LECTURE 3
INTERATOMIC FORCES

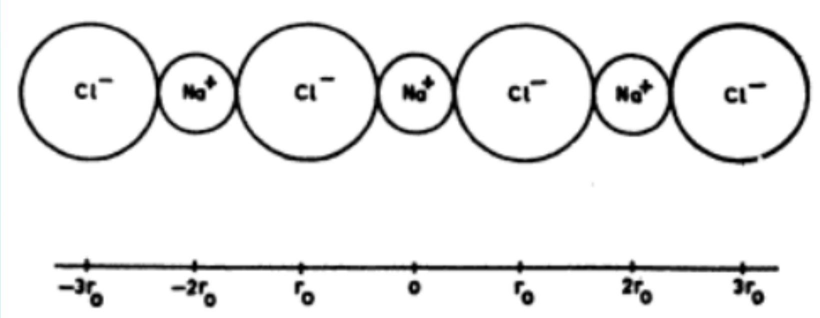
(Solid State physics S.O.Pillai)

http://202.141.40.218/wiki/index.php/
Unit-3:_Atomic_Cohesion_and_Crystal_Binding#FORCE_BETWEEN_ATOMS

Calculation of Madelung constt. of Ionic Crystal

Madelung constant (A) represents the effect of a specific geometrical array of ions on the electrostatic potential energy. It is a property of the crystal structure and depends on the lattice parameters, anion-cation distances, or molecular volume of the crystal.

Madelung constant (A) in a linear chain of ions of alternateive signs



The attractive Coulomb energy due to nearest neighbors is

$$-\frac{e^2}{4\pi\varepsilon_o r_o}+\left[-\frac{e^2}{4\pi\varepsilon_o r_o}\right]=-\frac{2e^2}{4\pi\varepsilon_o r_o}$$

The repulsive energy due to the two positive ions at a distance of $2r_o$ is

$$\frac{2e^2}{4\pi\varepsilon_o(2r_o)}$$

The attractive Coulomb energy due to two next neighbors at a distance $3r_o$ is

$$-\frac{2e^2}{4\pi\varepsilon_o(3r_o)}$$

And so on....

Thus the total energy due to all the ions in the linear array is

$$-\frac{2e^2}{4\pi\varepsilon_o r_o}+\frac{2e^2}{4\pi\varepsilon_o(2r_o)}-\frac{2e^2}{4\pi\varepsilon_o(3r_o)}+\ldots$$

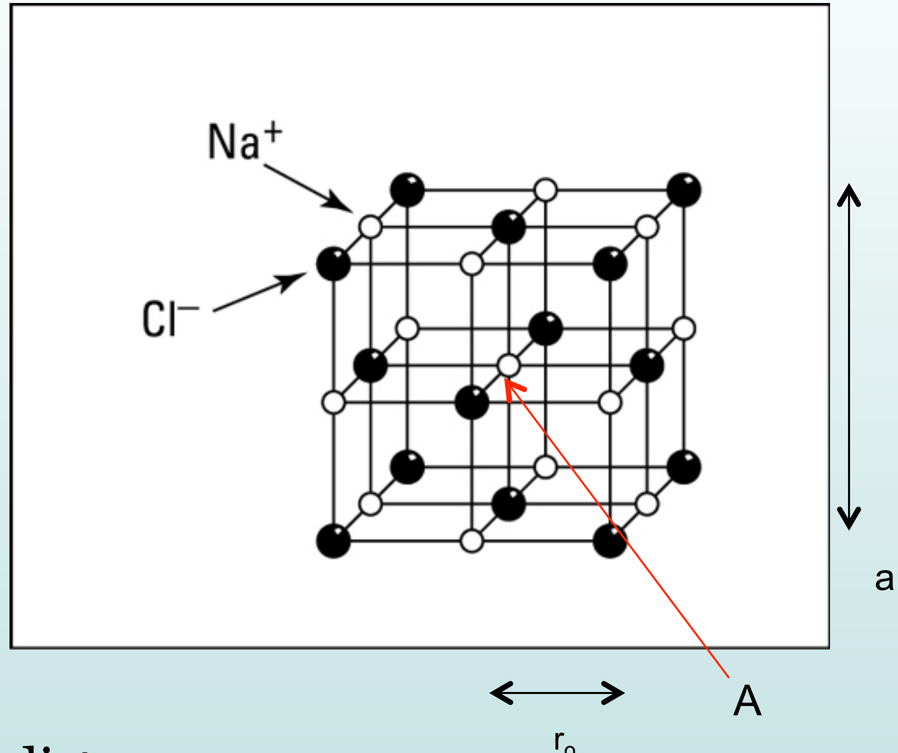
$$=-\frac{e^2}{4\pi\varepsilon_o r_o}\left[2\left(1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\ldots\right)\right]$$

$$=-\frac{e^2}{4\pi\varepsilon_o r_o}\left[2\log(1+1)\right]$$

$$=-\frac{e^2}{4\pi\varepsilon_o r_o}\left[2\log 2\right]$$

*Thus (2 log 2) is the Madelung constt. per molecule of the ionic solid. Hence (2*N_A *log 2) is the Madelung constant per mol of the ionic solid.*

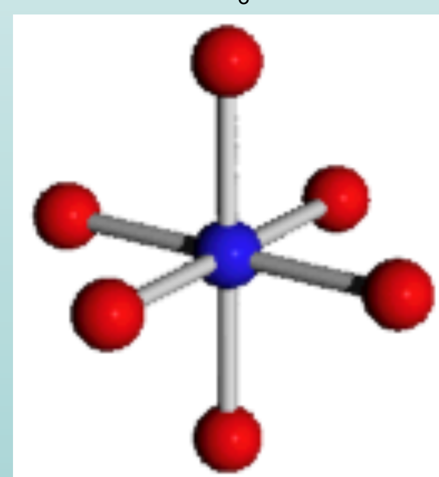
Madelung constant in 3D



- Na$^+$ is coordinated by 6 Cl$^-$ ions at a distance r_o.

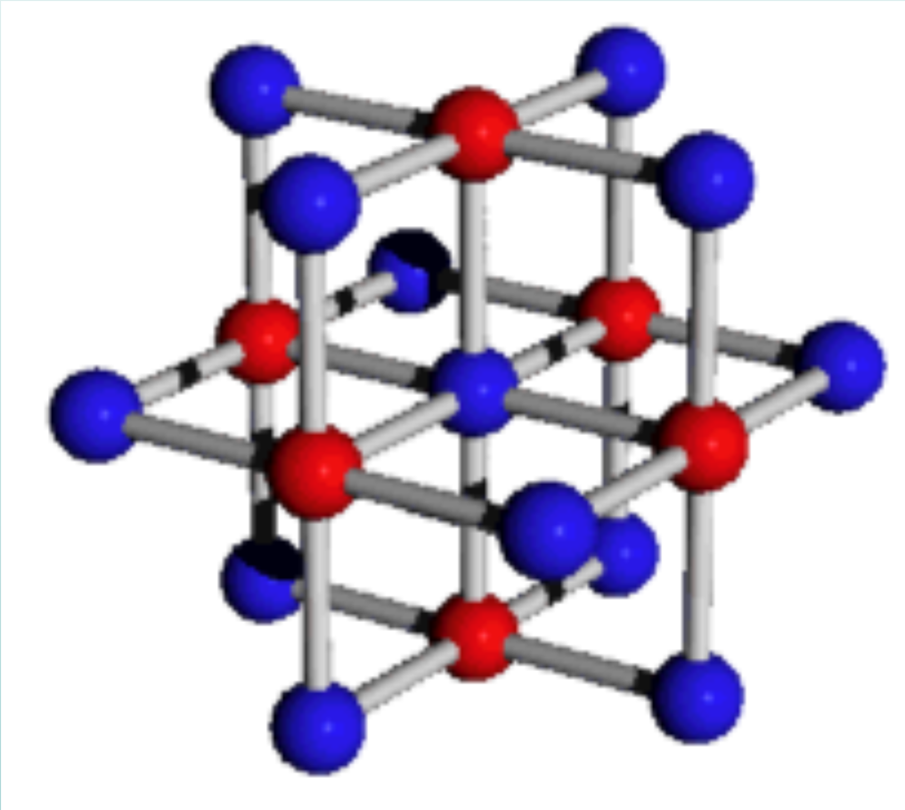
- Attractive potential energy

$$-\frac{6e^2}{4\pi\varepsilon_o r_o}$$



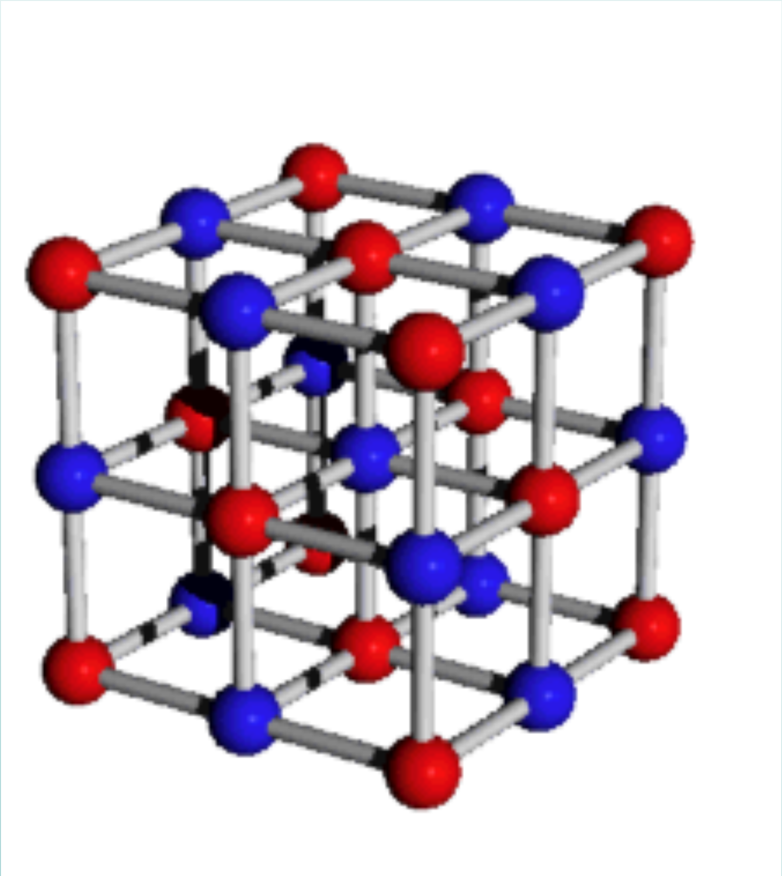
- Similarly, repulsive energy due to 12 Na^+ at $\sqrt{2}\, r_o$

$$\frac{12e^2}{4\pi\varepsilon_o\sqrt{2}r_o}$$



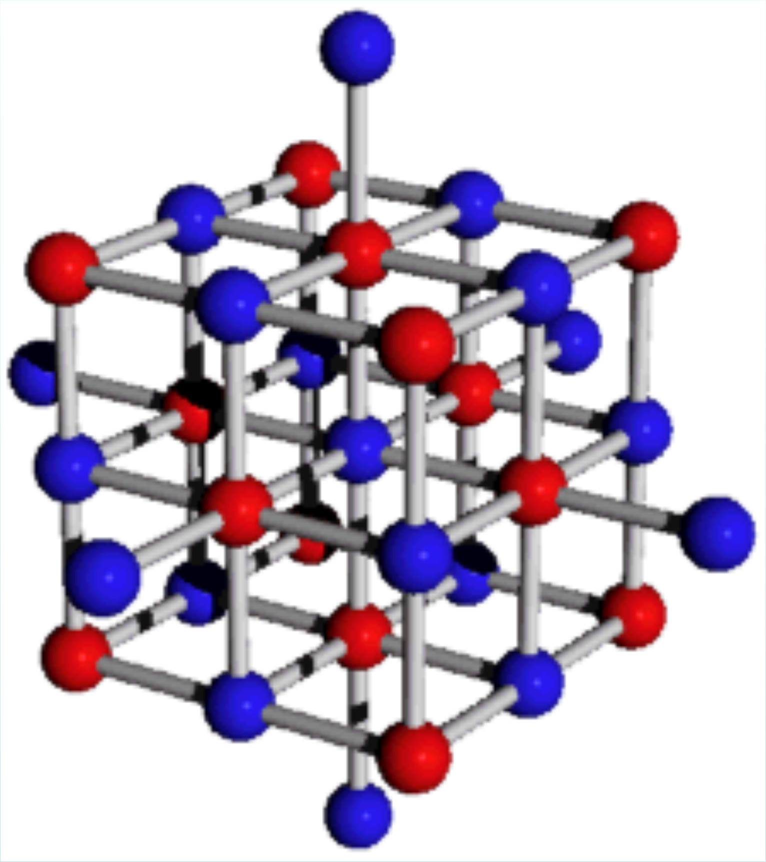
- Na^+ is coordinated by 8 Cl^- ions at a distance (body diagonal)$\sqrt{3}r_0$. Attractive potential energy

$$-\frac{8e^2}{4\pi\varepsilon_0\sqrt{3}r_0}$$



- Similarly, repulsive energy due to 6 Na^+ at $2r_o$

$$\frac{6e^2}{4\pi\varepsilon_o 2r_o}$$



Madelung constant in 3D

Thus the Coulomb energy of this Na^+ at A in the field of other ions is

$$U = -\frac{6e^2}{4\pi\varepsilon_o r_o} + \frac{12e^2}{4\pi\varepsilon\sqrt{2}_o r_o} - \frac{8e^2}{4\pi\varepsilon_o\sqrt{3}r_o} + \frac{6e^2}{4\pi\varepsilon_o 2r_o} + \ldots$$

$$U = -\frac{e^2}{4\pi\varepsilon_o r_o}\left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \ldots\right]$$

For mol of the crystal , the total Coulomb energy is

$$U = -\frac{N_A e^2}{4\pi\varepsilon_o r_o}\left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \ldots\right]$$

$$\boxed{U = -\frac{N_A e^2 A}{4\pi\varepsilon_o r_o}}$$

A→Madelung constant and A=1.75 for NaCl structure

$N_A = 6.022140857 \times 10^{23}$

Example S1

The potential energy function for the force between two particular ions, carrying charges +e and −e respectively, may be written as,

$$V = -\frac{Ae^2}{r} + \frac{B}{r^9}$$

(i) Find the equilibrium separation distance for these ions.

(ii) Find the potential energy at equilibrium separation.

Prob 2: What is cohesive energy? In a NaCl crystal , the equilibrium distance r_o between ions is 0.281 nm. Find the cohesive energy in NaCl. Given A=1.748 and n=9. Here IE is 5.13eV and EA is 3.6 0eV.

Prob 3: Calculation of c/a Ratio for an Ideal Hexagonal Close Packed Structure.