Defects in Crystals

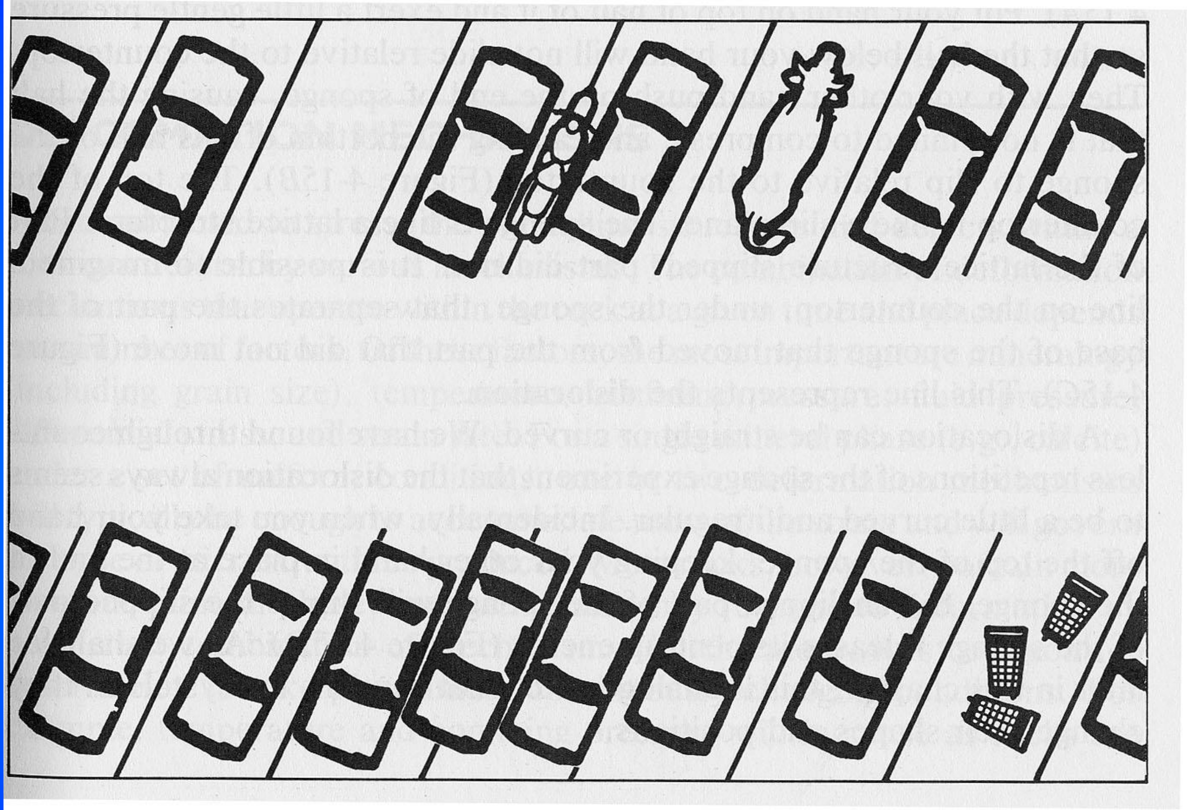
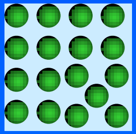
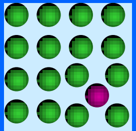
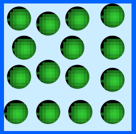


Image “borrowed” from http://comp.uark.edu/~pjansma/geol3513_25_defmechs1_04.ppt who got it from “Davis & Reynolds 1996.”

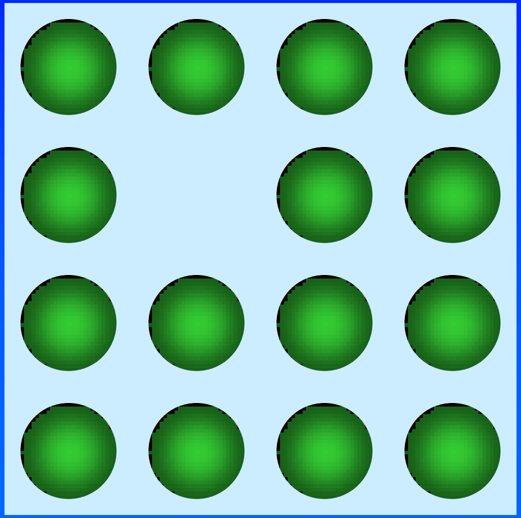
It's easy to think of real crystals as having these ideal structures.

In fact, no crystals are perfect; all crystals have defects. Crystals can have:

- The "right" atoms in "wrong" places. 
- "Wrong" atoms in "right" or "wrong" places. 
- Missing atoms. 
- Etc.

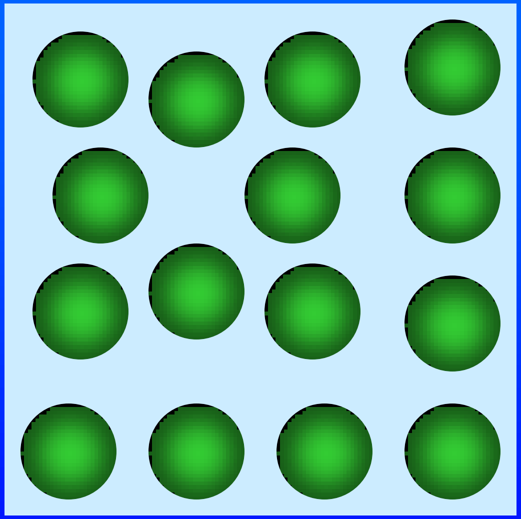
One type of defect is the ***point defect***.

There are three basic kinds of point defects.

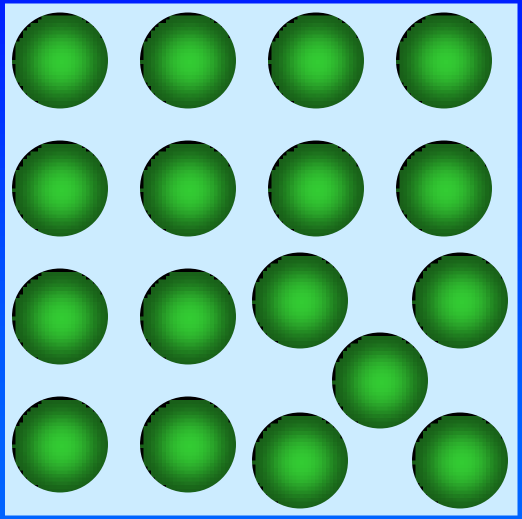


- (1) A vacancy.

Actually, a vacancy would probably look more like this:

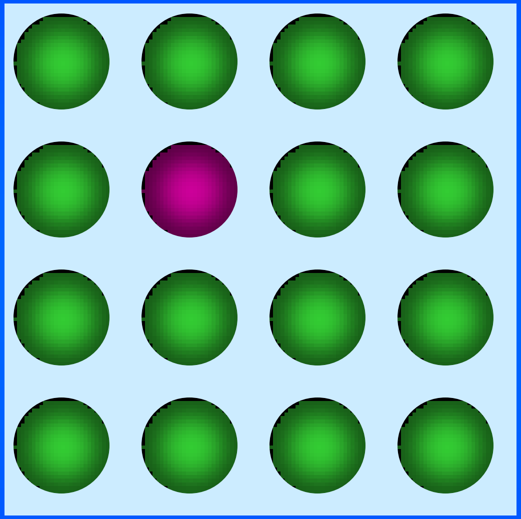


- (2) An interstitial.

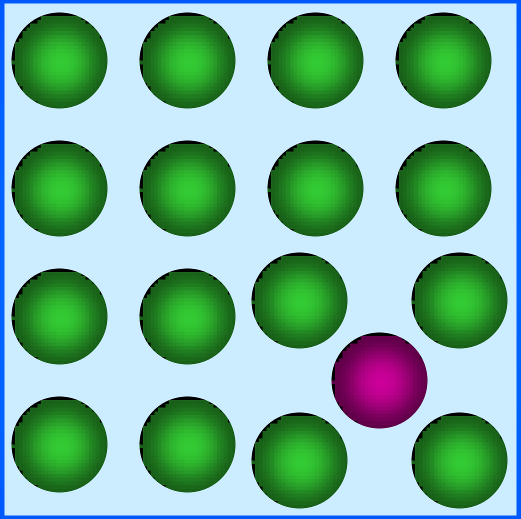


There is likely a vacancy somewhere else in the crystal, which supplied the interstitial atom.

- (3) An impurity, which could be either substitutional or interstitial.



substitutional



interstitial

Point defects makes diffusion in solids possible.

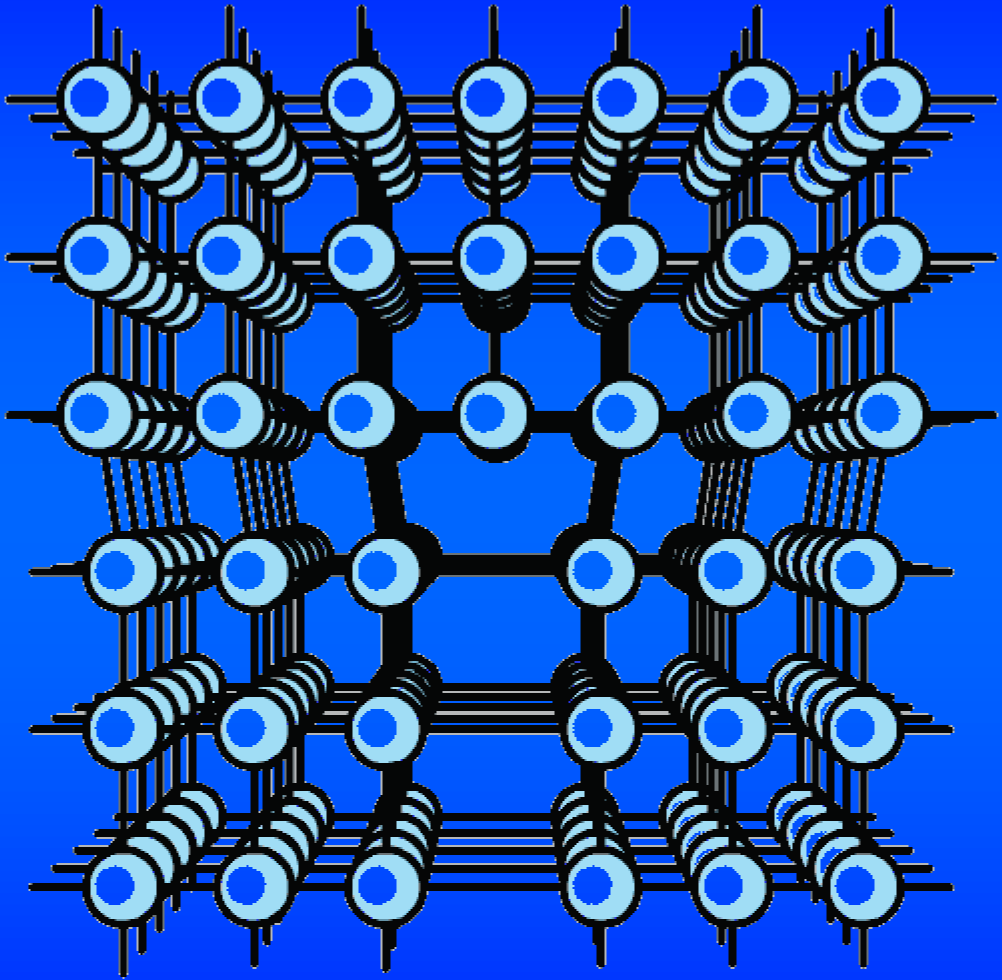
Either vacancies or interstitial atoms can migrate through a crystal.

Diffusion is strongly temperature dependent.

Higher dimensional defects include edge and screw dislocations. A dislocation occurs when a line of atoms is in the wrong place.

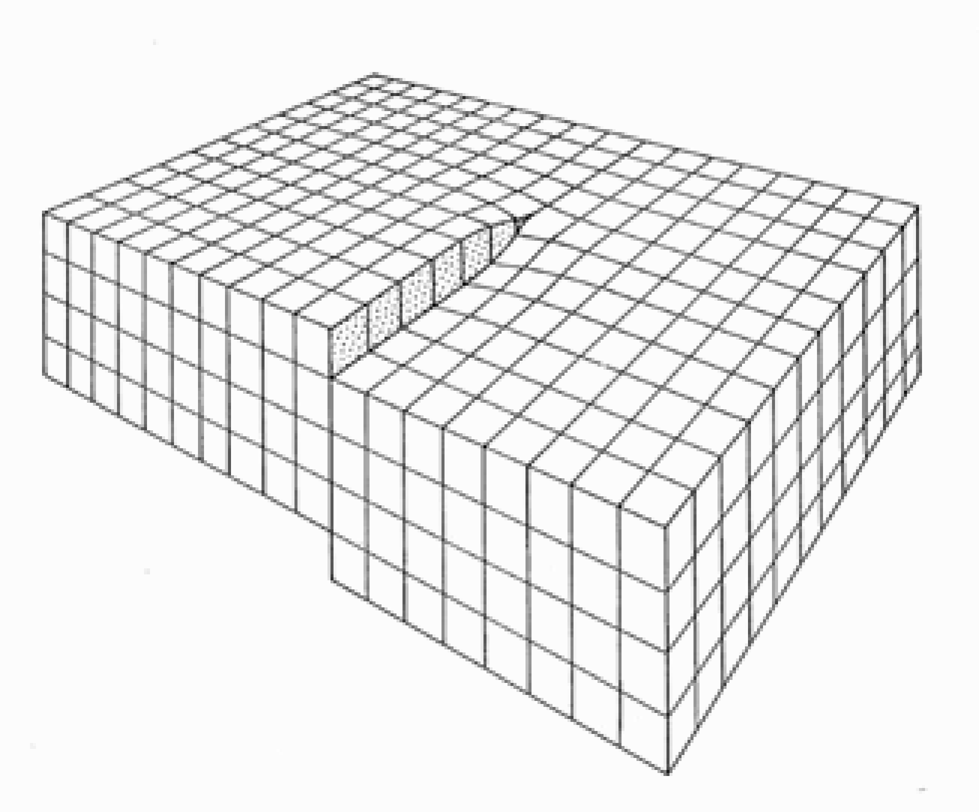
Dislocations are important but more difficult to deal with than point defects.

Edge dislocation are relatively easy to draw and visualize. See Figure 10.3.



http://uet.edu.pk/dmems/edge_dislocation.htm dead link spring 2005

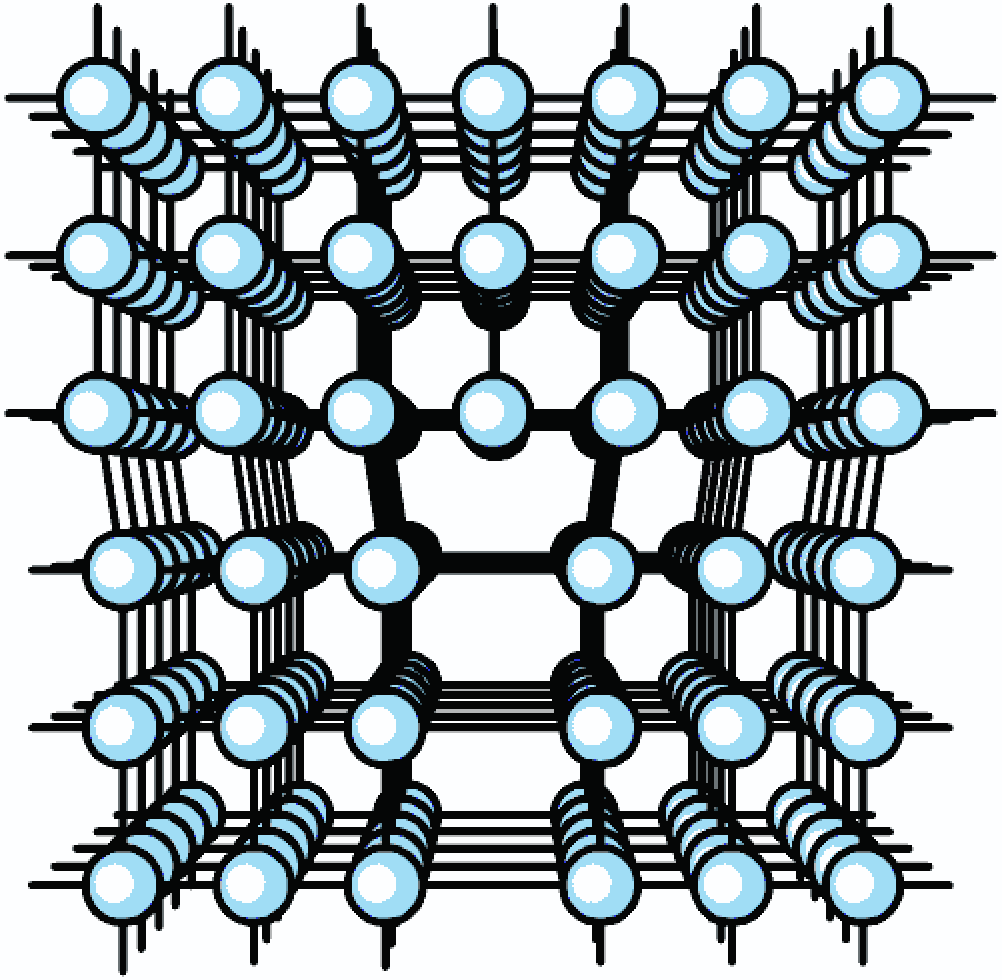
Screw dislocation are more difficult to draw. See Figures 10.4 and 10.5.



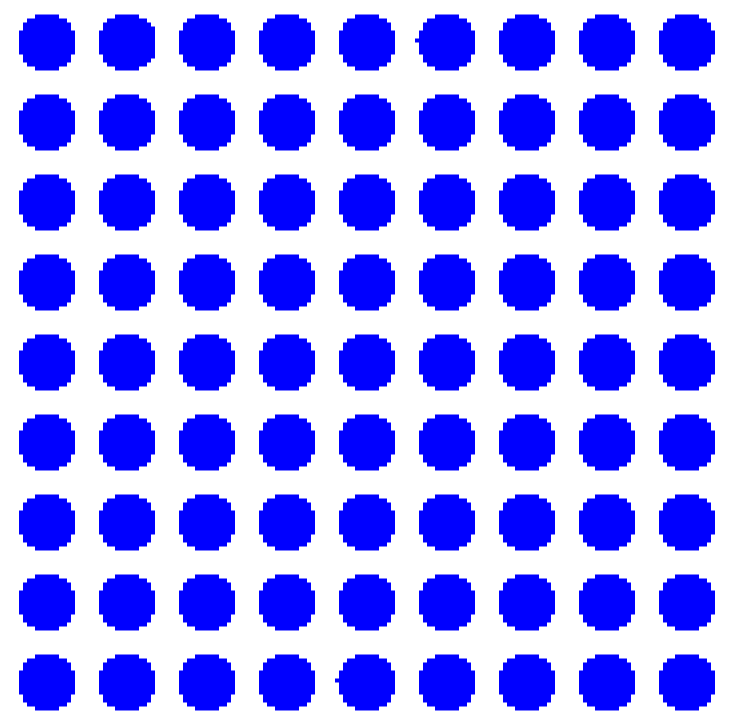
http://www.techfak.uni-kiel.de/matwis/amat/def_en/kap_5/backbone/r5_1_1.html

Atoms in crystals are not static, and neither are dislocations.

edge dislocation

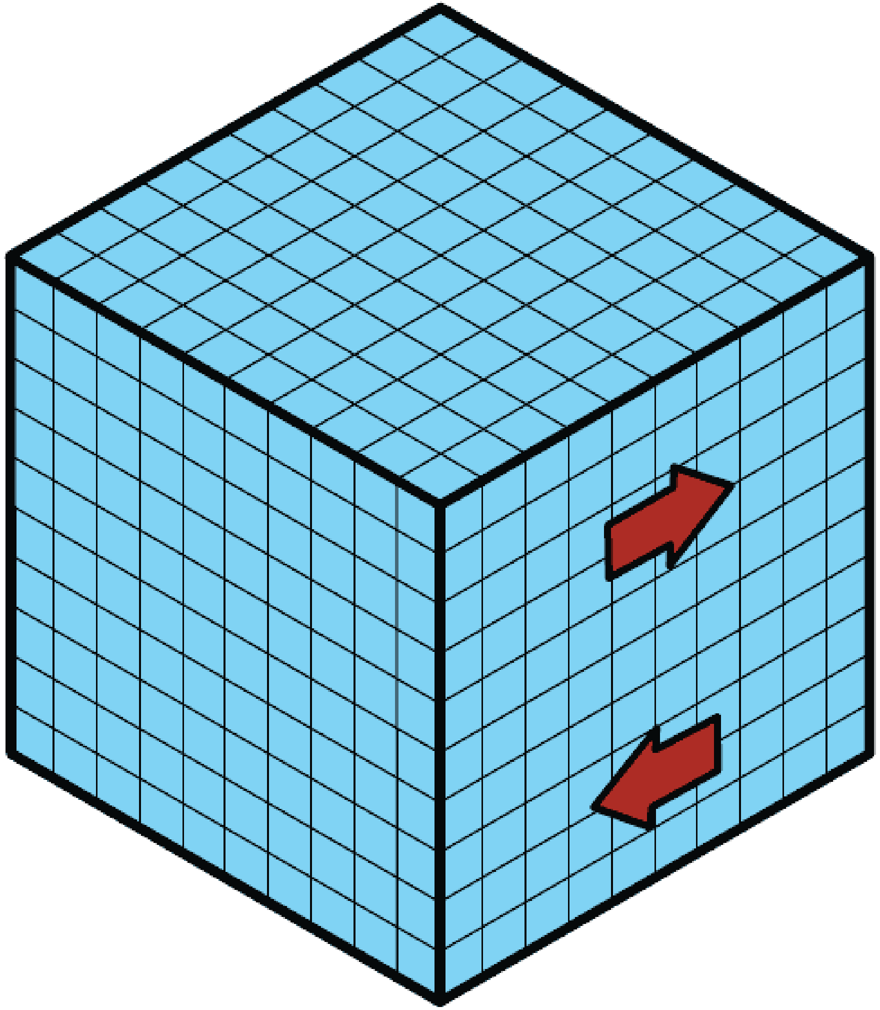


edge dislocation



http://www.techfak.uni-kiel.de/matwis/amat/def_en/kap_5/illustr/a5_1_1.html

screw dislocation



http://uet.edu.pk/dmems/screw_dislocation.htm

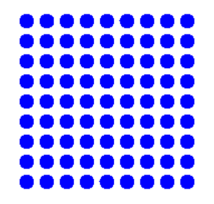
Work hardening (you have probably tried this at home).

Work hardening occurs when so many dislocations are formed in a material that they impede each others' motion.

Hard materials are usually brittle.

Annealing.

Heating (annealing) a crystal can remove dislocations. The edge dislocation animation from Germany we saw showed an edge dislocation being annealed out.



Annealing makes metals more ductile, and can be used to remove secondary phases in crystals.

10.2 Ionic Crystals

An atom with a low ionization energy can give up an electron to another atom with a high electron affinity. The result is an ionic crystal.

To calculate the stability of an ionic crystal, we need to consider all of the energies involved in its formation.

+	Positive energy is required to ionize an atom.
-	Energy is released when a highly electronegative atom gains an electron (energy becomes more -).
±	There are ± contributions to the energy from the Coulomb force between charged ions.
+	There is a + contribution to the energy from the overlap of core atomic electrons (the Pauli exclusion principle at work).

Remember that negative energies mean stable systems. If you add up all the above energies and get a more negative energy than for the separate, isolated atoms, then the ionic crystal is stable.

We'll go through that exercise soon.

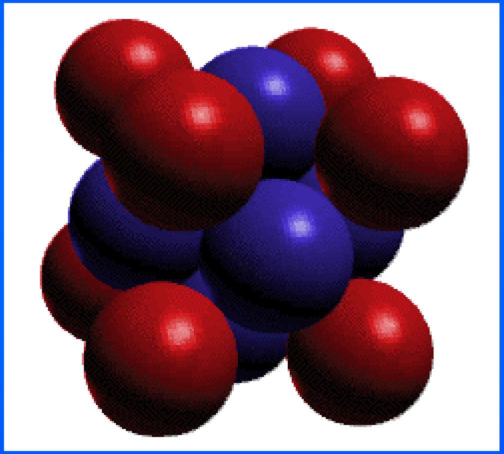
Ionic crystals are generally close-packed, because nature "wants" as many ions of different charge squeezed together as possible.

Like-charged ions never come in contact.

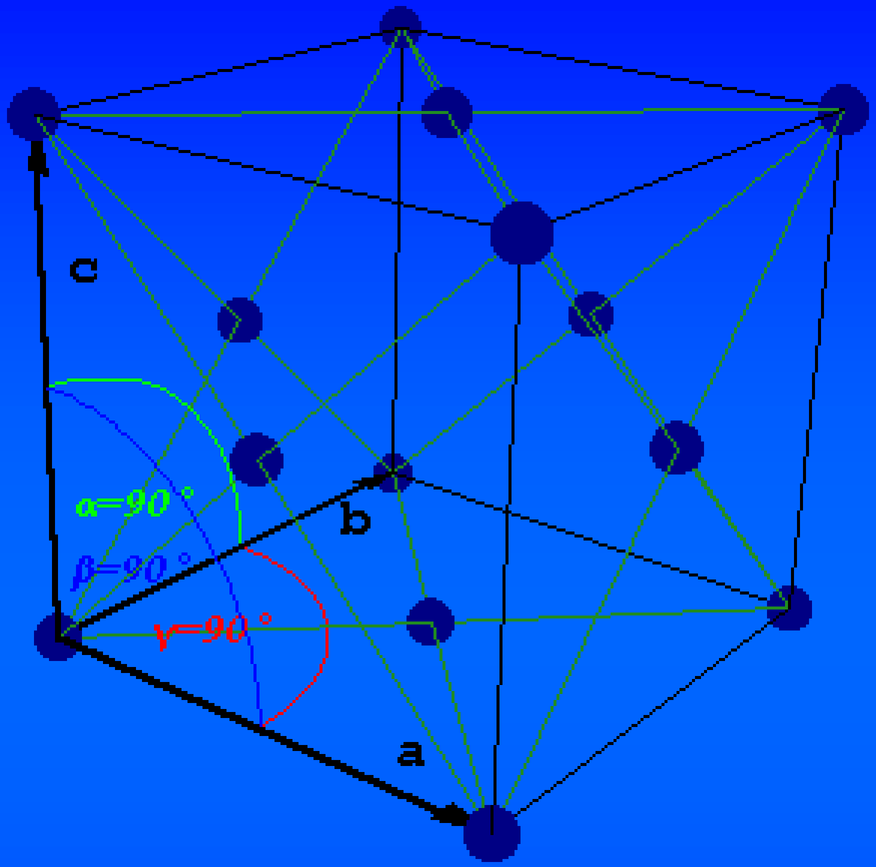
There are two primary structures for ionic crystals.

Face-centered cubic (fcc).

Face-Centered Cubic Structure

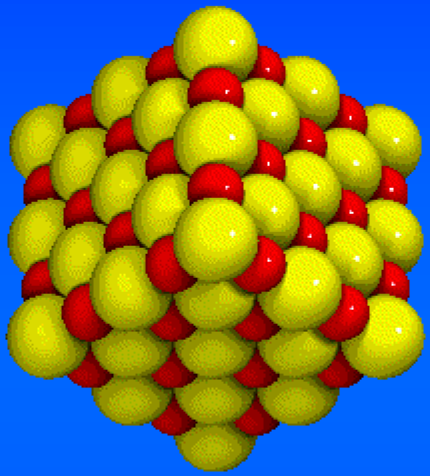


A sample static image from the
Animations for Introductory Chemistry CD-ROM
by John I. Gelder at Oklahoma State University

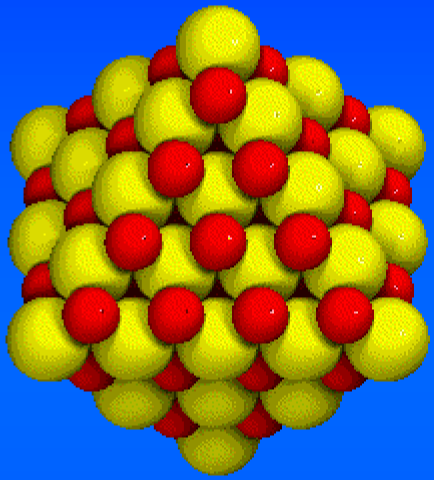


http://members.tripod.com/shiner17/Crystals/BravaisLattice/Cubic/FaceCenteredCubic.htm

An example of the fcc structure is sodium chloride (NaCl).



NaCl

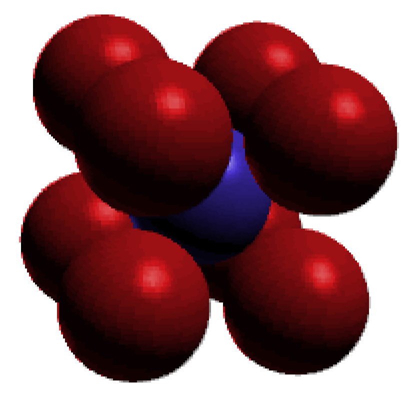


NaCl
a bit of the
front sliced off

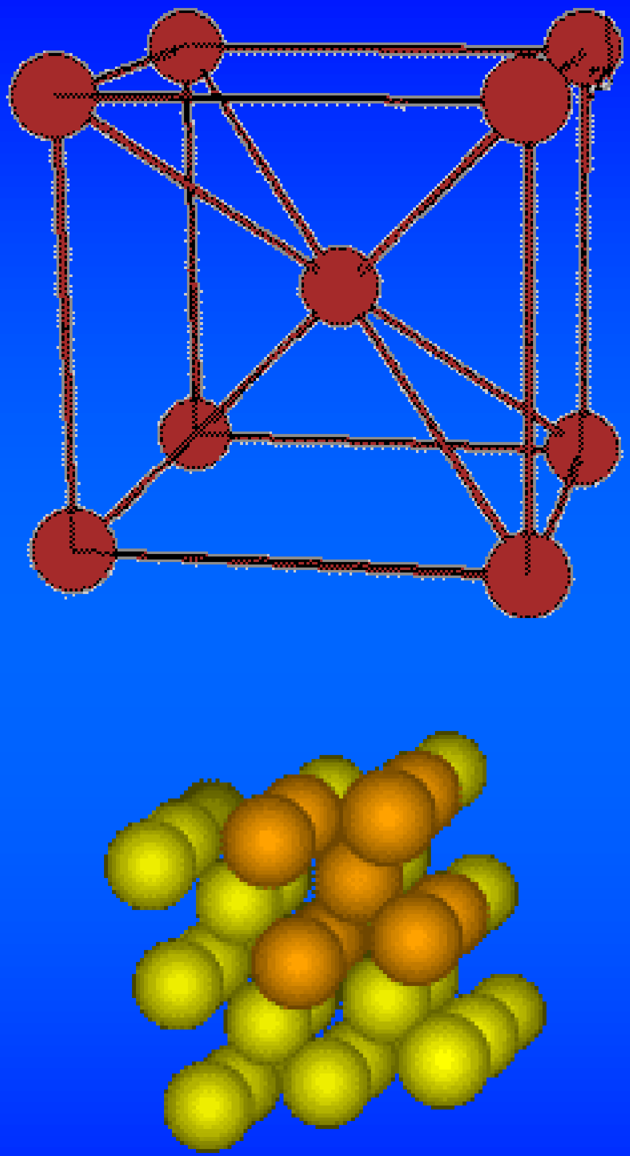
http://sbchem.sunysb.edu/msl/nacl.html

The other main ionic crystal structure is body-centered cubic (bcc).

Body-centered Cubic Unit Cell



A sample animation from the
Animations for Introductory Chemistry CD-ROM
by John I. Gelder at Oklahoma State University



An example of the bcc structure is cesium chloride (CsCl). Click here for a model you can manipulate.

It is not too difficult to calculate the energies involved in ionic bonding, so let’s do it.

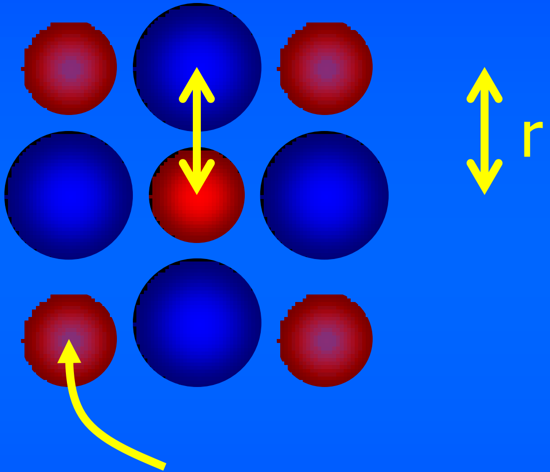
We begin by defining the ***cohesive energy*** of an ionic crystal as “the reduction in the energy per ion of the ionic crystal relative to the neutral atoms,” or “the energy per ion needed to break the crystal up into individual atoms.”

> Later Beiser implicitly generalizes this definition to all crystals.

Let's calculate the contribution to the cohesive energy from the Coulomb potential energy. Let's do it for an fcc structure, NaCl for example.

Let’s add up all contributions to the Coulomb energy from ion-ion interactions. Let's take a Na$^+$ ion as the reference* ion (NaCl is made of Na$^+$Cl$^-$ ions). We get the same result if we take a Cl$^-$ as the reference.

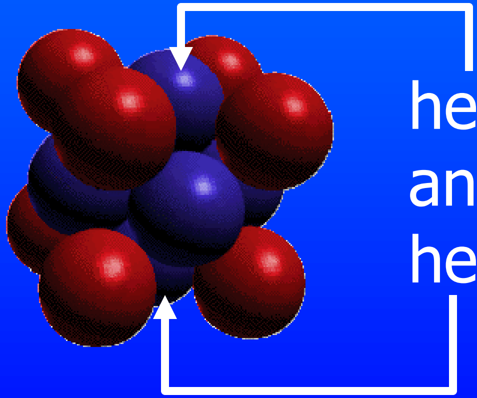
Here’s the reference ion.



showing these 4 Na’s just to help you get your bearings

Each Na+ ion has six Cl$^-$ nearest neighbors a distance r away. Here are four of them.

Where are the other two Cl’s?



here

and

here

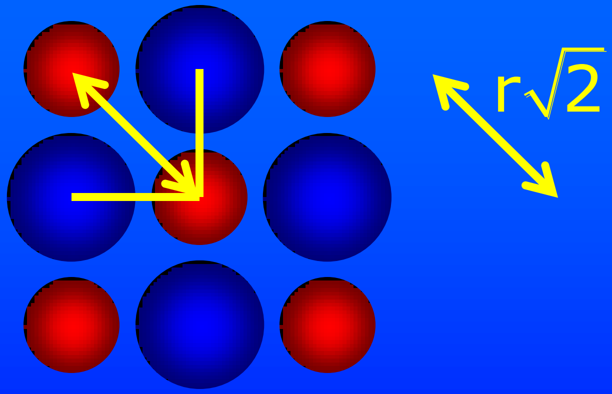
*Remember, the energy is calculated ***per ion***.

The contribution to the Coulomb potential from these six nearest neighbors is

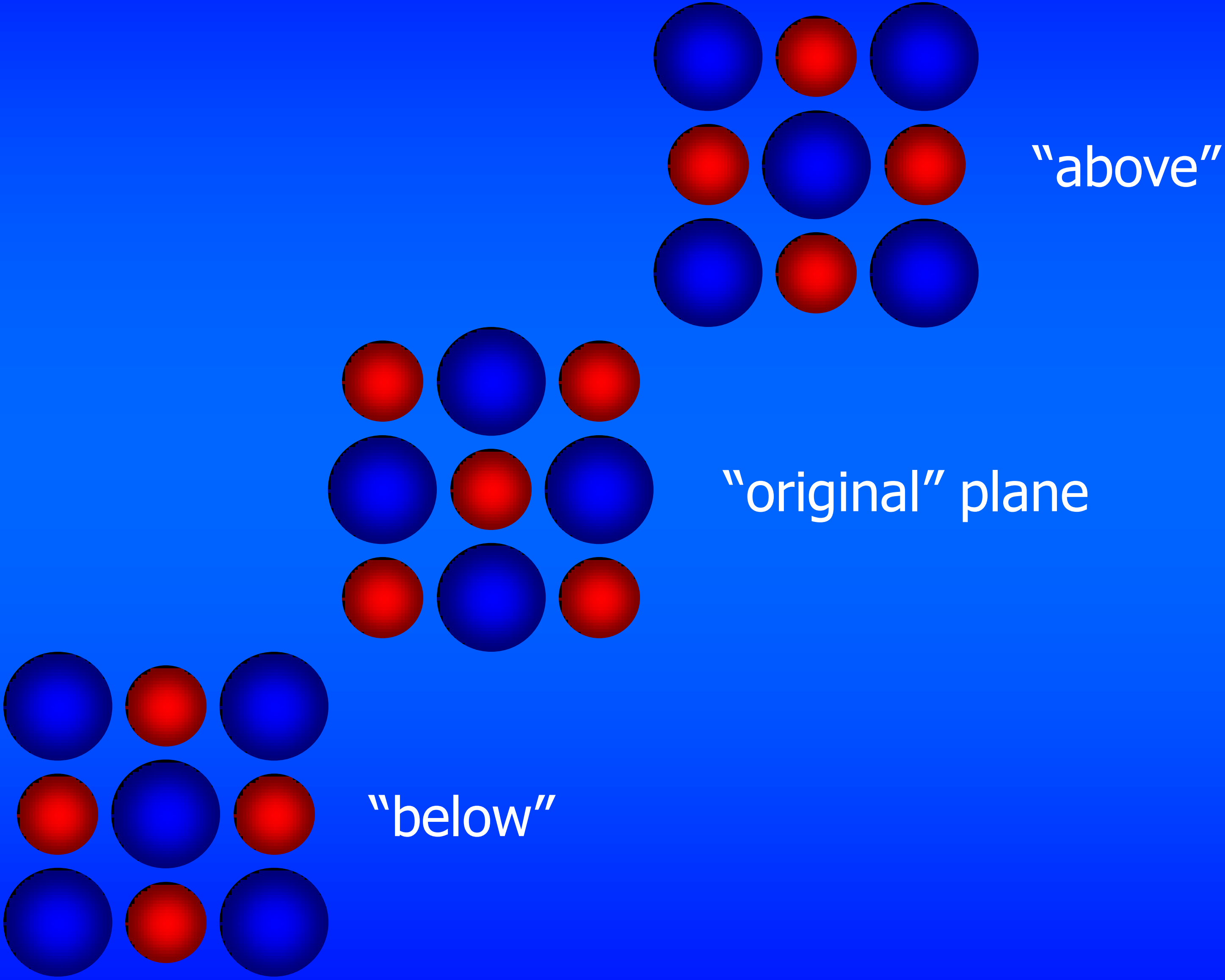
$$U_1 = \frac{6\,(+e)\,(-e)}{4\pi\varepsilon_0 r} = -\frac{6\,e^2}{4\pi\varepsilon_0 r} \;.$$

This represents a negative (more stable) contribution to the total energy.

Each Na^+ has 12 Na^+ next-nearest neighbors at a distance of $2^{1/2}r$. These are + ions, so the interaction is repulsive, and the contribution to the total energy is positive. This figure shows four of the next-nearest neighbors.



There are four more (red) in the plane above and four more in the plane below.



“above”

“original” plane

“below”

The contribution from the twelve next-nearest neighbors is

$$U_2 = + \frac{12\, e^2}{4\pi\varepsilon_0 r\sqrt{2}} \; .$$

This represents a positive (less stable) contribution to the total energy.

You could keep on like this for shell after shell. Pretty soon a pattern would emerge. After “many” shells, you get

$$U = -\frac{e^2}{4\pi\varepsilon_0 r}\left(6 - \frac{12}{\sqrt{2}} + \ldots\right) = -1.748\,\frac{e^2}{4\pi\varepsilon_0 r}$$

$$U = -\alpha\,\frac{e^2}{4\pi\varepsilon_0 r}$$

The constant α (which is constant only for a given type of structure) is known as the ***Madelung constant***. Beiser gives values of α for a couple of other structure types.

$$\alpha = \left(6 - \frac{12}{\sqrt{2}} + \ldots\right) = (6 - 8.485281 + \ldots)$$

The convergence of this series is very poor. You have to find a clever way to do this series if you want to calculate α with a reasonable amount of effort.

We've accounted for the Coulomb attraction. Beiser calls this $U_{coulomb}$ (using U instead of V as in the previous edition) so let's make it official:

$$\boxed{U_{coulomb} = -\alpha \frac{e^2}{4\pi\varepsilon_0 r}}$$

This isn’t the whole story!

$$U_{coulomb} = -\alpha \frac{e^2}{4\pi\varepsilon_0 r}$$

Note the - sign in the equation for U. The net coulomb interaction is attractive.

In fact, the closer the ions, the more negative the energy. The more negative, the more stable. What is the logical conclusion from this observation?

As r gets smaller and smaller, electron shells start to overlap, and electrons from different atoms share the same potential.

What does Pauli have to say about that?

Electrons would have to be promoted to higher energies to allow atoms to come closer together. The result is a more positive energy, i.e., a less stable crystal.

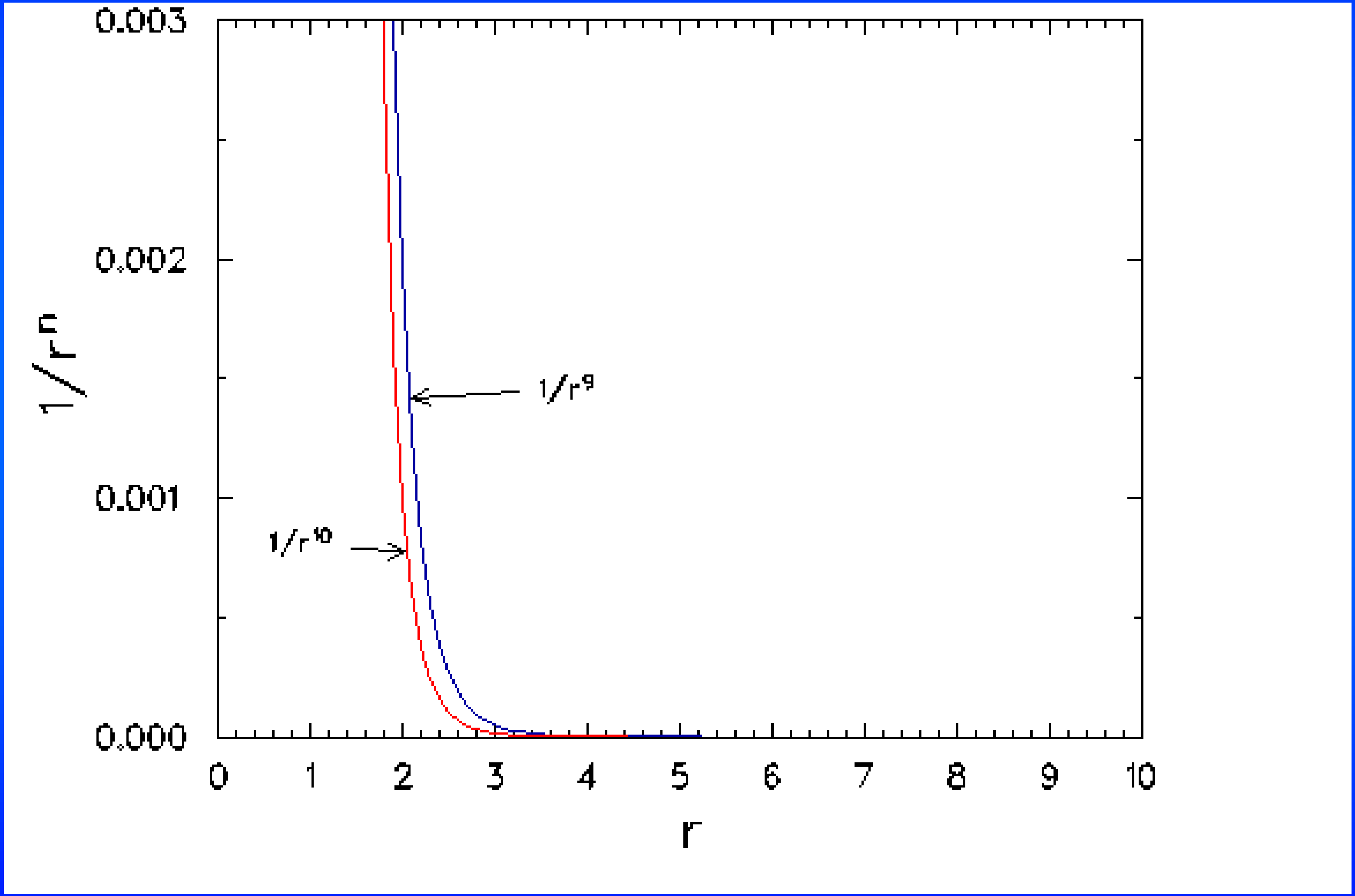
So we need to account for the repulsive forces that take over when electron shells start to overlap, and different electrons share the same set of quantum numbers.

We ***model*** this repulsive force with a potential of the form

$$\boxed{U_{repulsive} = \frac{B}{r^{n}},}$$

where n is some exponent. The exact value of n isn't too critical (see the figure on the next page).

A simple scale factor change could make $1/r^9$ and $1/r^{10}$ look nearly the same.



With the electron overlap repulsive energy accounted for, the potential energy of interaction of our Na^+ reference ion with all the other ions is

$$U_{total} = U_{coulomb} + U_{repulsive} = -\alpha \frac{e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n}.$$

Even though this says U_{total}, we are not done! Do not use this equation in a test/quiz problem!

For one thing, we have accounted for the total energy of interaction of the ions (that's what "total" means), but we haven't accounted for the energy required to ionize the neutral atoms.

For another thing, we have this adjustable parameter, B. (You do remember adjustable parameters?)

$U_{coulomb}$ was called $V_{lattice}$ in the previous text edition, so you'll see that terminology in homework solutions and prior exams.

At equilibrium the energy is minimized, which allows us to find B in terms of α and the equilibrium near-neighbor separation r_0.

$$0 = \left.\left(\frac{\partial U}{\partial r}\right)\right|_{r = r_0} = \frac{\alpha e^2}{4\pi\varepsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}}$$

$$\frac{\alpha e^2}{4\pi\varepsilon_0 r_0^2} = \frac{nB}{r_0^{n+1}}$$

$$B = \frac{\alpha e^2}{4\pi\varepsilon_0 n} r_0^{n-1}$$

In a sense, we have “adjusted” B to get the right answer (energy minimum at equilibrium).

Plugging B back into the expression for U gives the total potential energy at equilibrium separation. Beiser used to call it the lattice energy, V_{lat}. Now he calls it U_0.

$$\boxed{U_0 = -\alpha \frac{e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right).}$$

U_0 is the reduction in the energy of the ionic crystal relative to the ions at infinite separation.

We set out to calculate the cohesive energy, so we are **still** not done yet.

The cohesive energy, $E_{cohesive}$, takes into account the energy needed to create the ions.

Beiser doesn’t give an equation for the cohesive energy, so I’ll make one up. The energy of the ions is U_0. The energy to create a Na^+ ion is the ionization energy of Na. I’ll call that U_{ion}.

When a Cl atom combines with an electron to form Cl^-, energy is actually released. Chemists call this energy the electron affinity. I’ll write that U_{ea}.

$$\boxed{E_{coh,\, pair} = U_0 + U_{ion} + U_{ea} \, .}$$

You’ll see what “pair” means in a minute. Also, the numerical value of E_{coh} had better be negative, right?

U_{ion} is positive, because it is energy put into the crystal. U_{ea} is negative, because it is energy released from the crystal.

Part of your homework/quiz/exam responsibility is to get the right signs on these energies!

Oh, and one more thing. We've calculated the coulomb energy for our reference Na^+ with all other ions in the crystal, one pair at a time. Thus, U_0 is the energy per ion pair.

Also, U_{ion} is the energy to make Na^+ and U_{ea} is the energy released on making Cl^-. Thus $U_{ion} + U_{ea}$ represents the energy needed to make a Na^+Cl^- pair.

Beiser defines the cohesive energy as "per ion." Thus finally (and officially):

$$\boxed{E_{coh} = \frac{U_0 + U_{ion} + U_{ea}}{2}.}$$

Beiser on page 342 calculates the cohesive energy for NaCl.

A “typical” value for n is 9. The equilibrium distance r_0 between Na^+ and Cl^- ions is 0.281 nm.

Beiser calculates numerical values for the different energies, and then combines them to get the cohesive energy.

We know it’s better to do the problem algebraically first, and get numerical results only at the very end.

Let’s do it Beiser’s way here.

$$U_0 = -\alpha \frac{e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

only for NaCl structure!

$$U_0 = -(1.748)\frac{\left(1.6\times10^{-19}\right)^2}{4\pi\left(8.85\times10^{-12}\right)\left(0.281\times10^{-9}\right)}\left(1-\frac{1}{9}\right)$$

$$U_0 = -1.27\times10^{-18}\ \text{joules} = -7.96\ \text{eV}\ .$$

The ionization energy of Na is 5.14 eV and the electron affinity of Cl is 3.61 eV. With the correct signs, the energies are +5.14 eV and -3.61 eV. Make sure you understand why! Many of you will lose several points because of sign errors.

$$E_{coh} = \frac{U_0 + U_{ion} + U_{ea}}{2}$$

$$E_{coh} = \frac{-7.96\ \text{eV} + 5.14\ \text{eV} - 3.61\ \text{eV}}{2}$$

$$E_{coh} = -3.21\ \text{eV}$$

Great news! We got a – sign for the cohesive energy. You can sleep well at night knowing that NaCl is stable.

Wonder how it compares with experiment? The measured value is -3.28 eV. That's a 2% error. For this kind of calculation, the agreement is good.

Why did I bother with this rather lengthy calculation to show that NaCl is stable, when we already know it is stable?

Stupid?

Physicists may do stupid things, but we are not stupid.

Designer molecules! If you have an application that needs a compound with special properties, do you spend millions in the lab and hope you stumble across it… or do you spend a few hundred thousand on computational modeling that tells you what kind of compound to make?

The calculation we did is your first step towards making designer molecules.

Some properties of ionic crystals, which Beiser mentions briefly:

- They have moderately high melting points.
- They are brittle due to charge ordering in planes.
- They are soluble in polar fluids.