# Assignment 3

Due date: Friday, September 17

*Electrostatic energy of a crystal*

How much energy is released when sodium and chlorine ions are brought together (from infinity) to assemble a NaCl crystal? Although an ion is not exactly a point charge, outside a sphere that surrounds the outermost electrons, its electric field is identical to the electric field of a point charge (corresponding to the ion's net charge). So to the extent that the electron orbitals of the ions hardly overlap — a good approximation — you are in a position to answer this question.

To keep things simple you will work out the case of a two dimensional crystal (and not be challenged to make 3D drawings). The ions are arranged like a checkerboard with sodium at the centers of the black squares and chlorine centered on white. Let the distance between adjacent ions be $a$. Since all your pairwise Coulomb energies will be multiples of $U = Ke^2/a$, you should adopt this as your energy unit (and avoid a lot of unnecessary writing). For example, the energy of two adjacent ions in these units is simply $-1$.

You can think of each pair-energy term as "belonging" half to each ion in the pair. How much total energy belongs to each ion in a very large checkerboard crystal? Single out one sodium ion and let its position be $(0, 0)$. Now locate all ions up to a distance $a$ from the origin and find their contribution to the energy of the central ion. Next include all ions up to distance $\sqrt{2}a$. Continue in this way, adding successive shells of ions at distance $2a$, $\sqrt{5}a$, $\sqrt{8}a$, $3a$, etc. In this way you can develop a series of hopefully better approximations for the energy per ion in an infinite crystal:

$$\frac{1}{2}\left(-\frac{4}{1}\right)U$$

$$\frac{1}{2}\left(-\frac{4}{1}+\frac{4}{\sqrt{2}}\right)U$$

$$\frac{1}{2}\left(-\frac{4}{1}+\frac{4}{\sqrt{2}}+\frac{4}{2}\right)U$$

$$\frac{1}{2}\left(-\frac{4}{1}+\frac{4}{\sqrt{2}}+\frac{4}{2}-\frac{8}{\sqrt{5}}\right)U$$

etc.

Work out numerically the first five approximations. Do you see signs of convergence? Can you even feel confident about the sign of the energy?

To confirm that the energy per ion is indeed negative (and salt crystals are stable!) you will have to evaluate the energy differently. The trick is to build the crystal out of neutral units. As we saw already for the dipole, the electric field created by a neutral group of charges falls off more rapidly with distance, thereby making the interactions of distant groups weaker and improving the convergence of the energy sum. Choose as your neutral groups sets of two $+e$ and two $-e$ ions that form squares of side $a$. Let's call these "molecules". Because of their symmetry, our molecules do not produce even a dipole field at large distance, but a "quadrupole" field that falls off even faster.

Here's how you can reorganize your previous sum over individual ions into a sum over molecules to get a convergent sum for the energy. Start by interpreting the crystal as a crystal of molecules. The molecules are arranged on a square grid with spacing $2a$. To find the energy per molecule you sum over pairs of molecules as you did for the individual ions, where half of each pair-energy belongs to each molecule in the pair. You will also have to work out the energy internal to the molecule, i.e. that arising from all 6 pairs of its ions (all of these, not just half, belongs to the molecule). When all these energies are summed, the result is the electrostatic energy per molecule. Divide this by four to get the energy per ion.

What is the internal energy per molecule, $U_{00}$ (in units of $U = Ke^2/a$)?

What is the pair-energy for molecules separated by $(2a, 0)$, $U_{20}$?

What is the pair-energy for molecules separated by $(2a, 2a)$, $U_{22}$?

Work out the successive partial sums $U_{00}$, $U_{00} + 4U_{20}/2$, $U_{00} + 4U_{20}/2 + 4U_{22}/2$. Does this seem to converge? Divide your final sum by 4 to get the energy per ion.

Estimate the electrostatic energy in Joules, of one mole of NaCl, assuming the sum in the 3D case is $-0.874\,U$ per ion.

*Electrostatics in a spherical world*

Suppose the geometry of space is the surface of a sphere of radius $R$. There are point charges in this world and the electric fields they produce are entirely within this world, i.e. they are everywhere tangent to the surface of the sphere. The leading model of the 3D geometry of our actual world is exactly this type of curved world in one higher dimension (the 3D surface of a very large sphere that would be embedded in 4D).

Use the analog of Gauss's law in a 2D "sphere-world" to calculate the electric field of a point charge. Place a charge $q$ at the north pole, i.e. the point with spherical coordinate $\theta = 0$, and construct a Gaussian "surface" — a closed curve — surrounding it. By symmetry, the electric field will be directed everywhere from north to south (along lines of longitude) and will have a magnitude that only depends on $\theta$. Gauss's law relates the flux of electric field through a curve $\mathcal{C}$ and the charge enclosed like this:

$$\oint_{\mathcal{C}} \mathbf{E} \cdot d\mathbf{a} = q/\epsilon'.$$

The vector element $d\mathbf{a}$ is normal to the curve (and tangent to the sphere) and its magnitude equals the length of the curve-element. The constant $\epsilon'$ is the sphere-world counterpart of $\epsilon_0$. By using curves of constant $\theta$, i.e. lines of latitude, you should have no trouble calculating $E(\theta)$, the $\theta$-dependence of the point charge electric field magnitude.

What do you make of the behavior of the electric field at the antipodal point — the south pole — when the point charge is at the north pole? What do you conclude about the total charge in sphere-world?

Calculate the energy $U_{12}$ of a pair of charges $q_1$ and $q_2$ in sphere-world. Their separation will be measured by the angle $\theta_{12}$ they subtend at the center of the sphere. To fix $U_{12}$ absolutely you may set the energy to be zero when $\theta_{12} = \pi/2$ (there is no infinity in sphere-world).