



Lecture 2

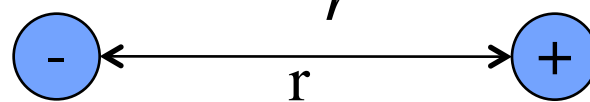
Bonds – Chapter 5



- 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.

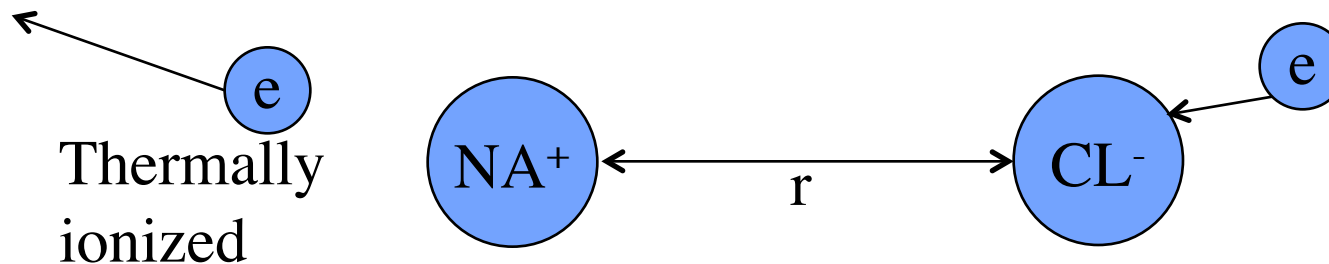
Properties of Bonds

- Coulomb attraction between opposite charges

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


A diagram showing two blue circles representing opposite charges. The left circle contains a minus sign (-) and the right circle contains a plus sign (+). A horizontal double-headed arrow connects the centers of the two circles, with the letter 'r' centered below it, representing the distance between the charges.

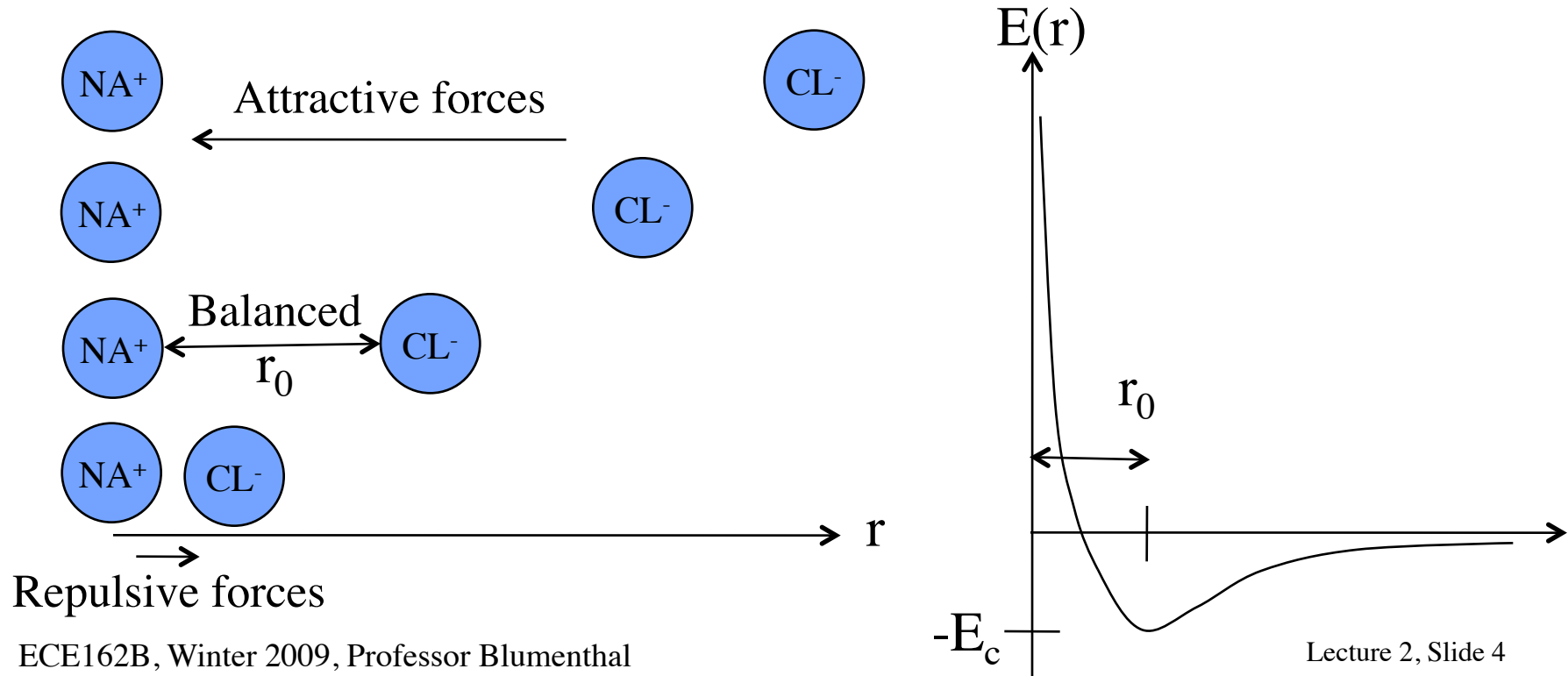
- How about Ionized atoms?



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

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

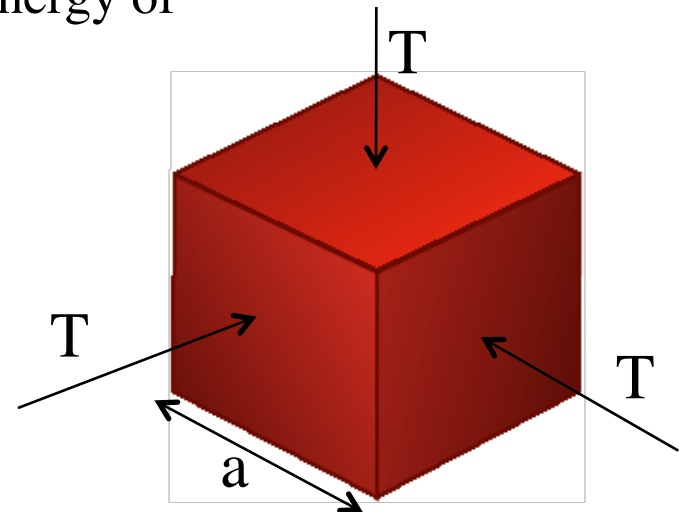
$$E(r_0 - \Delta r) = N_a a^3 E(r_0 - \Delta r)$$

Expanding into a Taylor series about r_0

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

The net increase in energy is

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



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

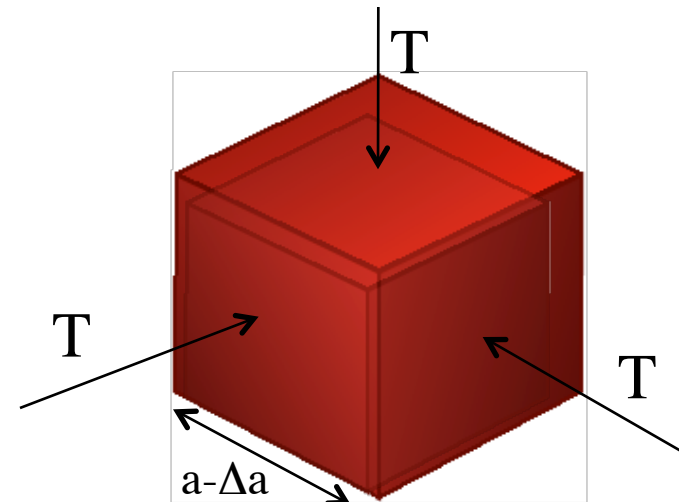
$$T = \frac{1}{3r_0} \left(\frac{\partial^2 E}{\partial r^2} \right)_{r=r_0} \frac{\Delta r}{r_0}$$

- The bulk elastic modulus c is defined as

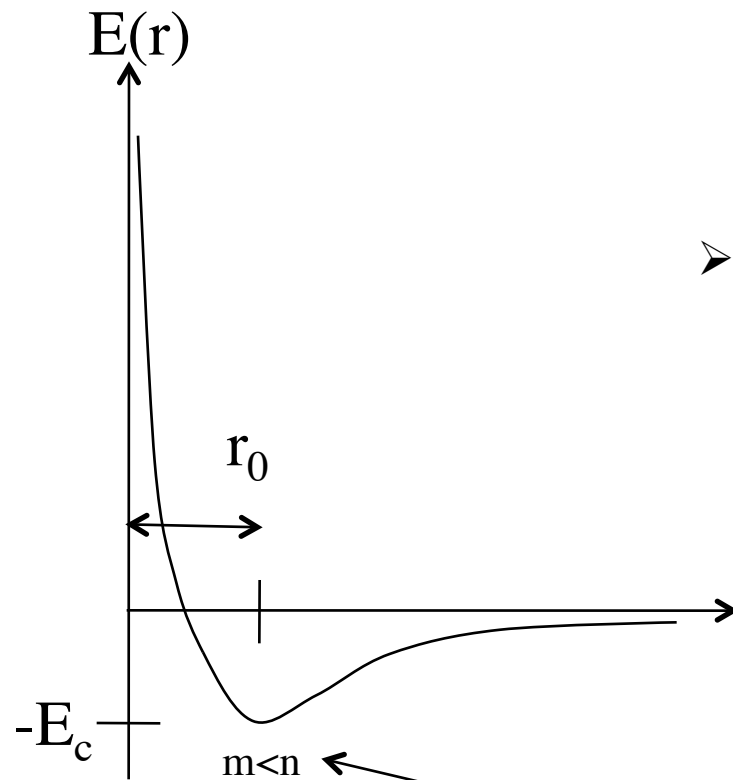
$$T = c \left(\frac{\Delta a^3}{a^3} \right) \cong c \left(\frac{3\Delta a}{a} \right) = c \left(\frac{3\Delta r}{r_0} \right)$$

Hook's
Law $\Rightarrow$

$$c = \frac{1}{9r_0} \left(\frac{\partial^2 E}{\partial r^2} \right)_{r=r_0}$$



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

$$6 \left(-\frac{q^2}{4\pi\epsilon_0} \frac{1}{a} \right)$$

- 12 Na ions bonded to each Na ion at a distance $a \sqrt{2}$

$$12 \left(\frac{q^2}{4\pi\epsilon_0} \frac{1}{a\sqrt{2}} \right)$$

- 8 Cl ions bonded to each Na ion at a distance $a \sqrt{3}$

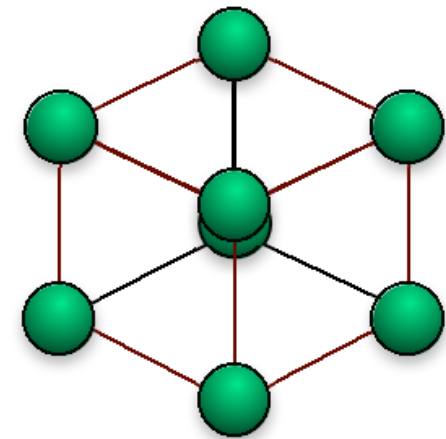
- Keep going $E_c = 6 \left(-\frac{q^2}{4\pi\epsilon_0} \frac{1}{a} \right) + 12 \left(\frac{q^2}{4\pi\epsilon_0} \frac{1}{a\sqrt{2}} \right) - 8 \left(\frac{q^2}{4\pi\epsilon_0} \frac{1}{a\sqrt{3}} \right) + \dots$

M is the
Madelung
Constant

$$E_c = -\frac{q^2}{4\pi\epsilon_0} \left(\frac{6}{a} - \frac{12}{a\sqrt{2}} + \frac{8}{a\sqrt{3}} + \dots \right)$$

$$E_c = -M \frac{q^2}{4\pi\epsilon_0 a}$$

Cubic Lattice Crystal



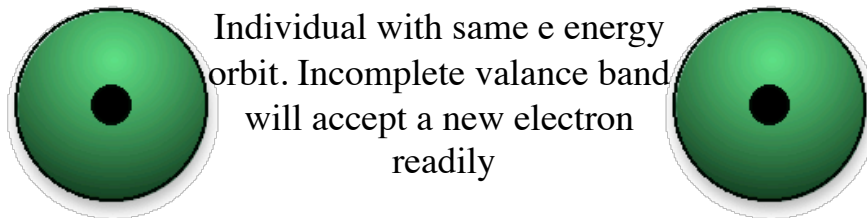
Metallic Bonds



- 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



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

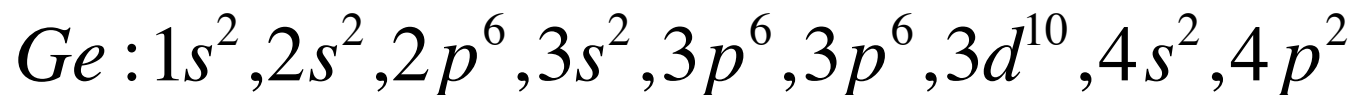
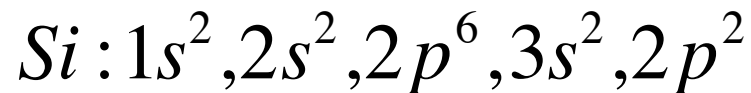
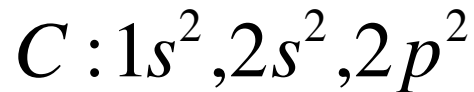


Covalent Bond



- 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



- 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

Van der Waals Forces



- What happens when we have an electrically neutral atom (not ionized) and there is no attraction to neighboring electrons?
- How do neutral atoms form bonds?
- The electron position density function fluctuates in time, forming a displacement between the electron and nucleus
 - This is called an oscillating dipole
- One dipole will generate a field (static or dynamic) that will distort nearby atoms into becoming dipoles (like oppose, opposites attract).
- Tendency on average is for attraction or the Van der Waals Force.