>• Relatively weak (&lt;100 kJ/mole or 1 ev/atom)</li><li>• Types of secondary bonds-<ol style="list-style-type: none"><li>1. Molecular bonds</li><li>2. Hydrogen bonds</li></ol></li></ul>

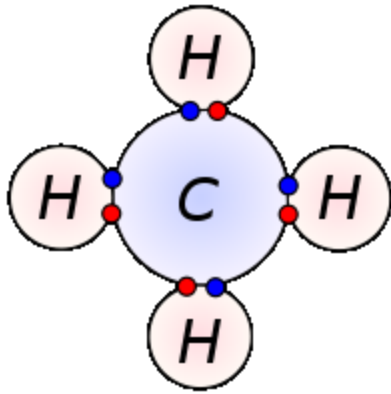
# Ionic Bonds



## Properties of Ionic Solids

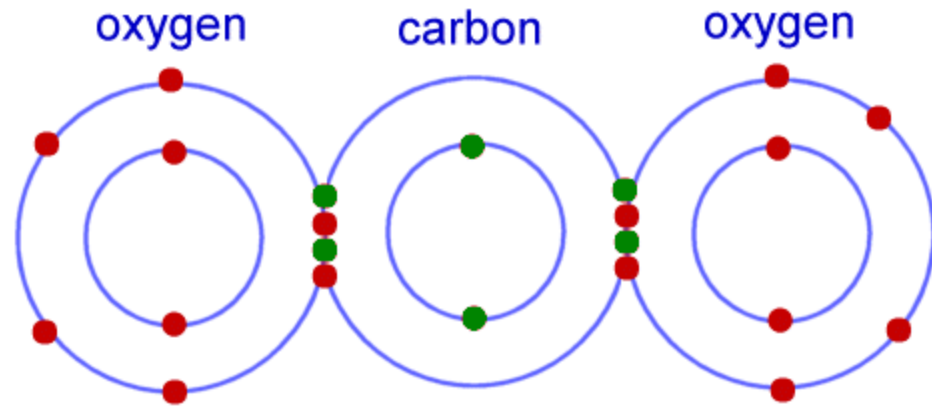
- Formed between Group I and VII elements.
- Systematic arrangements of +ve and -ve charges.
- Strong electrostatic attraction.
- Brittle and hard.
- Soluble in water and other polar liquids.
- Poor conductor of heat and electricity.
- Conducts electricity in solution form.
- High melting point because of high cohesive energy.
- High latent heat of fusion.

# Covalent Bonds

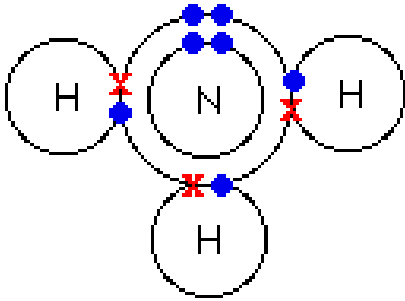


● Electron from hydrogen  
● Electron from carbon

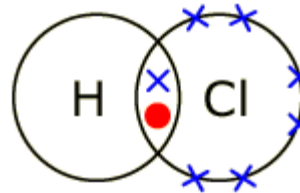
Methane



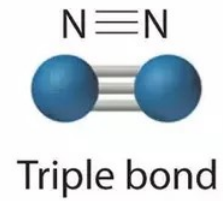
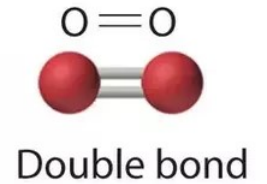
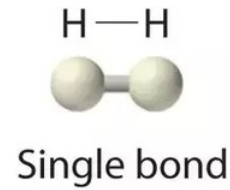
carbon dioxide



ammonia



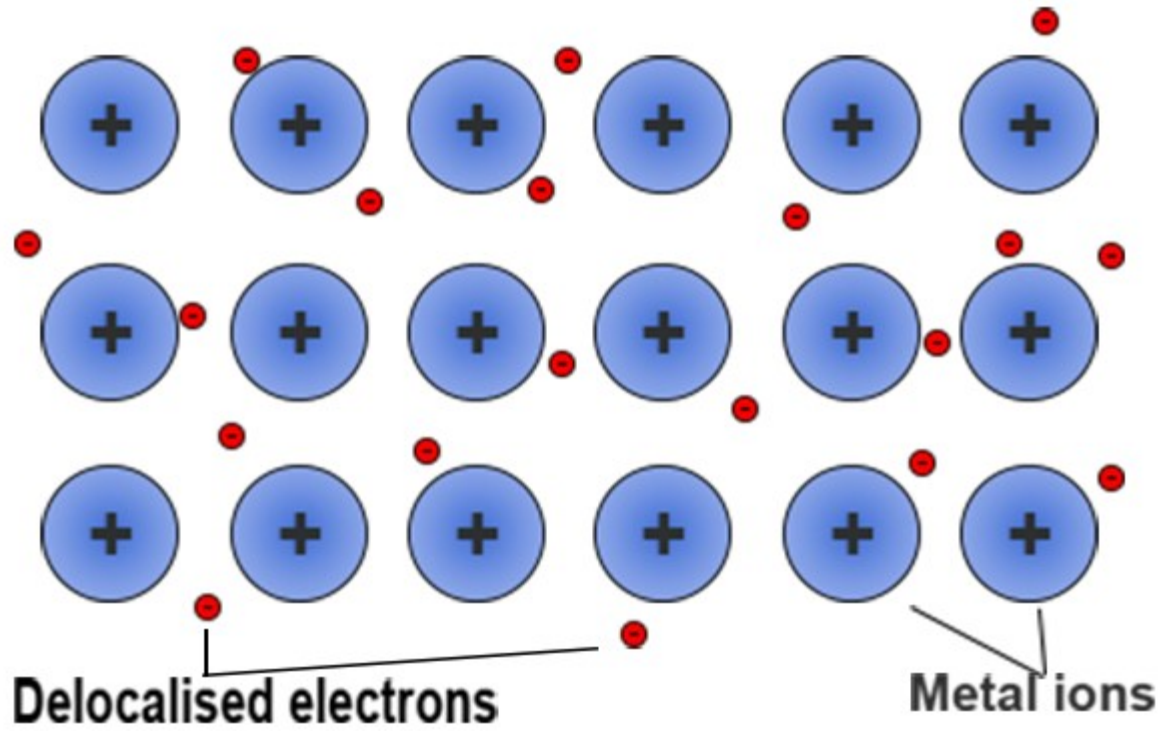
Hydrogen chloride



## Properties of Covalent Solids

- Forms between nonmetals or similar type of elements.
- Covalent bonds are highly directional in nature, that is why does not allow closely packed structure.
- They may be polar or non-polar in nature depending on the fact whether the electron pair is shared unequally or equally.
- Covalent crystals are very hard and cannot be deformed very easily.
- Usually soluble in non- polar liquids.
- Poor conductor of heat and electricity.
- High melting point and latent heat of fusion.

# Metallic Bonds

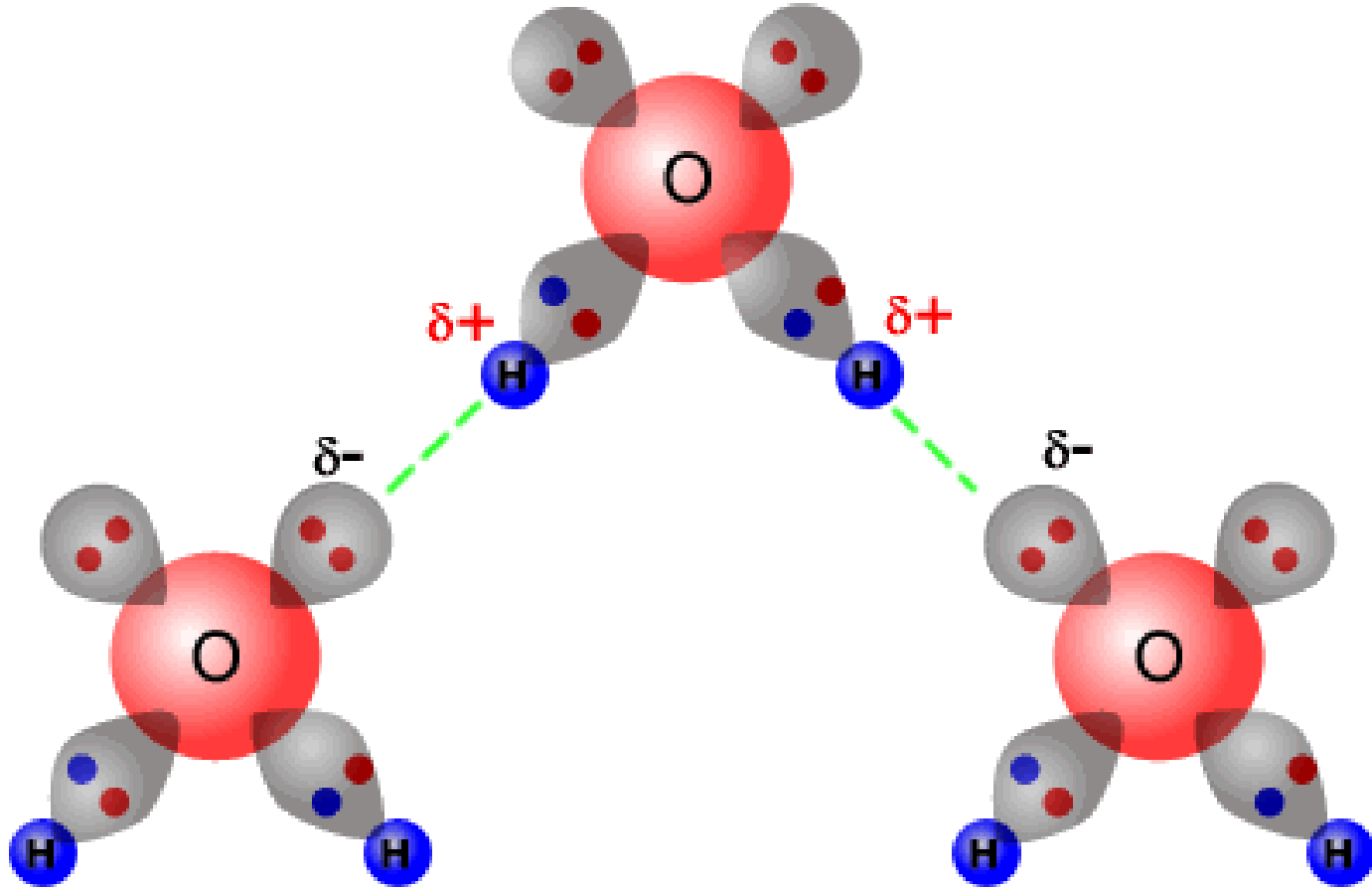




# Properties of Metals

- Metal is held together due to electrostatic attraction between +ve ions and electrons.
- Metallic bond is an unsaturated bond because it is formed neither due to well defined electron sharing nor electron transfer.
- This bond is weaker than other two saturated bonds - ionic and covalent.
- Metals are ductile and malleable.
- Good conductor of heat and electricity.
- Moderate to high melting point.
- Opaque to light, show photoelectric effect.

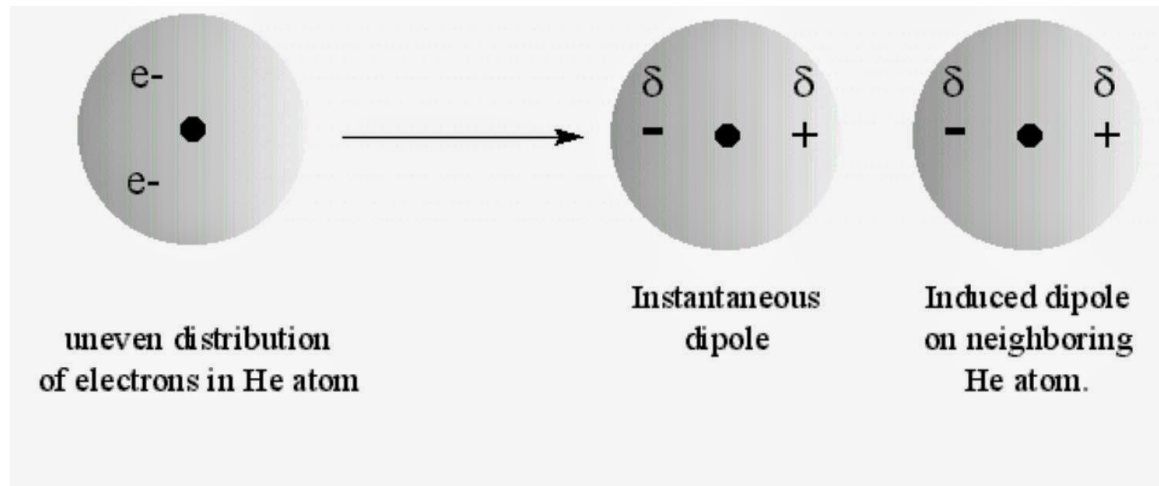
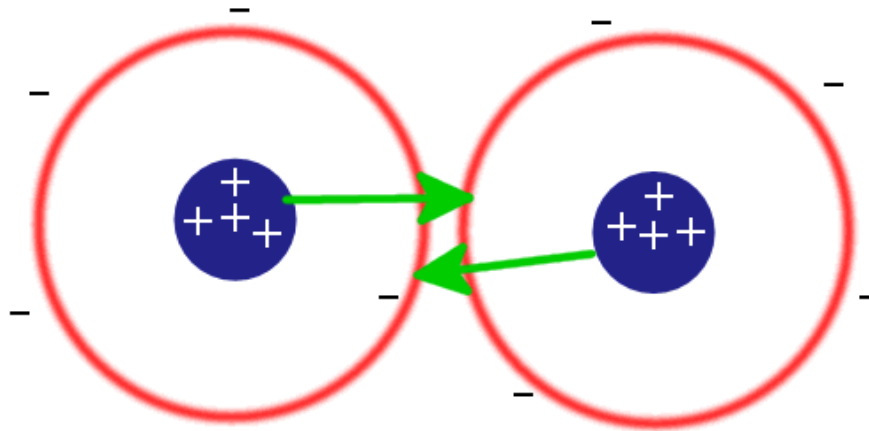
# Hydrogen Bonds



## Properties of Hydrogen Bonded Solids

- Hydrogen bond is weaker than primary bonds but stronger than molecular bond, it is largely ionic in character.
- It is directional in nature.
- Electrostatic interaction between electric dipole moments acts as the bonding forces.
- Hydrogen bonded solids have low melting point.
- Since there are no valance electrons available in the solids, they are good insulators of electricity.
- They are soluble in both polar and non-polar solvents.

# Molecular or Van der Waals Bonds



## Properties of Van der Waals Bonded Solids

- Van der Waals bond is weaker than Hydrogen bond.
  - It is non-directional in nature, soft type of material and may be crystalline and non-crystalline.
  - Van der Waals bonded solids have low melting point, they are volatile in nature and usually transparent to light.
  - Since there are no valence electrons available in the solids, they are good insulators of electricity.
  - They are soluble in both polar and non-polar solvents.
- ❑ Van der Waals force is weak but it exists everywhere.
  - ❑ It is responsible for the condensation of gases into liquid and freezing of liquid into solids in absence of any primary bonding force.
  - ❑ Van der Waals attraction between 2 molecules  $r$  distance apart is proportional to  $r^{-7}$ , when the molecules are very close.

## The characteristics of the attractive force between a polar and non-polar molecule:

The electric field  $\vec{E}$  a distance  $r$  from a dipole of moment  $\vec{p}$  is given by

Dipole electric field 
$$\vec{E} = \frac{1}{4\pi\epsilon_0} \left[ \frac{\vec{p}}{r^3} - \frac{3(\vec{p} \cdot \vec{r})}{r^5} \vec{r} \right]$$

From vector analysis,  $\vec{p} \cdot \vec{r} = pr\cos\theta$ ; where,  $\theta$  = the angle between  $\vec{p}$  and  $\vec{r}$ .

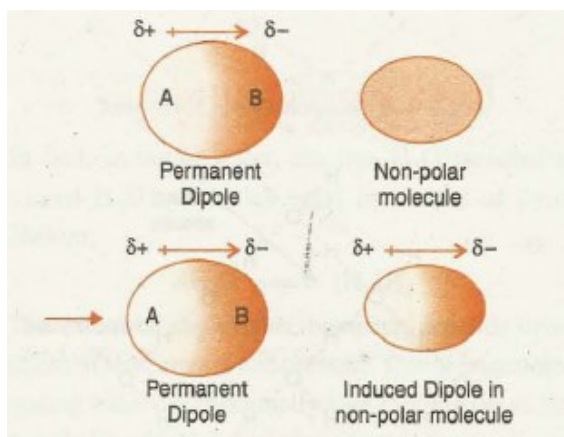
The field  $\vec{E}$  induces in the other non-polar molecule an electric dipole moment  $\vec{p}' \propto \vec{E}$ . Hence,  $\vec{p}' = \alpha\vec{E}$ ,  $\alpha$  = polarizability of the molecule.

The energy of the induced dipole in the electric field  $\vec{E}$  is

$$U = -\vec{p}' \cdot \vec{E} = -\alpha\vec{E} \cdot \vec{E} = -\frac{\alpha}{(4\pi\epsilon_0)^2} \left[ \frac{p^2}{r^6} - \frac{3p^2}{r^6} \cos^2\theta - \frac{3p^2}{r^6} \cos^2\theta + \frac{9p^2}{r^6} \cos^2\theta \right]$$

Interaction energy, 
$$U = -\frac{\alpha}{(4\pi\epsilon_0)^2} [1 + 3\cos^2\theta] \frac{p^2}{r^6} \propto \frac{1}{r^6}$$

Force = 
$$-\frac{dU}{dr} \propto \frac{1}{r^7}$$



## The bond energy and Madelung constant for NaCl Crystal

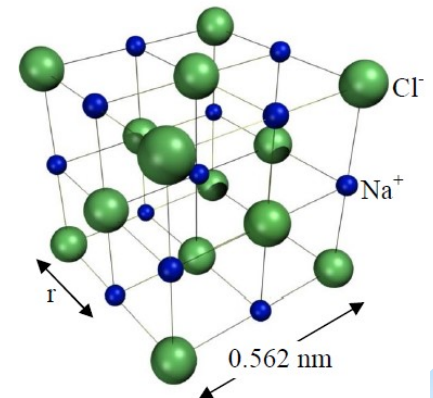
The cohesive energy is the work needed to remove an atom (or molecule) from the crystal and so indicates the strength of the bond holding it in place. Part of the cohesive energy is the electrical potential energy  $U_{\text{Coulomb}}$  of ions.

Let us consider an  $\text{Na}^+$  ion in crystal NaCl in which  $\text{Na}^+$  has six nearest neighbours  $\text{Cl}^-$  ions, each one are in  $r$  distance away. The potential energy of the  $\text{Na}^+$  ion due to this six  $\text{Cl}^-$  ion is therefore

$$U_1 = -\frac{6e^2}{4\pi\epsilon_0 r} \dots \dots \dots (1)$$

The next nearest neighbors are twelve  $\text{Na}^+$  ions, each on the distance  $\sqrt{2}r$  away.

$$U_2 = \frac{12e^2}{4\pi\epsilon_0 \sqrt{2}r} \dots \dots \dots (2)$$



When the summation is continued over all the positive and negative ions in a crystal of infinite size, the result is

$$U_{\text{Coulomb}} = -\frac{e^2}{4\pi\epsilon_0 r} \left( 6 - \frac{12}{\sqrt{2}} + \dots \right) \dots \dots \dots (3)$$

In general,

$$U_{\text{Coulomb}} = -\frac{\alpha e^2}{4\pi\epsilon_0 r} \dots \dots \dots (4)$$

Here the quantity  $\alpha$  is called the Madelung constant of the crystal, and it has the same value for the same structures.

Now the potential energy contribution of the exclusion principle has approximate form

$$U_{\text{Repulsive}} = \frac{B}{r^n} \dots \dots \dots (5)$$

The sign of  $U_{\text{repulsive}}$  is +ve, which corresponds to repulsion. The dependence on  $r^{-n}$  implies a short range force that increases as the interatomic distance  $r$  decreases.



The total potential energy of each ion due to its interactions with all the other ions is therefore,

$$U_{\text{Total}} = U_{\text{Coulomb}} + U_{\text{Repulsive}} = -\frac{\alpha e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n} \dots \dots \dots (6)$$

At equilibrium separation,  $r = r_0$ , of the ions,  $U$  is a minimum by definition, and so  $\frac{dU}{dr} = 0$ .

$$\left(\frac{dU}{dr}\right)_{r=r_0} = \frac{\alpha e^2}{4\pi\epsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}} = 0$$

$$B = \frac{\alpha e^2}{4\pi\epsilon_0 n} r_0^{n-1} \dots \dots \dots (7)$$

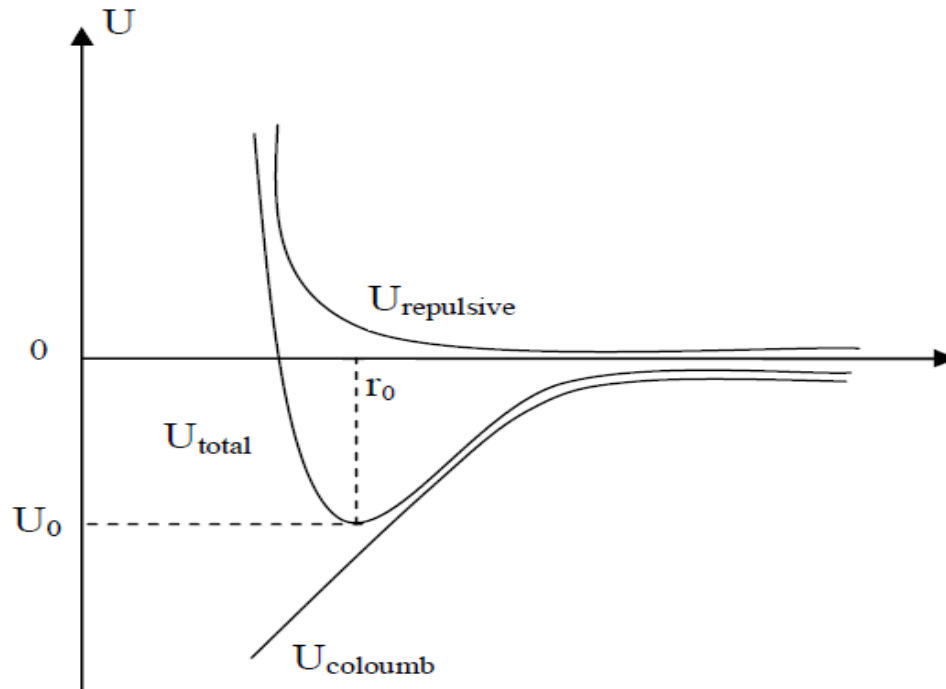
The total potential energy at the equilibrium separation is therefore,

$$U_0 = -\frac{\alpha e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right) \dots \dots \dots (8)$$

We must add this amount of **energy per ion pair** to separate an ionic crystal into individual ions.

The exponent  $n$  can be found from the observed compressibilities of ionic crystals. The average result is  $n \approx 9$ . which means that the repulsive force varies sharply with  $r$ .

Figure shows the variation of potential energy in an ionic crystal with ionic separation. The minimum value of  $U_{\text{total}}$  is  $U_0$  occurs at an equilibrium separation of  $r_0$ . Thus



Cohesive energy = Atom separation energy  
= Ion separation energy + Electron transfer energy

Na (atom) + 5.14 eV (ionization energy) → Na<sup>+</sup> + e<sup>-</sup>

Cl (atom) + e<sup>-</sup> → Cl<sup>-</sup> + 3.61 eV (electron affinity)

The electron transfer energy, E<sub>e- transfer</sub> = (5.14-3.61) eV = 1.53 eV

$$E_{\text{Cohesive}} = \frac{1}{2} \left[ -\frac{\alpha e^2}{4\pi\epsilon_0 r_0} \left( 1 - \frac{1}{n} \right) + E_{\text{e- transfer}} \right] \dots \dots \dots (9)$$

For separation of Na<sup>+</sup> or Cl<sup>-</sup>

The cohesive energy for NaCl molecule

$$E_{\text{Cohesive}} = \left[ -\frac{\alpha e^2}{4\pi\epsilon_0 r_0} \left( 1 - \frac{1}{n} \right) + E_{\text{e- transfer}} \right] \dots \dots \dots (10)$$