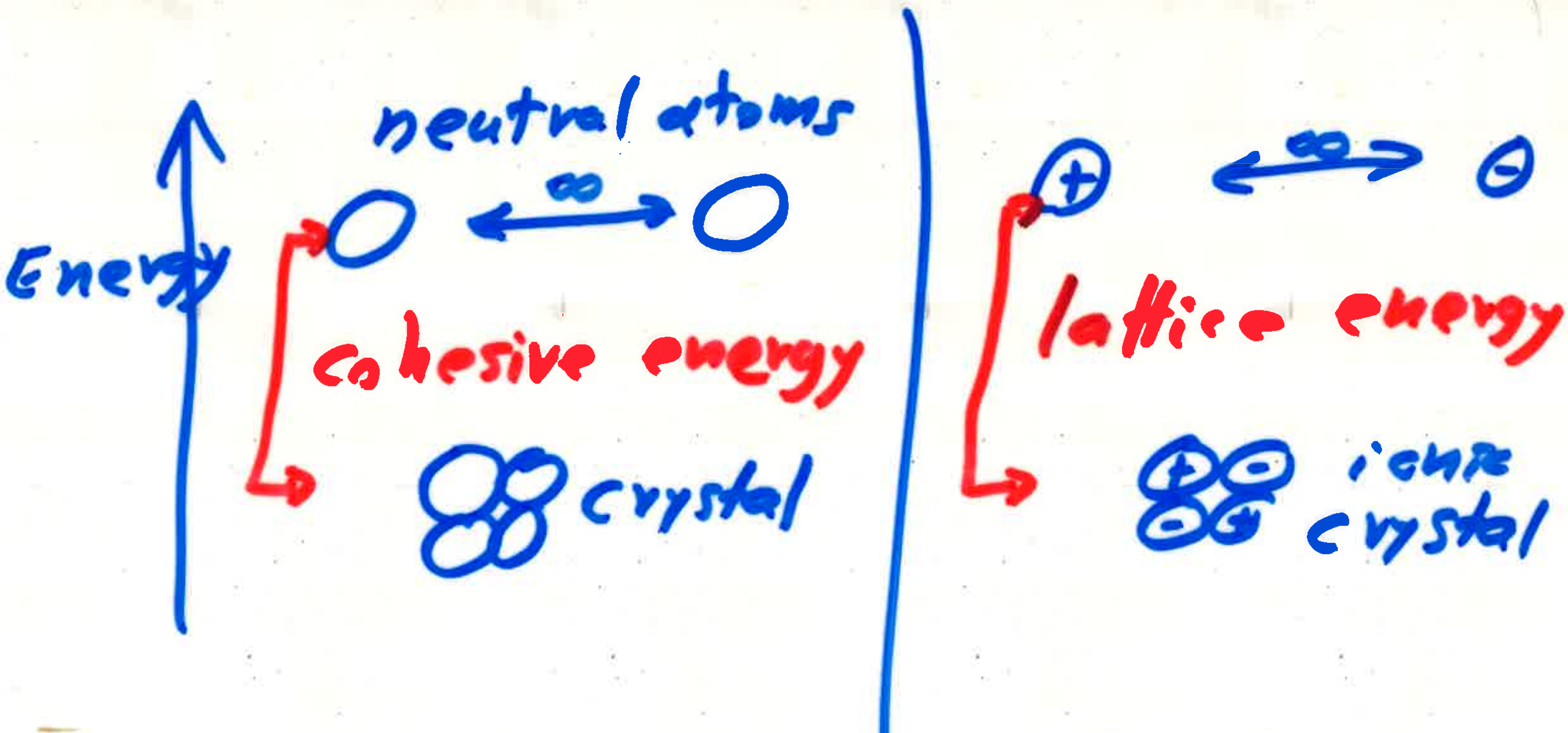
Crystal Binding

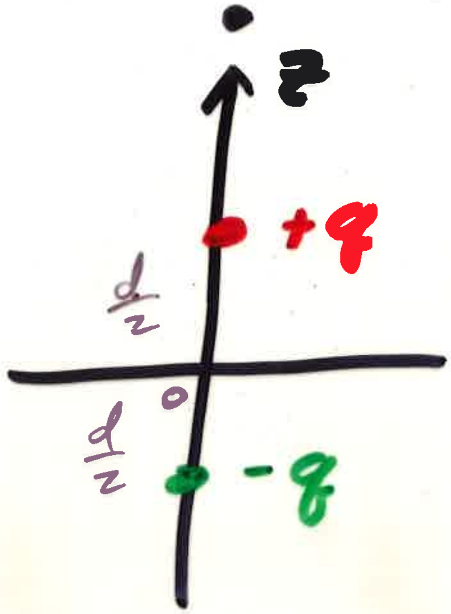
1. Van der Waals
2. Ionic
3. Covalent
4. Metal
5. Hydrogen



Ionic binding easy to understand

Coulomb attraction ⊕ $\vec{F}$ $\vec{F}$ ⊖

Inert gases : eg. Ne, Kr, Ar...



Find electric field on the z axis.

$$E(z) = \frac{q}{4\pi\epsilon_0}\frac{1}{(z-\frac{d}{2})^2} + \frac{(-q)}{4\pi\epsilon_0}\frac{1}{(z+\frac{d}{2})^2}$$

Expand with binomial series: $z \gg d$

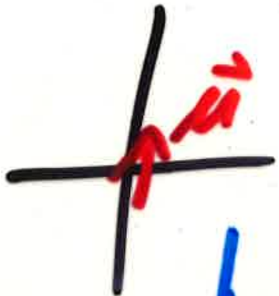
$$E(z) = \frac{q}{4\pi\epsilon_0}\left[\frac{1}{z^2}\right]\left[\frac{1}{(1-\frac{d}{2z})^2} - \frac{1}{(1+\frac{d}{2z})^2}\right]$$

$$= \frac{q}{4\pi\epsilon_0 z^2}\left[\left(1+\frac{d}{z}+\cdots\right) - \left(1-\frac{d}{z}+\cdots\right)\right]$$

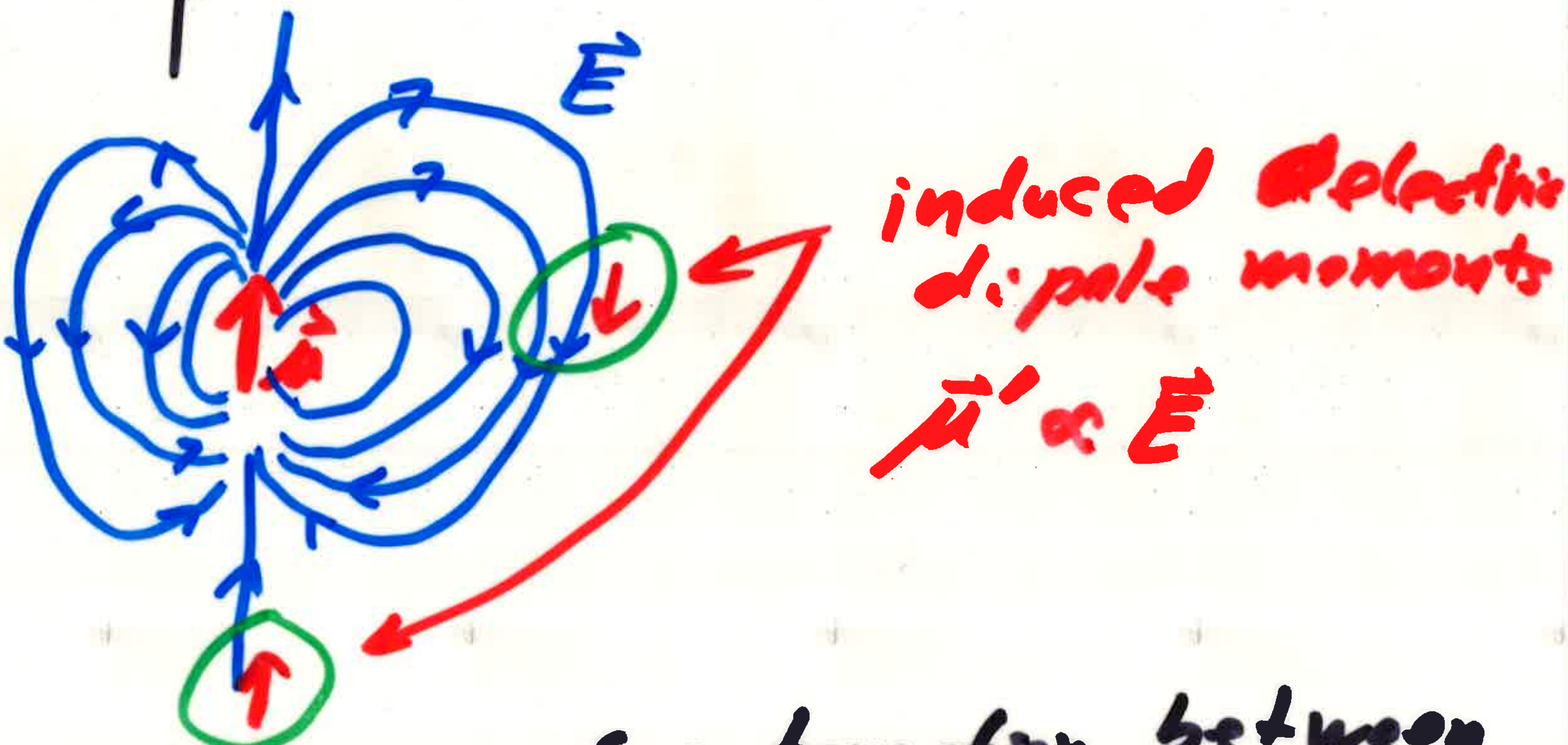
$$= \frac{q}{4\pi\epsilon_0 z^2}\frac{2d}{z} + \Theta\left(\frac{d^3}{z^5}\right)$$

Define $\mu = qd$

Dipole Electric field



$$\vec{E}(\vec{r}) = \frac{1}{4\pi\epsilon_0}\frac{1}{r^3}\left[3(\vec{\mu}\cdot\hat{r})\hat{r} - \vec{\mu}\right]$$



U = Energy of interaction between an electric dipole $\vec{\mu}$ and an electric field $\vec{E}$.

$$U = -\vec{\mu}\cdot\vec{E} \propto \frac{1}{r^6}$$

van der Waals - London binding

Ionic Crystals

Quantum Mechanics primer

Quantum numbers

n - principal, energy

ℓ - orbital, $0 \to n-1$

m_ℓ - magnetic, $\underbrace{-\ell, -\ell+1 \ldots 0 \ldots +\ell}_{2\ell+1}$

z projection of ℓ

s - spin $= \frac{1}{2}\hbar$

m_s - z projection of s $\quad -\frac{1}{2}, +\frac{1}{2}$

$\ell =$	0	1	2	3
	s	p	d	f

$1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^1$

Ionic Binding due to Coulomb interaction between ions.
Usually the ions have closed shells. → spheres.

Alkali metals: Li Na K Rb Cs Fr

Li: $1s^2 2s^1$

Na: $1s^2 2s^2 p^6 3s^1$

K: $1s^2 2s^2 p^6 3s^2 p^6 4s^1$

$Li^+, Na^+, K^+ \ldots$ → spheres

Halogens: F Cl Br I At

F: $1s^2 2s^2 p^5$

Cl: $1s^2 2s^2 p^6 3s^2 p^5$

$F^-, Cl^-, Br^- \ldots$ → spheres

Energy Accounting

Costs energy to ionize $Na \to Na^+$

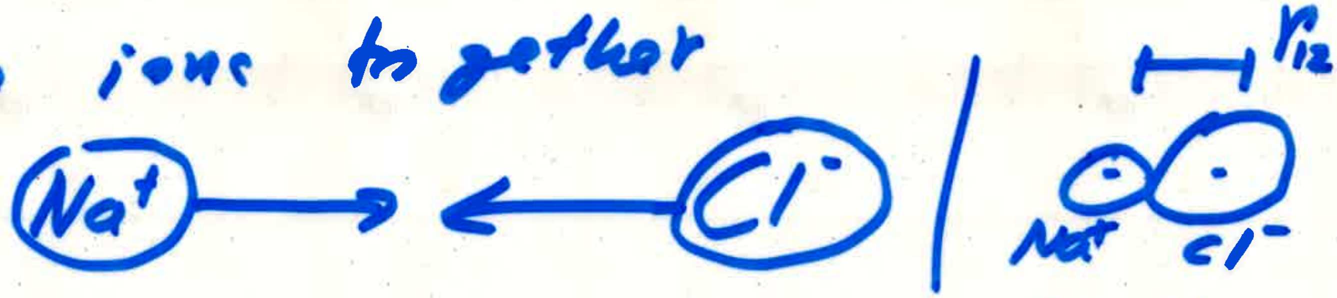
Get some energy back: $Cl \to Cl^-$

Cl^- has a lower energy than Cl neutral atom

$$E(Cl^-) - E(Cl) > 0$$

→ electron affinity.

Get even more energy by bringing the ions together



Coulomb interaction gives binding energy

$$U_{12} = \frac{k q_1 q_2}{r_{12}} < 0$$

because one q is positive one is negative

$$k = \frac{1}{4\pi\epsilon_0} \text{ (MKS)} \qquad k = 1 \text{ (c.g.s.)}$$

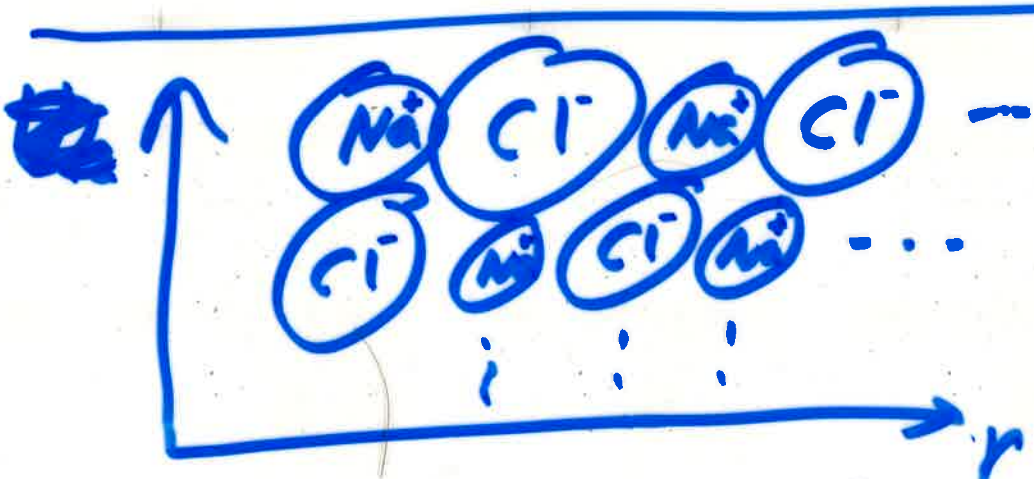
Ionic binding is <u>much</u> stronger than van der Waals.

Coul. $\frac{1}{R}$ vdW $\frac{1}{R^6}$

Repulsion at small distances

$$U_{12} = \frac{k q_1 q_2}{r} + \underline{\lambda e^{-\frac{r}{\rho}}}$$

Isolated pair is not a good approximation to binding energy since $\frac{1}{r}$ has a long range — need next-to nearest neighbors + $(\text{next-to})^p$ nearest neighbors.



Madelung constant for singly ionized atoms $q_1 = +q$, $q_2 = -q$

R is nearest neighbor distance.

$$r_{ij} \equiv p_{ij} R$$

p_{ij} ← number

$$U_{ij} = \begin{cases} -\dfrac{kq^2}{R} + \lambda e^{-\frac{R}{\rho}}, & \text{nearest neighbors} \\ \pm \dfrac{kq^2}{p_{ij} R} & \text{all other neighbors} \end{cases}$$

$$U_i = \sum_{\substack{j \\ j \neq i}}{}' U_{ij}$$

$$U_{\text{tot crystal}} = \sum_i U_i = N U_i$$

$$= N\left(z \lambda e^{-\frac{R}{\rho}} - \frac{kq^2}{R}\alpha\right)$$

z = # nearest neighbors (6 for NaCl)

Madelung constant $\alpha \equiv \sum_j{}' \dfrac{\pm 1}{p_{ij}}$

$p_{ij} = 1$ for nearest neighbors

Madelung constant for NaCl structure

z

nearest neighbors

$$\alpha = \sum \frac{\pm}{p_{ij}} = \frac{+6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2}$$

$r_{ij} = 1R$ $\quad r_{ij} = \sqrt{R^2+R^2}$ $\quad r_{ij} = \sqrt{R^2+R^2+R^2}$

next to nearest neighbors

Imagine a sphere centered on the reference ion.

Series does not converge.

$\Rightarrow$ use a cube instead of a sphere

$\Rightarrow$ Ewald sum. cf. App B. Kittel

$$U(R) = N\left(z\lambda e^{-\frac{R}{\rho}} - \frac{\alpha q^2}{R}\right) \quad (\text{cgs})$$

λ, ρ from a fit

Equilibrium separation between ions $\rightarrow R_0$

$$\left.\frac{dU(R)}{dR}\right|_{R=R_0} \overset{!}{=} 0 \Rightarrow N\left(\frac{-z\lambda}{\rho} e^{-\frac{R_0}{\rho}} + \frac{\alpha q^2}{R_0^2}\right) = 0$$

$$\Rightarrow \boxed{R_0^2 e^{-\frac{R_0}{\rho}} = \frac{\rho \alpha q^2}{z\lambda}} \quad (\text{cgs})$$

transcendental equation

can not solve for R_0

$$U(R_0) = N\left(z\lambda \underbrace{e^{-\frac{R_0}{\rho}}}_{\frac{\rho\alpha q^2}{z\lambda R_0^2}} - \frac{\alpha q^2}{R_0}\right)$$

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