

## \*Periodic lattices

as a result of the interatomic force balance in solids

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July 1, 2021

- \* Lattice definition.
- \* Crystal structure
- \* Crystal binding
- \* Madelung constant in the ionic crystal

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- \* The set of mathematical points to which the basis is attached is called lattice.
- \* The lattice in three dimensions may be defined by three translation vectors  $a_1, a_2, a_3$ , such that the arrangement of atoms in the crystal looks the same when viewed from the point  $r$  as when viewed from every point  $r'$  translated by an integral multiple of the:

$$r' = r + u_1 a_1 + u_2 a_2 + u_3 a_3 \quad (1)$$

Here  $u_1, u_2, u_3$  are arbitrary integers. The set of points  $r'$  defined by (1) for all  $u_1, u_2, u_3$  defines the lattice.

# Reciprocal lattice

- ✱ We can define a base in the reciprocal lattice. For example in 3D the first vector is given by

$$\vec{b}_1 = \frac{2\pi}{V} \vec{a}_2 \times \vec{a}_3$$

so that the first base vector in the reciprocal space is orthogonal to the second and third in the lattice. The same holds for  $\vec{b}_2, \vec{b}_3$  by permutation.

- ✱ The general basis transformation can be written:  $a_i \cdot b_j = 2\pi\delta_{ij}$

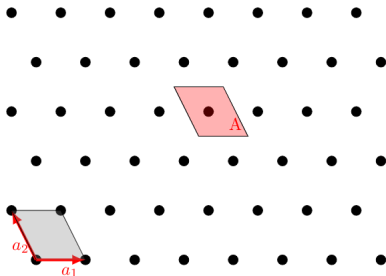


Figure 6: hexagonal lattice

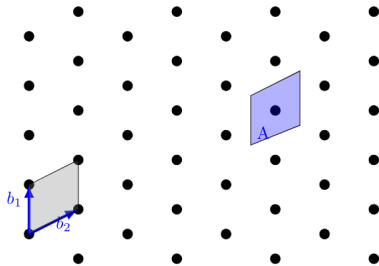
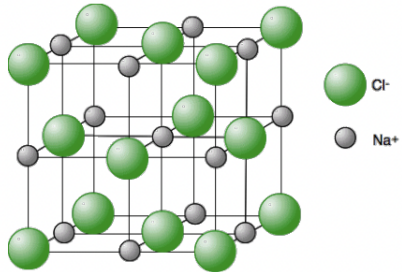


Figure 7: Reciprocal lattice

- ✱ The attractive electrostatic interaction between the negative charges and the positive charges is responsible for the formation of solids. In addition, we have also the repulsive term. The combined effect of attraction and repulsion give the lattice constant (usually indicated with  $a$ ), i.e. the distance between two sets of basis.

# Ionic Crystal

- ✱ The most common example of ionic crystal is the NaCl, made up of a positive ions  $Na^+$  and negative ions  $Cl^-$ .
- ✱ The long range interaction between ions is the electrostatic coulomb potential interaction ( $\pm \frac{q^2}{r}$ ). The ions arrange themselves in whatever crystal structure gives the strongest attractive interaction compatible with the repulsive interaction at short distances between ion cores. The main contribution to the binding energy of ionic crystals is electrostatic and is called the Madelung energy.





# Ionic Crystal Forces

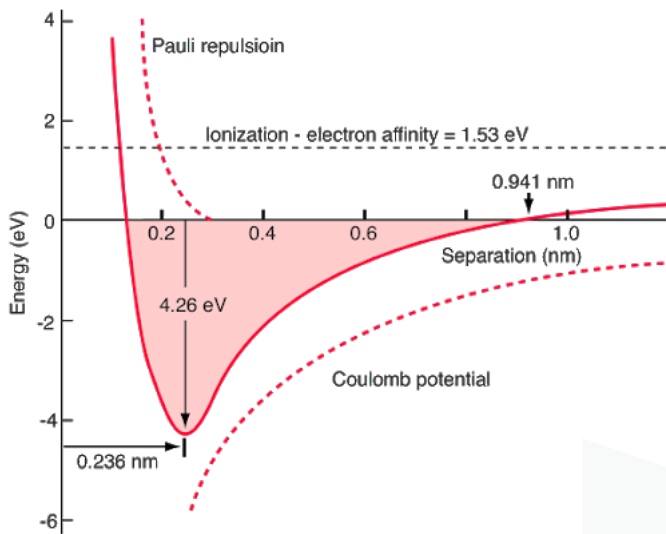


Figure 1: Caption

## Madelung constant

An clear example to understand the meaning of the Madelung constant is a unidimensional chain of NaCl. We can calculate the Madelung constant by looking at the potential ( $U_i = \sum_j U_{ij}$ ), which is felt by an atom (i). This potential has 2 components: The repulsive interaction and electrostatic interaction. The former ( $U_{ij}^{rep} = \lambda e^{-\frac{r_{ij}}{\rho}}$ ) acts only in the short-range between the ion cores, the latter ( $U_{ij}^{el} = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$ ) outweigh the repulsive component in longer distances. The main contribution to the binding energy of the crystal is electrostatic. So the total potential felt by an atom is:

$$\begin{aligned} U_i &= \sum_j U_{ij}^{rep} + U_{ij}^{el} \\ &= (z\lambda e^{-\frac{a}{\rho}} - \alpha \frac{1}{4\pi\epsilon_0} \frac{q^2}{a}) \end{aligned}$$

Where z indicate the number of neighbours and  $\alpha$  is the Madelung constant. As a consequence the total energy is given by:

$$U_{tot} = NU_i \quad (2)$$

## Madelung constant

So calculate the Madelung constant we can set up the origin in an arbitrary atom  $i$ .  
Let's choose a positive atom as reference atom:

$$\begin{aligned}U_i^{el} &= 2 \left( \frac{1}{4\pi\epsilon_0} \frac{q(-q)}{a} + \frac{1}{4\pi\epsilon} \frac{q(q)}{2a} + \frac{1}{4\pi\epsilon_0} \frac{q(-q)}{3a} \dots \right. \\&= 2 \left( \frac{q^2}{4\pi\epsilon_0 a} \left( -1 + \frac{1}{2} - \frac{1}{3} \dots \right. \right. \\&= -2 \frac{q^2}{4\pi\epsilon_0 a} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \\&= -\frac{q^2}{4\pi\epsilon_0 a} (2\ln(2))\end{aligned}$$

The sum is the Taylor expansion of  $\ln(1+x)$ . The factor 2 is needed because there are 2 ions at equal distance: one on the right and one on the left. Note that this assumption provides a better estimation of the Madelung constant when the lattice size increases. In conclusion, the Madelung constant  $\alpha$  for a 1D chain is equal to:  
 $2\ln(2)$

In order to find the distance between two lattice point at the equilibrium we have find the minimum of the total energy differentiating  $U_{tot}(r) = NU_i(r)$  with respect to  $r$  and find where  $U'_{tot}(r) = 0$ . The value of  $r$  that minimize the function  $U_{tot}$  has to satisfy the following condition:

$$r_{min}^2 e^{-\frac{r_{min}}{\rho}} = \frac{\rho \alpha q^2}{z\lambda} \quad (3)$$

By looking at this equation we see that  $r^2 e^{-\frac{r}{\rho}}$  is upper limited for  $r \geq 0$ . So the equation(3) has a solution only when the maximum is greater than  $\frac{\rho \alpha q^2}{z\lambda}$ . The maximum value of  $r^2 e^{-\frac{r}{\rho}}$  is given for  $r = 2\rho$ ; and by substituting this value in the equation(3) we get:

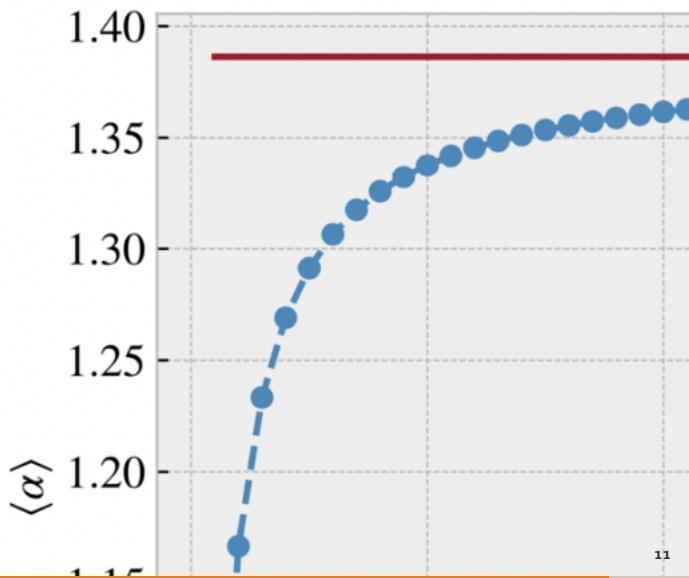
$$4\rho e^{-2} = \frac{\alpha q^2}{z\lambda}$$

Hence, in light of the above the condition on the parameters for the realisation of the crystal is:

$$\rho < \frac{e^2 \alpha q^2}{4z\lambda}$$

As  $U_{tot}(r)$  has a minimum, and the position  $r$  that gives the minimum value of the function doesn't depend on the crystal size, if  $N$  is large. I estimated numerically the equilibrium separation through the Newton method. Using the following parameters  $\rho = 0.32\text{\AA}$  and  $\lambda = 1\text{keV}$  taken from the Kittel, this yields to  $r_0 = 2.4\text{\AA}$ . Note, that this calculus has been made in 1D; in 3D the madelung constant is slightly lower, so the strength of the interaction is less giving a bigger spacing between the atoms  $r_0^{3D} \approx 2.82\text{\AA}$





**Figure 2:** Real behaviour considering few atoms, however the approximation  $N \gg 1$  already works very well for 50*atoms*. Usually in a crystal we have more than 50 atoms



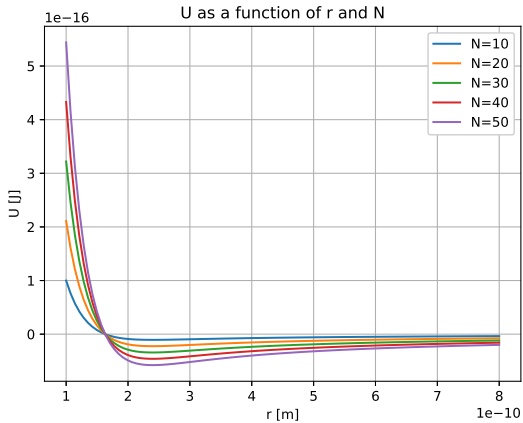


Figure 3: Considering the assumption  $N \gg 1$