Phys 570

Lecture #6

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Chapter 7: Energy Bands

Introduction

- The free electron model of metals gives us good insight into the heat capacity, thermal conductivity, electrical conductivity, magnetic susceptibility, and electrodynamics of metals.
- But the model fails to help us with other large questions:
  - *the distinction between metals, semimetals, semiconductors, and Insulators*
  - *the occurrence of positive values of the Hall coefficient*
  - *the relation of conduction electrons in the metal to the valence electrons of free Atoms*
  - *many transport properties, particularly magneto transport*

- Hence, we need to modify Fermi Electron Model to be able to answer these puzzles. We will see that little modification is just adequate.

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Introduction

- The difference between a good conductor and a good insulator is striking. The electrical resistivity of a pure metal may be as low as 10^{-10} Ω.cm at 1 K, apart from the possibility of superconductivity.
- The resistivity of a good insulator may be as high as 10^{22} Ω.cm.
- This range of 10^{32} may be the widest of any common physical property of solids.

- Every solid contains electrons. The important question for electrical conductivity is how the electrons respond to an applied electric field.
- electrons in crystals are arranged in energy bands.
- Bands are separated by band gaps (Forbidden Regions)
- Source of bands come from the interaction of the conduction electron waves with the ion cores of the crystal

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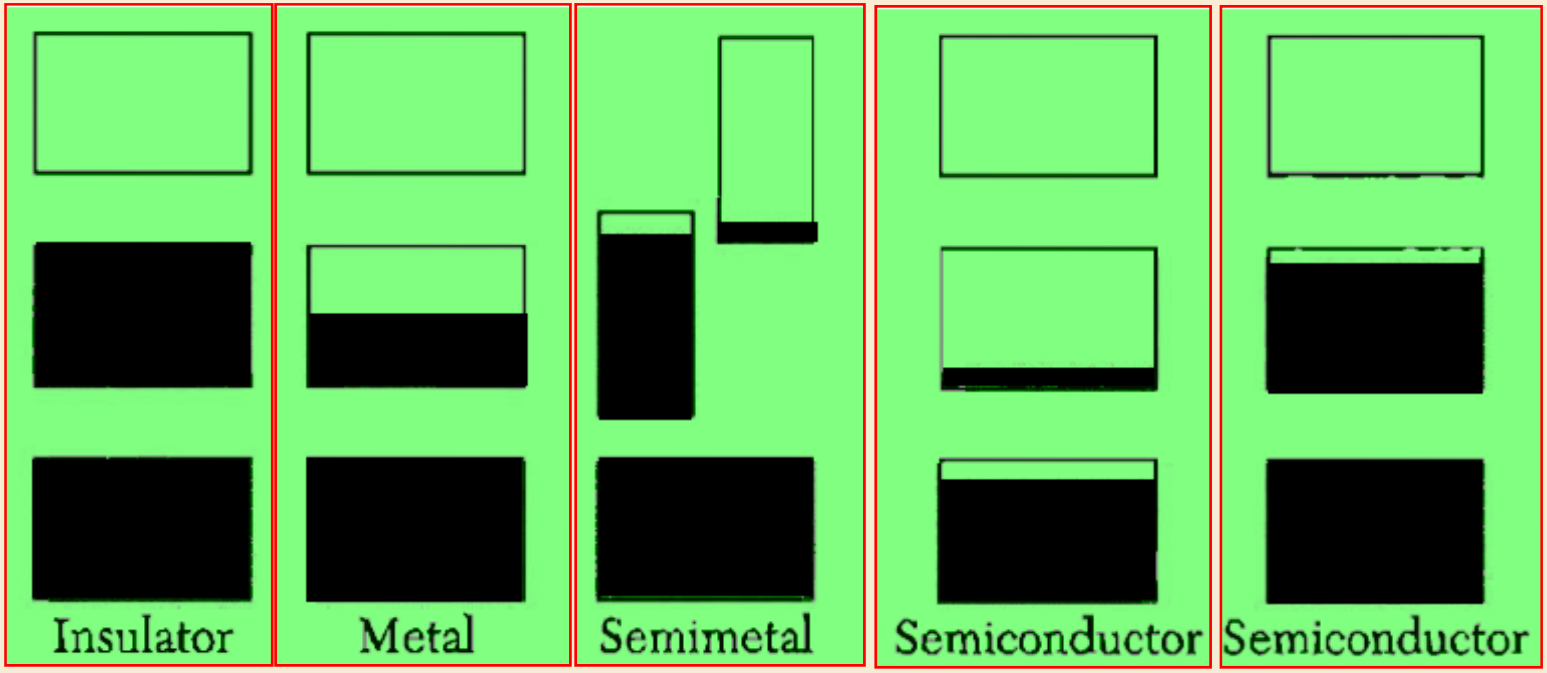
Insulators, Metals and Semiconductors

- ❑ Insulator: if the allowed energy bands are either filled or empty, for then no electrons can move in an electric field.
- ❑ Metal if one or more bands are partly filled.
- ❑ Semiconductor or a semimetal if one or two bands are slightly filled or slightly empty.



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Modifications needed for Free Electron Model

- To modify the Free Electron Model; we will assume that electron is not totally free. It has to respect the periodicity of the crystal.
- This will directly lead to the important result: band gap.
- Also; we introduce the concept of effective mass of electron m^* *which may be larger or* smaller than the free electron mass, or may even be negative.
- Negative and Positive effective mass can directly explain for +tive Hall coefficient.

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NEARLY FREE ELECTRON MODEL (1-D)

- On the free electron model the allowed energy values are distributed essentially continuously from zero to infinity

$$\varepsilon_k = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) \qquad (1)$$

From boundary conditions over a cube of side L :

$$k_x, k_y, k_z = 0; \pm\frac{2\pi}{L}; \pm\frac{4\pi}{L}; \ldots\ldots \qquad (2)$$

wavefunctions are of the form : $\psi_k(\mathrm{r}) = e^{i\mathrm{k.r}}$ (3)

- The band structure of a crystal can often be explained by the nearly free electron model for which the band electrons are treated as perturbed only weakly by the periodic potential of the ion cores. This model answers almost all the qualitative questions about the behavior of electrons in metals.

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Bragg Reflections

- Bragg reflection of electron waves in crystals is the cause of energy gaps. *At Bragg reflection wavelike solutions of the Schrodinger equation do not exist, as in Fig. 2 (Forbidden Region)*

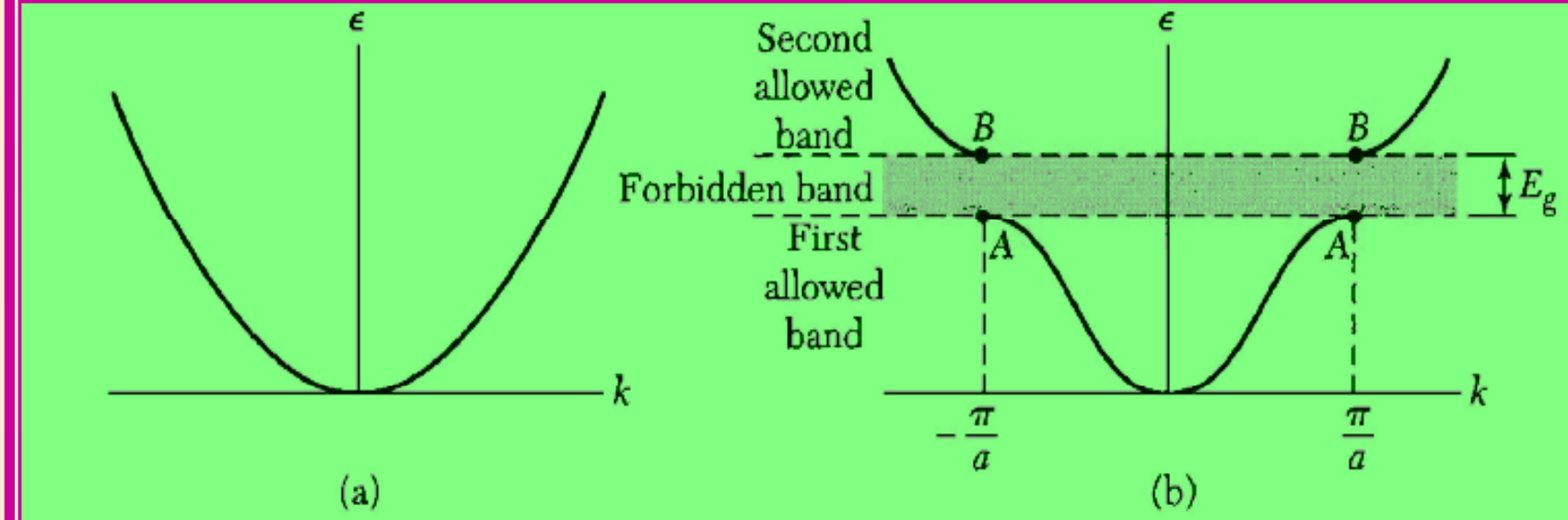

Figure 2 (a) Plot of energy ϵ versus wavevector k for a free electron. (b) Plot of energy versus wavevector for an electron in a monatomic linear lattice of lattice constant a. The energy gap E_g shown is associated with the first Bragg reflection at $k = \pm\pi/a$; other gaps are found at higher energies at $\pm n\pi/a$, for integral values of n.

- Fig. 2, in (a) for entirely free electrons and in (b) for electrons that are nearly free, but with an energy gap at $k = \pm\pi/a$. *The Bragg* condition $(\mathbf{k} + \mathbf{G})^2 = \mathbf{k}^2$ for diffraction of a wave of wavevector **k** becomes in one dimension:

$$k = \pm\frac{1}{2}G = \pm\frac{n\pi}{a} \quad \text{(in 1-D)} \qquad (4)$$

- where $G = 2\pi n/a$ is a reciprocal lattice vector and n is an integer. The first reflections and the first energy gap occur at $k = \pm\pi/a$. The region in k space between $-\pi/a$ and π/a is the first **Brillouin zone of this lattice.** Other energy gaps occur for other values of the integer n.
- 2nd **Brillouin zone** is located between: $\pm 2\pi/a$ *and so on.*

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Bragg Reflections lead to Band Gap

- Electron waves will move only inside the B.Z.
- All waves stop and Reflect at the borders of the B.Z. (From forbidden regions).
- we will have 3 different types of Waves:
  - Moving to the Right → (will be reflected to the left from π/a)
  - Moving to the Left ← (will be reflected to the right from $-\pi/a$)
  - Standing waves (time independent. Do not move).
- Consequently: Standing waves can be used to describe the case.
- We can form two different standing waves from the two traveling waves:

$$e^{+i\pi x/a} = \cos(\pi x/a) + i\sin(\pi x/a) \quad \rightarrow$$

$$e^{-i\pi x/a} = \cos(\pi x/a) - i\sin(\pi x/a) \quad \leftarrow$$

$$\text{or: } e^{\pm i\pi x/a} = \cos(\pi x/a) \pm i\sin(\pi x/a)$$

- Hence; we have 2 standing waves: Even (+) and odd (-):

$$\left.\begin{aligned}\psi(+) &= e^{+i\pi x/a} + e^{-i\pi x/a} = 2\cos(\pi x/a)\\ \psi(-) &= e^{+i\pi x/a} - e^{-i\pi x/a} = 2i\sin(\pi x/a)\end{aligned}\right\} \quad (5)$$

- In one dimension; solution to the Schrödinger equation at the boundaries of Brillouin Zone are standing waves.

Origin of the Energy Gap

- The two standing waves Ψ(+) and Ψ(-) pile up electrons at different regions, and therefore the two waves have different values of the potential energy in the field of the ions of the lattice. This is the origin of the energy gap.
- Waves traveling in different directions have different energies, leading to energy gap.

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NEARLY FREE ELECTRON MODEL

- Let us consider the probability density ρ for both + and – (even and odd) functions.
- ρ is expressed as: $\rho=\psi^{*}\psi=|\psi|^{2}$
- For pure travelling wave: $\psi = e^{ikx}$ ➔ $\rho=\psi^{*}\psi=|\psi|^{2} = e^{-ikx}\, e^{ikx} =1$
- This mean that probability of finding electron = 100% (ρ = const.)
- But in our case (Nearly Free Electron), ρ is not Const.

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

$$\rho(-) = |\psi(-)|^{2} \alpha \sin^{2}(\frac{\pi x}{a})$$

- Accordingly; for even functions (+): ρ = 1 only at specific values of x; namely at: x =0, a, 2a, ….
- For odd functions (-): ρ = 1 only at: x = 1/2 a, 3/2 a, 5/2 a ….

- Hence; even function probability has its values max (=1) when the Pot. Energy is at lowest values (just at the Ions).
- On the other hand; odd function probability has its values max (=1) in the middle locations between the Ions.
- In other words: (+) function piles up electrons near the Ions while the (-) function piles up electrons in places mid-distance from two ions.
- This leads to an energy gap between the two pools of electrons.
- If we calculate the expectation values (average energy) in these three cases: + , -, and Free electron (travelling wave): we have:
- that of $\rho(+)$ is lower than that of Free Electron
- that of $\rho(-)$ is above that of Free Electron.
- Result is: $\mathbf{E_g}$ difference in energy between the $\rho(+)$ and $\rho(-)$
- This is the origin of the Band Gap.

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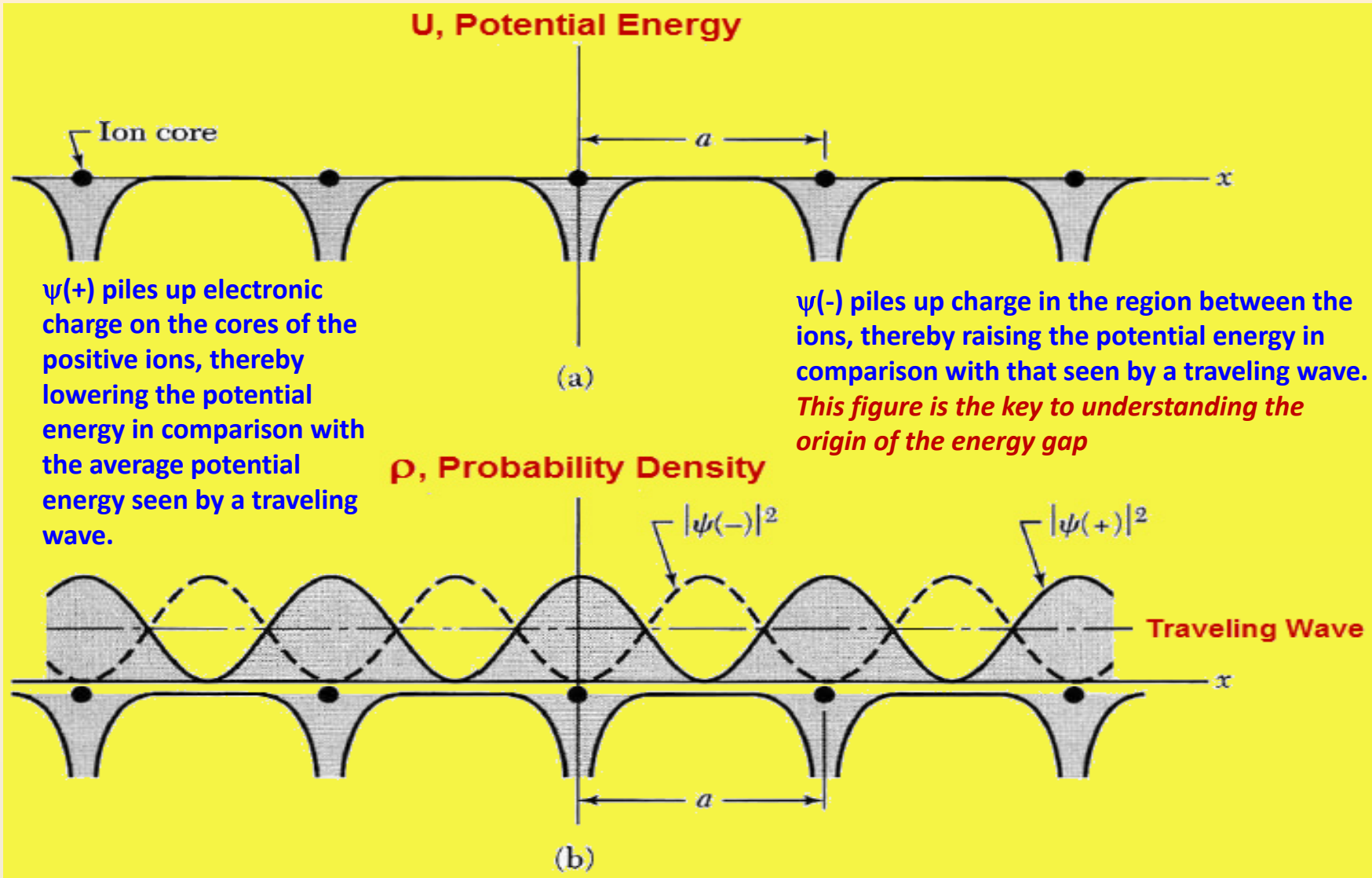
NEARLY FREE ELECTRON MODEL



ψ(+) piles up electronic charge on the cores of the positive ions, thereby lowering the potential energy in comparison with the average potential energy seen by a traveling wave.

ψ(-) piles up charge in the region between the ions, thereby raising the potential energy in comparison with that seen by a traveling wave.

This figure is the key to understanding the origin of the energy gap

- Let us suppose that the potential energy of an electron in the crystal at point *x is:*

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

The first-order energy difference between the two standing wave states is :

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

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

$$= U \qquad (6)$$

- We see that the gap is equal to the Fourier component of the crystal potential.

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BLOCH FUNCTIONS

- F. Bloch proved the important theorem that the solutions of the Schrodinger equation for a periodic potential must be of a special form:

$$\psi_k(r) = u_k(r) e^{ik.r} \qquad (7)$$

- $u_k(r)$ *has same periodicity of the crystal with* $u_k(r) = u_k(r + T)$
- T is the translation vector of the lattice in normal space.
- Eq. (7) means that:

*The eigenfunctions of the wave equation for a periodic potential are the product of a plane wave exp(i**k**.**r**) times a function $u_k(r)$ with the periodicity of the crystal lattice.*

- Bloch functions can he assembled into wave packets to represent electrons that propagate freely through the potential field of the ion cores.

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Proof of BLOCH FUNCTIONS

- We consider *N identical lattice points on a ring of length Na. The potential energy is* periodic in *a, with U(x) = U(x + sa), where s is an integer.*
- symmetry of the ring leads to:

$$\psi(x+a) = C\psi(x) \tag{8}$$

where C is a constant. Then, on going once around the ring:

$$\psi(x+Na) = \psi(x) = C^N \psi(x)$$

bccause ψ(x) must be single-valued.

It follows that C is one of the N roots of unity, or:

$$C = e^{i2\pi s/N} \qquad s = 0,1,2,\ldots,N-1 \tag{9}$$

satisfies (8), provided that $U_k(x)$ has the periodicity a, so that $U_k(x) = U_k(x+a)$.

This is the Bloch result (7).