Series can be very tricky…

In lecture 2

The difficulties of infinite series are discussed by analysing the strange behaviour of bond summations in ionic crystals….

Ionic Bonding

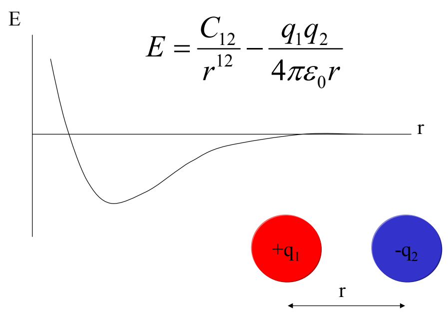
Consider the energy of an ionic crystal, eg: Na^+Cl^-, $Mg^{2+}O^{2-}$

To a good approximation each pair of ions interacts through a;

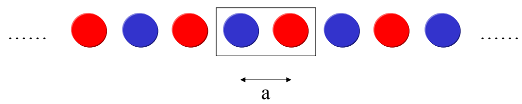
- short range repulsion ~$(1/r)^{12}$
- **long range** electrostatic ~$(1/r)$

Pair Interaction

$$E = \frac{C_{12}}{r^{12}} - \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$



Simplify: A 1-dimensional crystal

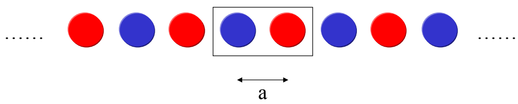


A line of charges $+q$, $-q$ with spacing a

What is the energy per ion of this object ?

The short range sum is straightforward but the long range electrostatic sum is **not**…

Easy to write down the series



The electrostatic energy is…

$$E = -\frac{2q^2}{4\pi\varepsilon_0 a}\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \ldots\right) \quad \text{Joules/ion}$$

i.e. The Alternating Harmonic Series

$$S = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \cdots$$

We'll come back to this but first of all consider the Harmonic Series – when all the signs are +.

The Harmonic Series

The convergence of a series is not always immediately apparent from inspection ?

The *harmonic series* "should" converge by the nth term test !

$$S = 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} +$$

Analysing the Harmonic Series

$$S = 1 + \frac{1}{2} + \left(\frac{1}{3} + \frac{1}{4}\right) + \left(\frac{1}{5} + \frac{1}{6} + \frac{1}{7} + \frac{1}{8}\right) +$$
$$+ \left(\frac{1}{9} + \frac{1}{10} + \frac{1}{11} + \frac{1}{12} + \frac{1}{13} + \frac{1}{14} + \frac{1}{15} + \frac{1}{16}\right)$$

$$S = 1 + \frac{1}{2} + s_1 + s_2 + s_3 + \ldots + s_n$$

And so….

Each of the partial sums, s_n, contains 2^n terms each of which has a smallest term $1/2^{n+1}$.

So, each $s_n > 2^n.(1/2^{n+1}) = 1/2$.

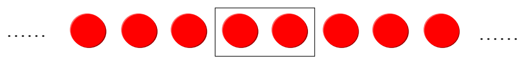
So,

$$S > 1 + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \ldots..$$

which, diverges to infinity…

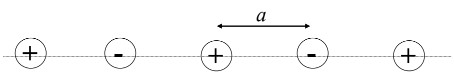
Is this obvious from the Chemistry ?

$$E = \frac{2q^2}{4\pi\varepsilon_0 a}\left(1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \frac{1}{5} + \ldots\right) \quad \text{Joules/ion}$$



The Harmonic Series corresponds to a chain of atoms of the same charge – obviously unstable…?

Ionic Bonding !



The energy of a chain of ions of alternating charge (q) separation a is;

$$E = -\frac{2q^2}{4\pi\varepsilon_0 a}\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \ldots\right) \quad \text{Joules/ion}$$

This is the alternating harmonic series….

So – what is the energy of rocksalt Na^+Cl^- ?

The Alternating Harmonic Series

$$E = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \ldots = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n}$$

This series is *conditionally convergent* in short we can make it converge to *any answer* we want…

!?

Conditional Convergence

The limit of the alternating harmonic series depends on how we arrange the sum of the terms, so…

We can make it converge to any number - for example 2.0000

Note: There are an infinite number of terms and we can add them in *any order* – however we decide to do that we will never run out of positive or negative terms.

Alternating Harmonic Series = 2.000

Strategy:

- Sum just positive terms to get a sum > 2
- Subtract a single negative term
- Add more positive terms until > 2
- Subtract a single negative term
- Repeat for ever

And… it must converge to 2.

Alternating Harmonic Series = 2.000

$$1+\frac{1}{3}+\frac{1}{5}+....+\frac{1}{15}=2.021800422$$

$$-\frac{1}{2}=1.521800422$$

$$+\frac{1}{17}+\frac{1}{19}+\frac{1}{21}+.....+\frac{1}{41}=2.004063454$$

$$-\frac{1}{4}=1.754063454$$

$$+\frac{1}{43}+\frac{1}{45}+.....+\frac{1}{69}=2.009446048$$

Etc…

How odd is that ?

This may seem very strange.

But..

The analysis is **correct**.

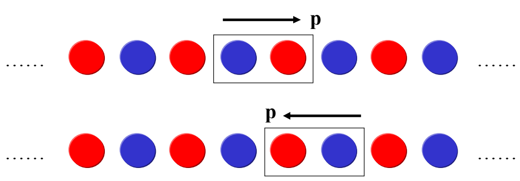
We have an infinite number of +ve and –ve terms – it doesn't matter that we are using more +ve ones than –ve ones…

The sum, and thus the energy of a rocksalt crystal, converges to any number you want !!

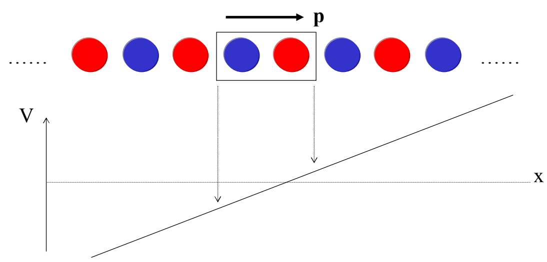
Why ?

The Coulomb interaction is very long range.

Note: the apparently arbitrary choice of repeat unit (unit cell) generates different electrostatic dipoles



Dipoles generate fields



Each cell contributes a dipole and the fields grows and grows as you walk along the chain..

The Coulomb interaction is tricky..

For each different choice of cell you get a different dipole and a different long range field – the energy of the chain has a different energy for each…

What is the true energy of the chain ?

In nature crystals are very careful to grow without long range fields !