

Crystal Bonding

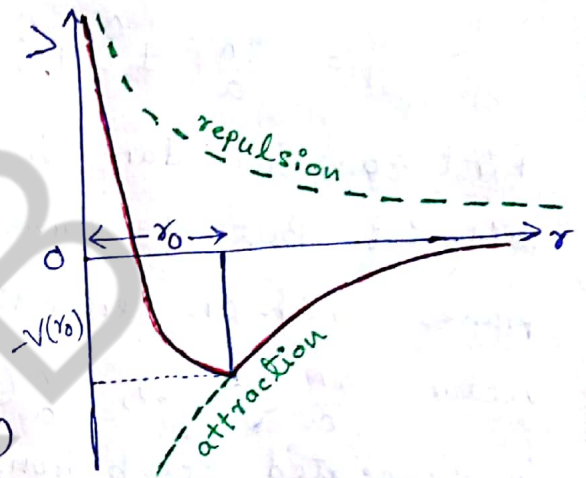
The ability to hold the atoms/ions together is called bonding. Atoms vibrate in lattice & nucleus due to heavy mass is almost at rest. So electrostatic interaction happens between electron cloud & distribution of electron leads to 5 types of bonding due to (a) "attractive force" of negatively charged electron cloud of one atom with positive nuclear charge of other atom (b) "repulsive force" of overlapping negatively charged electron clouds & positively charged nucleus of two atoms.

"spring effect" \rightarrow attraction \rightarrow repulsion.

$$F = - \frac{dV}{dr}$$

attractive force = negative potential.

repulsive force = positive potential.



cohesive/binding energy $V(r_0)$ (negative)
dissociation energy $-V(r_0)$ (positive)

Cohesive energy of a solid is the energy that will be given out in forming a crystal by bringing neutral atoms from ∞ to equilibrium separation r_0 .

Suppose $V_{\text{attractive}} \propto r^{-m}$ & $V_{\text{repulsive}} \propto r^{-n}$

$$\therefore \text{Cohesive energy } V = V_{\text{attractive}} + V_{\text{repulsive}} = -A r^{-m} + B r^{-n}$$

$$\& \text{ force } F = - \frac{dV}{dr} = m A r^{-(m+1)} - n B r^{-(n+1)}$$

$$\text{at } r=r_0, F=0 = m A r_0^{-(m+1)} - n B r_0^{-(n+1)}$$

$$\text{or } r_0^{m-n} = \frac{A}{B} \frac{m}{n}$$

$$\begin{aligned} \text{Then equilibrium potential energy } V(r_0) &= -A r_0^{-m} + B r_0^{-n} \\ &= -A r_0^{-m} \left(1 - \frac{B}{A} r_0^{m-n} \right) = -A r_0^{-m} \left(1 - \frac{m}{n} \right) \end{aligned}$$

For V to be minimum, it must be concave upwards curvature,
 $\left. \frac{d^2V}{dr^2} \right|_{r=r_0} > 0$ or $\left[-m(m+1)A r^{-(m+2)} + n(n+1)B r^{-(n+2)} \right]_{r=r_0} > 0$

$$\text{or } -m(m+1) + n(n+1) \frac{B}{A} r_0^{m-n} > 0$$

$$\text{or } -m(m+1) + n(n+1) \frac{m}{n} \frac{B}{A} > 0$$

$$\text{or } n-m > 0 \quad \text{or } n > m. \quad \text{Thus to form a chemical bond, we always need repulsive force be of shorter range than attractive force.}$$

Types of bonding 5 types of bonding exist

(a) Ionic bond (transfer of valence electron): NaCl, LiF.

(b) Covalent bond (sharing of valence electrons): Diamond, SiC.

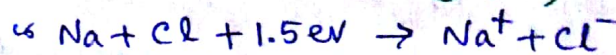
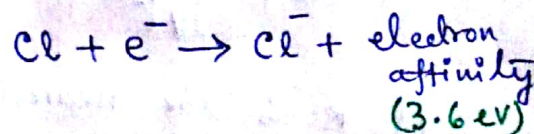
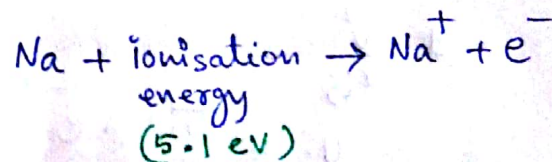
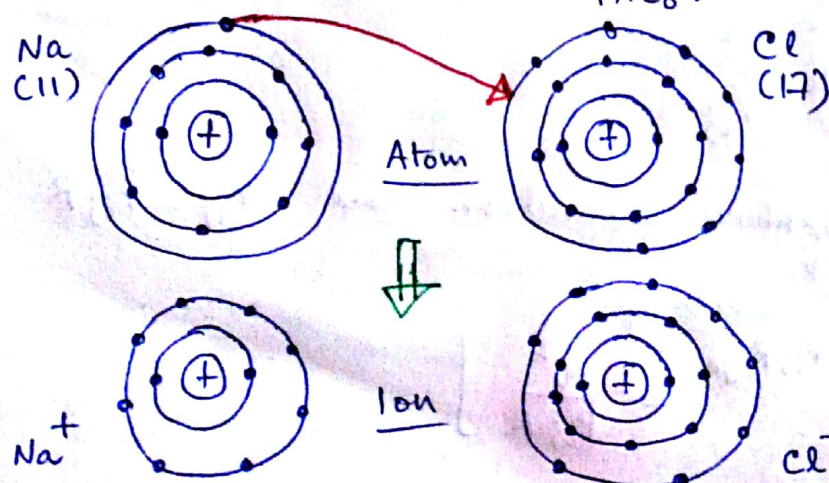
(c) Metallic bond (free nature of valence electron): Cu, Ag, Fe

(d) Hydrogen bond ($V \propto r^{-2}$): Ice

(e) van der Waal's bonding (dipole-dipole interaction)

Ionic / Electrovalent Bonding

Transfer of electrons from an electropositive element to electronegative element, to create $+ -$ ion. Electronegative element of large electron affinity accommodate extra added electron to complete outermost valence orbit to stabilize. Oppositely charged ions attract $V_{\text{attraction}} = -\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r}$



$$Z_1 = Z_2 = 1.$$

So potential energy $V = -\frac{e^2}{4\pi\epsilon_0 r_0} = -\frac{(1.6 \times 10^{-19})^2}{4\pi \times 8.85 \times 10^{-12} \times 2.4 \times 10^{-10}}$
 $(r_0 = 2.4 \text{ \AA})$
 $= -\frac{9.6 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = -6 \text{ eV}.$

So net energy released $= 5.1 - 3.6 - 6 = -4.5 \text{ eV}.$

Cohesive energy

Binding energy calculated by Born & Madelung in 1910 extended by Mayer.

assumptions : (a) Ionic crystals are formed by positive & negative ions with spherical charge distribution. (b) Force of attraction depends on inter-ionic distance & isotropic (orientation independent), (c) Electrostatic interaction (Madelung energy $V_a = -\frac{\alpha q^2}{4\pi\epsilon_0 r}$, α = Madelung constant) contributes to cohesive energy

According to Born-Madelung theory interaction energy U_i on ion i due to all j other ions, $U_i = \sum_{j \neq i} U_{ij}$

U_i consists of two parts:

1. Short range central field repulsive potential βr_{ij}^{-n} between $+$ & $-$ ions which was modified by $\lambda e^{-r_{ij}/\rho}$, λ = strength, ρ = range of interaction (screened Coulomb)
2. Attractive or repulsive long ranged coulomb force with energy $\pm \frac{q^2}{r_{ij}}$

$$\therefore U_i = \sum_{j \neq i} \left[\lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}} \right]$$

If R is the nearest neighbour separation then $r_{ij} = p_{ij} R$ where p_{ij} is a dimensionless quantity.

$$\text{Then } U_i = \sum_{j \neq i} \left[\lambda e^{-p_{ij} R/\rho} \pm \frac{q^2}{p_{ij} R} \right]$$

$$= Z\lambda e^{-R/\rho} \pm \sum_{j \neq i} \frac{q^2}{p_{ij} R} = Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}$$

where Z is number of nearest neighbour of i^{th} ion & $\alpha = \pm \sum \frac{1}{p_{ij}}$ is called Madelung constant

If the crystal contain $2N$ ions or N molecules, then

$$U_{\text{total}} = N U_i = N \left[Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R} \right]$$

at equilibrium distance $R = R_0$, $\frac{dU_{\text{total}}}{dR} = 0$

$$\therefore -\frac{Z\lambda}{\rho} e^{-R_0/\rho} + \frac{\alpha q^2}{R_0^2} = 0$$

$$\text{or } e^{-R_0/\rho} = \frac{\rho \alpha q^2}{Z\lambda R_0^2}$$

$$\therefore U_{\text{total}} = N \left[Z\lambda \frac{\rho \alpha q^2}{Z\lambda R_0^2} - \frac{\alpha q^2}{R_0} \right] = -\frac{N\alpha q^2}{R_0} \left(1 - \frac{\rho}{R_0} \right)$$

Madelung energy

contribution from short range repulsion

$$U_i = -\frac{\alpha q^2}{R_0} \left(1 - \frac{\rho}{R_0} \right)$$

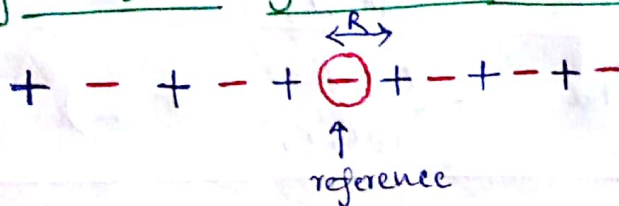
or in SI units,

$$U_i = -\frac{\alpha q^2}{4\pi\epsilon_0 R_0} \left(1 - \frac{\rho}{R_0} \right)$$

as $\frac{\rho}{R_0} \rightarrow 0$ repulsive interaction is very short range.

In $\alpha = \sum \pm \frac{1}{p_{ij}}$, $+$ is used for +ve ion & $-$ for -ve ion if i^{th} ion is -ve. & we consider repulsive interaction effective for nearest neighbours only.

Madelung constant for a 1D lattice



$$\alpha = \sum_{j \neq i} \pm \frac{1}{p_{ij}}, \quad \frac{\alpha}{R} = \sum_{j \neq i} \pm \frac{1}{p_{ij} R} = \pm \sum_{j \neq i} \frac{1}{r_{ij}}$$

$$\therefore \frac{\alpha}{R} = 2 \left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \dots \right]$$

$$\alpha = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]$$

↑ due to both side of reference ion

$$\text{but } \ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

$$\text{if } x=1, \ln 2 = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots$$

$$\therefore \alpha = 2 \ln 2 = 1.38$$

Madelung constant for NaCl crystal

Nearest neighbour to -ive (reference) ion = 6 +ive ions with

$P_{ij} = P = 1$. 12 -ive ions at $P = \sqrt{2}$. 8 +ive ions at $P = \sqrt{3}$.

6 -ive ions at $P = \sqrt{4}$ & so on

$$\alpha = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots = 1.748$$

Bigger α , more cohesive energy, greater stability of structure

Cohesive energy for repulsive core potential $\propto r^{-n}$

$$V_i = V_{\text{attractive}} + V_{\text{repulsive}} = -\frac{\alpha q^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$$

$$\text{at } r=r_0, V \text{ is minimum, } \left. \frac{dV}{dr} \right|_{r=r_0} = 0 = \frac{\alpha q^2}{4\pi\epsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}}$$

$$\propto B = \frac{\alpha q^2 r_0^{n-1}}{4\pi\epsilon_0 n}$$

$$\therefore V_i = -\frac{\alpha q^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n} \right)$$

$$\propto \text{for } 2N \text{ molecules, } V_{\text{tot}} = -\frac{N\alpha q^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n} \right)$$

for NaCl, $\alpha = 2 \ln 2$,

$$V_{\text{tot}} = -\frac{2Nq^2 \ln 2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n} \right)$$

Bulk modulus of ionic crystals

Volume strain = $\frac{dV}{V}$, change in pressure dp , Bulk modulus

$$B = - \left. \frac{dp}{dV/V} \right|_{R=R_0} \text{, Using 1}^{\text{st}} \text{ law of thermodynamics, } dG = dU + p dV$$

$$\therefore \frac{dU}{dV} = -p \quad (dG=0) \quad \text{or} \quad \frac{d^2U}{dV^2} = - \frac{dp}{dV}$$

$$\therefore B = V \left. \frac{d^2U}{dV^2} \right|_{R=R_0}$$

Volume occupied by $\frac{1}{2}$ molecule $\rightarrow R_0^3$

volume occupied by 1 molecule $\rightarrow 2R_0^3$

volume occupied by N molecule $\rightarrow 2NR_0^3$
($2N$ ions)

volume of unit cell $\rightarrow (2R_0)^3 = 8R_0^3$ because $a = 2R_0$

$$V = 2NR^3, \quad \frac{dV}{dR} = 6NR^2 \quad \text{and} \quad \left. \frac{dU}{dR} \right|_{R=R_0} = 0$$

$$\therefore \frac{d^2U}{dV^2} = \frac{d}{dV} \left(\frac{dU}{dV} \right) = \frac{d}{dV} \left(\frac{dU}{dR} \cdot \frac{dR}{dV} \right) = \frac{d}{dV} \left(\frac{dU}{dR} \right) \cdot \frac{dR}{dV} + \frac{dU}{dR} \cdot \frac{d^2R}{dV^2}$$

$$= \frac{d}{dR} \left(\frac{dU}{dR} \right) \frac{dR}{dV} \cdot \frac{dR}{dV} + \frac{dU}{dR} \cdot \frac{d^2R}{dV^2} = \frac{d^2U}{dR^2} \cdot \left(\frac{dR}{dV} \right)^2 + \frac{dU}{dR} \cdot \frac{d^2R}{dV^2}$$

$$\therefore \left. \frac{d^2U}{dV^2} \right|_{R=R_0} = \frac{d^2U}{dR^2} \cdot \left(\frac{dR}{dV} \right)^2 = \frac{1}{(6NR_0^2)^2} \left. \frac{d^2U}{dR^2} \right|_{R=R_0}$$

$$\therefore B = V \left. \frac{d^2U}{dV^2} \right|_{R=R_0} = 2NR_0^3 \cdot \frac{1}{36N^2R_0^4} \left. \frac{d^2U}{dR^2} \right|_{R=R_0} = \frac{1}{18NR_0} \left. \frac{d^2U}{dR^2} \right|_{R=R_0}$$

We learned that $U_{\text{total}} = N \left[ZA e^{-R/\rho} - \frac{\alpha q^2}{R} \right]$

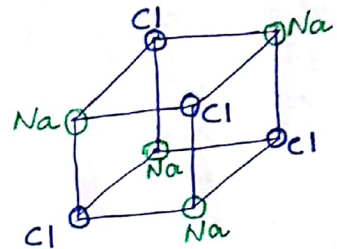
$$\therefore \frac{dU_{\text{total}}}{dR} = - \frac{NZA}{\rho} e^{-R/\rho} + \frac{N\alpha q^2}{R^2}$$

$$\frac{d^2U_{\text{total}}}{dR^2} = \frac{NZA}{\rho^2} e^{-R/\rho} - \frac{2N\alpha q^2}{R^3}, \quad \text{also } e^{-R_0/\rho} = \frac{\rho \alpha q^2}{ZAR_0^2}$$

$$\therefore B = \frac{1}{18NR_0} \left[\frac{NZA}{\rho^2} e^{-R_0/\rho} - \frac{2N\alpha q^2}{R_0^3} \right] = \frac{1}{18NR_0} \left[\frac{NZA}{\rho^2} \cdot \frac{\rho \alpha q^2}{ZAR_0^2} - \frac{2N\alpha q^2}{R_0^3} \right]$$

$$B = \frac{\alpha q^2}{18R_0^4} \left(\frac{R_0}{\rho} - 2 \right)$$

From B & R_0 , range of repulsive interaction can be calculated.



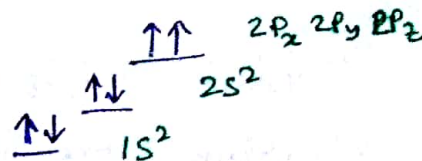
(equilibrium separation)

Covalent Bonding

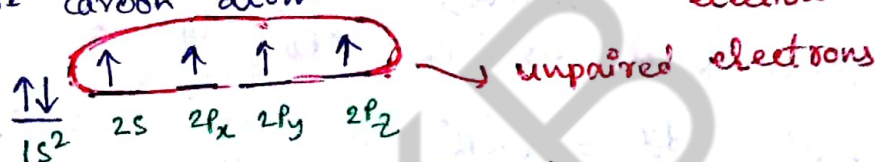
Equal sharing of electrons between neighbouring atom with incomplete outermost shell. Unlike isotropic bonds in ionic, these are directional, due to electron's restricted orbital motion.

Covalent bond can happen due to overlap of s-orbital with opposite spin paired electrons (like H_2) or hybrid bonding due to overlapping s & p orbitals.

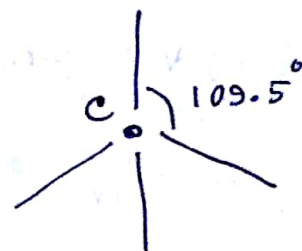
for single carbon atom $C_6 = 1s^2 2s^2 2p^2$



But when more carbon atom comes close

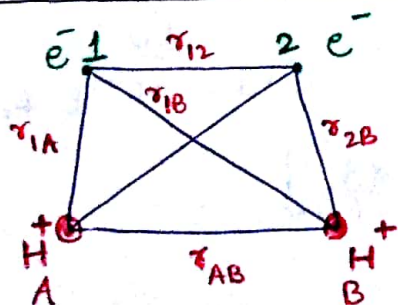


So 4-bonds can form with bond angle 109.5° in a regular tetrahedron using 4 unpaired electrons in 2s, 2p orbital.



(sp^3 hybridization) \Rightarrow Diamond, Si, Ge etc.

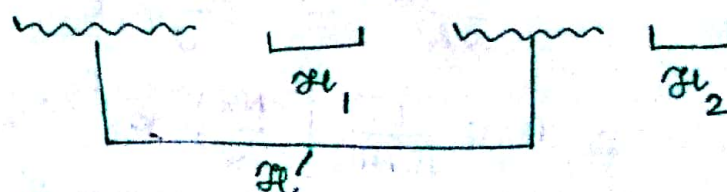
Heitler-London theory



A & B are H^+ nucleus (hydrogen atom) with two electrons 1 & 2 in $1s^1$ orbital. Ψ_{1A}, Ψ_{2B} are eigenfunction of A, B atoms.

Total Hamiltonian is
$$\mathcal{H} = \frac{e^2}{r_{AB}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}}$$

$\mathcal{H}_1, \mathcal{H}_2$ = potential energy of electron 1 & 2 (without overlap)



\mathcal{H}' = exchange potential (interaction)

When there is no spin-orbit coupling, A & B are far apart

$$\Psi(\vec{r}_1 \vec{s}_1; \vec{r}_2 \vec{s}_2) = \underbrace{\psi_{1A} \psi_{2B}}_{\text{space}} \underbrace{\phi_{1A} \phi_{2B}}_{\text{spin}} \quad \text{with Pauli exclusion principle}$$

principle $\Psi(\vec{r}_1 \vec{s}_1; \vec{r}_2 \vec{s}_2) = -\Psi(\vec{r}_2 \vec{s}_2; \vec{r}_1 \vec{s}_1)$.

We can write the Schrödinger equation for the two electron system

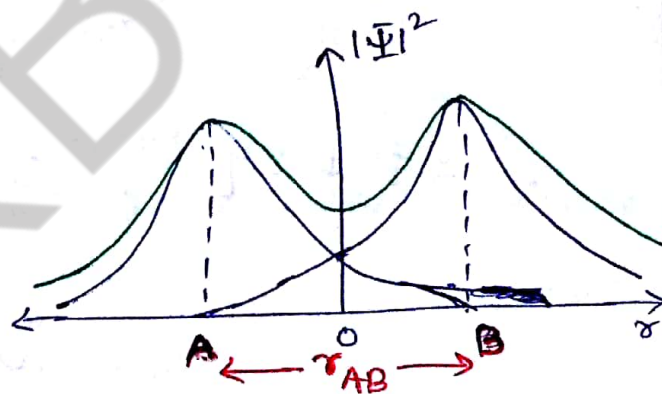
$$-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) \Psi + (\mathcal{H}_1 + \mathcal{H}_2) \Psi = E \Psi \quad (\text{no overlap})$$

$$\begin{aligned} \therefore \nabla_1^2 \psi_{1A} + \frac{2m}{\hbar^2} (E_1 - \mathcal{H}_1) \psi_{1A} &= 0 \\ \nabla_2^2 \psi_{2B} + \frac{2m}{\hbar^2} (E_2 - \mathcal{H}_2) \psi_{2B} &= 0 \end{aligned} \quad \left. \begin{array}{l} \text{H-atom solution in} \\ \text{radial part, spherical} \\ \text{polar \& azimuthal part} \end{array} \right\}$$

$$\psi_{1A} \sim \frac{1}{\sqrt{\pi} a_0^3} e^{-\frac{r_{1A}}{a_0}}, \quad \psi_{2B} \sim \frac{1}{\sqrt{\pi} a_0^3} e^{-\frac{r_{2B}}{a_0}}, \quad E_1 = E_2 = -\frac{e^2}{a_0}$$

[a_0 = Bohr orbit radius]

For 2-H atom $\Psi = \psi_{1A} \psi_{2B}$ is the wavefunction & $|\Psi|^2$ is probability of finding both electrons.



But they are indistinguishable, so

due to exchange degeneracy $\psi_{2A} \psi_{1B}$ is also a wavefunction.

Superpositions are also wavefunction Ψ_S (symmetric), Ψ_A (antisymmetric)

$$\Psi_S = \frac{1}{\sqrt{2+2S}} (\psi_{1A} \psi_{2B} + \psi_{2A} \psi_{1B}),$$

$$\Psi_A = \frac{1}{\sqrt{2-2S}} (\psi_{1A} \psi_{2B} - \psi_{2A} \psi_{1B})$$

$$S = \iint (\psi_{1A} \psi_{2B})^* (\psi_{2A} \psi_{1B}) d\tau_1 d\tau_2$$

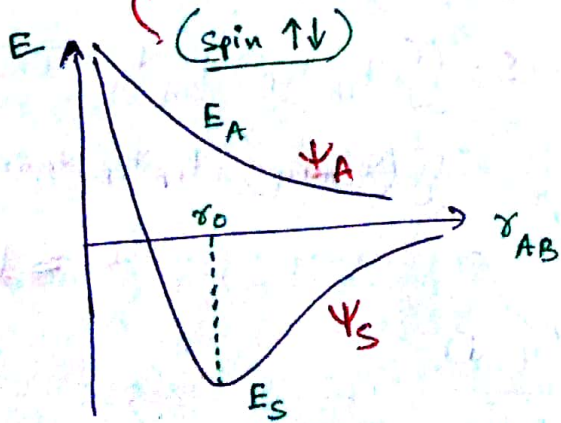
$$= \iint (\psi_{2A} \psi_{1B})^* (\psi_{1A} \psi_{2B}) d\tau_1 d\tau_2$$

$$= \text{overlap integral} \leq 1$$

$$\therefore H = E_0 + E_0 + \mathcal{H}' = 2E_0 + \mathcal{H}'$$

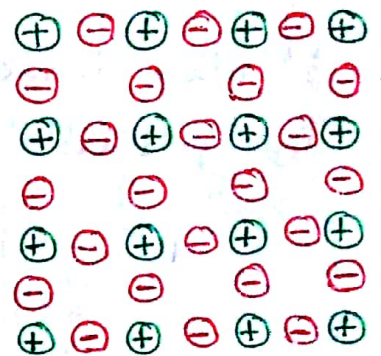
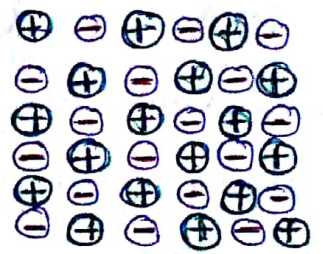
Exchange interaction is $E' = \frac{\int \Psi^* \mathcal{H}' \Psi d^3r}{\int \Psi^* \Psi d^3r}$

with $\Psi = \frac{1}{\sqrt{2 \pm 2S}} (\psi_{1A} \psi_{2B} \pm \psi_{2A} \psi_{1B})$.



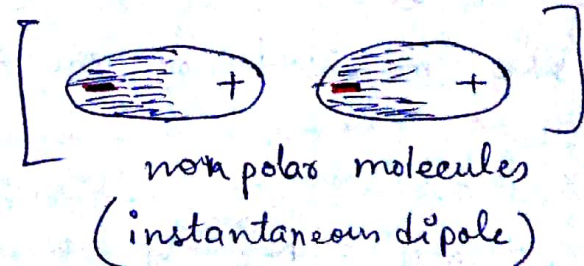
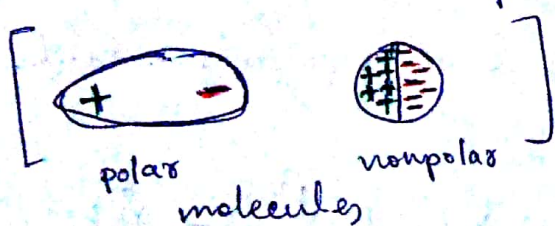
Metallic Bonding

Ionisation energy is low and high electrical conductivity. They have vacant valency orbitals & have very few valency electrons compared to the number of valency orbitals. These electrons in the outermost orbit are loosely bound (conduction/free electrons) & 1 or 2 can be detached from parent atom due to attraction of neighbouring atom cores. These mobile electrons move from one kernel (positively charged atom) to other in metal lattice, & in the process bind two or more kernels together, by electrostatic interaction (partial). Because electrons are delocalized, do not have directional polarity & weak than covalent bond. They are easy to shear, opaque & lustrous appearance because they radiate light energy of different frequency.



Vander Wall's bonding in molecular crystals

Inert gases attract with weak attractive force, although their outermost electron orbits are completely filled so they have no valence electrons. Force of attraction $\propto r^{-7}$ so very short range.



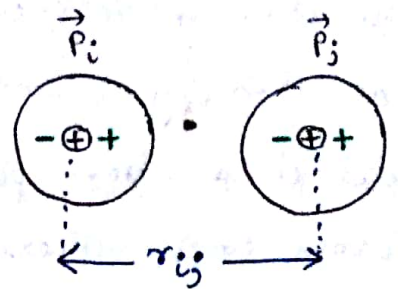
dipole-dipole, dipole-induced dipole interaction.

These bonds are around 0.1 eV/bond & break by temperature fluctuations at room temperature. As temperature is reduced, vanderwaal's force dominate & matter transform from gas to liquid or solid.

Binding energy of Inert gas crystals

Dipole-dipole interaction produces a weak attractive force.

Fluctuation of charge distribution on j^{th} atom induces instantaneous dipole moment \vec{P}_i on i^{th} atom. This produces field \vec{E} at centre of the j^{th} atom



$$E_i = \frac{2P_j}{r_{ij}^3}$$

$$\text{Instantaneous dipole moment } P_j = \alpha E_i = \frac{2\alpha P_i}{r_{ij}^3}$$

\therefore Potential energy of the dipole moments is

$$U_{\text{atr}} = -\frac{2P_i P_j}{r_{ij}^3} = -\frac{4\alpha P_i^2}{r_{ij}^6} \propto -\frac{1}{r_{ij}^6} \rightarrow \text{short range}$$

\downarrow attractive

$$= -\frac{B}{r_{ij}^6}$$

Repulsive interaction is due to overlap of electron clouds of atoms i & j (Pauli's exclusion principle)

$$U_{\text{rep}} = \frac{C}{r_{ij}^{12}} \quad \therefore U_{ij} = -\frac{B}{r_{ij}^6} + \frac{C}{r_{ij}^{12}} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

ϵ is the magnitude of the energy & σ represents extent.

Cohesive energy

$$U_{\text{tot}} = N U_i = N \sum_{j \neq i} U_{ij} = \frac{1}{2} N (4\epsilon) \sum_j \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

substituting $r_{ij} = r_{ij} R$

$$U_{\text{tot}} = 2NE \left[\sum_j \left(\frac{\sigma}{r_{ij} R} \right)^{12} - \sum_j \left(\frac{\sigma}{r_{ij} R} \right)^6 \right] = 2NE \left[12.131 \left(\frac{\sigma}{R} \right)^{12} - 14.454 \left(\frac{\sigma}{R} \right)^6 \right]$$

for fcc crystal.

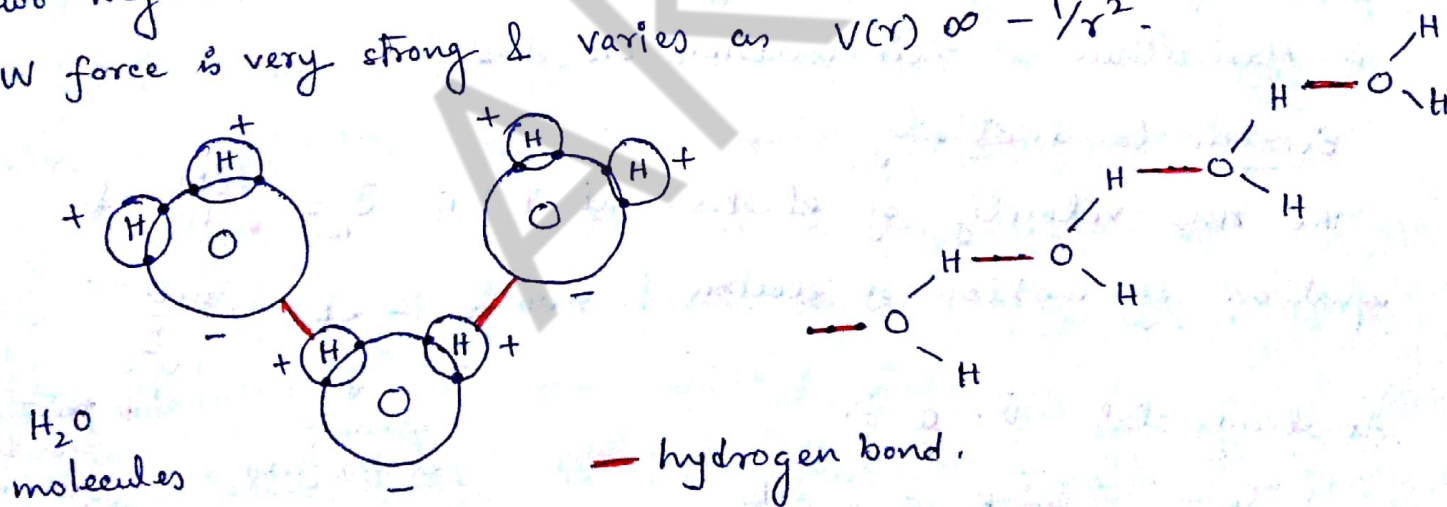
$$\left. \frac{dU_{\text{tot}}}{dR} \right|_{R=R_0} = 0 \Rightarrow R_0/\sigma = 1.09.$$

$$\text{and } U_{\text{tot}} = 2NE \left[12.131 \left(\frac{\sigma}{R_0} \right)^{12} - 14.454 \left(\frac{\sigma}{R_0} \right)^6 \right] = -8.6 NE$$

This is the cohesive energy of the inert gas crystal at absolute zero temperature & zero pressure.

Hydrogen Bonding

A special type of vanderWaal bond happens between hydrogen atom, which has 1 electron loses to other atom leaving behind a poorly shielded proton. The proton (H^+ ion) has two negative ions to attract & its radius is 10^{-15} m , so the VW force is very strong & varies as $V(r) \propto -1/r^2$.



Interaction between oppositely charged ends of permanently polarized molecules with having H-atom is called the Hydrogen bond.

<p>VW $\sim 2-7 \text{ kJ/mole}$</p> <p>H-bond $\sim 10 \text{ kJ/mole}$</p>	<p>Metallic $\sim 20-100 \text{ kJ/mole}$</p> <p>Covalent $\sim 170-244 \text{ kJ/mole}$</p> <p>Ionic $\sim 184 \text{ kJ/mole}$</p>	cohesive energy
--	---	-----------------