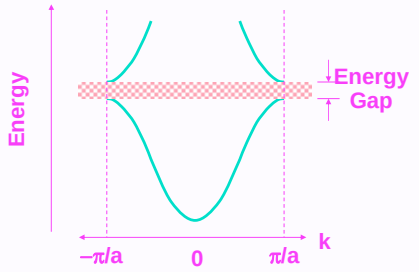
Lecture 15 - Energy Bands for Electrons - continued

Lecture 15: Energy Bands for Electrons in Crystals - continued (Kittel Ch. 7)



Outline

- **Electrons in crystals**
  - **Electrons in a periodic potential**
  - **Bloch Theorem**
- **Quantitative calculations for nearly free electrons**
  - **Equivalent to Bragg diffraction**
  - **Energy Bands and standing waves at the Brillouin Zone Boundary**
  - **Energy gaps**
- **Energy Bands in three dimensions**
- **Metals vs insulators - simple arguments**
- **(Read Kittel Ch 7)**

From last time

Schrodinger Equation

- Basic equation of Quantum Mechanics

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

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

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

Representing V as a periodic function

- We have seen (Lecture 4; Kittel Ch 2) that any periodic function can be written as Fourier series

$$f(\underline{r}) = \Sigma_{\underline{G}} f_{\underline{G}} \exp(i \underline{G} \cdot \underline{r})$$

where the $\underline{G}$'s are reciprocal lattice vectors

$$\underline{G}(m_1,m_2,\ldots) = m_1 \underline{b}_1 + m_2 \underline{b}_2 + m_3 \underline{b}_3$$

- Check: A periodic function satisfies $f(\underline{r}) = f(\underline{r} + \underline{T})$ where $\underline{T}$ is any translation

$$\underline{T}(n_1,n_2,\ldots) = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3$$

where the n's are integers

- Thus $V(\underline{r}) = \Sigma_{\underline{G}} V_{\underline{G}} \exp(i \underline{G} \cdot \underline{r})$
- And $V(\underline{r})$ = real $\Rightarrow V_{\underline{G}} = V^*_{-\underline{G}}$
- If the crystal is symmetric ($V(\underline{r}) = V(-\underline{r})$), then $V_{\underline{G}} = V_{-\underline{G}}$

Schrodinger Equation - Again

- In a periodic crystal

$$[- (\hbar^2/2m)\nabla^2 + \Sigma_{\underline{G}} V_{\underline{G}} \exp(i \underline{G} \cdot \underline{r})] \Psi (\underline{r}) = E \Psi (\underline{r})$$

- Now expand $\Psi (\underline{r}) = \Sigma_{\underline{k}} c_{\underline{k}} \exp(i \underline{k} \cdot \underline{r})$
- Note we do NOT assume Ψ is periodic! It is a wave!
- What is $\underline{k}$?
  Just as before for electrons in a box, we assume $\Psi(\underline{r})$ is periodic in a large box (L x L x L) which leads to

$$k = \pm m (2\pi/L), \; m = 0,1,..$$

Schrodinger Equation - Continued

- Then the Schrodinger Eq.beomes:

$$\Sigma_{\underline{k}} c_{\underline{k}} [\lambda_{\underline{k}} \exp(i \underline{k} \cdot \underline{r}) + \Sigma_{\underline{G}} V_{\underline{G}} \exp(i (\underline{k} + \underline{G}) \cdot \underline{r})] = E \Sigma_{\underline{k}} c_{\underline{k}} \exp(i \underline{k} \cdot \underline{r})$$

where

$$\lambda_{\underline{k}} = (\hbar^2/2m) |\underline{k}|^2$$

- By re-labeling the sums, this can be written

$$\Sigma_{\underline{k}} \{ [\lambda_{\underline{k}} - E] c_{\underline{k}} + \Sigma_{\underline{G}} V_{\underline{G}} c_{\underline{k}-\underline{G}} \} \exp(i \underline{k} \cdot \underline{r}) = 0$$

- Equating terms with the same r dependence on the two sides on the equation, we find what Kittel calls the "Central Equation"

$$[\lambda_{\underline{k}} - E] c_{\underline{k}} + \Sigma_{\underline{G}} V_{\underline{G}} c_{\underline{k}-\underline{G}} = 0$$

Lecture 15 - Energy Bands for Electrons - continued

"Central Equation" for electron bands

- What is the interpretation of the equation:

$$[\lambda_{\underline{k}} - E\,]\, c_{\underline{k}} + \Sigma_{\underline{G}}\, V_{\underline{G}}\, c_{\underline{k}-\underline{G}} = 0$$

- If $V_{\underline{G}} = 0$ (no potential - free electrons) then each $\underline{k}$ is independent and each wavefunction is

$$\Psi_{\underline{k}}(\underline{r}) = c_{\underline{k}} \exp(i\,\underline{k}\cdot\underline{r})\ ;\ E = \lambda_{\underline{k}} = (\hbar^2/2m)\,|\,\underline{k}\,|^2$$

- If $V_{\underline{G}} \neq 0$, then each $\underline{k}$ is mixed with $\underline{k} - \underline{G}$ where $\underline{G}$ is any reciprocal lattice vector -- the solution is

$$\Psi_{\underline{k}}(\underline{r}) = \Sigma_{\underline{G}}\, c_{\underline{k}-\underline{G}} \exp(i\,(\underline{k} - \underline{G})\cdot\underline{r})$$

Yet to be determined

Bloch Theorem - I

- One of the most important ideas in the course!
- In a general crystal, the wave function for an electron has the form:

$$\Psi_{\underline{k}}(\underline{r}) = \Sigma_{\underline{G}}\, c_{\underline{k}-\underline{G}} \exp(i\,(\underline{k} - \underline{G})\cdot\underline{r})$$

which can be written

$$\Psi_{\underline{k}}(\underline{r}) = \exp(i\,\underline{k}\cdot\underline{r})\, u_{\underline{k}}(\underline{r})$$

where $u_{\underline{k}}(\underline{r})$ is the periodic function

$$u_{\underline{k}}(\underline{r}) = \Sigma_{\underline{G}}\, c_{\underline{k}-\underline{G}} \exp(-i\,\underline{G}\cdot\underline{r})$$

Bloch Theorem - II

- The general form is

$$\Psi_{\underline{k}}^{n}(\underline{r}) = \exp(i\,\underline{k}\cdot\underline{r})\, u_{\underline{k}}^{n}(\underline{r})$$

where $u_{\underline{k}}^{n}(\underline{r})$ is a periodic function. Here n labels different bands

- Key Points:
  1) Each state is labeled by a wave vector $\underline{k}$
  2) $\underline{k}$ can be restricted to the first Brillouin Zone
  This may be seen since

$$\Psi_{\underline{k}+\underline{G}'}(\underline{r}) = \exp(i\,(\underline{k} + \underline{G}')\cdot\underline{r})\, u_{\underline{k}+\underline{G}'}(\underline{r})$$
$$= \exp(i\,\underline{k}\cdot\underline{r})\, u'_{\underline{k}}(\underline{r})$$

where $u'_{\underline{k}}(\underline{r}) = \exp(i\,\underline{G}\cdot\underline{r})\, u_{\underline{k}+\underline{G}'}(\underline{r})$ is just another periodic function

Bloch Theorem - III

- Thus a wavefunction in a crystal can always be written

$$\Psi_{\underline{k}}^{n}(\underline{r}) = \exp(i\,\underline{k}\cdot\underline{r})\, u_{\underline{k}}^{n}(\underline{r})$$

where: $u_{\underline{k}}^{n}(\underline{r})$ is a periodic function
n labels different bands
$\underline{k}$ is restricted to the first Brillouin Zone

- In limit of large system
  k becomes continuous
  n is discrete index: n = 1,2,3, ….

Bloch Theorem - IV

- "Energy Bands" for electrons in crystals
- Recall the "Central Equation"

$$[\lambda_{\underline{k}} - E_{\underline{k}}^{n}\,]\, c_{\underline{k}} + \Sigma_{\underline{G}}\, V_{\underline{G}}\, c_{\underline{k}-\underline{G}} = 0$$

- The eigenvalues of the equation are the energies $E_{\underline{k}}^{n}$ which depend upon the wavevector k and the index n:
  $E_{\underline{k}}^{n}$ are the "energy bands"
  n labels different bands
  $\underline{k}$ is restricted to the first Brillouin Zone
- In limit of large system
  $E_{\underline{k}}^{n} \Rightarrow E^{n}(\underline{k})$ becomes a continuous function of k
  n is discrete index: n = 1,2,3, ….

Solving "Central Equation" - I

- Simple cases where we can solve

$$[\lambda_{\underline{k}} - E\,]\, c_{\underline{k}} + \Sigma_{\underline{G}}\, V_{\underline{G}}\, c_{\underline{k}-\underline{G}} = 0$$

- Consider the case where the potential $V_{\underline{G}}$ is very weak. Then we can find an accurate approximate solution. This is called the "nearly-free-electron" approximation.
- For k near BZ boundary, the wave $\exp(i\,\underline{k}\cdot\underline{r})$ is mixed strongly with $\exp(i\,(\underline{k} - \underline{G})\cdot\underline{r})$, where $\underline{G}$ is the one (and only one) vector that leads to $|\,\underline{k}\,| \sim |\,\underline{k} - \underline{G}\,|$
- Let $V = V_{\underline{G}} = V_{-\underline{G}}$ for that $\underline{G}$

Lecture 15 - Energy Bands for Electrons - continued

Solving "Central Equation" - II

- Leads to two coupled equations

$$[\lambda_{\underline{k}} - E]\, c_{\underline{k}} + V c_{\underline{k-G}} = 0$$

$$[\lambda_{\underline{k-G}} - E]\, c_{\underline{k-G}} + V c_{\underline{k}} = 0$$

- or

$$\begin{vmatrix} [\lambda_{\underline{k}} - E] & V \\ V & [\lambda_{\underline{k-G}} - E] \end{vmatrix} = 0$$

- Solution

$$E^{\pm} = (1/2)(\lambda_{\underline{k}} + \lambda_{\underline{k-G}}) \pm (1/2)[(\lambda_{\underline{k}} - \lambda_{\underline{k-G}})^2 + V^2]^{1/2}$$

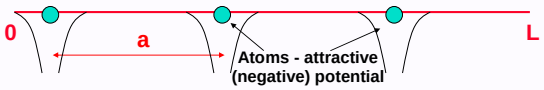
and

$$c_{\underline{k-G}} = [(\lambda_{\underline{k}} - E)/V]\, c_{\underline{k}}$$

Example in one dimension

- A 1-dimensional crystal has a periodic potential

$$V(x) = \Sigma_G V_G \exp(iGx)$$



- In the nearly free electron approximation, we assume the potential is very weak. For a state near a zone boundary k ~ π/a, we consider only

$V = V_G$, where $G = 2\pi/a$

(and we neglect the other G's)

Example in one dimension

- At the zone boundary: k = π/a, k-G = -π/a and

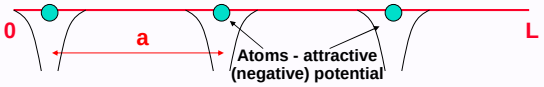
$$\lambda_{\underline{k}} = \lambda_{\underline{k-G}} = (\hbar^2/2m)(\pi/a)^2$$

- From a previous slide, the energies are given by

$$E^{\pm} = (1/2)(\lambda_{\underline{k}} + \lambda_{\underline{k-G}}) \pm (1/2)[(\lambda_{\underline{k}} - \lambda_{\underline{k-G}})^2 + V^2]^{1/2}$$

- Solution for k = π/a: $E^{\pm} = \lambda_{\underline{k}} \pm (1/2)\, V$
- With eigenvectors $c_{\underline{k-G}} = [(\lambda_{\underline{k}} - E)/V]\, c_{\underline{k}} = \pm c_{\underline{k}}$
- This means that

$$\Psi(x) = \Sigma_k c_k \exp(ikx) = c_k[\exp(ikx) \pm \exp(i(k-G)x)]$$
$$= c_k[\exp(i\pi x/a) \pm \exp(-i\pi x/a)]$$



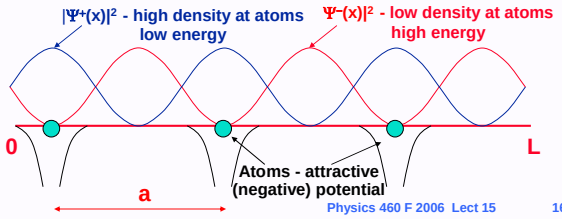
Interpretation of Standing waves at Brillouin Zone boundary

- Bragg scattering at k = π/a leads to the two possible combinations of the right and left going waves:

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

with density

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

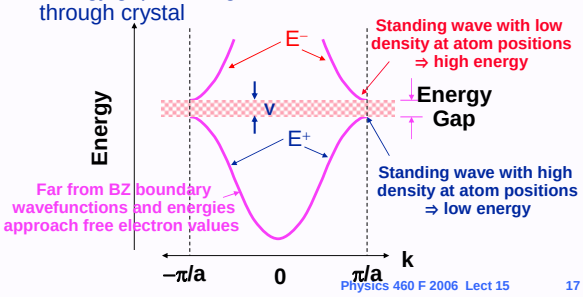


Nearly Free Electrons on a line

- Bands changed greatly only at zone boundary

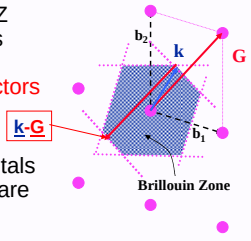
Standing wave at zone boundary

Energy gap -- energies at which no waves can travel through crystal



These conclusions also apply in general in 2 and 3 dimensions

- In ALL crystals states at the boundary of the Brillouin Zone are standing waves
- For each state **k** at the BZ boundary, there is always an equivalent state **k-G** where **G** is one of the vectors of the reciprocal lattice



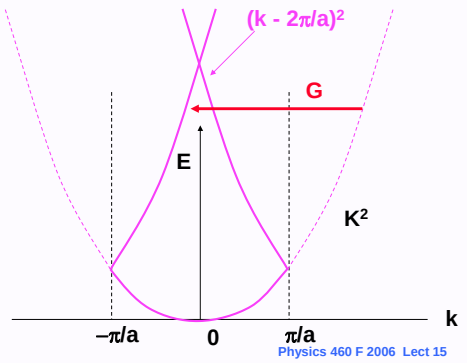
- This happens in ALL crystals since the BZ boundaries are defined by $|\underline{k} \cdot \underline{G}| = G^2/2$, so that $|(\underline{k}-\underline{G}) \cdot \underline{G}| = G^2/2$

Lecture 15 - Energy Bands for Electrons - continued

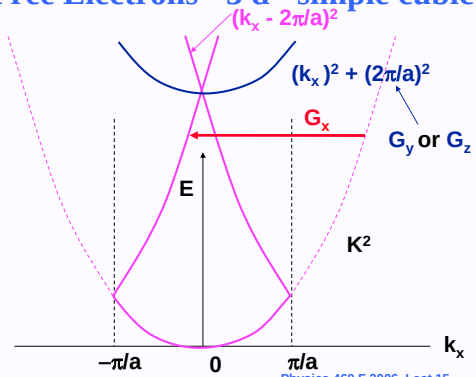
How to apply the nearly-free electron aproximation in general crystals

- First find free electron bands plotted in BZ
- The energy is ALWAYS $E(\underline{K}) = (\hbar^2/2m)\,|\,\underline{K}\,|^2$ but now we "reduce" $\underline{K}$ to BZ, i.e., we define the "reduced" $\underline{k}$ by
  $\underline{K} = \underline{k} + \underline{G}$ or $\underline{k} = \underline{K} - \underline{G}$
- Then add effects of potential

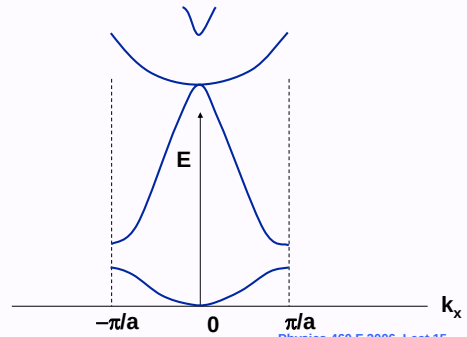
Free Electrons - 1 d



Free Electrons - 3 d - simple cubic



Nearly Free Electrons - 3d - schematic



Summary so far

- **We have solved the "Central Equation" in the "nearly-free electron approximation"**
- **The results apply to all types of crystals but we have assumed the potential is "weak" which is not always true**
- **Which conclusions will ALWAYS apply in all crystals?**
  - **The Bloch Theorem**
  - **Standing waves and gaps at the BZ boundary**
  - **Continuous curves ("energy bands") E (Discussion in class)**
- **Why are these results important?**

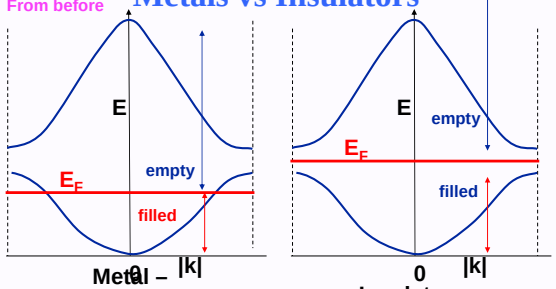
Metals vs Insulators

- **How can we use the results so far to determine which crystals will be metals? Which can be insulators?**

Lecture 15 - Energy Bands for Electrons - continued

Metals vs Insulators

From before



Metal – the Fermi Energy E_F is in the band "partially filled band"

Insulator – the Fermi Energy E_F is in the band gap "filled band"

Metals vs Insulators

- **How can we know when the Fermi energy will be in the band? In the gap?**

Sums and Integrals over k points

- We often need to sum or integrate over k to find total quantities, for example the total number of filled states in the bands.
- We can use idea of periodic boundary conditions on box of size L x L x L
  Exactly the same as for phonons, electrons in a box,...
- Volume per k point = $(2\pi/L)^3$
- Total number of k points in in BZ
  $N_{k\text{-point}} = V_{BZ}/(2\pi/L)^3 = (2\pi/a)^3(L/2\pi)^3 = (L/a)^3 = N_{cell}$
- Rules:
  $N_{k\text{-point}} = N_{cell}$
  $(2\pi/L)^3 \Sigma_{\underline{k}} \rightarrow \int dk$ or $(1/N_{k\text{-point}}) \Sigma_{\underline{k}} \rightarrow (1/V_{BZ}) \int dk$

Sums and Integrals over k points

- **Important conclusion from previous slide:**
- The number of k points in a band equals the number of cells in the crystal
  $N_{k\text{-point}} = N_{cell}$
- This may seem meaningless for an infinite crystal, but it is correct if it is understood properly:
  In the limit of a large crystal, the surface effects become negligible. The states approach a continuum with the density of points in k space given by:
  $(2\pi/L)^3 \Sigma_{\underline{k}} \rightarrow \int dk$ or $(1/N_{k\text{-point}}) \Sigma_{\underline{k}} \rightarrow (1/V_{BZ}) \int dk$

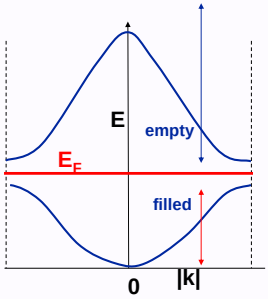
Metals vs Insulators

- **Important Conclusion – one of the most important in the course!**
- The energies of the electron states are "bands" $E^n(\underline{\mathbf{k}})$. For each band (n = 1,2, …) $E^n(\underline{\mathbf{k}})$ varies continuously as a function of $\underline{\mathbf{k}}$ inside the BZ.
- At the boundary of the BZ the states are standing waves. There are energy gaps and the group velocity $dE^n/d\underline{\mathbf{k}} = 0$ at the boundary.
- Electrons obey the exclusion principle. 2 electrons per primitive cell of the crystal fill a band. Any additional electrons must go into the next band, and so forth.

• An odd number of electrons per primitive cell ALWAYS leads to a partially filled band – a METAL
• An even number MAY lead to an insulator – see later

Metals vs Insulators

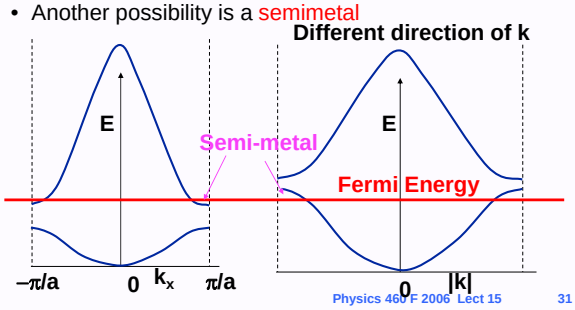
- An even number of electrons per cell leads to an insulator if the Fermi energy is in a gap everywhere in the BZ



Lecture 15 - Energy Bands for Electrons - continued

Metals vs Insulators

- An even number of electrons per cell leads to an insulator if the Fermi energy is in a gap everywhere in the BZ
- Another possibility is a semimetal



Metals vs Insulators

- A band holds two electrons per cell of the crystal
- Therefore an crystal with an odd number of electrons per cell MUST* be a metal!
  Partially filled bands lead to Fermi energy and "Fermi surface" in k space
  Conductivity because states can change and scatter when electric field is applied
- A crystal with an even number of electrons per cell MAY be an insulator!
  Electrons "frozen"
  Gap in energy for any excitations of electrons
- *caveat later

Metals vs Insulators

- Examples
- Na – 1 valence electron/atom = 1 valence electron/cell
- Cu – 10 d electrons + 1 s electron in the atom – discuss in class
- NaCl – 1 + 7 = 8 valence electrons/cell
- Xe - 8 valence electrons/atom
- Solid H_2 - discuss in class
- Si - 4 valence electrons/atom - discuss in class

Summary

- **"Central Equation" – General for ALL crystals**
- **We solved the problem in the "nearly-free electron approximation" where we assume the potential is "weak"**
- **Some results apply to ALL types of crystals:**
  The Bloch Theorem
  Standing waves and gaps at the BZ boundary
  Continuous curves ("energy bands") $E^n(k)$
- **We can predict that some materials most be metals, and other materials can be insulators -- simply by counting electrons!**

Next time

- **Semiconductors**
- **What is a semiconductor?**
- **We have established that there can be gaps and filled bands – from this starting point we can understand how the electrons in some materials will have interesting, large changes with temperature, "doping", electric fields, . . .**
- **(Read Kittel Ch 8)**