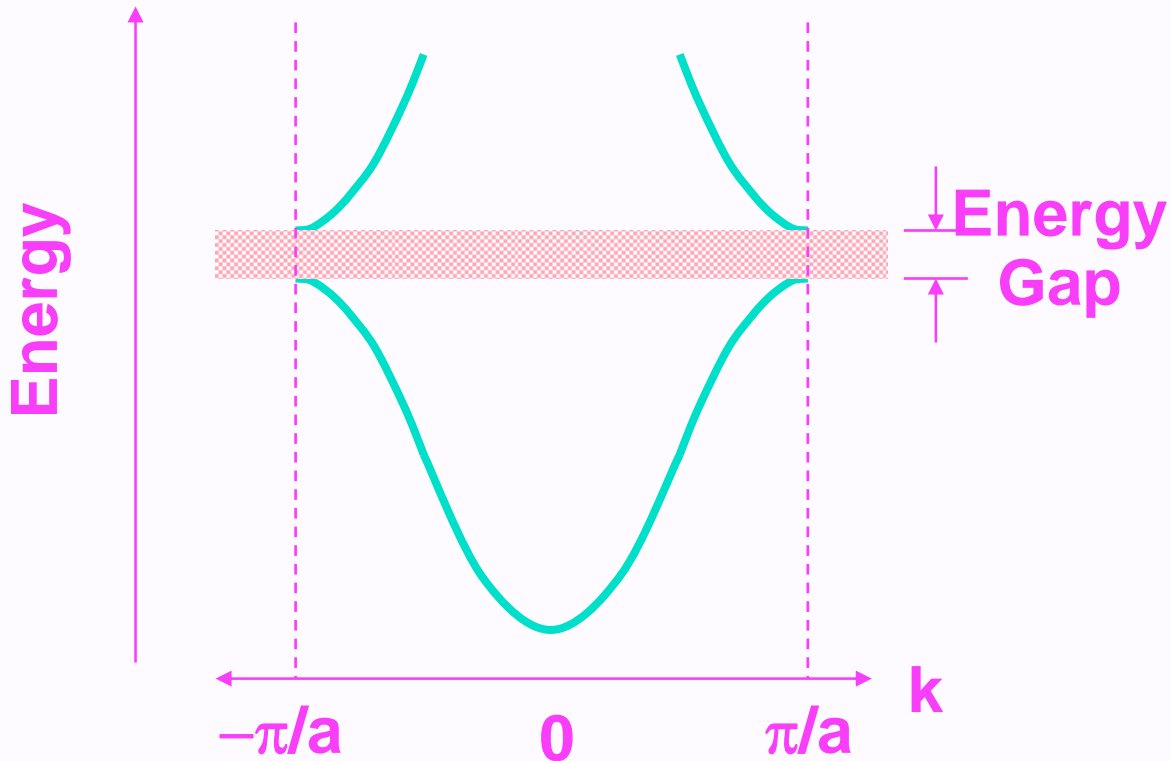


Lecture 15: Energy Bands for Electrons in Crystals - continued

(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)**

Schrodinger Equation

- Basic equation of Quantum Mechanics

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

where

m = mass of particle

$V(\underline{\mathbf{r}})$ = potential energy at point $\underline{\mathbf{r}}$
 $\nabla^2 = (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$

E = eigenvalue = energy of quantum state

$\Psi (\underline{\mathbf{r}})$ = wavefunction

$n (\underline{\mathbf{r}}) = | \Psi (\underline{\mathbf{r}}) |^2 =$ probability density

- **Key Point for electrons in a crystal:** The potential $V(\underline{\mathbf{r}})$ 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

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

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

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

- Check: A periodic function satisfies

$$f(\underline{\mathbf{r}}) = f(\underline{\mathbf{r}} + \underline{\mathbf{T}}) \text{ where } \underline{\mathbf{T}} \text{ is any translation}$$

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

where the n 's are integers

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

Schrodinger Equation - Again

- In a periodic crystal

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

- Now expand $\Psi (\underline{\mathbf{r}}) = \sum_{\underline{\mathbf{k}}} c_{\underline{\mathbf{k}}} \exp(i \underline{\mathbf{k}} \cdot \underline{\mathbf{r}})$

- Note we do NOT assume Ψ is periodic! It is a wave!

- What is $\underline{\mathbf{k}}$?

Just as before for electrons in a box, we assume

$\Psi (\underline{\mathbf{r}})$ is periodic in a large box (L x L x L) which leads to

$$\mathbf{k} = \pm m (2\pi/L), m = 0, 1, \dots$$

Schrodinger Equation - Continued

- Then the Schrodinger Eq. becomes:

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

where

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

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

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

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

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

“Central Equation” for electron bands

- What is the interpretation of the equation:

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

- 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

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

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:

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

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

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

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

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

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: $n = 1, 2, 3, \dots$

Bloch Theorem - IV

- “Energy Bands” for electrons in crystals
- Recall the “Central Equation”

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

- The eigenvalues of the equation are the energies $E_{\underline{k}}^n$ which depend upon the wavevector \underline{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 \underline{k}
 - n is discrete index: $n = 1, 2, 3, \dots$

Solving “Central Equation” - I

- Simple cases where we can solve

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

- 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}

Solving “Central Equation” - II

- Leads to two coupled equations

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

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

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

- Solution

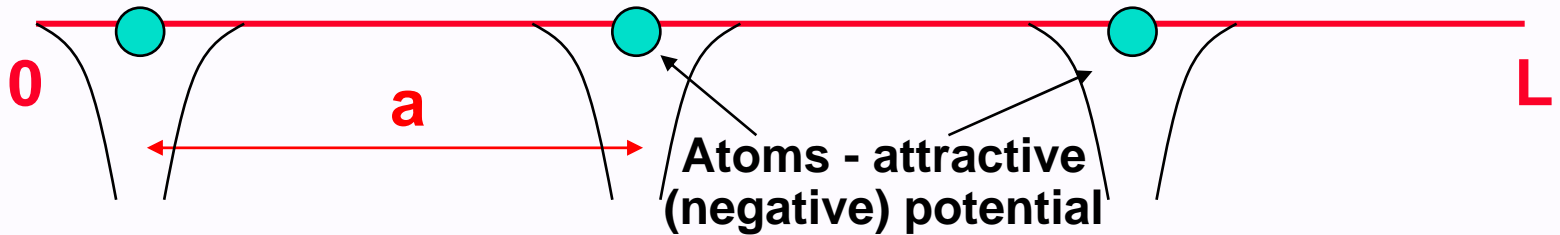
$$E^{\pm} = (1/2) (\lambda_{\underline{k}} + \lambda_{\underline{k}-\underline{G}}) \pm (1/2) [(\lambda_{\underline{k}} - \lambda_{\underline{k}-\underline{G}})^2 + V^2]^{1/2}$$

and

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

Example in one dimension

- A 1-dimensional crystal has a periodic potential
$$V(x) = \sum_G V_G \exp(iGx)$$



- In the nearly free electron approximation, we assume the potential is very weak. For a state near a zone boundary $k \sim \pi/a$, we consider only
$$V = V_G, \text{ where } G = 2\pi/a$$

(and we neglect the other G 's)

Example in one dimension

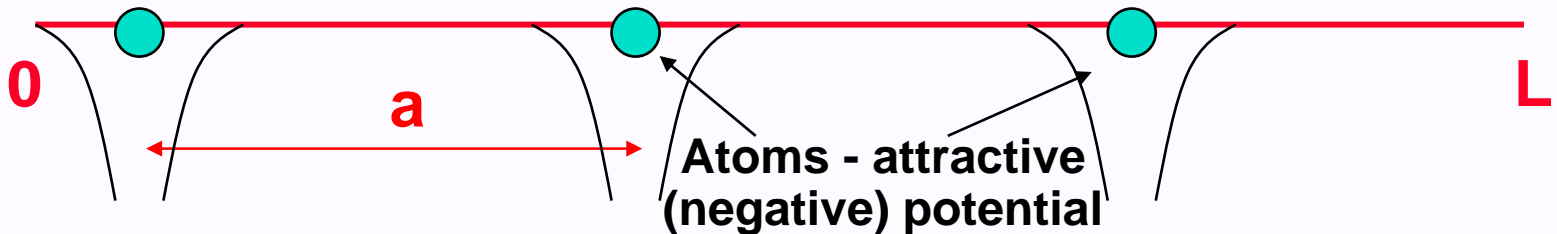
- At the zone boundary: $k = \pi/a$, $k-G = -\pi/a$ and

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

$$\Psi(x) = \sum_{\underline{k}} c_{\underline{k}} \exp(i\mathbf{k}x) = c_{\underline{k}} [\exp(i\mathbf{k}x) \pm \exp(i(\mathbf{k}-\mathbf{G})x)]$$

$$= c_{\underline{k}} [\exp(i\pi x/a) \pm \exp(-i\pi x/a)]$$



Interpretation of Standing waves at Brillouin Zone boundary

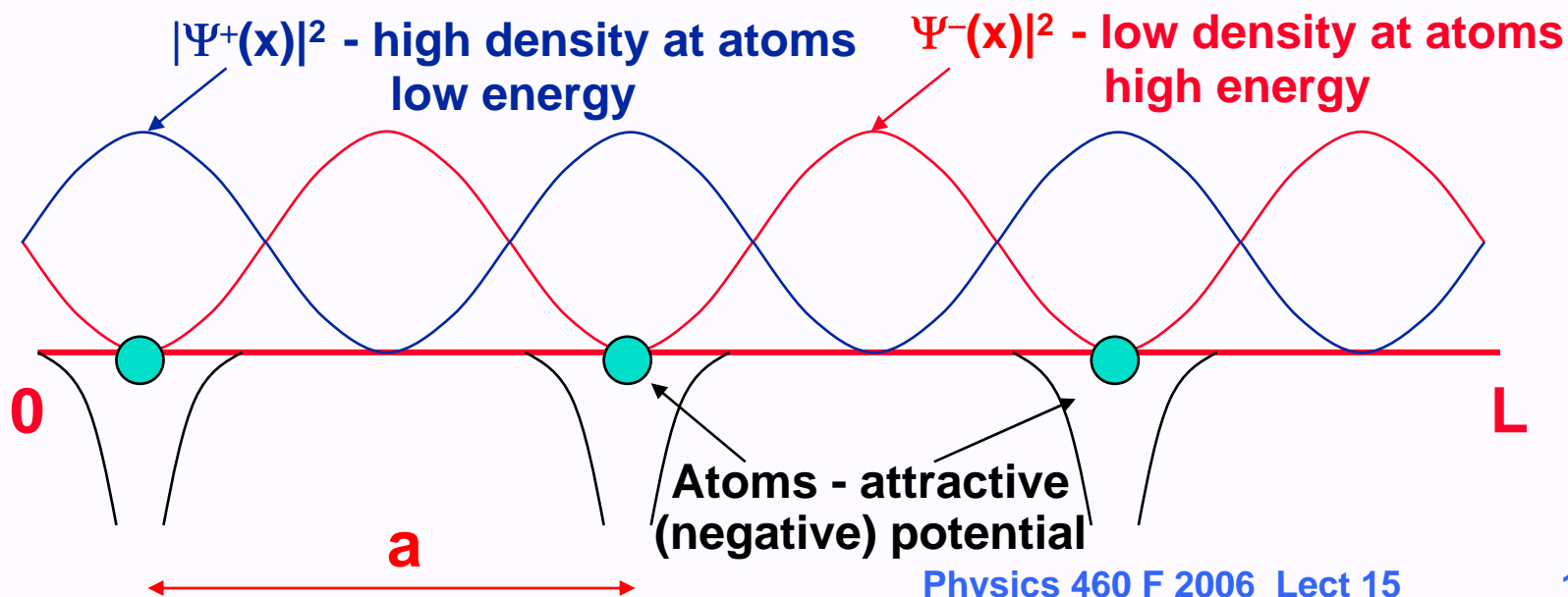
- Bragg scattering at $k = \pi/a$ leads to the two possible combinations of the right and left going waves:

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

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

with density

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

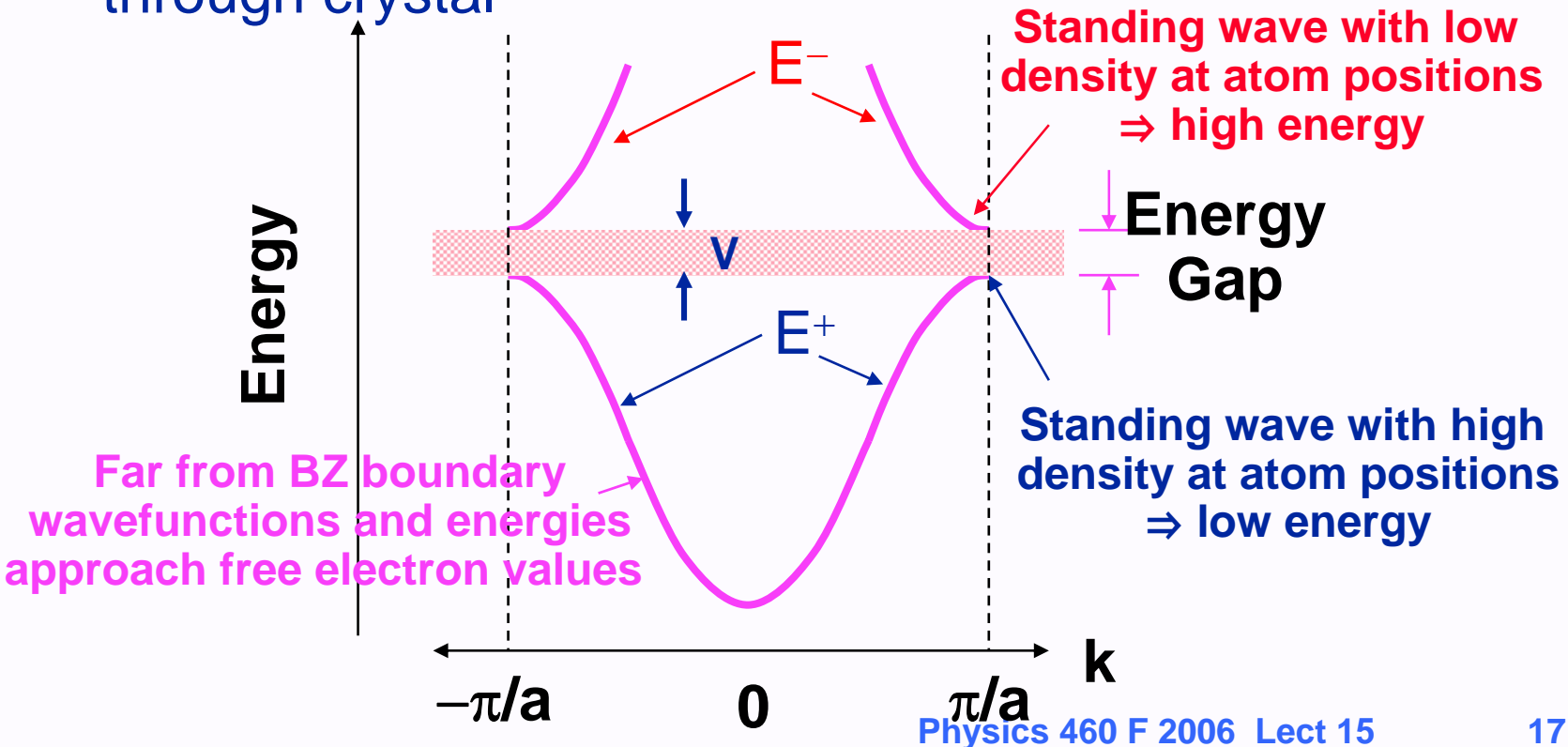


Nearly Free Electrons on a line

- Bands changed greatly only at zone boundary

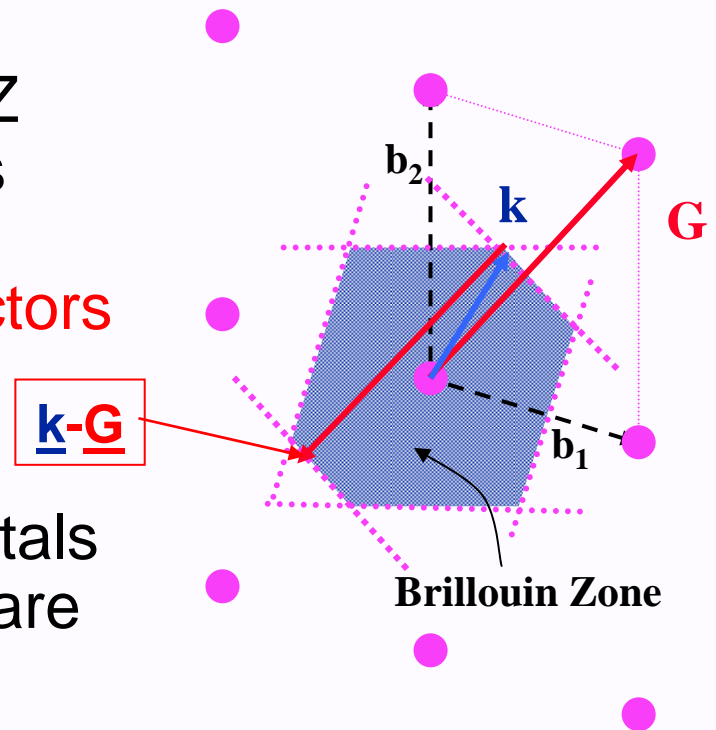
Standing wave at zone boundary

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 \underline{k} at the BZ boundary, there is always an equivalent state $\underline{k}-\underline{G}$ where \underline{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 $|(\underline{k}-\underline{G}) \cdot \underline{G}| = G^2/2$



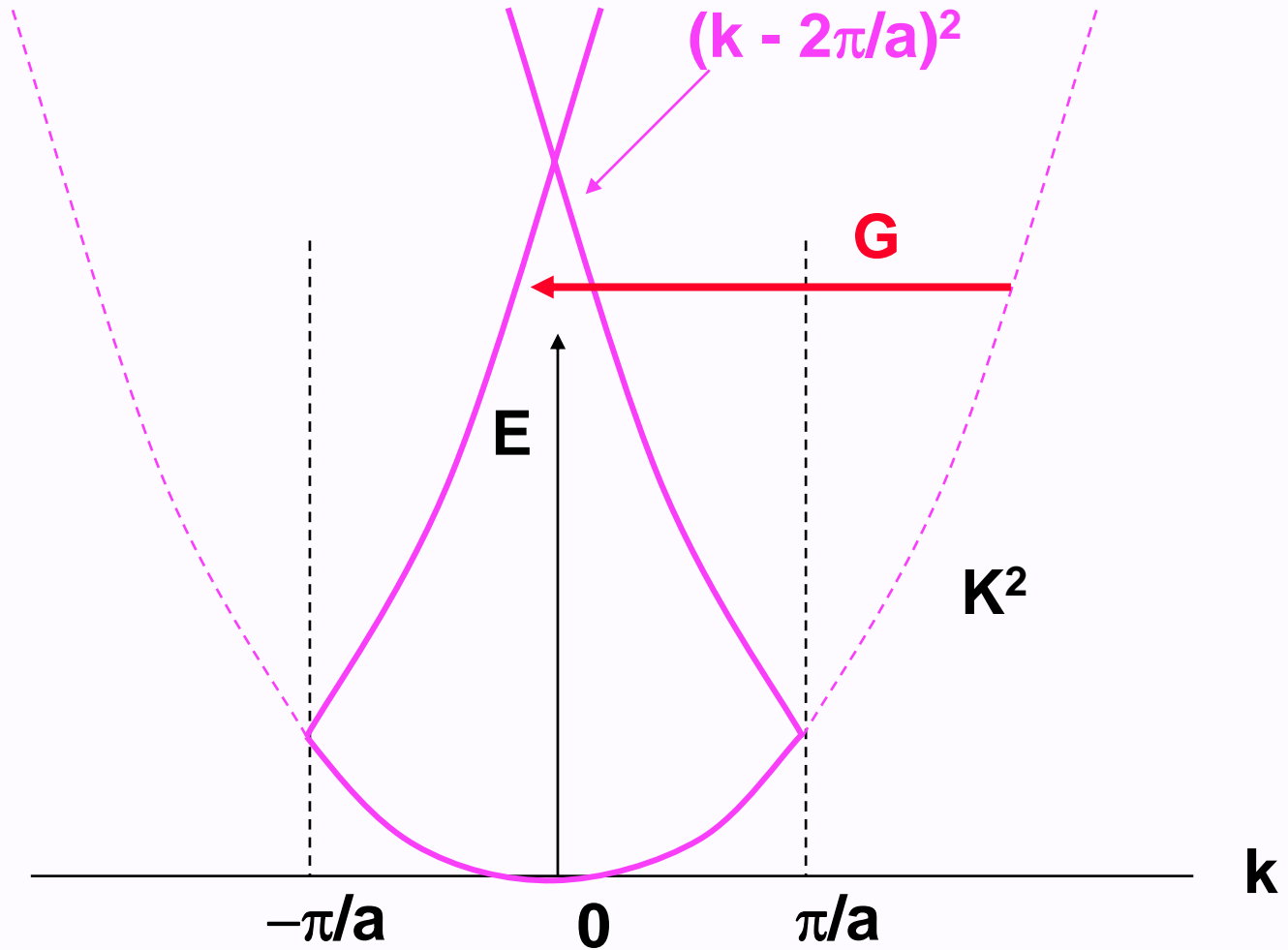
How to apply the nearly-free electron approximation in general crystals

- First find free electron bands **plotted in BZ**
- The energy is **ALWAYS** $E(\underline{\mathbf{K}}) = (\hbar^2/2m) |\underline{\mathbf{K}}|^2$ but now we “reduce” $\underline{\mathbf{K}}$ to BZ, i.e., **we define the “reduced” $\underline{\mathbf{k}}$ by**

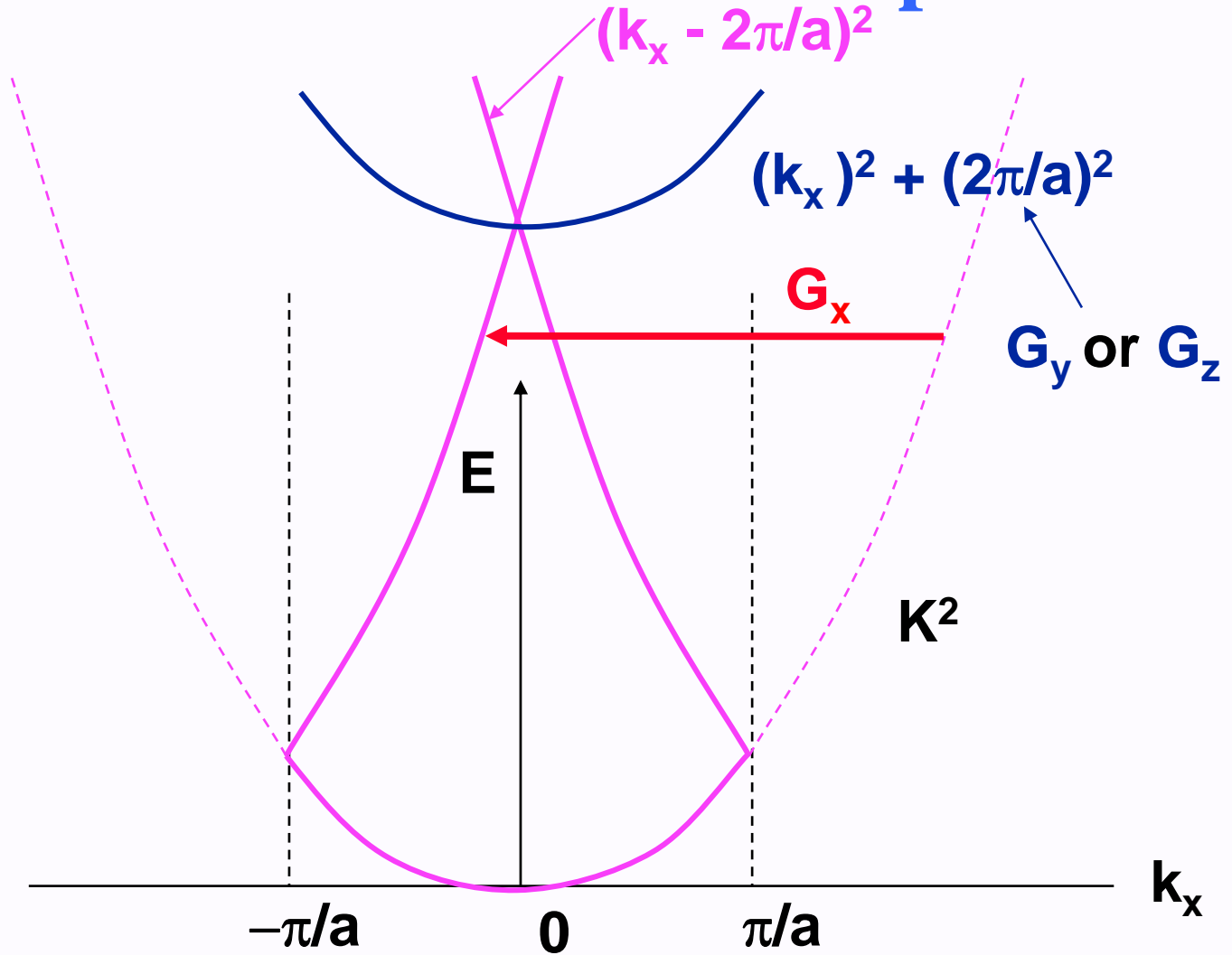
$$\underline{\mathbf{K}} = \underline{\mathbf{k}} + \underline{\mathbf{G}} \quad \text{or} \quad \underline{\mathbf{k}} = \underline{\mathbf{K}} - \underline{\mathbf{G}}$$

- Then add effects of potential

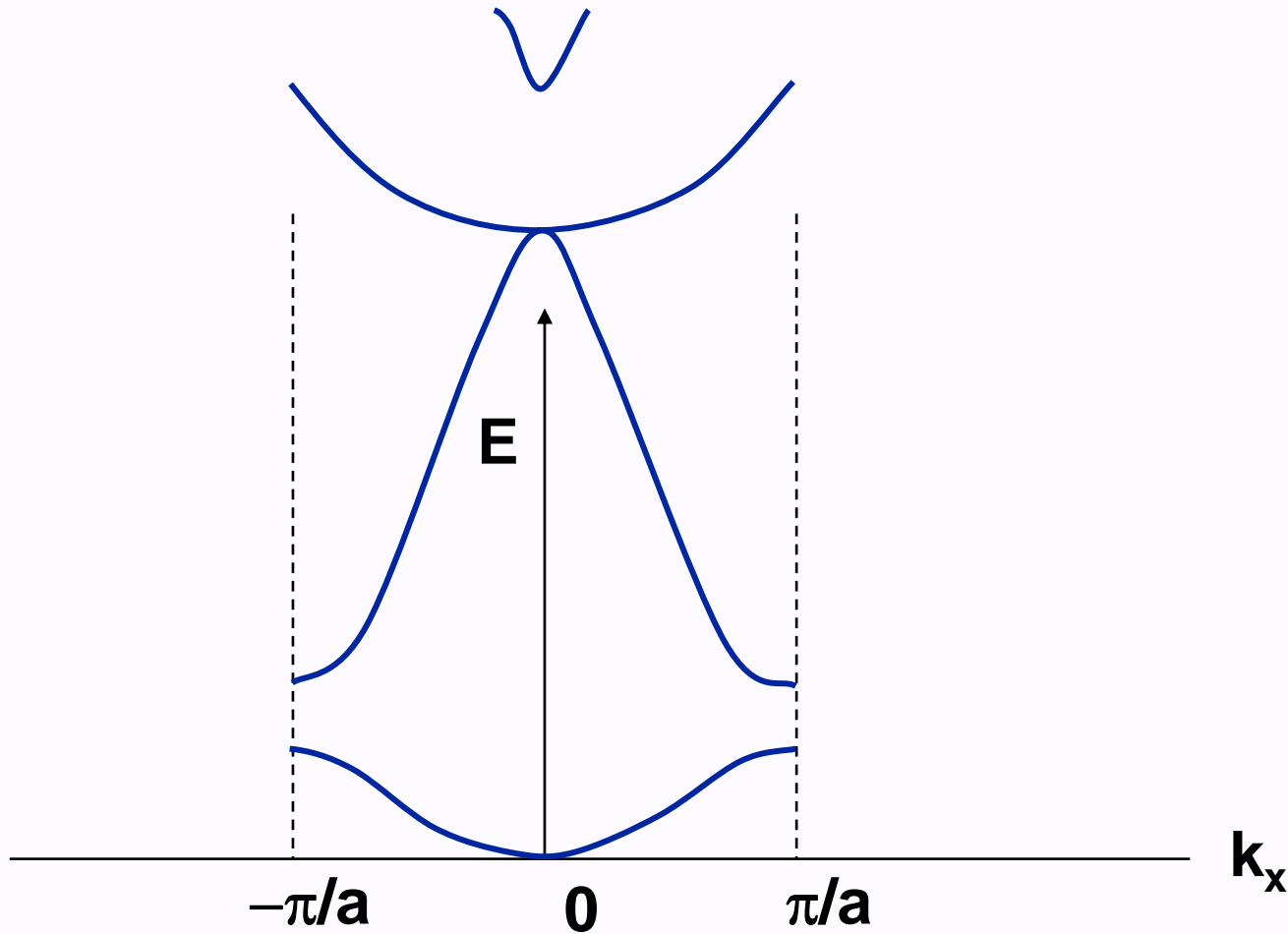
Free Electrons - 1 d



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)

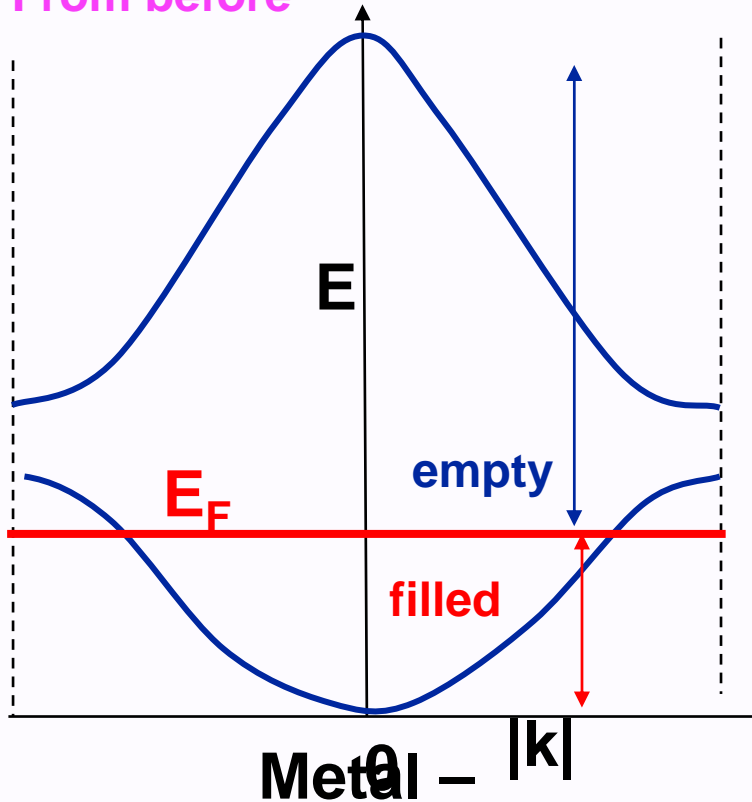
- **Why are these results important?**

Metals vs Insulators

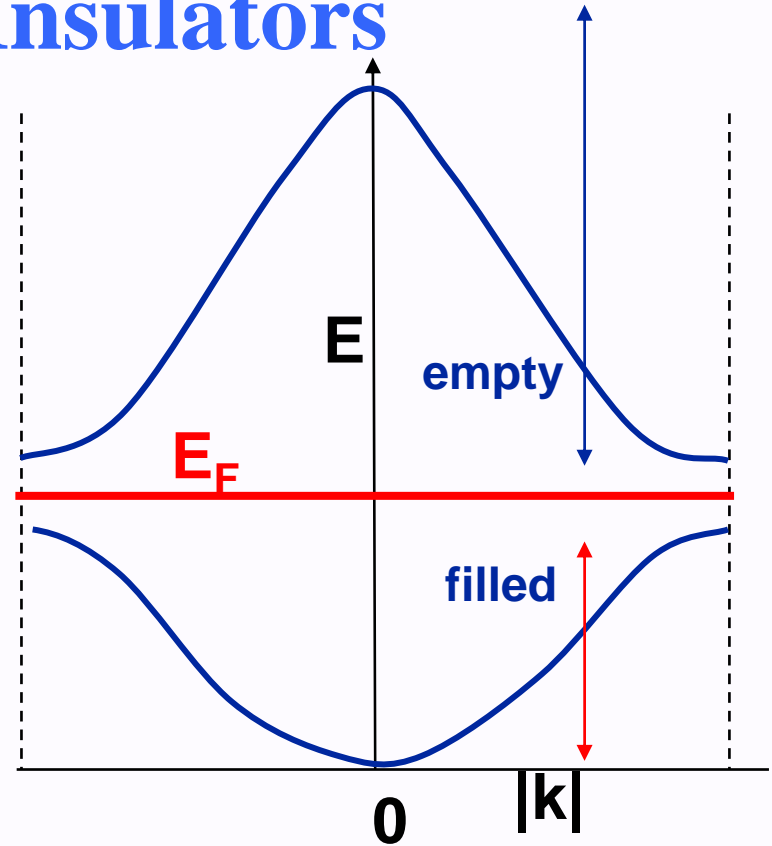
- **How can we use the results so far to determine which crystals will be metals? Which can be insulators?**

Metals vs Insulators

From before



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



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

$$N_{\text{k-point}} = V_{\text{BZ}} / (2\pi/L)^3 = (2\pi/a)^3 (L/2\pi)^3 = (L/a)^3 = N_{\text{cell}}$$

- Rules:

$$N_{\text{k-point}} = N_{\text{cell}} \\ (2\pi/L)^3 \sum_{\underline{k}} \rightarrow \int dk \quad \text{or} \quad (1/N_{\text{k-point}}) \sum_{\underline{k}} \rightarrow (1/V_{\text{BZ}}) \int dk$$

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

$$N_{\text{k-point}} = N_{\text{cell}}$$

- 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:

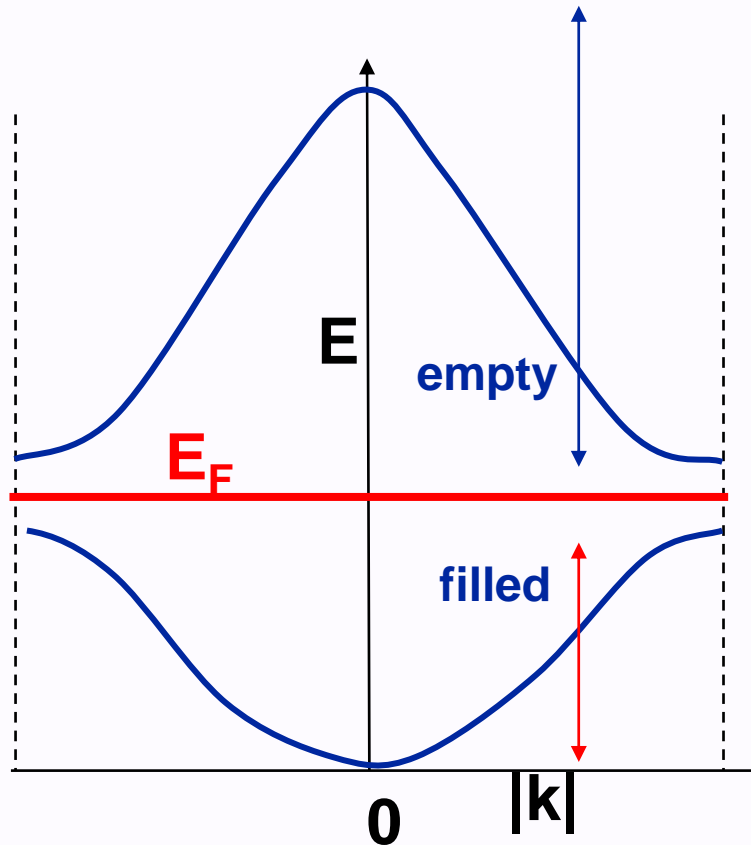
$$(2\pi/L)^3 \sum_{\underline{k}} \rightarrow \int d\underline{k} \quad \text{or} \quad (1/N_{\text{k-point}}) \sum_{\underline{k}} \rightarrow (1/V_{\text{BZ}}) \int d\underline{k}$$

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 ($n = 1, 2, \dots$) $E^n(\underline{\mathbf{k}})$ 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**

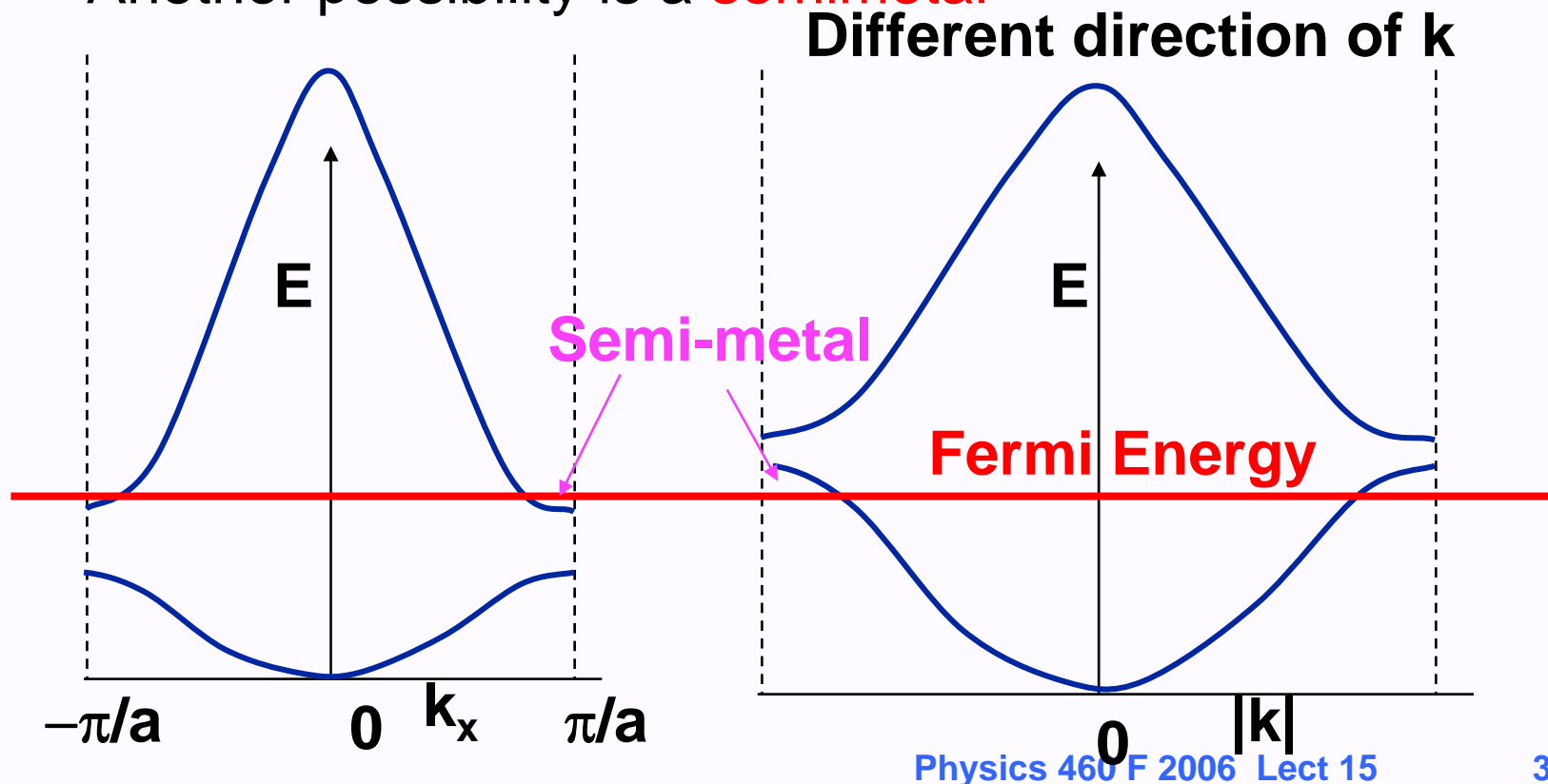
Metals vs Insulators

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



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 H₂ - 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”) $E^n(\mathbf{k})$**
- **We can predict that some materials must 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)**