ECE 340
Lecture 4: Bonding Forces and Energy Bands

Class Outline:

- Crystal Diffraction
- Crystal Bonding
- Energy Band Formation
Key Questions

• Why is the Bohr model useful?
• What is the Schrödinger equation?
• What is a wavefunction?
• What are the most common chemical bonds?
• What are energy bands?
• What is an energy gap?
Crystal Diffraction

Last time, we discussed crystal lattices and structure. How can we determine this?

- Crystal structure is determined in experiment by studying the diffraction of suitable wave sources from particular sets of crystal planes.

- X-ray diffraction is most widely exploited in practice and arises from the interaction of the incoming wave with the electron cloud of each atom in the crystal.

- SCHEMATIC ILLUSTRATION OF X-RAY DIFFRACTION BY AN ATOM IN A CRYSTAL.

- THE ELECTRIC FIELD ASSOCIATED WITH THE INCOMING X-RAY ACCELERATES THE CLOUD OF ELECTRONS THAT SURROUND THE ATOM.

- THE ACCELERATED ELECTRONS THEN_EMIT_SO-CALLED SECONDARY X-RAYS WITH THE SAME PHASE AND WAVELENGTH AS THE INCIDENT RADIATION.

- WE MAY THEREFORE CONSIDER EACH ATOM IN THE CRYSTAL TO BE A SOURCE OF SECONDARY WAVES.

- THE STRENGTH OF THE SECONDARY X-RAYS IS DETERMINED BY THE SCATTERING POWER OF THE ATOM WHICH QUANTITY IS KNOWN AS THE ATOMIC FORM FACTOR.
Crystal Diffraction

The incident rays will scatter off the crystal.

- The CRUCIAL feature of the atomic form factor is that it is a STRONG function of scattering angle because the atom does NOT scatter X-rays in an isotropic manner.
- The reason for the anisotropic scattering is the FINITE size of the atom itself which is COMPARABLE to the wavelength of the X-rays.
  - Consequently secondary X-rays that leave the atom from different parts of the electron cloud are NOT in exact phase with each other.
  - Since the phase difference is more significant for the more backscattered waves the form factor decreases with increasing scattering angle.

The form factor essentially measures the scattering power of an atom.

- The form factor decreases with increasing scattering angle indicating that X-rays are most likely to be scattered in the forward direction.
- This variation is illustrated schematically here.
Crystal Diffraction

Now consider an incident beam of x-rays...

- Each plane causes a reflection of a small portion of the incident rays.
  - This number is usually a few percent of the total incident beam.
- Waves in successive planes interfere with one another
  - This process is critical for the observation of crystal diffraction.

*SCHEMATIC IMAGE ILLUSTRATING THE REFLECTION OF AN INCOMING X-RAY BEAM FROM A PARTICULAR SET OF CRYSTAL PLANES*

*BECAUSE OF THE STRONG ANGULAR DEPENDENCE OF THE ATOMIC FORM FACTOR WE MAY CONSIDER THAT ONLY A SMALL FRACTION OF THE INCOMING WAVE IS REFLECTED BY ANY GIVEN PLANE*
**Crystal Diffraction**

Typically, rays incident from an arbitrary angle interfere destructively

- For reflection from a set of crystal planes with spacing $d$ and with incident illumination of wavelength.
- There is a special set of angles for which the interference is constructive and so for which strong reflection of the X-ray beam occurs.
- This set of angles is given by the Bragg condition which is obtained by considering the interference of waves reflected from two successive planes.

\[
\frac{(2d \sin \theta)}{\lambda}
\]

* A PHASE-DIFFERENCE therefore exists between the two waves which may be written as

\[
2d \sin \theta = n\lambda, \quad n = 1, 2, 3, \ldots
\]
Crystal Diffraction

How is it done experimentally?

- In the figure below, we show the measured variation of the reflected X-ray intensity at an incident angle for a crystalline sample of silicon carbide (SiC).
- A major peak is observed at $2\Theta = 36^\circ$ at an incident wavelength of 1.9 Å corresponding to an interplane spacing of 3.2 Å.
- This agrees with the known lattice spacing of silicon (111).

Y. Sun et al. 
J. Appl. Phys. 82, 2334 (1997)
To explain the spectrum of photon emissions in hydrogen, Bohr proposed the following:

1. Electrons exist in certain stable orbits. This assumption implies that the orbiting electron does not give off radiation as classical electromagnetics would require of a charge experiencing angular acceleration.

2. The electron may shift to an orbit of higher or lower energy, thereby gaining or losing energy equal to the energy difference between the two layers.

3. The angular momentum of the electron in an orbit is always an integral multiple of Planck’s constant divided by 2π.

\[ E_H = \frac{m_0 q^4}{2(4\pi\varepsilon_0\hbar n)^2} = -\frac{13.6 \text{ eV}}{n^2} \]

\( n = 1, 2, 3, \ldots \)
Crystal Bonding

The Schrödinger Equation:

- The Bohr model explains some things but is inadequate to explain many other observable phenomena.

- Use wave mechanics - Schrödinger equation

- Based on three essential postulates:

  1. Each particle in the system is defined by a wavefunction. The wavefunction and its space derivative are continuous, finite and single valued.

  2. We must express the normal classical quantities with the new quantum mechanical formulations.

  3. The probability of finding a particle with a given wavefunction within a volume should be unity.
Crystal Bonding

Using the Schrödinger Equation: Free electron gas

\[ \nu = 0 \]

\[ \psi(x, y, z) = \psi(x + L, y, z) \]

\[ \psi(x, y, z) = \psi(x, y + L, z) \]

\[ \psi(x, y, z) = \psi(x, y, z + L) \]

The solution wavefunctions:

\[ \psi(x) = \exp(i k_x \cdot x) \]

Momentum space becomes discretized...

\[ k_x = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \ldots \]
Crystal Bonding

Ionic Bonding: NaCl

Sodium (Na)^+  Chlorine (Cl)^-

P: 11  N: 12  P: 17  N: 18

Na^+  Cl^-

z
y
x

\[ a \]
Crystal Bonding

Metallic Bonding: Sodium (Na)

- Outer shell is only partially filled
- Screening by other charges makes the valence electron very loosely bound.
- Outer electron contributed to crystal as a whole.
- Bonding can be very complex depending on the compound involved.
Crystal Bonding

The most important type of bonding: Covalent

- Look to the simplest materials – Hydrogen
  - By assuming that only one electron is present, we can neglect the interaction of electrons in the molecule.
  - We can still understand the critical features.
- Consider the case of two atoms A and B with ground state wavefunctions shown below:
  - The resulting molecule is a superposition of the two atomic wavefunctions

\[ \psi_{\pm} = \psi_A \pm \psi_B \]

Symmetric State
Crystal Bonding

But another combination of wavefunctions exists.

- The antisymmetric wavefunction gives a reduced probability of finding the electron between the two atoms.
  - The solution to the Schrödinger equation shows that the symmetric state lies lower in energy.
  - The symmetric state is referred to as the bonding state and the antisymmetric state is referred to as the anti-bonding state.

\[ \psi_A \quad \psi_- \quad \psi_B \quad \psi_-\psi_* \]
Crystal Bonding

Visualizing the bonding vs. anti-bonding states

• The variation of the total energy of the hydrogen molecule as a function of inter-atomic separation is shown for the bonding and anti-bonding states.
• There is no minimum present in the anti-bonding state indicating the absence of a stable molecular state.
• In the bonding state there is a minimum which defines a stable molecular state at a certain inter-atomic separation.
• When this occurs there is an enhanced probability of finding the electron between the two atoms.

- With the atoms far apart from each other the bonding and anti-bonding states are equal in energy.
- At such large separations the total energy of the two atoms is equal to that of a pair of independent hydrogen atoms.
- As the inter-atomic separation is reduced however the energy of the bonding state decreases faster than that of the anti-bonding state.
- The existence of a minimum energy in the bonding state determines the equilibrium separation of the hydrogen atoms in the molecule.
Crystal Bonding

Now we can examine elemental and compound semiconductors.

- Each atom shares bonds with 4 other atoms.
- Silicon bonds are covalent, but compound semiconductors have a mix of ionic and covalent bonds.
  - Depends on separation on periodic table.

When silicon atoms COMBINE to form a crystal the s- and p- orbitals HYBRIDIZE to form so-called $sp^3$ ORBITALS that are mixtures of the s- and p-orbitals.
Energy Band Formation

Bring atoms together, the wavefunctions begin to overlap.

Large Separation

Small Separation
Energy Band Formation

In a single atom, electrons are trapped in a potential well. When many atoms combine and form a crystal, the atomic potentials overlap, giving rise to a periodic variation.

Diagram showing energy levels and periodic variation in potential.
**Energy Bands**

We conclude by looking at the **free electron model**...

$$E_k = \frac{\hbar^2}{2m} \left( k_x^2 + k_y^2 + k_z^2 \right)$$

Allowed energy values:

So, let's look at a 1D crystal with periodic boundary conditions:

$$\psi(x, y, z) = \psi(x + L, y, z)$$

Wavefunction solutions are in the form of travelling waves:

$$\psi(x) = \exp(ik_x \cdot x)$$

Solutions to the Schrödinger equation discretize the allowed values:

$$k_x = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; ...$$

$${n_{x,y,z}} = \begin{array}{ccccccc} -3 & -2 & -1 & 0 & 1 & 2 & 3 \end{array}$$

$$\rightarrow k_x$$
If the wavevectors at $k_x = \pm \frac{\pi}{a}$, satisfy the **Bragg condition**

$$2d \sin \theta = n\lambda, \quad n = 1, 2, 3, \ldots$$

Then the resultant wave is a combination of left and right going waves (Standing wave):

$$\psi(+) = \exp\left(\frac{i\pi x}{a}\right) + \exp\left(-\frac{i\pi x}{a}\right) \rightarrow 2 \cos\left(\frac{\pi x}{a}\right)$$

$$\psi(-) = \exp\left(\frac{i\pi x}{a}\right) - \exp\left(-\frac{i\pi x}{a}\right) \rightarrow 2i \sin\left(\frac{\pi x}{a}\right)$$

Examine the density:

$$\rho(+) = |\psi(+)|^2 \propto \cos^2\left(\frac{\pi x}{a}\right)$$

$$\rho(-) = |\psi(-)|^2 \propto \sin^2\left(\frac{\pi x}{a}\right)$$
To find the energy gap, we look at the energies:

Let's assume that the potential in our crystal can be written as:

\[ U(x) = U \cos\left(\frac{2\pi x}{a}\right) \]

The energy gap is the energy difference between these two standing waves:

\[ E_g = \int_0^1 dx U(x) \left[ |\psi(+)|^2 - |\psi(-)|^2 \right] \]

\[ = 2 \int_0^1 dx U \cos\left(\frac{2\pi x}{a}\right) \left[ \cos^2\left(\frac{\pi x}{a}\right) - \sin^2\left(\frac{\pi x}{a}\right) \right] \]

\[ = U \]
By putting the atoms together, we get an energy gap.

- The top band is referred to as the “conduction” band. At low temperatures it is mostly empty of electrons.
- The bottom band is referred to as the “valence” band. At low temperatures it is almost entirely filled with electrons.