Ionic Crystals

Quantum Mechanics primer

Quantum numbers

n - principal, energy

l - orbital, $0 \rightarrow n-1$

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

z projection of l

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

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

$l=$	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^+ ... → 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^-... → spheres

Energy Accounting

Costs energy to ionize Na → Na^+

Get some energy back: Cl → 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

Na^+ ⟶ ⟵ Cl^-

Coulomb interaction gives binding energy

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

because one q is positive, one is negative

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

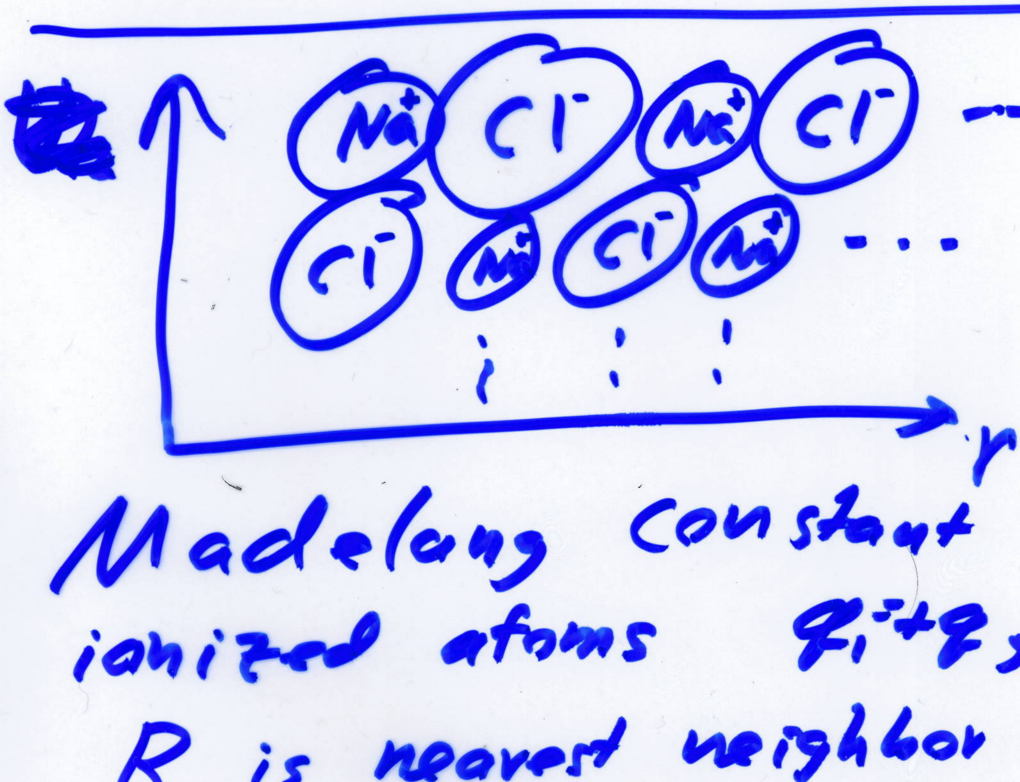
Ionic binding is <u>much</u> stronger than van der Waals.

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 + (next-to)^p nearest neighbors.



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

R is nearest neighbor distance.

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

number

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

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

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

$$= N\Big(\underset{\uparrow}{z} \lambda e^{-\frac{R}{\rho}} - \frac{kq^2 \alpha}{R}\Big)$$

\# nearest neighbors (6 for NaCl)

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

$p_{ij} = 1$ for nearest neighbors

Remember for van der Waals

Lennard-Jones sums

$\boxed{\text{fcc}}$ $\sum_j{}' \rho_{ij}^{-6} = 14.45\ldots \qquad \sum_j{}' \rho_{ij}^{-12} = 12.13\ldots$

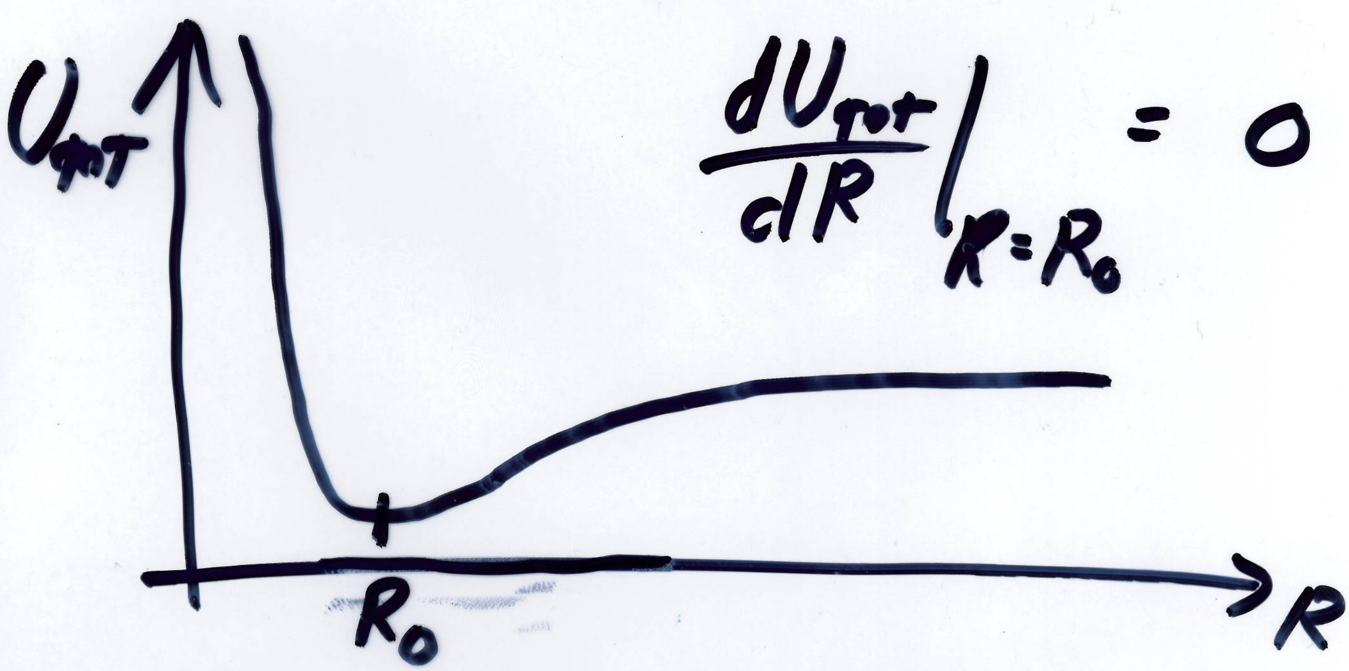
Madelang

NaCl $\quad \alpha = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{2}$

$\alpha = 1.7475$

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

$$\left.\frac{dU_{TOT}}{dR}\right|_{R=R_0} = 0$$



Must be careful in computing α!

e.g. one-dimensional crystal

$$\cdots \oplus \ominus \oplus \underbrace{\ominus \quad \oplus}_{R} \ominus \cdots$$

$$Z = 2$$

$$\alpha = \sum_j{}' \frac{\pm 1}{p_{ij}} = 2\left[\frac{+1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \cdots\right]$$

alternating harmonic series

conditionally (not absolutely) convergent.

$$\left|\frac{1}{1}\right| + \left|-\frac{1}{2}\right| + \left|\frac{1}{3}\right| + \left|-\frac{1}{4}\right| + \cdots$$

$$1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4}$$ does not converge $\rightarrow \infty$

Grouped like this

$$\left(1 - \frac{1}{2}\right) + \left(\frac{1}{3} - \frac{1}{4}\right) + \left(\frac{1}{5} - \frac{1}{6}\right) + \cdots$$

$$\rightarrow \ln(2)$$

Taylor expansion $\ln(1+x)$

$$= x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$$

$x=1 \rightarrow \ln(2) = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \cdots$

<u>But</u> different grouping

$$\left(1 - \frac{1}{2} - \frac{1}{4}\right) + \left(\frac{1}{3} - \frac{1}{6} - \frac{1}{8}\right) + \left(\frac{1}{5} - \frac{1}{10} - \frac{1}{12}\right) + \cdots$$

$$\rightarrow \frac{\ln(2)}{2}$$

Madelung energy

$$\boxed{-\frac{N\alpha q^2}{R_0}}$$
