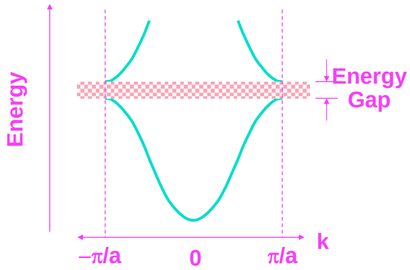
Lecture 14 - Energy Bands for Electrons in Crystals

Lecture 14: Energy Bands for Electrons in Crystals (Kittel Ch. 7)

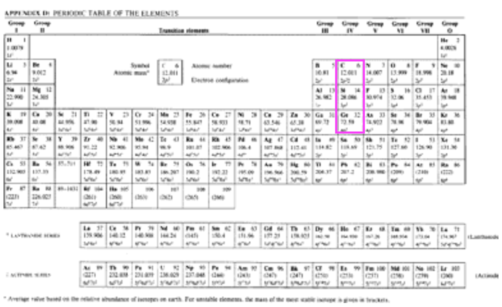


Outline

- Recall the solution for the free electron gas (Jellium)
  - Simplest model for a metal
  - Free electrons in box of size L x L x L (artificial but very useful)
  - Schrodinger equation can be solved
  - States classified by k with $E(k) = (\hbar^2/2m) |\underline{k}|^2$
  - Periodic boundary conditions convenient: Leads to k_x = integer x $(2\pi/L)$, etc.
  - Pauli Exclusion Principle, Fermi Statistics
- Questions: (Answered in the next few lectures)
  - Why are some materials insulators, some metals?
  - What is a semiconductor? What makes them useful?
- Electrons in crystals
  - First step - NEARLY free electrons in a crystal
  - Simple picture - Bragg diffraction leads to standing waves at the Brillouin Zone boundary and to energy gaps
- (Read Kittel Ch 7)

Questions for understanding materials:

- Why are most elements metallic - special place of semiconductors between metals and insulators



How can we understand that some materials are insulators or semiconductors?

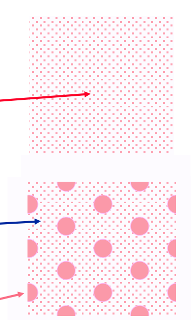
- To answer this question we must consider electrons in a crystal
- The key is the quantum wave nature of electrons in a crystal
  - **A great success of quantum theory in the 1920's and 1930's**
- The nuclei are arranged in a periodic crystalline array

This changes the energies of the electrons and leads to different behavior in different crystals

- Here we will see the basic effects
- Next time – a more complete derivation

Understanding Electrons in Crystals

- **Electron Gas**
  Simplest possible model for a metal - electrons are completely "free of the nuclei" - nuclei are replaced by a smooth background -- "Electrons in a box"
- **Real Crystal -**
  Potential variation with the periodicity of the crystal



Attractive (negative) potential around each nucleus

Schrodinger Equation

- Basic equation of Quantum Mechanics

$$[- (\hbar^2/2m) \nabla^2 + V(\mathbf{r})] \Psi(\mathbf{r}) = E \Psi(\mathbf{r})$$

where
- m = mass of particle
- $V(\mathbf{r})$ = potential energy at point $\mathbf{r}$
- $\nabla^2 = (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$
- E = eigenvalue = energy of quantum state
- $\Psi(\mathbf{r})$ = wavefunction
- $n(\mathbf{r}) = |\Psi(\mathbf{r})|^2$ = probability density

- Key Point for electrons in a crystal: The potential $V(\mathbf{r})$ has the periodicity of the crystal

Lecture 14 - Energy Bands for Electrons in Crystals

Schrodinger Equation

- How can we solve the Schrodinger Eq.

  $[- (\hbar^2/2m)\nabla^2 + V(\mathbf{r})] \Psi (\mathbf{r}) = E \Psi (\mathbf{r})$

  where $V(\mathbf{r})$ has the periodicity of the crystal?

- Difficult problem - This is the basis of current research in the theory of electrons in crystals

- We will consider simple cases as an introduction
  One dimension
  Nearly Free Electrons
  Kronig-Penny Model

Next Step for Understanding Electrons in Crystals

- **Simplest extension of the Electron Gas model**

- **Nearly Free electron Gas - Very small potential variation with the periodicity of the crystal**

Very weak potentials with crystal periodicity

- **We will first consider electrons in one dimension**

Consider 1 dimensional example

- If the electrons can move freely on a line from 0 to L (with no potential),

0 ———————————— **L**

then we have seen before that :

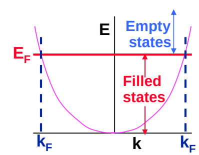
- Schrodinger Eq. In 1d with V = 0
  $- (\hbar^2/2m)\, d^2/dx^2\, \Psi (x) = E \Psi (x)$
- If we have periodic boundary conditions ($\Psi (0) = \Psi (L)$) then the solution is:

  $\Psi (x) = L^{-1/2} \exp(ikx)$, $k = \pm m (2\pi/L)$, $m = 0,1,..$

  $E (k) = (\hbar^2/2m) | k |^2$

Electrons on a line

- For electrons in a box, the energy is just the kinetic energy
  $E (k) = (\hbar^2/2m) k^2$
- Values of k fixed by the box, $k = \pm m (2\pi/L)$, $m = 0, 1, . . .$



- The lowest energy state is for electrons is to fill the lowest states up to the Fermi energy E_F and Fermi momentum k_F – two electrons (spin up and spin down) in each state
- This is a metal – the electrons can conduct electricity as we described before

How can we understand that some materials are insulators or semiconductors?

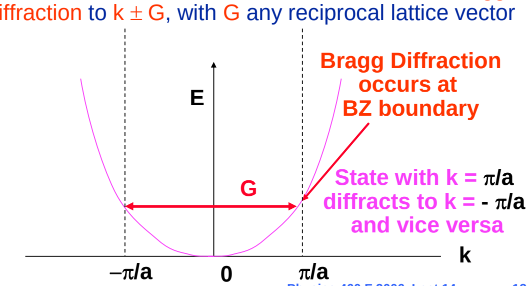
- To answer this question we must consider electrons in a crystal
- The nuclei are arranged in a periodic crystalline array

  This changes the energies of the electrons and leads to different behavior in different crystals

- Here we will see the basic effects
- Next time – a more complete derivation

Electrons on a line with potential V(x)

- What happens if there is a potential V(x) that has the periodicity a of the crystal?
- An electron wave with wavevector k can suffer Bragg diffraction to $k \pm G$, with G any reciprocal lattice vector



Lecture 14 - Energy Bands for Electrons in Crystals

Interpretation of Standing waves at Brillouin Zone boundary

- Bragg scattering at $k = \pi/a$ leads to the two possible standing waves. Each is a combination of the right and left going waves $\exp(i\,\pi x/a)$ and $\exp(-i\,\pi x/a)$:

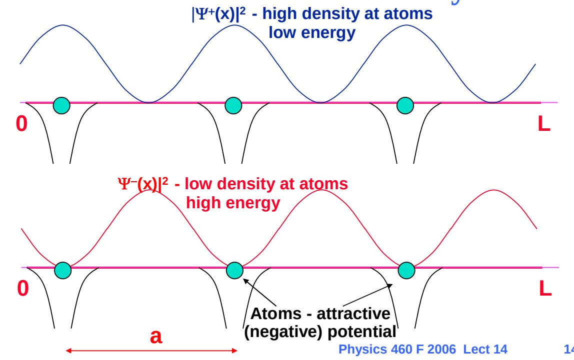
$$\Psi^{+}(x) = \exp(i\,\pi x/a) + \exp(-i\,\pi x/a) = 2\cos(\pi x/a)$$
$$\Psi^{-}(x) = \exp(i\,\pi x/a) - \exp(-i\,\pi x/a) = 2i\sin(\pi x/a),$$

The density of electrons for each standing wave is:

$$|\Psi^{+}(x)|^2 = 4\cos^2(\pi x/a)$$
$$|\Psi^{-}(x)|^2 = 4\sin^2(\pi x/a)$$

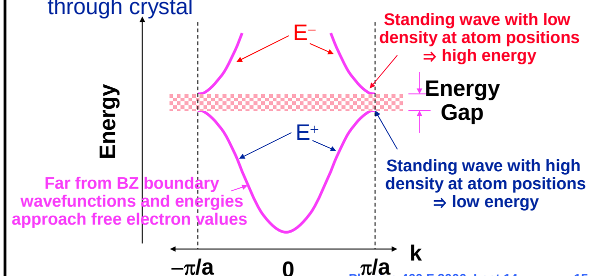
- (Recall standing phonon waves at the zone boundary)

Interpretation of Standing waves at Brillouin Zone boundary



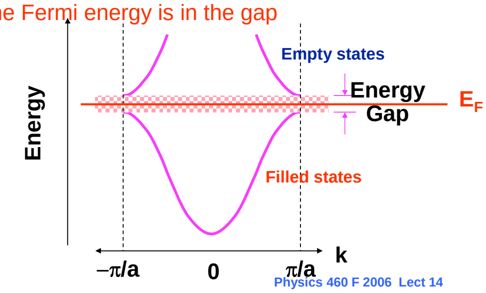
Nearly Free Electrons on a line

- Bands changed greatly only at zone boundary
  Standing wave at zone boundary
  Energy gap -- energies at which no waves can travel through crystal



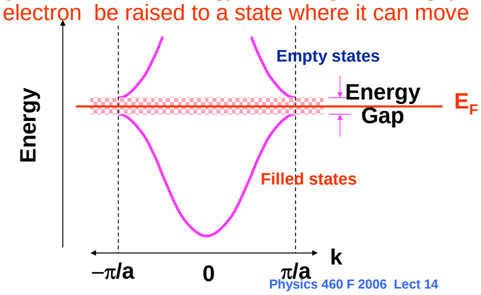
How does this help us understand that some materials are insulators or semiconductors?

- If there are just the right number of electrons to fill the lower band and leave the upper band(s) empty
- The Fermi energy is in the gap



This is an insulator (or a semiconductors)!

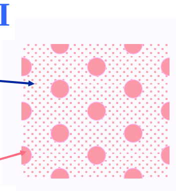
- If the Fermi energy is in the gap, then the electrons are not free to move!
- Only if one adds an energy as as large as the gap can an electron be raised to a state where it can move



Summary I

- **Real Crystal - Potential variation with the periodicity of the crystal**

  Attractive (negative) potential around each nucleus



- **Potential leads to:**
  Electron bands - E(k) different from free electron bands
  Band Gaps
- **More next time on Consequences for crystals**

Lecture 14 - Energy Bands for Electrons in Crystals

Summary II

- Electrons in crystals
  - Build upon the solution for free electrons
  - Consider "nearly free electrons" – first step in understanding electrons in crystals
- Simple picture of how Bragg diffraction leads to standing waves at the Brillouin Zone boundary and to energy gaps
- This is the basic idea for understanding why are some materials are insulators, some are metals, some are semiconductors
- In the following lectures, this will be developed and applied – especially for understanding semiconductors

Next time

- Bloch Theorem
  - Bloch states for electrons in crystals
  - Energy Bands
  - Band Gaps
- Kronig-Penny Model
- General solutions in Fourier Space
- Energy Bands and Band Gaps
  - Basis for understanding metals, insulators, and semiconductors
- (Read Kittel Ch 7)