Lecture 2

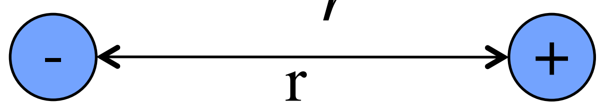
Bonds – Chapter 5

- Reading Assignment
  - Chapter 5
- Simplest atom is the Hydrogen Atom
  - 1 electron + 1 proton
- What keeps the atom together?
  - All systems seek to be at the energy minimum
  - Somehow the electron in its orbit around the proton is a minimum energy configuration compared to closer or farther away.

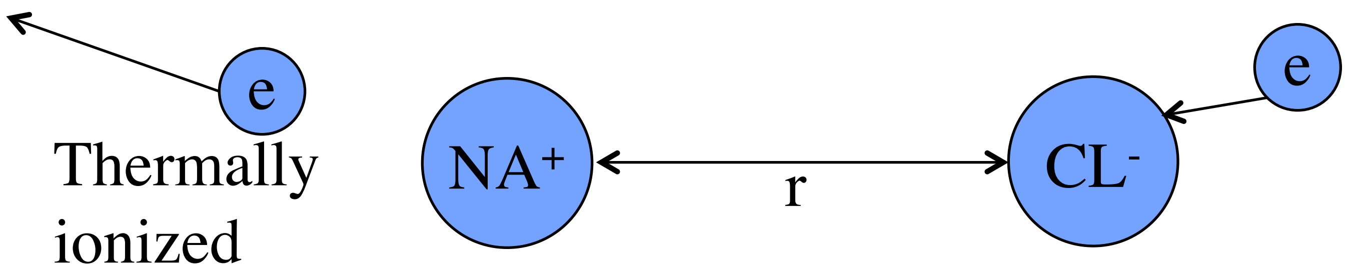
Properties of Bonds

- Coulomb attraction between opposite charges

$$F \propto \frac{1}{r^2}$$

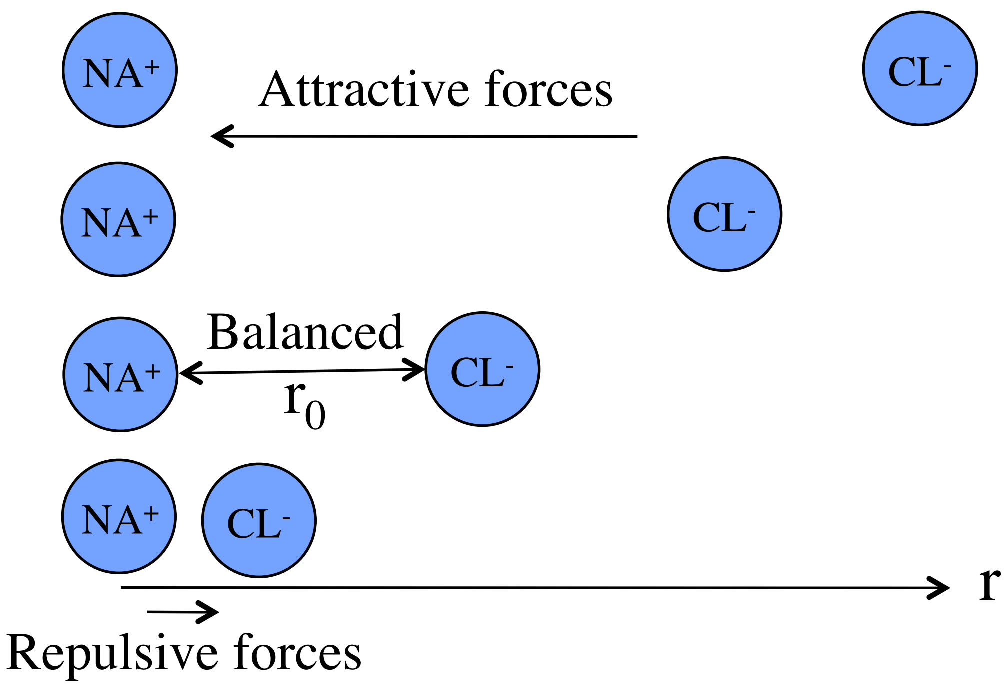


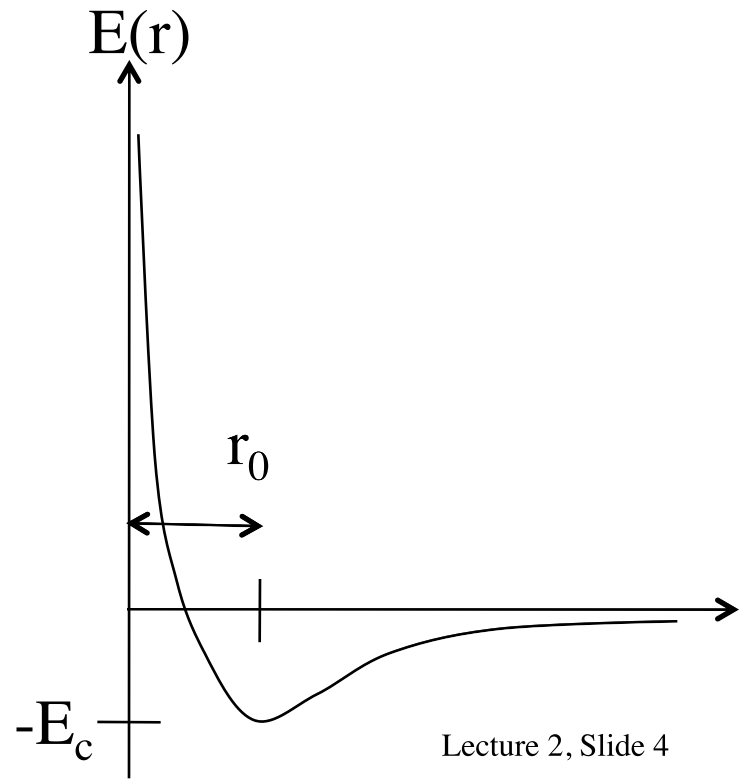
- How about Ionized atoms?



Equilibrium

- Equilibrium
  - Where is the minimum energy distance for two oppositely charged particles?





Attractive vs. Repulsive Forces

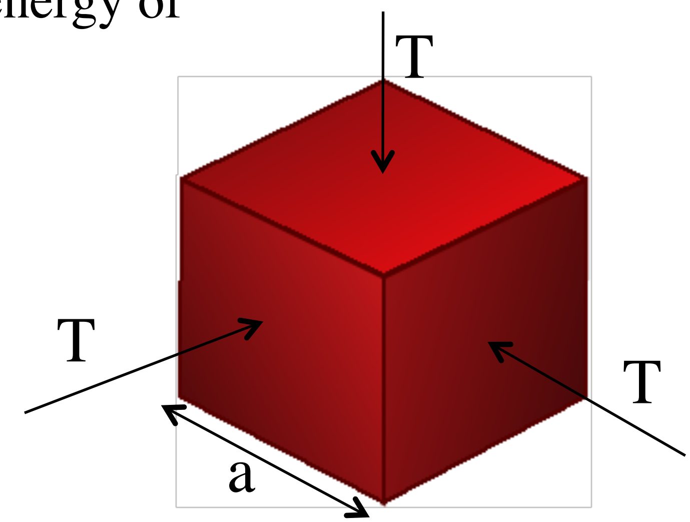
- We understand the electrostatic attraction, but why do the particles or ions repel each other below a certain distance?
  - Atoms will distort due to rules of electronic states and the atoms will want to push each other away to minimize this distortion
  - For particles, there is a momentum associated with a state, this momentum generates a force outwards, in a direction opposite from electrostatic attractive
- But this is a mechanical picture – there is also a more complex quantum mechanical picture.

Crystals

- We can also look at why atoms might organize themselves into a crystalline structure as the lowest energy formation
  - Consider *r* as the inter-atomic distance -***Equilibrium Position***
  - If we squeeze the atoms together (put energy into the lattice) they will start to resist (energy will increase) and when we let go they will return to the minimum energy state – ***Equilibrium Position***
  - Define the elastic properties of the solid as the response to external mechanical forces

Bulk Elastic Constant of a Solid

- Consider a cubic piece of material, density N_a per volume, and energy per atom E_0
- What is the energy change under isotropic compression (equal force from all sides)?
- A cube of linear dimension *a*, uniformly compressed by stress T applied to each of 6 sides, will have a net increase in energy of



$$E(r_0) = N_a a^3 E(r_0)$$

$$E(r_0 - \Delta r) = N_a a^3 E(r_0 - \Delta r)$$

Expanding into a Taylor series about r_0

$$E(r_0 - \Delta r) \approx E(r_0) + \frac{1}{2}\left(\frac{\partial^2 E}{\partial r^2}\right)_{r=r_0}\left(\Delta r^2\right) + \cdots$$

The net increase in energy is

$$\Delta E = \frac{1}{2}\left(\frac{\partial^2 E}{\partial r^2}\right)_{r=r_0}\left(\Delta r^2\right)$$

Bulk Elastic Constant of a Solid

- If each atom distance compresses Δr, then the total change in linear dimension is $(a/r_0)\ \Delta r$ and each face compresses by $(1/2)\ (a/r_0)\ \Delta r$ and the total work done to compress the material is

$$\text{Total Work Done on Material} = \frac{6}{2} T a^2 \left(\frac{a}{2r_0}\right) \Delta r$$

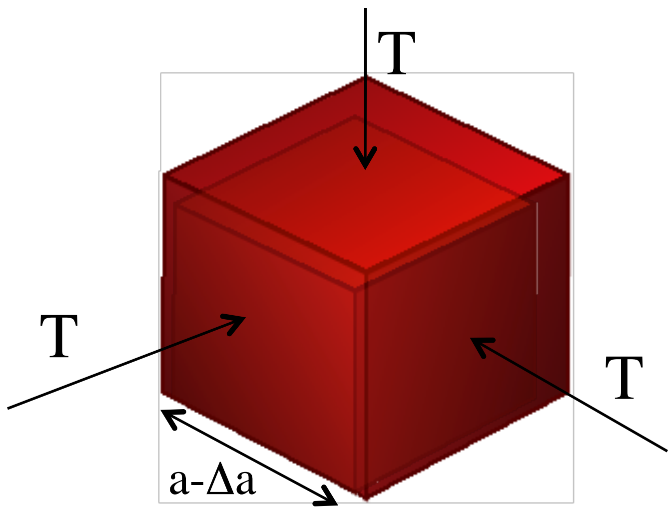
- From the Taylor expansion we can equate the total energy increase and the work done to solve for T

$$T = \frac{1}{3r_0}\left(\frac{\partial^2 E}{\partial r^2}\right)_{r=r_0} \frac{\Delta r}{r_0}$$

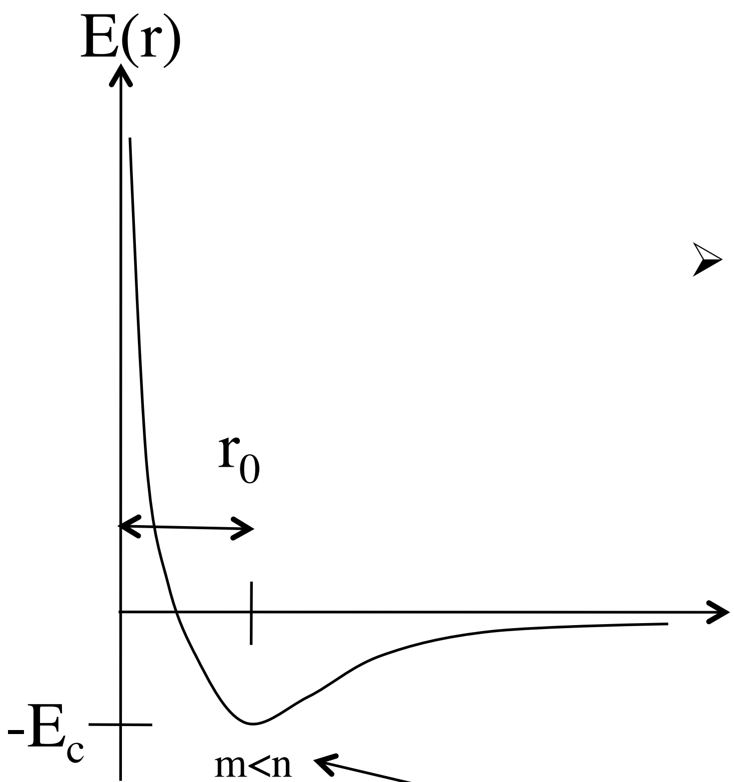
- The bulk elastic modulus c is defined as

$$T = c\left(\frac{\Delta a^3}{a^3}\right) \cong c\left(\frac{3\Delta a}{a}\right) = c\left(\frac{3\Delta r}{r_0}\right)$$

Hook's Law ⇒ $$\boxed{c = \frac{1}{9r_0}\left(\frac{\partial^2 E}{\partial r^2}\right)_{r=r_0}}$$



Energy Minimum



- Approximating the curve to the left by

$$E(r) = \underbrace{\frac{A}{r^n}}_{\text{repulsion}} - \underbrace{\frac{B}{r^m}}_{\text{attraction}}$$

- The energy minimum is obtained by differentiating with respect to r and setting equal to zero

$$\frac{dE(r)}{dr} = -n\frac{A}{r^{n-1}} + m\frac{B}{r^{m-1}} = -nr\frac{A}{r^n} + mr\frac{B}{r^m} = 0$$

$$mr\frac{B}{r^m} = nr\frac{A}{r^n}$$

$$\frac{m}{n}\frac{B}{r^m} = \frac{A}{r^n} = E(r_0) + \frac{B}{r^m}$$

$$E(r_0) = E_c = \frac{B}{r_0^m}\left(\frac{m}{n} - 1\right)$$

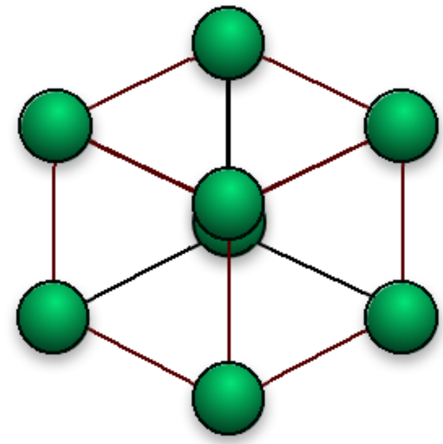
Bond Types

- Ionic bonds
- Metallic bonds
- Covalent bond
- Van der Waals bond
- Mixed bonds

Ionic Bonds

- How much energy would it take to take this crystal apart?
  - This is the ***Cohesive Energy*** E_c
  - Summing the electrostatic forces of the crystal
    - 6 Cl ions bonded to each Na ion at distance *a* $$6\left(-\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a}\right)$$
    - 12 Na ions bonded to each Na ion at a distance *a sqrt(2)* $$12\left(\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a\sqrt{2}}\right)$$
    - 8 Cl ions bonded to each Na ion at a distance *a sqrt(3)*
    - Keep going ……

Cubic Lattice Crystal



$$E_c = 6\left(-\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a}\right) + 12\left(\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a\sqrt{2}}\right) - 8\left(\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a\sqrt{3}}\right) + \cdots$$

M is the *Madelung* Constant

$$E_c = -\frac{q^2}{4\pi\varepsilon_0}\left(\frac{6}{a} - \frac{12}{a\sqrt{2}} + \frac{8}{a\sqrt{3}} + \cdots\right)$$

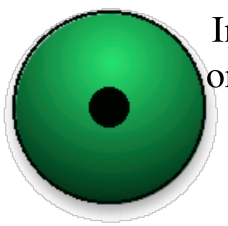
$$E_c = -M\frac{q^2}{4\pi\varepsilon_0 a}$$

Metallic Bonds

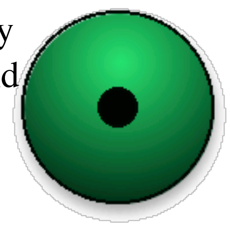
- A metal can be thought of as a lattice of thermally vibrating atoms with a sea of free, conducting electrons scattering off each other and the fixed atoms.
- But these electrons are confined for the most part to the metal and we have to do some work to remove them from the metal
- The metallic bond is similar to the ionic bond in that electrostatic forces generated by the moving electrons play a key role in keeping the lattice together

Covalent Bond

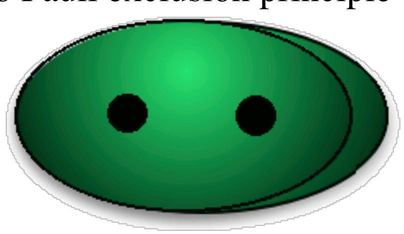
- Sometimes called the ***Valence*** bond
- Sharing of electrons between atoms
  - But really from a quantum mechanical state, a sharing of electron states
- Consider for example two Hydrogen atoms that come close to one another



Individual with same e energy orbit. Incomplete valance band will accept a new electron readily



Each atom wants to take e from other atom, but there is no preference, so they must share. Since they occupy same space, they must adjust according to Pauli exclusion principle



Covalent Bond

- In general the Covalent bond is very strong
  - Electrons are not easily removed (bond broken) or free to conduct
  - Insulator
- In some material systems (compound) the covalent bond is more easily broken and the electrons freed by breaking this bond can conduct
  - Semiconductor

Covalent Bond Examples

$$C: 1s^2, 2s^2, 2p^2$$

$$Si: 1s^2, 2s^2, 2p^6, 3s^2, 3p^2$$

$$Ge: 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3p^6, 3d^{10}, 4s^2, 4p^2$$

- What do these atoms have in common?
  - 2 s and 2 p electrons in the outer shells
  - Symmetry of outer s electronics is broken and minimum energy state is for them to join the p electrons in the other atom
  - For this example, C, Si, Ge, there are essentially 4 electrons arranged symmetrically around the atoms in the crystal forming the covalent bonds