



# Chapter 8 Energy Bands II

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- 8.1 Semiclassical motion of electrons**
- 8.2 Electron motion in a constant electric field**
- 8.3 Electron motion in a constant magnetic field**
- 8.4 Fermi Surface & Density of States**
- 8.5 Experimental measurement of Fermi Surface**
- 8.6 Energy bands in some typical metals**
- 8.7 Success and Failure of electron band theory**



# 8.1 Semiclassical Motion of Electrons

## I. Average velocity in a crystal

Consider a electron eigen state  $\psi_{n\vec{k}}$

Electron has *no fixed velocity*, but has an average value

$$\bar{v}_n(\vec{k}) = \frac{1}{m} \int \psi_{n\vec{k}}^* \hat{p} \psi_{n\vec{k}} d\vec{r}$$

$$\hat{p} = -i\hbar\nabla$$

due to Bloch theorem:

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r})$$



$$\bar{v}_n(\vec{k}) = \frac{1}{m} \int u_{n\vec{k}}^*(\hat{p} + \hbar\vec{k}) u_{n\vec{k}} d\vec{r}$$

$u_{n\vec{k}}(\vec{r})$  satisfies:

$$\left[ -\frac{\hbar^2}{2m} (\nabla + i\vec{k})^2 + V(\vec{r}) \right] u_{n\vec{k}}(\vec{r}) = \varepsilon_n(\vec{k}) u_{n\vec{k}}(\vec{r})$$

$$\left[ \frac{(\hat{p} + \hbar\vec{k})^2}{2m} + V(\vec{r}) \right] u_{n\vec{k}}(\vec{r}) = \varepsilon_n(\vec{k}) u_{n\vec{k}}(\vec{r})$$

$$\hat{H}_{\vec{k}} = \frac{(\hat{p} + \hbar\vec{k})^2}{2m} + V(\vec{r})$$



$$\hat{H}_{\vec{k}} u_{n\vec{k}}(\vec{r}) = \varepsilon_n(\vec{k}) u_{n\vec{k}}(\vec{r})$$

take  $\nabla_{\vec{k}} = \frac{\partial}{\partial \vec{k}}$ :

$$\begin{aligned} & \frac{\hbar}{m} (\hat{p} + \hbar \vec{k}) u_{n\vec{k}}(\vec{r}) + \hat{H}_{\vec{k}} \nabla_{\vec{k}} u_{n\vec{k}}(\vec{r}) \\ &= [\nabla_{\vec{k}} \varepsilon_n(\vec{k})] u_{n\vec{k}}(\vec{r}) + \varepsilon_n(\vec{k}) \nabla_{\vec{k}} u_{n\vec{k}}(\vec{r}) \end{aligned}$$

left multiply  $u_{n\vec{k}}^*(\vec{r})$ , and take integral over  $\vec{r}$ :

$$\begin{aligned} & \frac{\hbar}{m} \int u_{n\vec{k}}^*(\vec{r}) (\hat{p} + \hbar \vec{k}) u_{n\vec{k}}(\vec{r}) d\vec{r} + \int u_{n\vec{k}}^*(\vec{r}) \hat{H}_{\vec{k}} \nabla_{\vec{k}} u_{n\vec{k}}(\vec{r}) d\vec{r} \\ &= \nabla_{\vec{k}} \varepsilon_n(\vec{k}) \int u_{n\vec{k}}^*(\vec{r}) u_{n\vec{k}}(\vec{r}) d\vec{r} + \varepsilon_n(\vec{k}) \int u_{n\vec{k}}^*(\vec{r}) \nabla_{\vec{k}} u_{n\vec{k}}(\vec{r}) d\vec{r} \end{aligned}$$



Hamiltonian is a Hermitian operator, the second terms cancel

$$\vec{v}_n(\bar{k}) = \frac{1}{\hbar} \nabla_{\bar{k}} \epsilon_n(\bar{k})$$

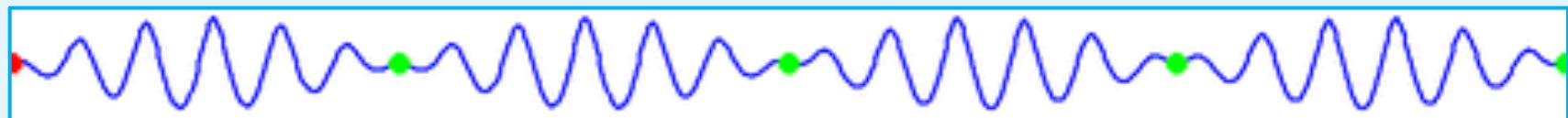
Quantum mechanical wave package, a Bloch wave.

## Kind Reminder: phase and group velocities

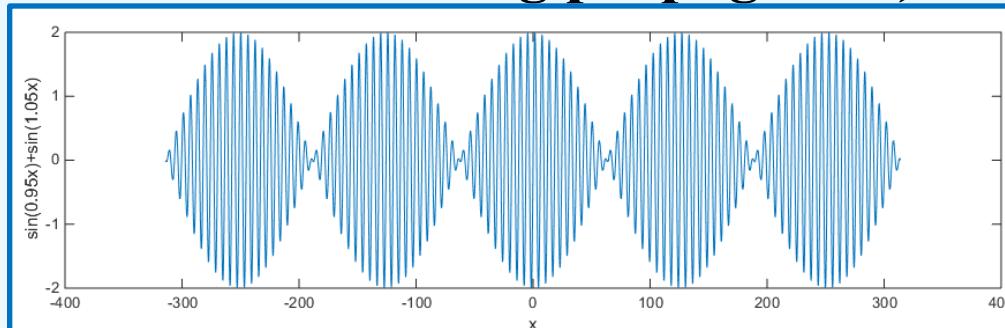
**phase velocity:** the rate at which the phase of the wave propagates in space, for a pure lattice wave with specific frequency  $\omega$  and lattice vector  $q$

$$v_p = \frac{\omega}{q}$$

$$v_p = \frac{\lambda}{T}$$



**group velocity:** describe the speed of the *envelope* of the wave packet (given a small range of  $q$ , such that the envelope *does not distort* too much during propagation).



$$v_g = \frac{\partial \omega}{\partial q}$$



Bloch wave with vectors near  $\bar{k}$  (in the range of  $\Delta\bar{k}$ )

constitutes a wave packet  $\bar{k}$ , whose **group velocity** is:

$$\vec{v} = \nabla_{\bar{k}} \omega(\bar{k}) \quad \omega(\bar{k}) \text{ —— frequency}$$

use  $\epsilon(\bar{k}) = \hbar\omega(\bar{k})$ , the velocity of Bloch electron is:

$$\boxed{\vec{v} = \frac{1}{\hbar} \nabla_{\bar{k}} \epsilon(\bar{k})}$$

■ **velocity  $\vec{v}$  is perpendicular to the isoenergy surface in  $\bar{k}$  space**

When the isosurface is not a sphere,  $\vec{v}$  is generally not parallel to  $\bar{k}$ .



free electrons:

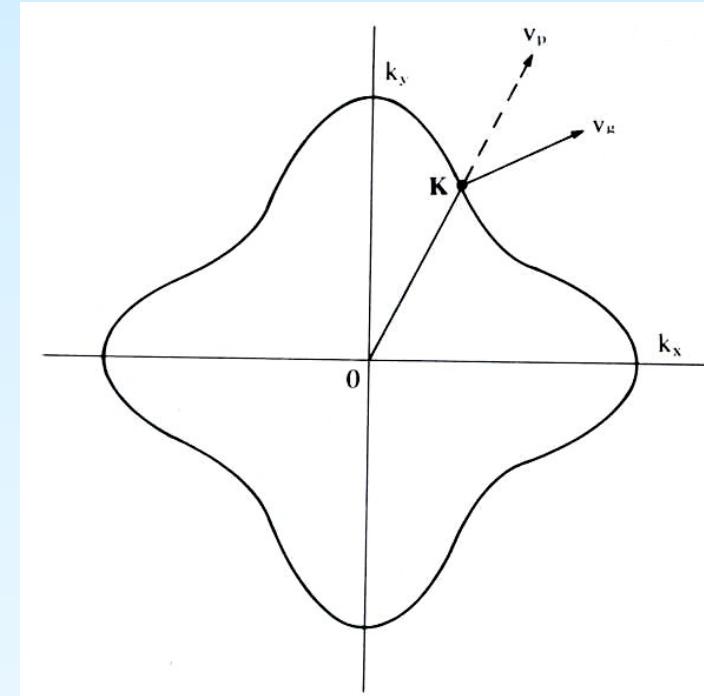
$$\bar{v} = \frac{\bar{p}}{m} = \frac{\hbar \bar{k}}{m}$$

$$\bar{v} \propto \bar{k} \quad \bar{v} \parallel \bar{k}$$

### ■ Average velocity of crystal electron

depends on  $\varepsilon_n(\bar{k})$  and  $\bar{k}$ .

$$\varepsilon(\bar{k}) = \varepsilon(-\bar{k}) \quad \bar{v}(\bar{k}) = -\bar{v}(-\bar{k})$$



## II. Semiclassical model of electron motion

*Response* of crystal electron to external fields—treated classically

*Electron state* in periodic lattice—quantum mechanical way (in terms of energy band theory).



## Bloch electron in an external force $\vec{f}$

The *electron energy change* equals the *work* external force does in an *unit time*:

$$\frac{d\epsilon(\bar{k})}{dt} = \vec{f} \cdot \vec{v}$$

$$\frac{d\epsilon(\bar{k})}{dt} = \nabla_{\bar{k}}\epsilon(\bar{k}) \frac{d\bar{k}}{dt} = \hbar\vec{v} \frac{d\bar{k}}{dt}$$

$$\hbar\vec{v} \frac{d\bar{k}}{dt} = \vec{f} \cdot \vec{v}$$

$$\boxed{\vec{f} = \hbar \frac{d\bar{k}}{dt}}$$

The changing ratio of  $\bar{k}$  is proportional to **external force**  $\vec{f}$ , and has the same direction.

- ✓ In a similar form as Newton's second law, but with only external forces  $\vec{f}$ .



$\hbar\vec{k}$  quasi momentum

✓ Electron in an external electric & magnetic fields

$$\hbar \frac{d\vec{k}}{dt} = -e [\vec{E}(\vec{r}, t) + \vec{v}_n(\vec{k}) \times \vec{B}(\vec{r}, t)]$$

### III. Acceleration and Effective Mass

#### 1. Acceleration

$$\vec{a} = \frac{d\vec{v}}{dt} = \frac{d}{dt} \left[ \frac{1}{\hbar} \nabla_{\vec{k}} \epsilon(\vec{k}) \right] = \frac{1}{\hbar} \left[ \frac{d}{d\vec{k}} \nabla_{\vec{k}} \epsilon(\vec{k}) \frac{d\vec{k}}{dt} \right]$$

$$= \frac{1}{\hbar^2} \nabla_{\vec{k}} \nabla_{\vec{k}} \epsilon(\vec{k}) \cdot \vec{f}$$

1D case:  $a = \frac{1}{\hbar^2} \frac{d^2 \epsilon}{dk^2} \cdot f$



## 2. Effective mass

1D:

$$\mathbf{a} = \frac{1}{\hbar^2} \frac{\mathbf{d}^2 \boldsymbol{\varepsilon}}{\mathbf{d}\mathbf{k}^2} \cdot \mathbf{f} \quad \mathbf{f} = \mathbf{m}^* \mathbf{a}$$

$$\mathbf{m}^* = \frac{\hbar^2}{\mathbf{d}^2 \boldsymbol{\varepsilon} / \mathbf{d}\mathbf{k}^2}$$

3D:

$$\vec{a} = \frac{1}{\hbar^2} \nabla_{\vec{k}} \nabla_{\vec{k}} \boldsymbol{\varepsilon}(\vec{k}) \cdot \vec{f}$$

in a tensor form:

$$\begin{pmatrix} \mathbf{a}_x \\ \mathbf{a}_y \\ \mathbf{a}_z \end{pmatrix} = \left( \frac{1}{\mathbf{m}^*} \right) \begin{pmatrix} \mathbf{F}_x \\ \mathbf{F}_y \\ \mathbf{F}_z \end{pmatrix}$$



$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_n(\vec{k})}{\partial k_i \partial k_j}$$

$i, j = x, y, z$

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \begin{pmatrix} \frac{\partial^2 \varepsilon}{\partial k_x^2} & \frac{\partial^2 \varepsilon}{\partial k_x \partial k_y} & \frac{\partial^2 \varepsilon}{\partial k_x \partial k_z} \\ \frac{\partial^2 \varepsilon}{\partial k_x \partial k_y} & \frac{\partial^2 \varepsilon}{\partial k_y^2} & \frac{\partial^2 \varepsilon}{\partial k_y \partial k_z} \\ \frac{\partial^2 \varepsilon}{\partial k_x \partial k_z} & \frac{\partial^2 \varepsilon}{\partial k_y \partial k_z} & \frac{\partial^2 \varepsilon}{\partial k_z^2} \end{pmatrix}$$

Diagonal terms along the principal axes:

$$\frac{1}{m_\alpha^*} = \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_n(\vec{k})}{\partial k_\alpha^2} \quad \alpha = x, y, z$$



- ✓ Effective mass is a rank-2 tensor (a matrix), generally the acceleration of electrons is *not necessarily parallel to external forces*. Due to the fact that electrons not only “feels” external forces, but are also affected by periodic potentials.
- ✓ Effective mass includes the effects of crystal potentials, leaving the acceleration of electrons and external force in a simple relation.

Effective mass is related to the *electron state* and *structure of energy bands*.

band bottom: “+” sign

band top: “-” sign

## 8.2 Electron Motion in a Constant Electric Field

### I. Electron in a constant electric field

Under the external field  $\vec{E}$

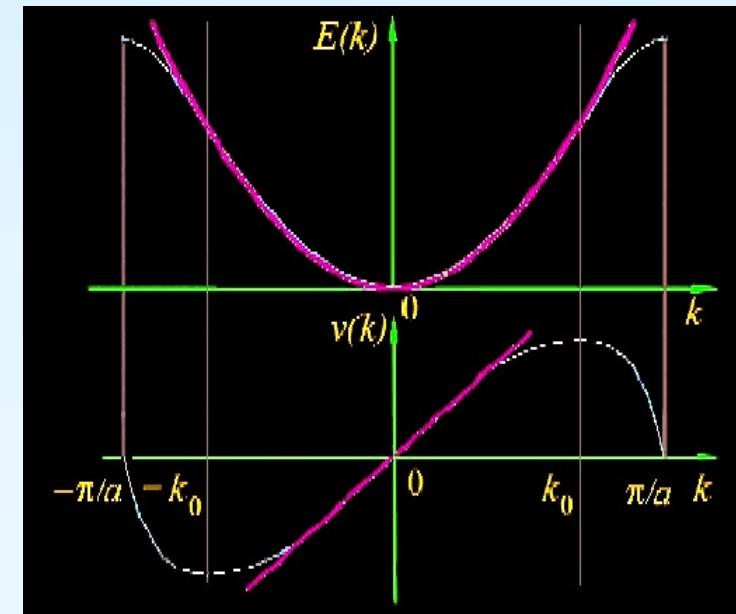
$$\hbar \frac{d\vec{k}}{dt} = -e\vec{E}$$

$$\frac{d\vec{k}}{dt} = -\frac{e\vec{E}}{\hbar}$$

Since electrons distribute

uniformly in  $k$ -space, every single state move in the same velocity:

$$\vec{k}(t) = \vec{k}(0) - \frac{e\vec{E}t}{\hbar}$$





## II. Energy band filling and conductivity

**full band:** a band with all  $2N$  energy levels filled

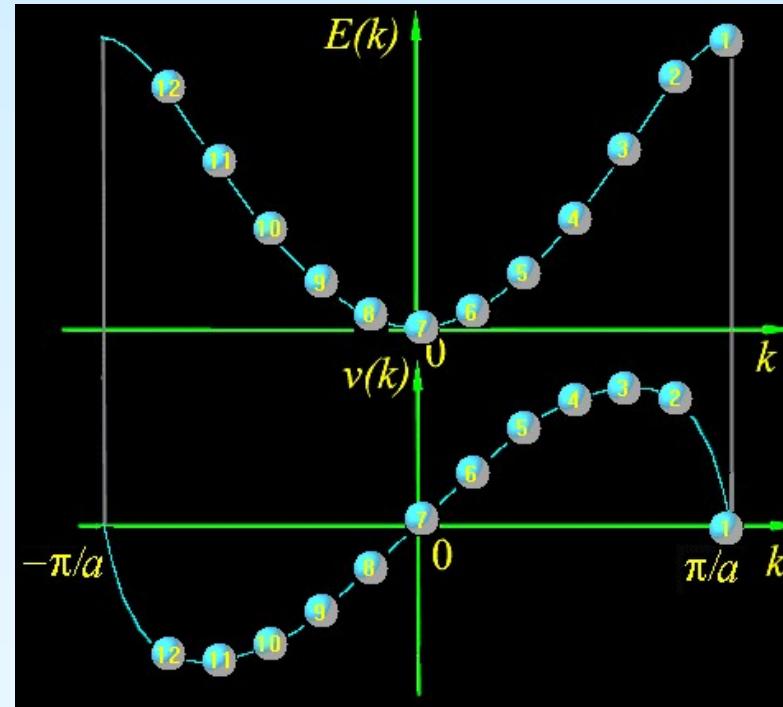
**partially filled band:** some of the levels are occupied by electrons

For each band:

$$\varepsilon(\vec{k}) = \varepsilon(-\vec{k}) \quad \vec{v}(-\vec{k}) = -\vec{v}(\vec{k})$$

**Electrons of  $\vec{k}$  and  $-\vec{k}$  have the same velocity, moving oppositely.**

**Absence of external fields:** full/partially filled band,  $\vec{k}$  and  $-\vec{k}$  electrons move anti-parallel and their contributions cancel, giving rise to no net electrical current.



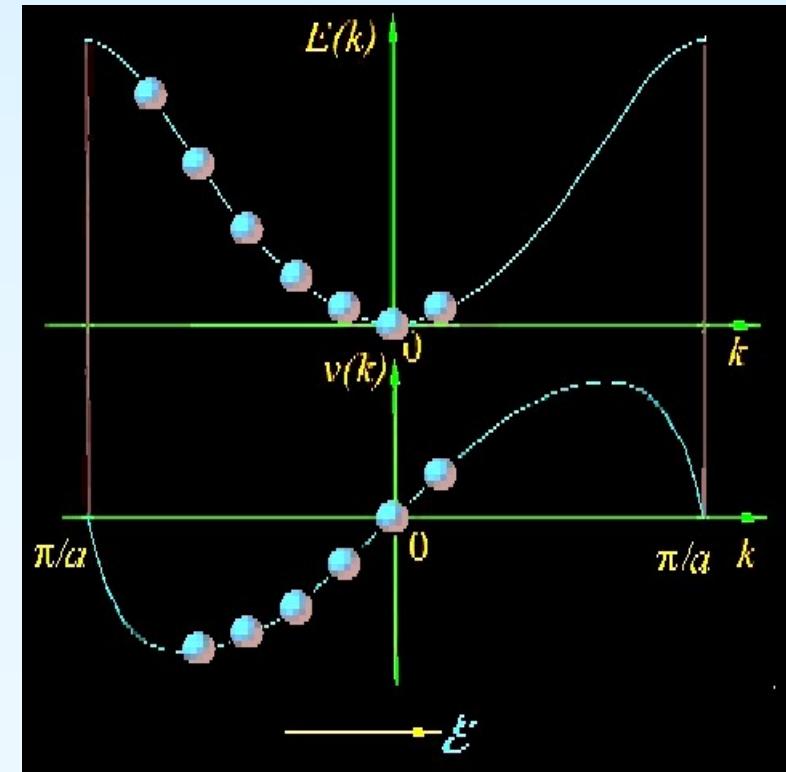
**presence of external field:**

■ **full band:** under external fields, all electron states change from one  $\vec{k}$  state to another with the same rate. Due to the periodicity of lattice,  $k$ -distribution is intact and no net current can be produced in this way.

**■ Partially filled band:**

Only a part of states are occupied by electrons. Due to the effect of external fields, the final  $k$ -distribution will be *asymmetric*, making two different numbers of electrons moving parallel and anti-parallel to fields, and thus a net electricity can exist.

✓ Partially filled band can conduct electricity under external fields





### III. Nearly full band and hole

There exist one state  $\bar{k}$  unoccupied by electron, now the band is not fully filled——**nearly full band**.

A current  $I_{\bar{k}}$  is induced by applying an external field.

If we put an electron in state  $\bar{k}$ , the current of the electron is:

$$-e\bar{v}(\bar{k})$$

By filling this single electron, the energy band is full and net electrical current is:

$$I_{\bar{k}} + (-e\bar{v}(\bar{k})) = 0$$

$$I_{\bar{k}} = e\bar{v}(\bar{k})$$



when state  $\vec{k}$  is unoccupied, electricity in a nearly full band is just like being produced by a positive charge  $e$ , whose velocity is the same as that of a electron in state  $\vec{k}$ . Such a carrier is called a **hole**.

Collective motion of a big number of electrons can be effectively described as the motion of a few holes.

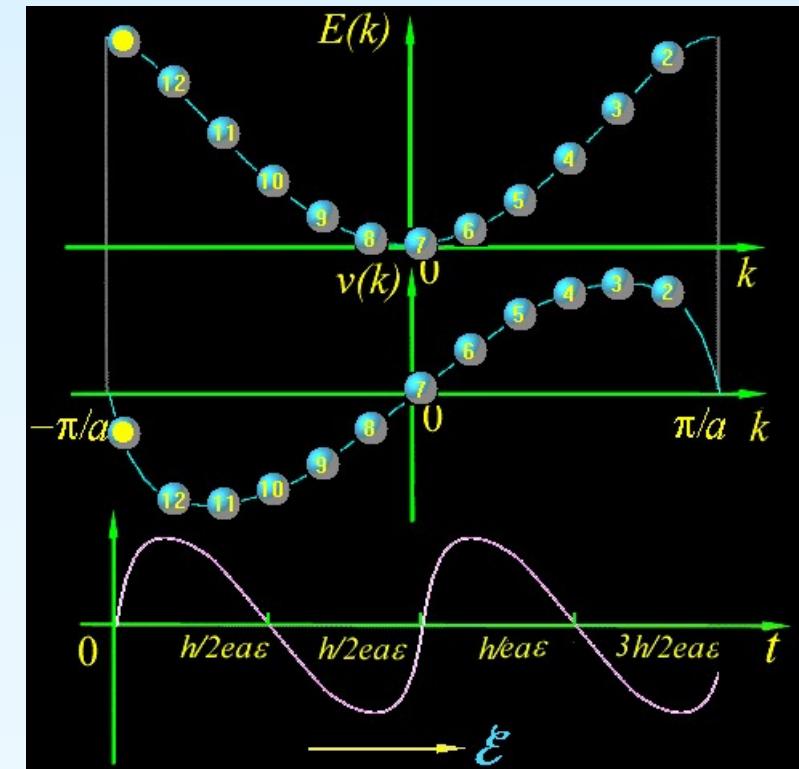
Under electric field  $\vec{E}$ , all the electron states in nearly full band moves following the equation  $\vec{f} = \frac{d(\hbar\vec{k})}{dt}$ .  
Acceleration of the empty state is:

$$\frac{d\vec{v}(\vec{k})}{dt} = \frac{1}{m_e^*} (-e\vec{E})$$

Generally, empty state exists near band top, which corresponds to negative effective mass  $m_e^*$ , define the effective mass of hole as:

$$m_h^*(\vec{k}) = -m_e^*(\vec{k})$$

$$\frac{d\vec{v}(\vec{k})}{dt} = \frac{e\vec{E}}{m_h^*(\vec{k})}$$



Hole can be regarded as a particle with both positive charge and effective mass.



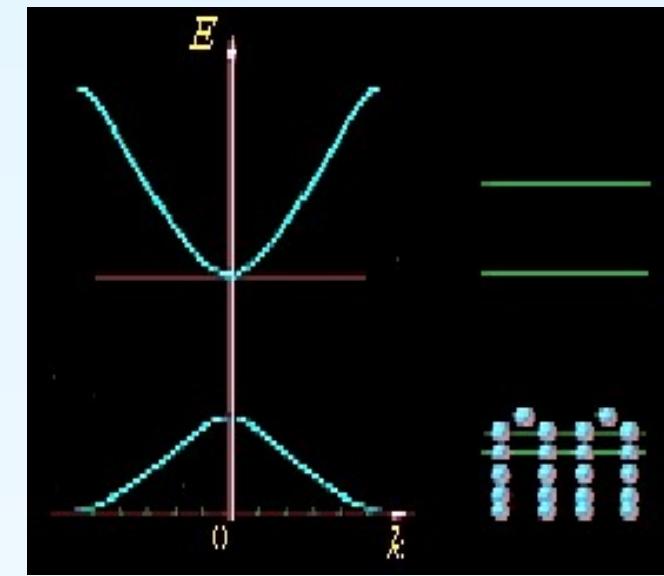
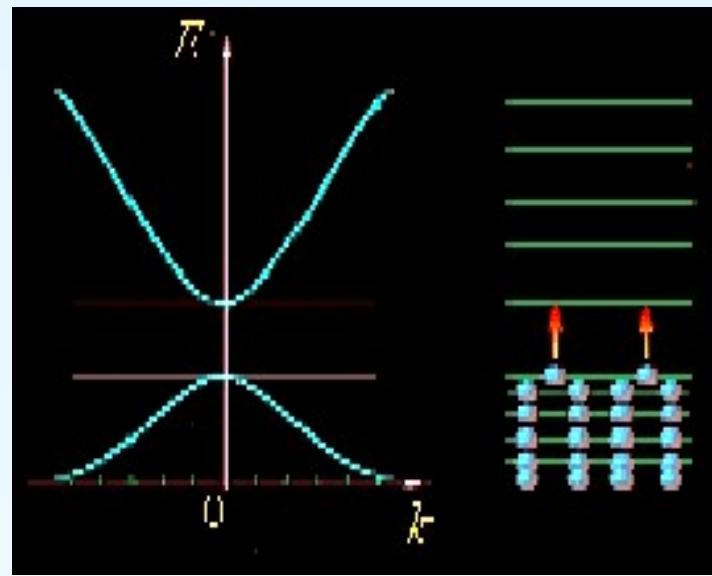
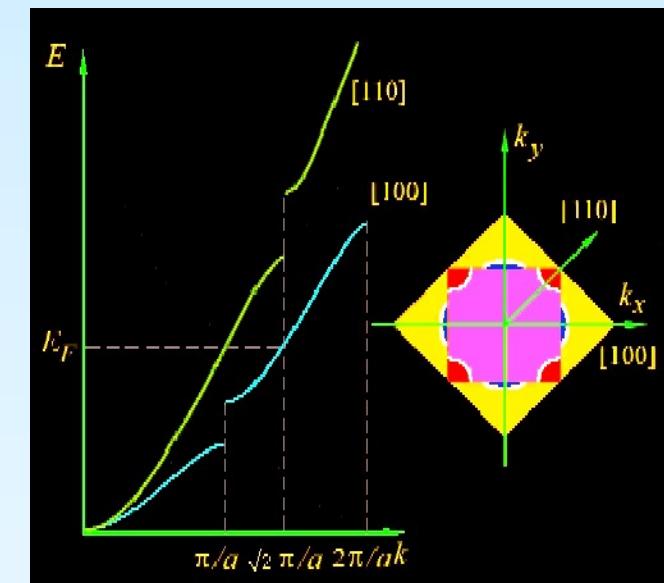
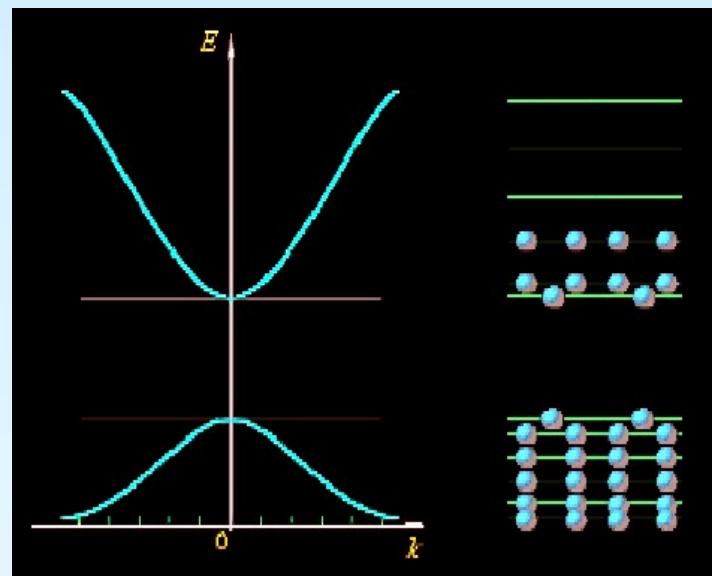
## IV. Conductor, Semiconductor, and Insulator

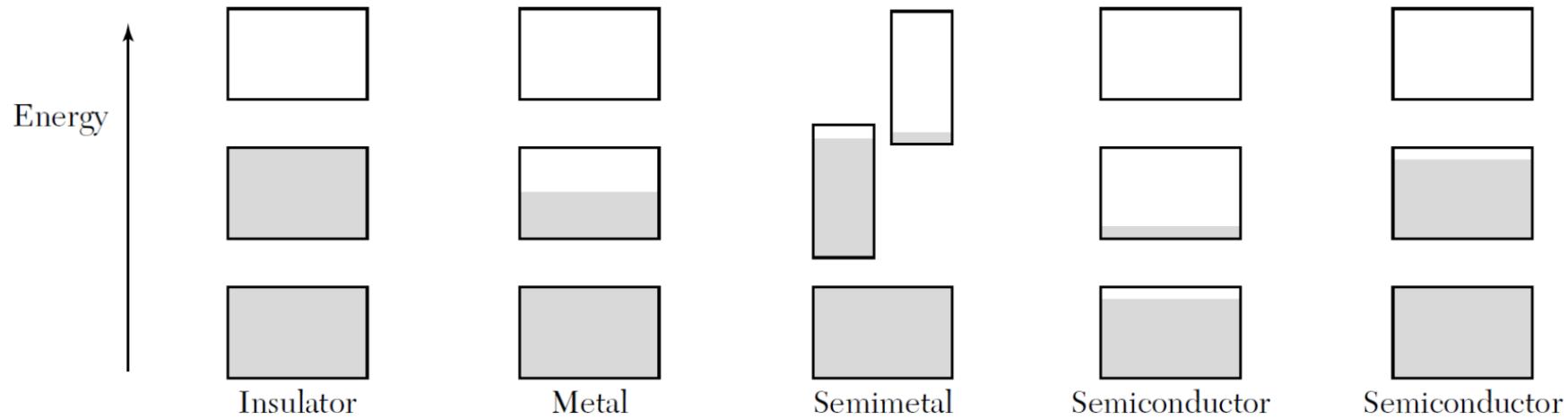
- ✓ In practical crystals, electrons fill up energy bands from low energy to high, until the band where valence electrons occupy ---valence band.
- ✓ The higher bands are empty---empty band. The energy interval between *top of valence band* and *bottom of nearest empty band* is called **forbidden band (gap)**.

Conductor: valence band is partially filled

non-conductor:

- { semimetal—full band, but gap vanishes or has band overlaps
- semiconductor—full band, but gap is narrow (0-2eV)
- insulator—full band and gap is wide (much larger than 2eV)





**Figure 1** Schematic electron occupancy of allowed energy bands for an insulator, metal, semimetal, and semiconductor. The vertical extent of the boxes indicates the allowed energy regions; the shaded areas indicate the regions filled with electrons. In a **semimetal** (such as bismuth) one band is almost filled and another band is nearly empty at absolute zero, but a pure **semiconductor** (such as silicon) becomes an insulator at absolute zero. The left of the two semiconductors shown is at a finite temperature, with carriers excited thermally. The other semiconductor is electron-deficient because of impurities.



## 8.3 Electron Motion in a Constant Magnetic Field

### I. Semiclassical motion of electrons in a constant magnetic field

when only constant magnetic field is present:

$$\vec{v}(\vec{k}) = \frac{1}{\hbar} \nabla_{\vec{k}} \epsilon(\vec{k})$$

$$\hbar \frac{d\vec{k}}{dt} = -e \vec{v}(\vec{k}) \times \vec{B}$$

suppose  $\vec{B}$  is along z direction

➤ since  $\frac{d\vec{k}}{dt} \perp \vec{B}$ , we have  $\frac{d\vec{k}}{dt} \cdot \vec{B} = 0 \quad \frac{dk_z}{dt} = 0$

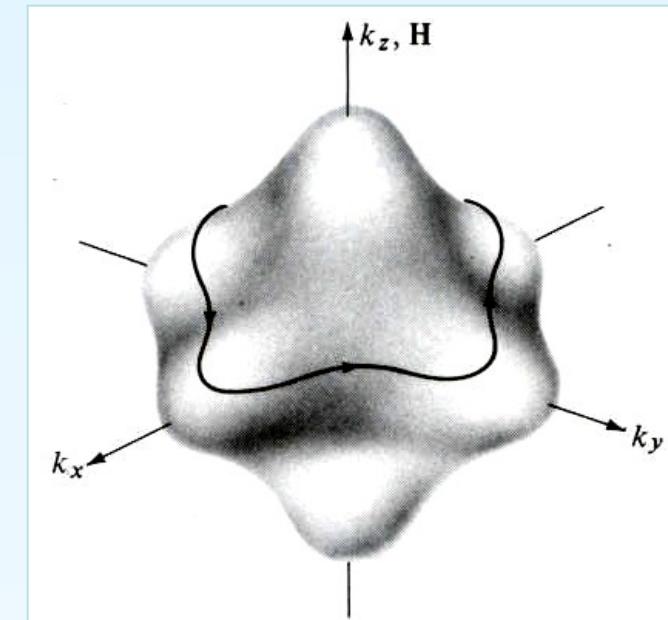
$$\rightarrow k_z = c$$

The component of  $\vec{k}$  parallel to the magnetic field is a constant.

➤ since  $\frac{d\vec{k}}{dt} \perp \vec{v}$ ,  $\frac{d\vec{k}}{dt} \bullet \vec{v} = 0 \rightarrow \frac{d\varepsilon(\vec{k})}{dt} = 0$

Energy of electron  $\varepsilon(\vec{k})$  do not change with time, electrons are moving on the isosurface in  $\vec{k}$  space.

Electrons move along the cross line between plane normal to magnetic field  $\vec{B}$  and the isoenergetic surface.





### 1. free electron:

$$\varepsilon(\bar{k}) = \frac{\hbar^2 k^2}{2m}$$

substitute it into E.O.M: 
$$\begin{cases} \vec{v}(\bar{k}) = \frac{\hbar \bar{k}}{m} \\ \frac{d\bar{k}}{dt} = -\frac{e}{m} \bar{k} \times \vec{B} \end{cases}$$

their components: 
$$\begin{cases} \frac{dk_x}{dt} = -\frac{eB}{m} k_y \\ \frac{dk_y}{dt} = \frac{eB}{m} k_x \\ \frac{dk_z}{dt} = 0 \end{cases}$$

$k_z$  is a constant, electron is in a uniform circular motion ( $k_x - k_y$  plane).

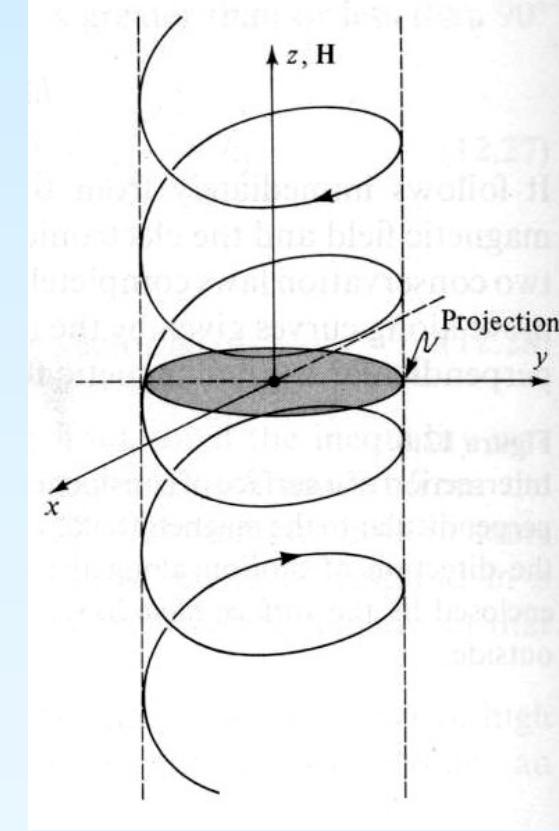


Period:  $T = \frac{2\pi m}{eB}$

Angular Frequency:  $\omega_c = \frac{2\pi}{T} = \frac{eB}{m}$  —— cyclotron frequency

Isoenergetic surface of free electron is sphere, the intersection line with planes normal to  $k_z$  are a series of circles.

$$\left\{ \begin{array}{l} \frac{dv_x}{dt} = -\frac{eB}{m} v_y \\ \frac{dv_y}{dt} = \frac{eB}{m} v_x \\ \frac{dv_z}{dt} = 0 \end{array} \right.$$



Free electron is in a *linear uniform motion* along magnetic field, and in a *uniform circular motion* perpendicular to it. As a result, **the electron is in a helical motion in real space.**



## 2. Bloch electrons

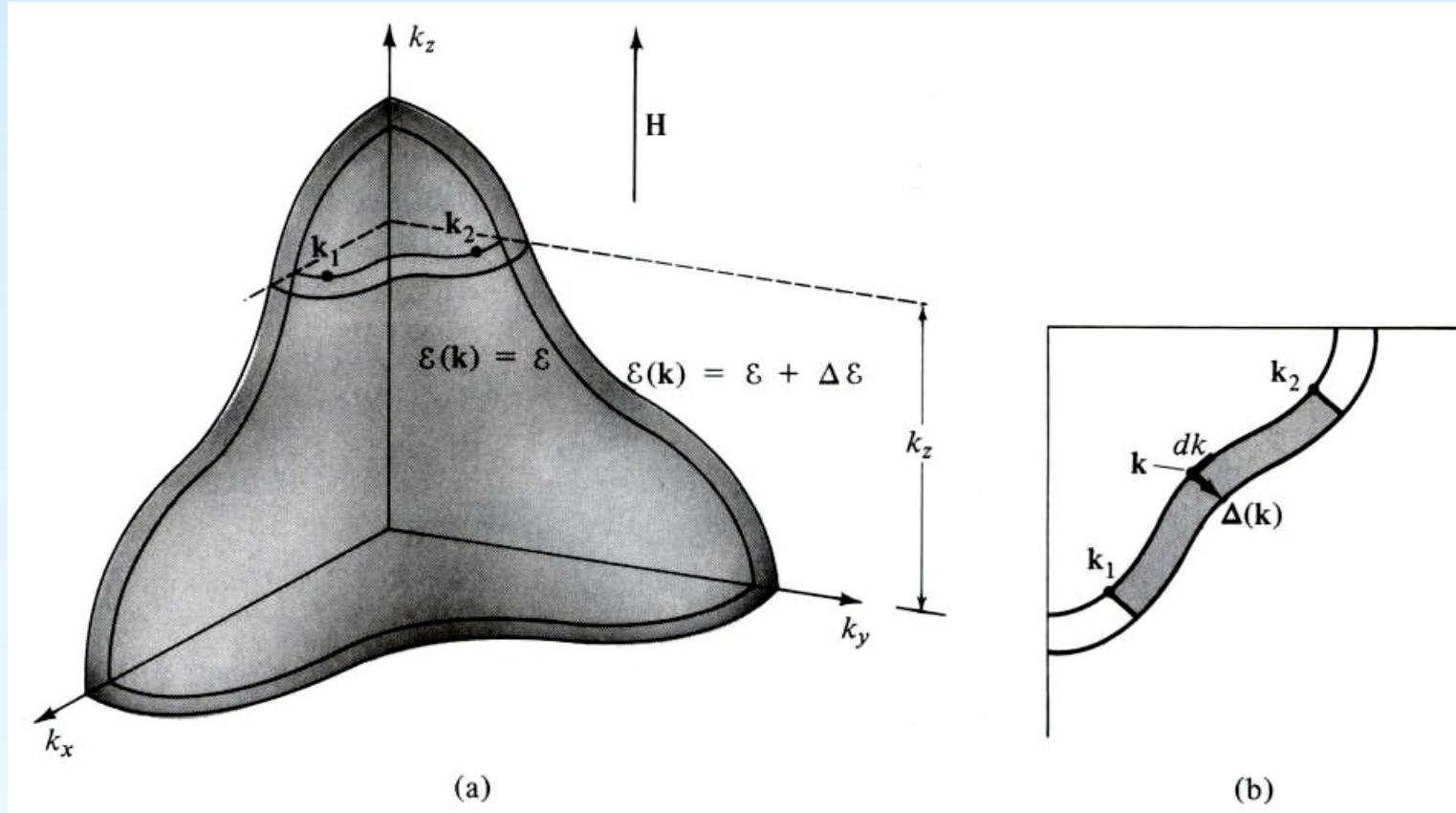
Isoenergetic surface is not necessarily a sphere, and the orbit is not necessarily a circle.

$$\omega_c = \frac{eB}{m_c^*} \quad m_c^* \text{ —cyclotron motion mass}$$

Period:

$$T(\varepsilon, k_z) = \frac{2\pi}{\omega_c} = \frac{\oint dk}{dk/dt} = \frac{\hbar}{eB} \oint \frac{dk}{|v_{\perp}|}$$

$v_{\perp}$  component of electron velocity perpendicular to magnetic field



$\Delta(\vec{k})$ — a vector pointing from  $\varepsilon$  to  $\varepsilon + d\varepsilon$ , perpendicular to electron orbits, and passes through  $\vec{k}$  point.

$$\Delta\varepsilon = \hbar|v_{\perp}|\Delta(\vec{k})$$



$$T(\varepsilon, k_z) = \frac{2\pi}{\omega_c} = \frac{\hbar^2}{eB} \oint \frac{\Delta(\vec{k}) dk}{\Delta\varepsilon} = \frac{\hbar^2}{eB} \frac{\partial}{\partial\varepsilon} A(\varepsilon, k_z)$$

$A(\varepsilon, k_z)$  ---- area in  $\vec{k}$  space surrounded by orbit  $(\varepsilon, k_z)$ .

$$\omega_c = \frac{2\pi}{\hbar^2} \frac{eB}{\partial\varepsilon / \partial A(\varepsilon, k_z)}$$

orbital property

$$m_c^* = \frac{\hbar^2}{2\pi} \frac{\partial}{\partial\varepsilon} A(\varepsilon, k_z)$$

Unit vector  $\hat{B}$  is along the direction of magnetic field:

$$\hat{B} \times \left( \hbar \frac{d\vec{k}}{dt} \right) = \hat{B} \times [-e\vec{v}(\vec{k}) \times \vec{B}] \quad \rightarrow$$



$$\hbar \hat{\mathbf{B}} \times \left( \frac{d\vec{k}}{dt} \right) = -eB \frac{d}{dt} \vec{r}_\perp$$

$$\vec{r}_\perp(t) - \vec{r}_\perp(0) = -\frac{\hbar}{eB} \hat{\mathbf{B}} \times [\vec{k}(t) - \vec{k}(0)]$$

In the direction perpendicular to field, the real space orbit of electrons is to rotate the  $\vec{k}$  space orbit by  $90^\circ$  with respect to the field direction, and multiply a factor of  $\hbar/eB$ .

Along magnetic field (z) direction:

$$z(t) = z(0) + \int_0^t v_z(t) dt \quad v_z = \frac{1}{\hbar} \frac{\partial \epsilon}{\partial k_z}$$

For free electron, it is linear uniform motion; while for Bloch electrons this is not necessarily true.



## II. Free Electrons in a constant Magnetic Field: A Quantum Theory

Absence of field:  $\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2$

Presence of field:  $\hat{H} = \frac{1}{2m} (\hat{p} + e\vec{A})^2$

$\vec{A}$  is magnetic vector potential.

Uniform field along  $z$  axis, i.e.,

$$\vec{B} = (0, 0, B)$$

$$\vec{A} = (0, Bx, 0)$$

Schrödinger Equation:

$$\frac{1}{2m} (-i\hbar\nabla + eBx\hat{y})^2 \psi(\vec{r}) = \varepsilon \psi(\vec{r})$$



$$\varepsilon(k_z, \nu) = \frac{\hbar^2 k_z^2}{2m} + \left(\nu + \frac{1}{2}\right) \hbar \omega_c$$

$$\nu = 0, 1, 2, \dots$$

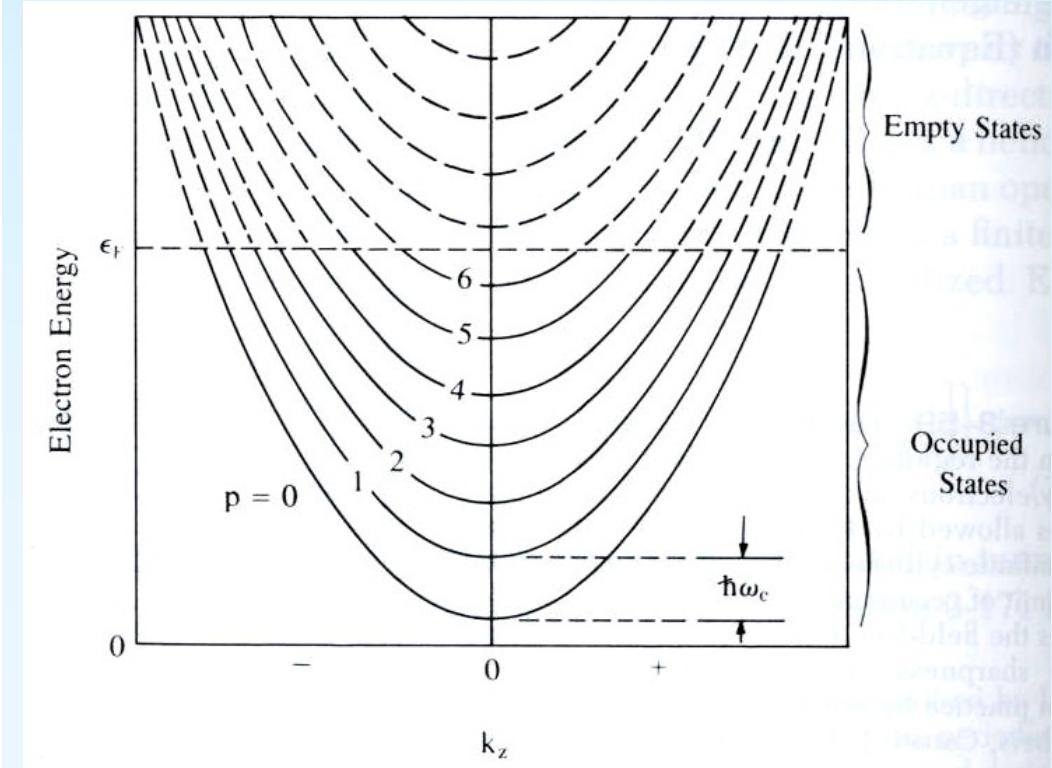
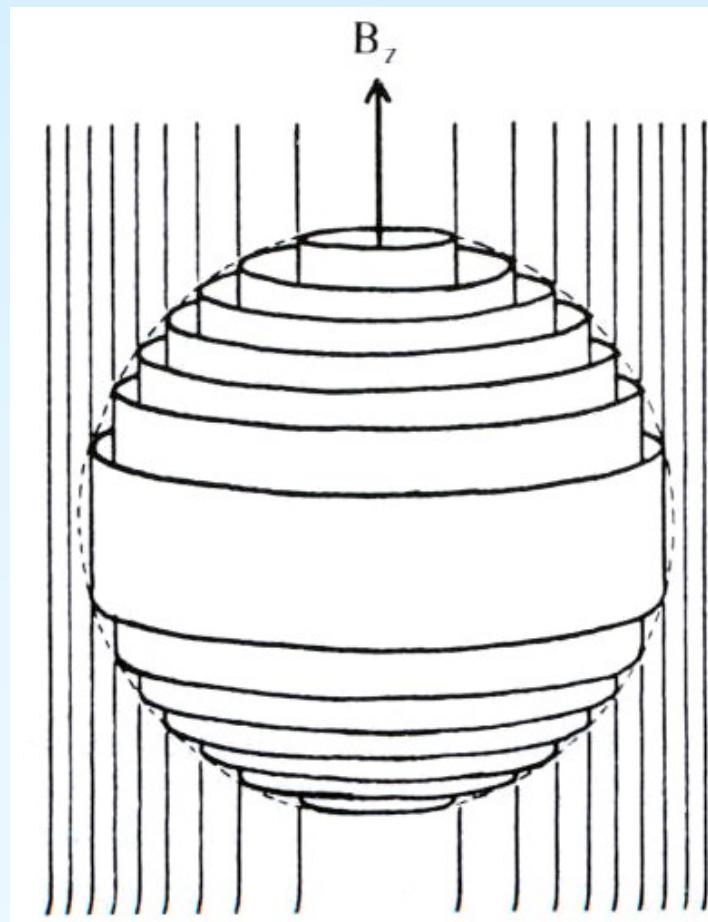
$$\varepsilon_{\nu+1}(k_z) - \varepsilon_\nu(k_z) = \hbar \omega_c$$

$$\omega_c = \frac{eB}{m} \quad \text{——cyclotron frequency} \quad k_z = \frac{2\pi}{L} n_z \quad n_z \text{ an integer}$$

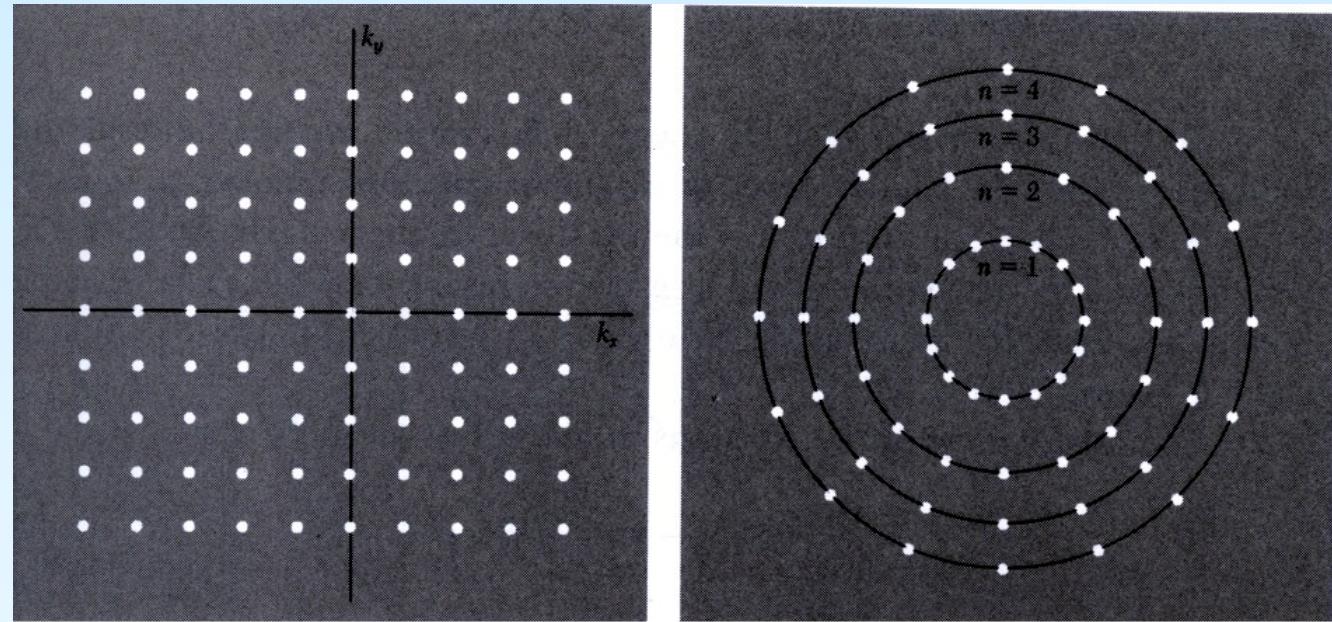
compared to free electron eigen energy:

$$\varepsilon(\bar{k}) = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m}$$

- ✓ After applying a magnetic field along z axis, the electron is still in a linear uniform motion along z axis, with energy  $\hbar^2 k_z^2 / 2m$ .
- ✓ Perpendicular to magnetic field, electron motion is quantized, change from continuous energy  $\hbar^2 k_x^2 / 2m + \hbar^2 k_y^2 / 2m$  to a series of 1D sub-band  $(\nu + 1/2)\hbar \omega_c$  ——Landau Level.



In  $k$ -space, the allowed states collapsed to the Landau rings.



Area between two N.N. Landau rings,

$$\Delta A = \pi \Delta(k_x^2 + k_y^2) = \frac{2\pi m \Delta E}{\hbar^2} = \frac{2\pi m \hbar \omega_c}{\hbar^2} = \frac{2\pi e B}{\hbar}$$

A constant proportional to external field, the degeneracy of each Landau ring is

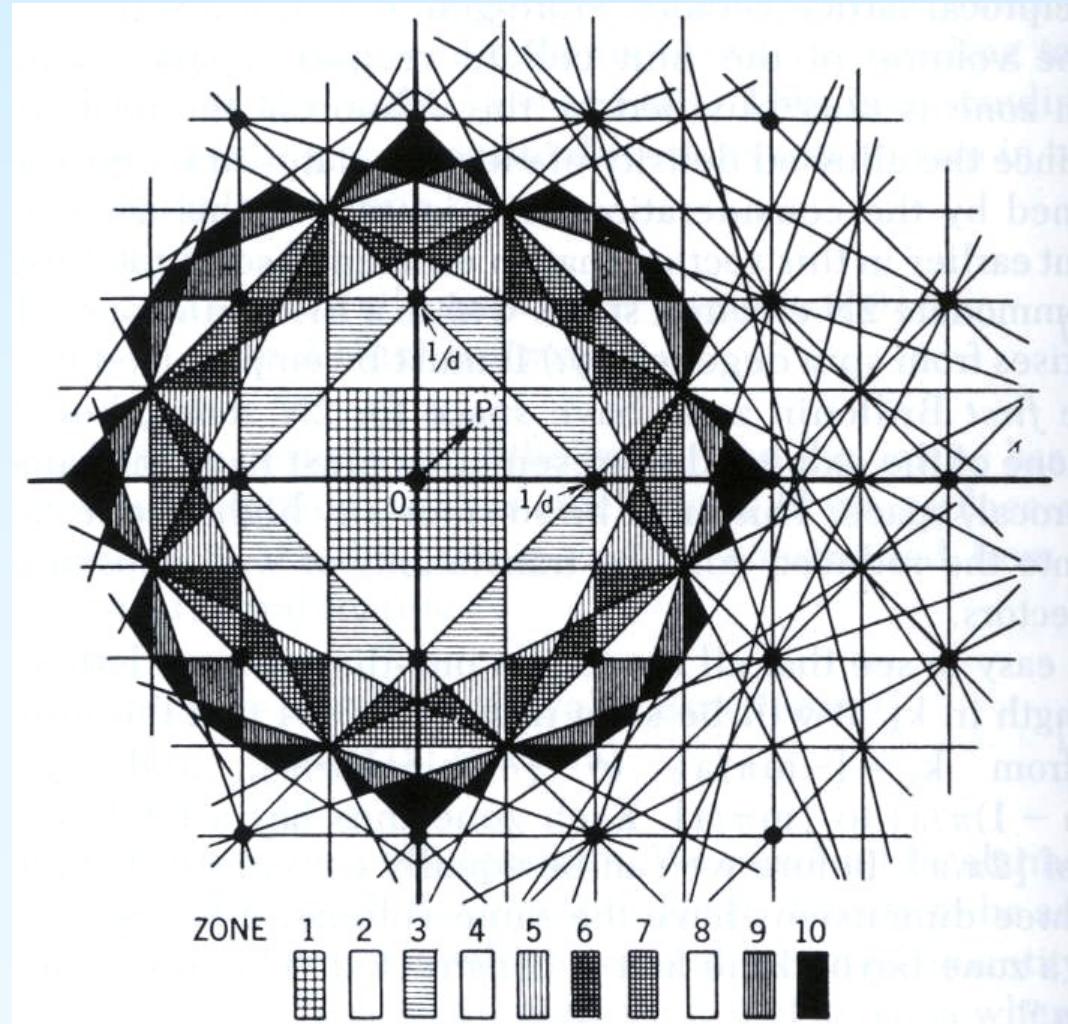
$$p = \Delta A \cdot \frac{L^2}{4\pi^2} \cdot 2 = \frac{2e}{h} BL^2$$



# 8.4 Fermi Surface & Density of States

## I. Higher Brillouin Zone

Consisted of independent blocks, each of which has the same volume as the reciprocal primitive cell.





## II. Fermi Surface

### 1. Ground State Fermi Energy of Free Electron Gas

- ✓ **Ground State:** electrons fill up the quantum states from low energy to high levels (Pauli Exclusive Principle). All the states below Fermi energy  $\varepsilon_F$  are full, while those higher than  $\varepsilon_F$  are empty.
- ✓ The interface between occupied and unoccupied  $k$ -levels —**Fermi Surface.**

Free Electron:  $\varepsilon(k) = \frac{\hbar^2 k^2}{2m}$       **Fermi Surface is a sphere**

$N$  electrons  $\vec{k}$  fills up a ball of radius  $k_F$  in  $k$ -space.

$$k_F = (3\pi^2 n)^{1/3} \quad n \text{——electron density}$$



### 2. Construction of Fermi Surface

(1) Free electron Fermi surface (take square lattice as an example)

$$k_F = (2\pi n)^{1/2}$$

(a) plot extended B.Z.

(b) plot Fermi circle

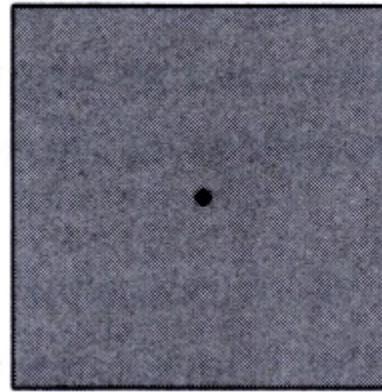
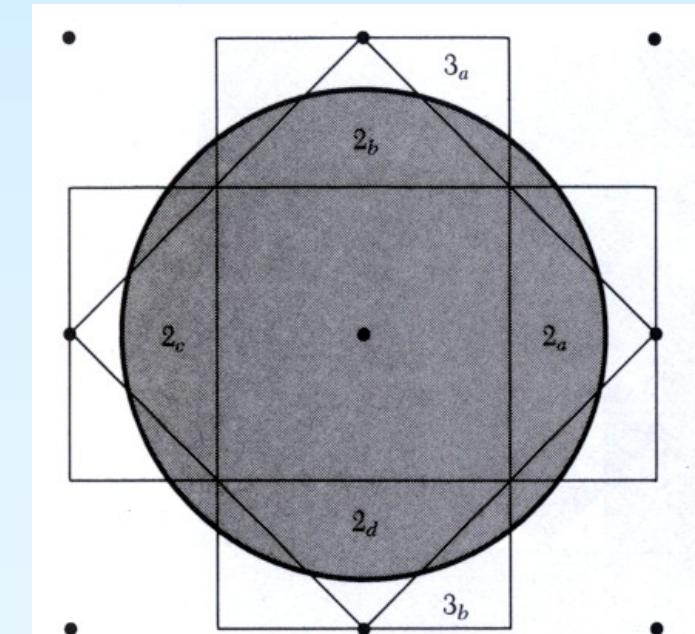
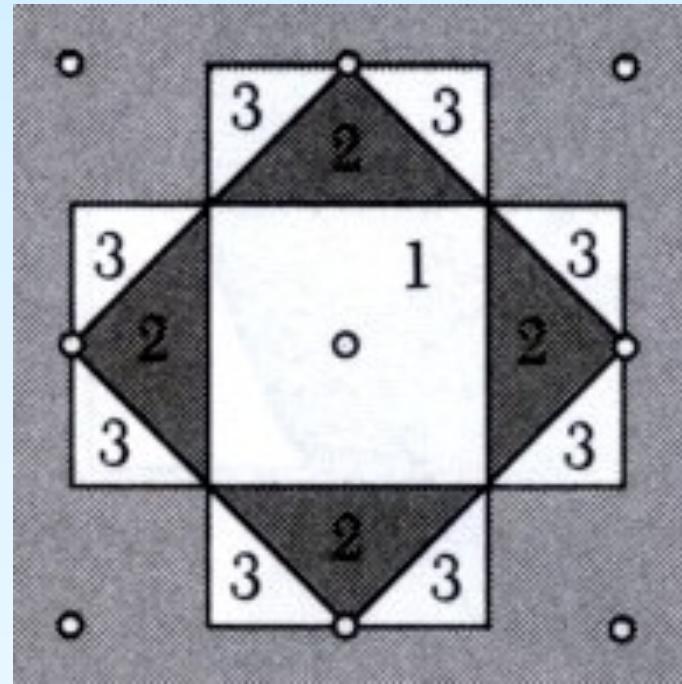
Shape and size of B.Z. are determined by crystal structure,

Fermi radius is related to electron density in crystal.

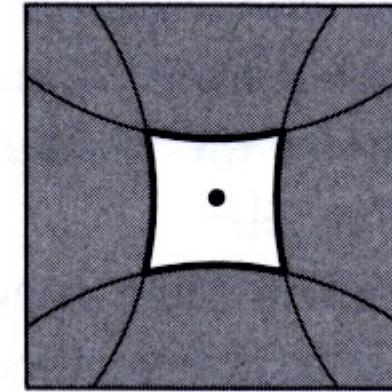
(c) move the Fermi sectors in extended B.Z. to the equivalent position of reduced B.Z.



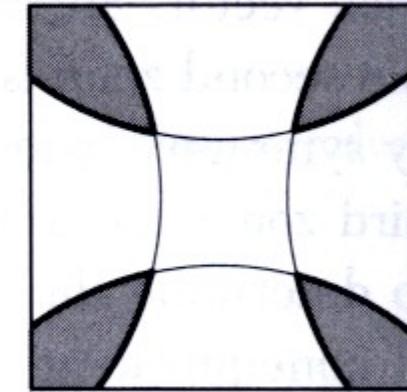
## 8.4 Fermi Surface & Density of States



1st zone



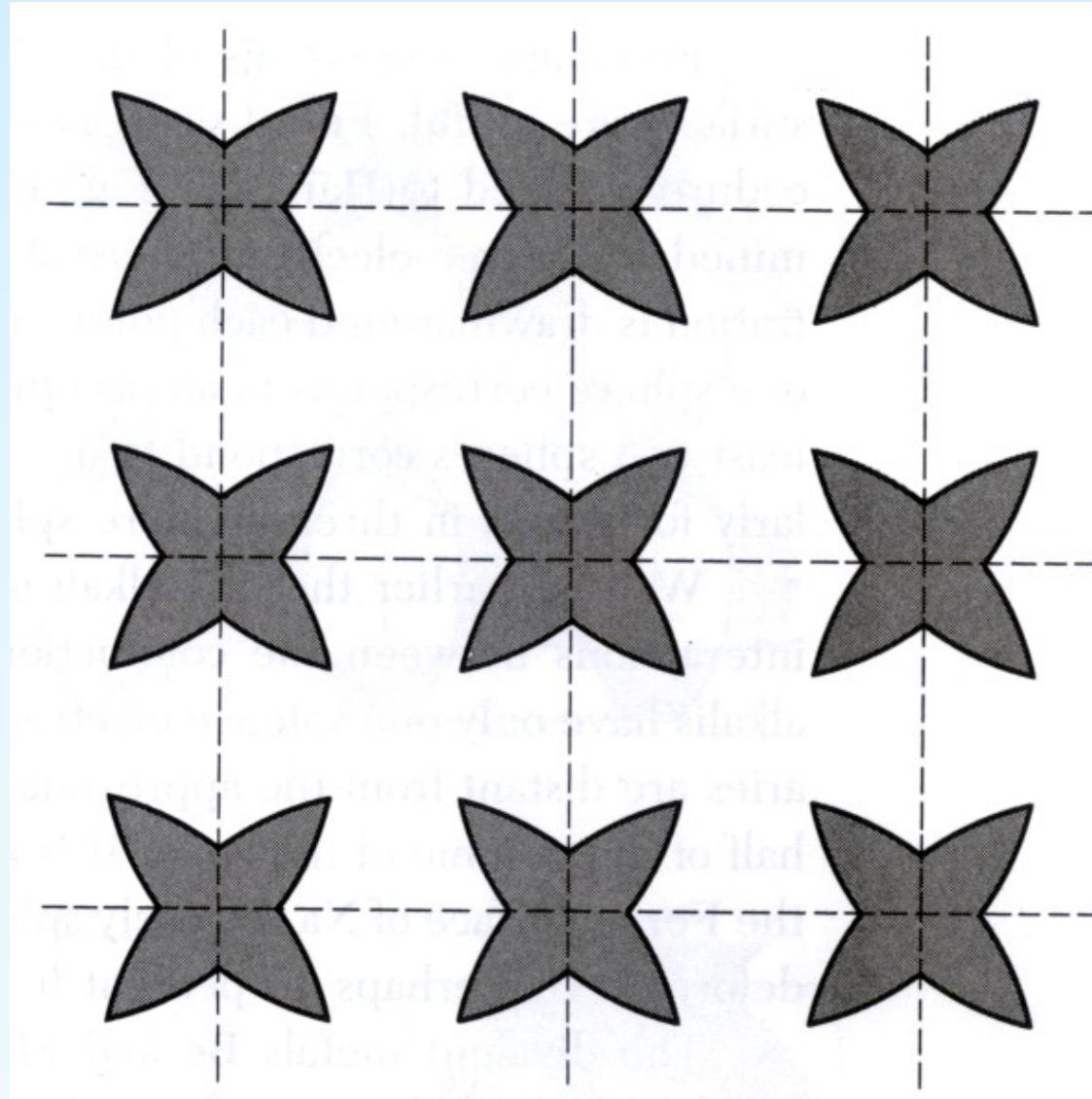
2nd zone



3rd zone



## 8.4 Fermi Surface & Density of States



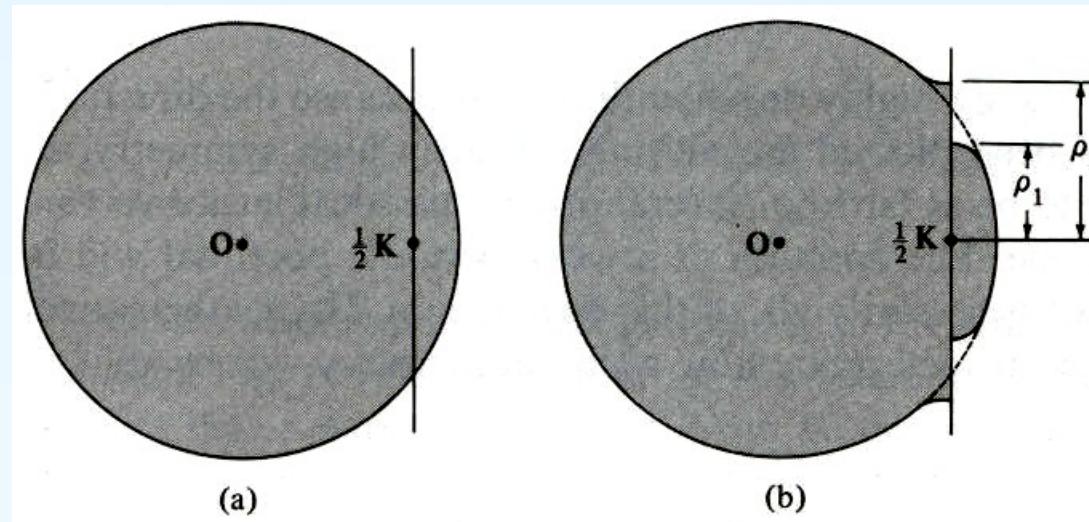
Fermi Surface in 3rd B.Z. (a extended zone representation)

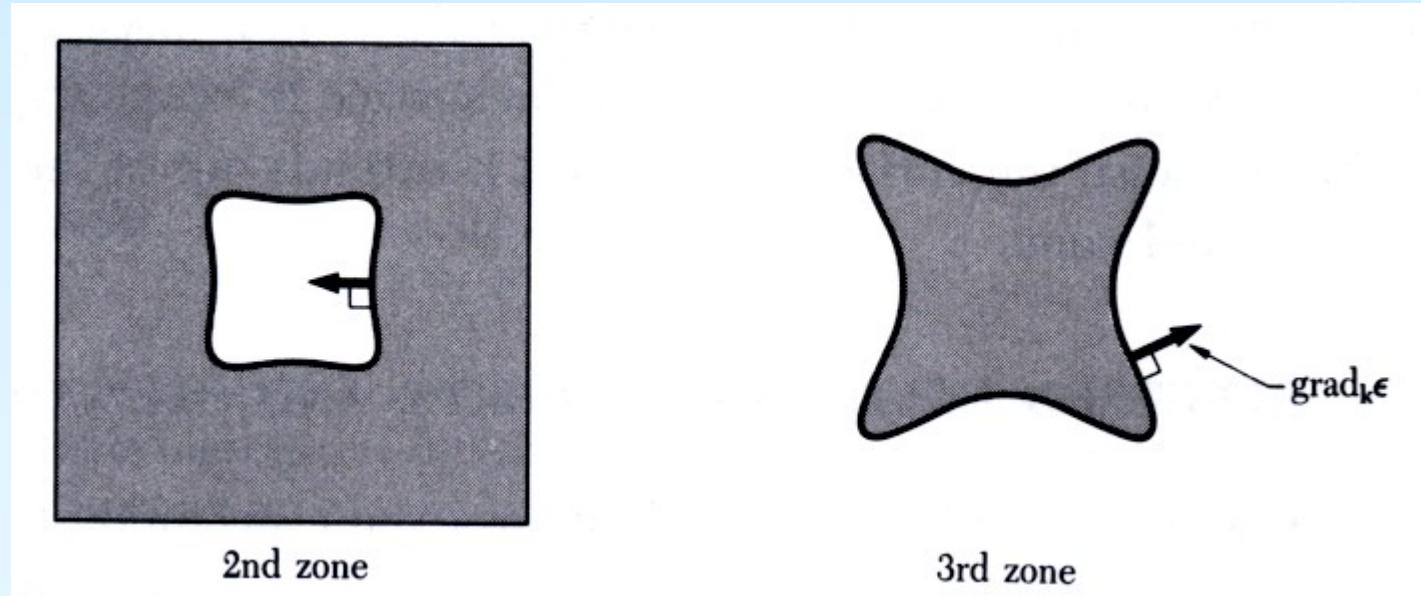


### (2) Fermi Surface of Nearly Free Electrons

Presence of periodic potential makes the Fermi surface no more a sphere. The corrections are as followings:

- (a) Energy jumps at B.Z. boundary
- (b) Isoenergetic surfaces are perpendicular to BZ boundary
- (c) Periodic potential smoothens the corners/edges of Fermi surface





### III. Density of States (D.O.S.)

DOS  $g(\varepsilon)$ : # of electron states (spin degrees of freedom included) in unit energy interval, in sample of unit volume.

DOS of  $n$ -th energy band:  $g_n(\varepsilon)$      $\rightarrow$      $g(\varepsilon) = \sum_n g_n(\varepsilon)$



In  $\bar{k}$  space, # of states with energy within  $\varepsilon \sim \varepsilon + d\varepsilon$  are:

$$\Delta Z = \frac{V}{(2\pi)^3} \Delta V$$

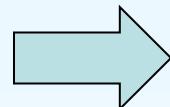
$\Delta V$  : volume in  $k$ -space, between  $\varepsilon \sim \varepsilon + d\varepsilon$  isoenergetic surfaces.

$$\Delta V = \int ds dk_{\perp}$$

$dk_{\perp}$  : distance between two isoenergetic surfaces (normal direction)

$$\Delta \varepsilon = dk_{\perp} |\nabla_k \varepsilon(\bar{k})|$$

$\nabla_k \varepsilon(\bar{k})$  is energy change along normal direction of isosurface



$$\Delta Z = \frac{V}{(2\pi)^3} \int \frac{ds}{|\nabla_k \varepsilon(\bar{k})|} \Delta \varepsilon$$



$$g(\varepsilon) = \frac{1}{(2\pi)^3} \int \frac{ds}{|\nabla_k \varepsilon(\vec{k})|}$$

Each  $k$ -state can contain two electrons of opposite spin orientation

$$g_n(\varepsilon) = \frac{1}{4\pi^3} \int \frac{ds}{|\nabla_k \varepsilon_n(\vec{k})|}$$

Free electron density of states:

$$g(\varepsilon) \propto \sqrt{\varepsilon}$$

Nearly free electrons:

- Vicinity of original point: isoenergetic surface is a sphere, like the free electrons

## 8.4 Fermi Surface & Density of States

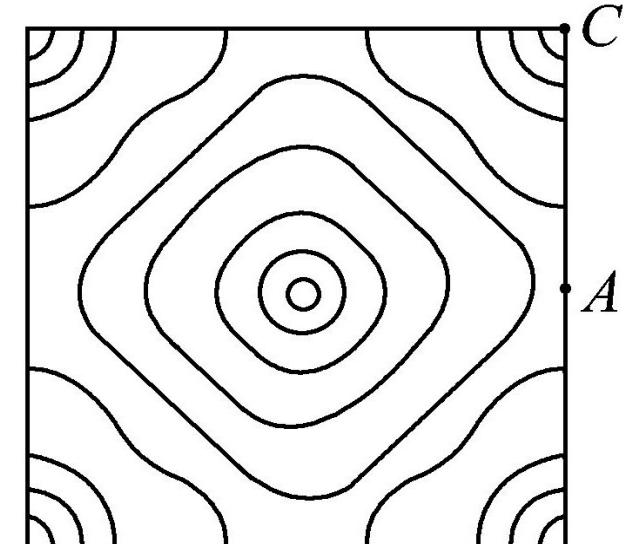
■ Close to BZ boundary: isoenergetic surface is convex→larger enclosed volume →larger DOS

boundary A:  $g(\varepsilon) \rightarrow g_{\max}(\varepsilon)$

$\varepsilon > \varepsilon_A$     $g(\varepsilon)$  decreases

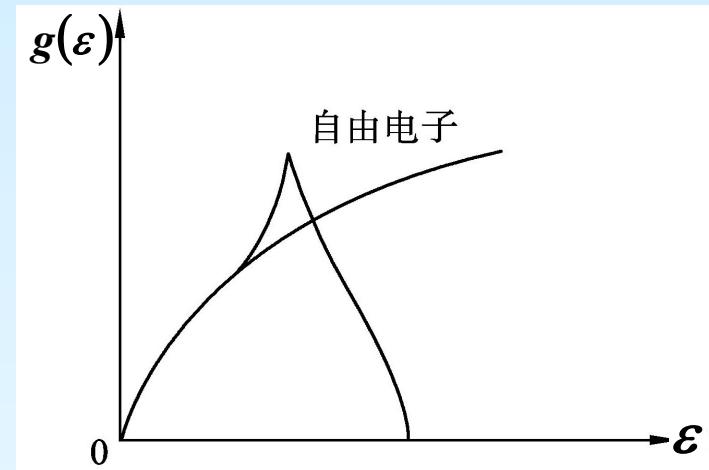
$$\varepsilon(k) = \varepsilon(-k); \frac{\partial \varepsilon}{\partial k} \Big|_k = \frac{\partial \varepsilon}{\partial k} \Big|_{-k}$$

$$\varepsilon(k) = \varepsilon(k + G); \frac{\partial \varepsilon}{\partial k} \Big|_k = \frac{\partial \varepsilon}{\partial k} \Big|_{k+G}$$



Energy gradient is zero at BZ boundary

$$k = \pm \frac{1}{2}G; \frac{\partial \varepsilon}{\partial k} \Big|_{\frac{1}{2}G} = - \frac{\partial \varepsilon}{\partial k} \Big|_{-\frac{1}{2}G} = \frac{\partial \varepsilon}{\partial k} \Big|_{-\frac{1}{2}G} = 0$$



van Hove singularity:

for some  $k$  point,  $|\nabla_k \epsilon| = 0$ , giving may rise to a divergent  $g(\epsilon)$   
which is still 3D integrable:  $g(\epsilon)$  is finite, but  $dg(\epsilon) / d\epsilon$   
diverges.



## 8.5 Experimental Measurement of Fermi Surface

**Research of Fermi surface:** magnetoresistance, anomalous skin effect, cyclotron resonance, Shubnikov-de Haas effect, and de Haas –van Alphen effect.

### I. Orbital quantization of Bloch electrons

With Onsager & Lifshitz *semiclassical* approximation, the electron orbitals in magnetic fields are *quantized* according to Bohr-Sommerfeld relation:

$$\oint \vec{p} \cdot d\vec{r} = (\nu + \gamma) 2\pi\hbar$$

$\nu$  is an integer,  $\gamma$  is phase correction factor,  $\gamma=1/2$  for free electrons.



In magnetic field:  $\vec{p} = \hbar\vec{k} - e\vec{A}$

$\vec{A}$  is vector potential:  $\vec{B} = \nabla \times \vec{A}$

$$\oint \vec{p} \cdot d\vec{r} = \oint (\hbar\vec{k} - e\vec{A}) \cdot d\vec{r}$$

take integral of  $\hbar \frac{d\vec{k}}{dt} = -e\vec{v}(\vec{k}) \times \vec{B}$

$\hbar\vec{k} = -e\vec{r} \times \vec{B} = -e(y\hat{x} - x\hat{y})B$ , from which we get

$$\nabla \times \hbar\vec{k} = 2e\vec{B}$$

Due to Stokes Theorem:  $\oint \vec{F} \cdot d\vec{l} = \iint (\nabla \times \vec{F}) \cdot d\vec{S}$

$$\oint (\hbar\vec{k} - e\vec{A}) \cdot d\vec{r} = \iint e\vec{B} \cdot d\vec{S} = eBA_r$$

$A_r$ : Area surrounded by electron orbitals in real space.



$$eBA_r = (\nu + \gamma)2\pi\hbar \quad A_r = \frac{2\pi\hbar}{eB}(\nu + \gamma)$$

Area of electron orbitals in  $\vec{k}$  space:

$$A_v(k_z) = \left( \frac{eB}{\hbar} \right)^2 A_r = \frac{2\pi eB}{\hbar}(\nu + \gamma)$$

quantized with  $\frac{2\pi eB}{\hbar}$  as unit

Remember:

$$\vec{r}_\perp(t) - \vec{r}_\perp(0) = -\frac{\hbar}{eB} \hat{B} \times [\vec{k}(t) - \vec{k}(0)]$$

In Fermi surface experiments we may be interested in the increment of B for which two successive orbits, v and v+1, *have the same area in k-space on the Fermi surface*. The areas are equal when

$$\rightarrow A\left(\frac{1}{B_{v+1}} - \frac{1}{B_v}\right) = \frac{2\pi e}{\hbar}$$



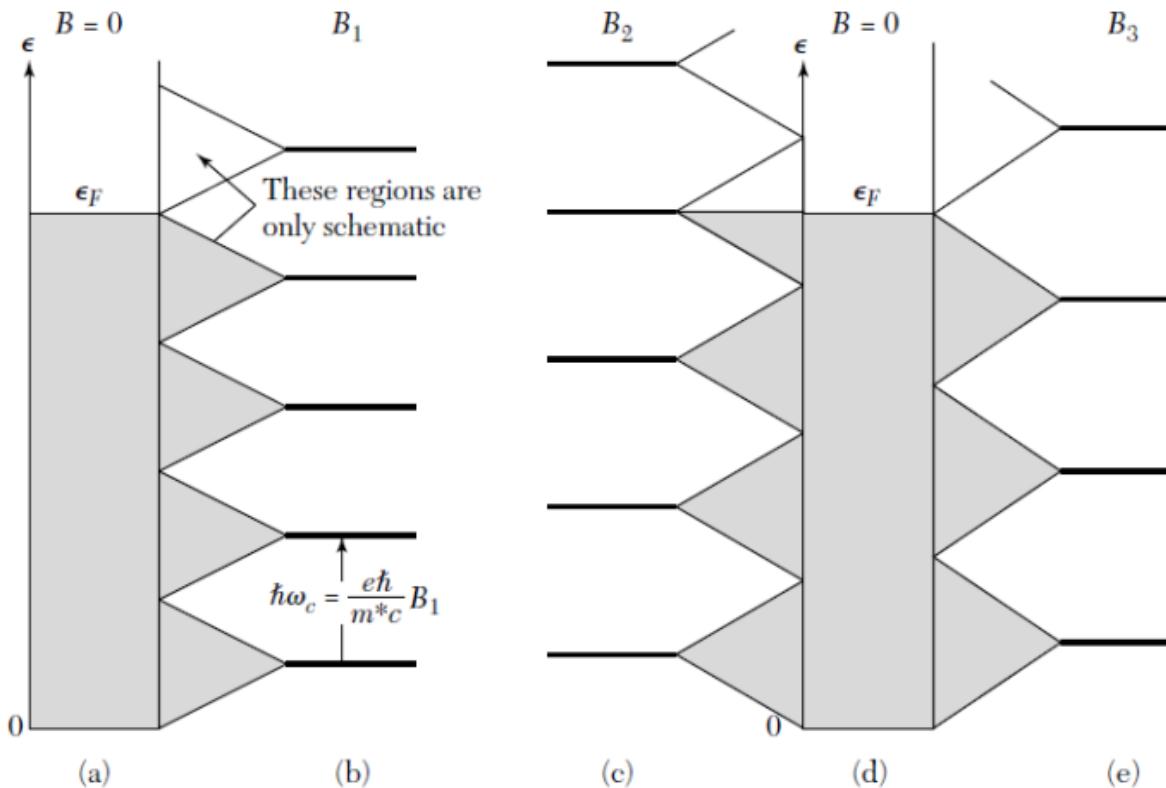
## II. de Haas-van Alphen effect, 1930

Magnetic susceptibility of metal *oscillates* with changing inverse of magnetic field ( $1/B$ )

- ✓ Related to the behavior of electrons near Fermi surface in strong magnetic field
- ✓ Due to quantization of electron orbitals in magnetic fields
- ✓ The shape of Fermi surface can be obtained by measuring oscillation period

Apply a strong magnetic field to a *pure* sample (containing free electrons) at *low temperatures*

$T = 0\text{ K}$  and  $B = 0$ , all the energy levels below Fermi energy are all filled, and the levels above are all empty.



**Figure 23** Explanation of the de Haas-van Alphen effect for a free electron gas in two dimensions in a magnetic field. The filled orbitals of the Fermi sea in the absence of a magnetic field are shaded in *a* and *d*. The energy levels in a magnetic field are shown in *b*, *c*, and *e*. In *b* the field has a value  $B_1$  such that the total energy of the electrons is the same as in the absence of a magnetic field: as many electrons have their energy raised as lowered by the orbital quantization in the magnetic field  $B_1$ . When we increase the field to  $B_2$  the total electron energy is increased, because the uppermost electrons have their energy raised. In *e* for field  $B_3$  the energy is again equal to that for the field  $B = 0$ . The total energy is a minimum at points such as  $B_1, B_3, B_5, \dots$ , and a maximum near points such as  $B_2, B_4, \dots$ .

$$D = \Delta A \cdot \frac{L^2}{4\pi^2} \cdot 2 = \frac{2e}{h} BL^2$$

The electron transfer to lower Landau levels can occur because their degeneracy  $D$  increases as  $B$  is increased.



Suppose at  $B = B_1$ , critical energy of  $v$ -th subband is  $\varepsilon_F$

$$\varepsilon_v = \left(v + \frac{1}{2}\right) \hbar \frac{eB_1}{m} = \varepsilon_F$$

$B$  enhances, and  $\varepsilon_{v-1}$  enhances correspondingly, at  $B = B_2$ ,

$$\varepsilon_{v-1} = \left(v - \frac{1}{2}\right) \hbar \frac{eB_2}{m} = \varepsilon_F$$

when field increases from  $B_1$  to  $B_2$ , total energy changes from maximum to minimum and then to maximum again, and accomplishes a period of change, who satisfies:

$$\Delta\left(\frac{1}{B}\right) = \frac{1}{B_1} - \frac{1}{B_2} = \frac{e\hbar}{m\varepsilon_F}$$

total energy changes with a period  $\Delta(1/B)$

Magnetic Moment:  $M(B) = -\frac{\partial E}{\partial B}$  and

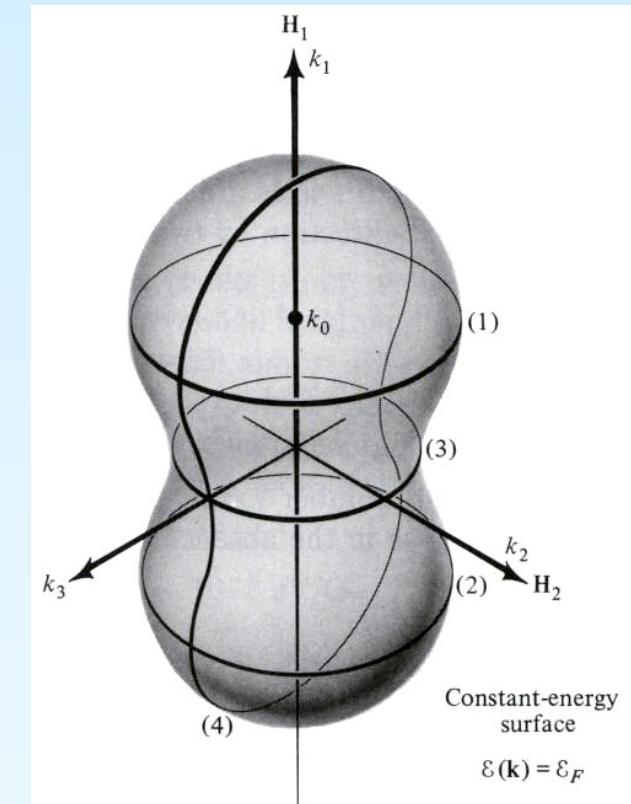
susceptibility changes periodically  $1/B$

$$A\left(\frac{1}{B_{v+1}} - \frac{1}{B_v}\right) = \frac{2\pi e}{\hbar} \quad \rightarrow \quad \Delta\left(\frac{1}{B}\right) = \frac{e\hbar}{m\varepsilon_F} = \frac{2\pi e}{\hbar A_e(\varepsilon_F, k_z)}$$

$$A_e = \frac{2\pi m}{\hbar^2} \varepsilon_F \quad \text{——Fermi surface}$$

### Measurement of Fermi surface:

For Bloch electrons, there are also quantization in magnetic fields. Total energy, magnetic susceptibility, and other quantities oscillate with respect to  $1/B$ , with period inversely proportional to the cross section of Fermi surface perpendicular to magnetic field.





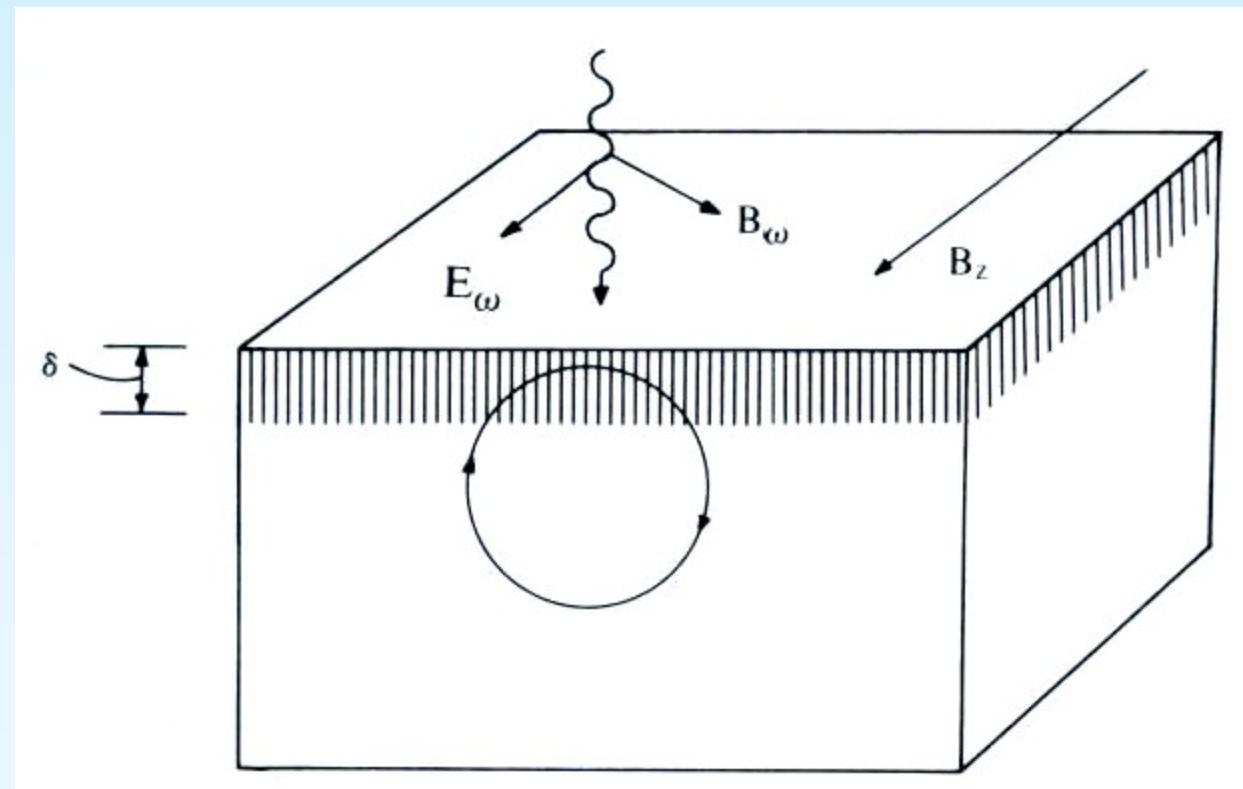
Change the direction of magnetic field, and measure the period, one can get the cross section  $A_e$  on the corresponding direction.

Collect  $A_e$  on different directions, one can determine the shape of Fermi surface.

### III. Electron cyclotron resonance (ECR)

Crystal electrons are in a cyclotron motion under a magnetic field, with frequency  $\omega_c = \frac{eB}{m_c^*}$

Apply a second magnetoelectric field with high frequency  $\omega$ , perpendicular to the constant field. When  $\omega = \omega_c$ , energy of alternating magnetic field can be absorbed by ECR, thus determine the *effective mass* of electron.





# 8.6 Band structure of typical metals

## I. Alkali metals

**Li, Na, K, Rb, Cs:** monovalent metal.

crystal structure: BCC

reciprocal lattice: FCC

**free electron:** Fermi sphere with radius  $k_F$

$$k_F^3 = 3\pi^2 n \quad n = \frac{2}{a^3} \quad a \text{ is lattice constant}$$

$$k_F = \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} \frac{2\pi}{a} = 0.620 \frac{2\pi}{a}$$



shortest distance between center to a face of First BZ  
(dodecahedron):

$$k_{\min} = 0.707 \frac{2\pi}{a}$$

$$\frac{k_F}{k_{\min}} = 0.877$$

spherical Fermi surface is completely contained in first BZ

- ✓ Agree with experimental results.
- Valence electron in alkali metals behaves quite much like free electron. One can use free electron gas theory to discuss the transport properties of alkali metals.



## II. Noble Metal

Cu, Ag, Au: an s-electron in outer shell, s-band and d-band has some overlap

Crystal Structure: FCC

Reciprocal Lattice: BCC

1st B.Z.: Truncated Octahedron

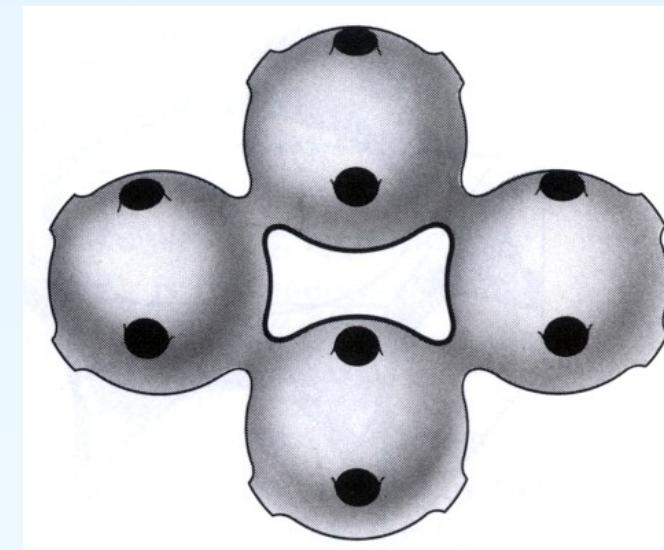
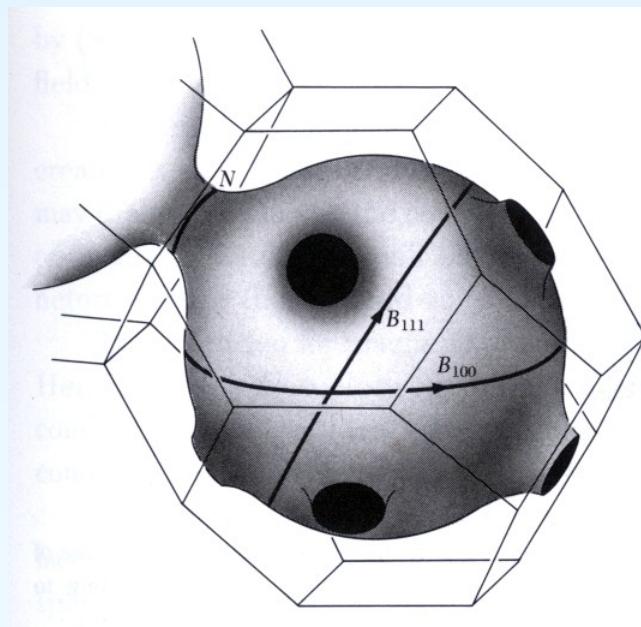
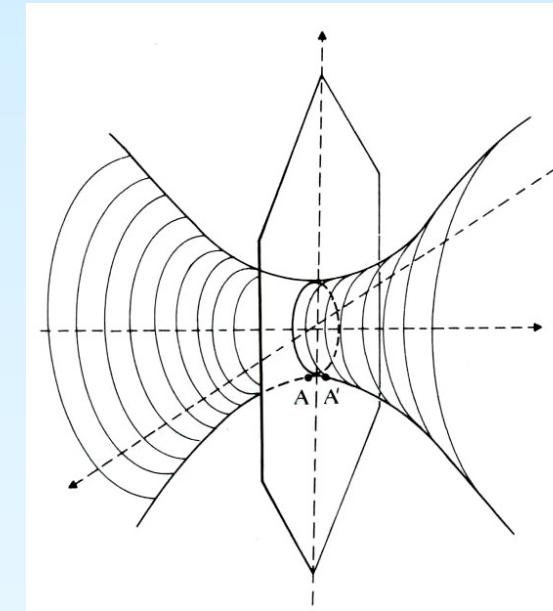
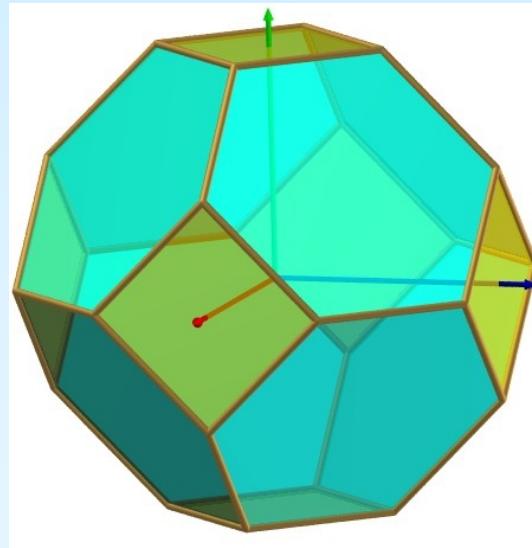
s electron: free electron, Fermi surface is also within 1st BZ,  
but quite close to interface along <111> direction:

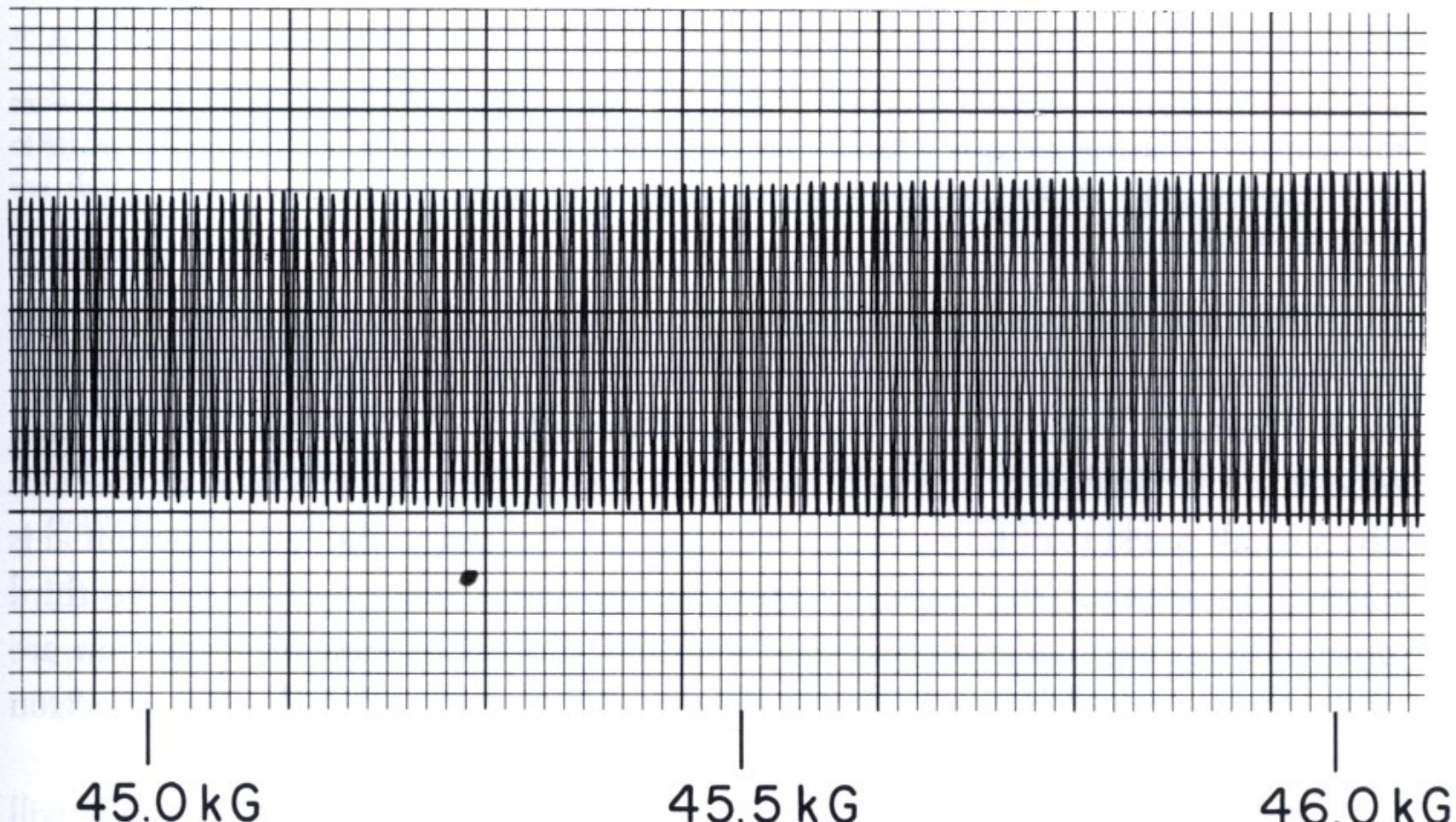
$$\frac{k_F}{k_{\min}} = 0.903$$

Fermi sphere is distorted along these directions, and makes contacts with adjacent Fermi surface through center of eight hexagonal faces.



## 8.6 Band structure of typical metals





dHvA effect of gold,  $B//[110]$

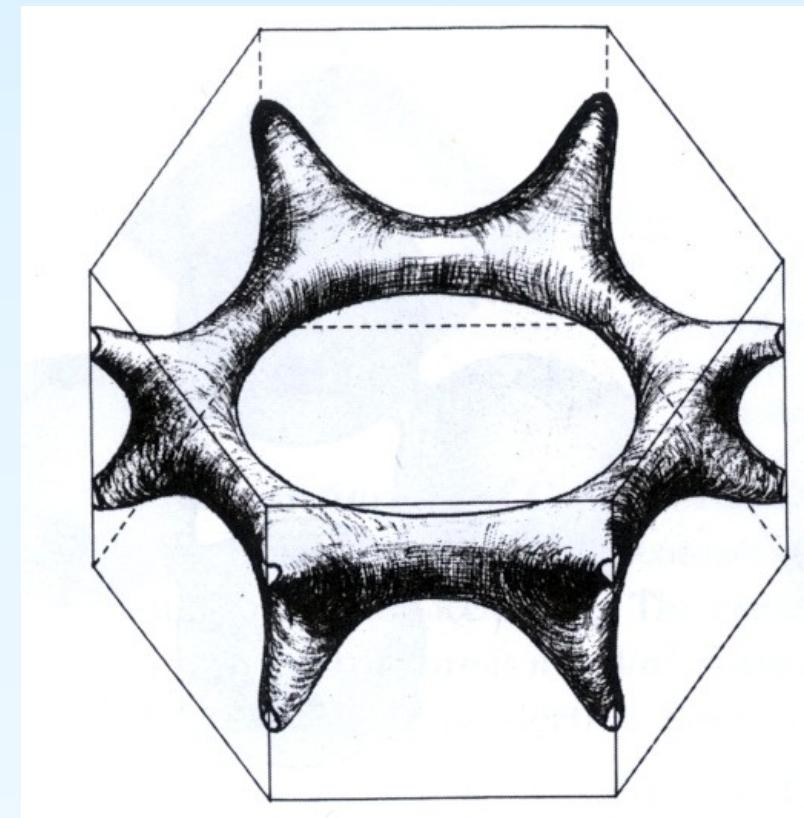
### III. Divalent metal

Be, Mg, Zn, Cd: hexagonal closely packed (h.c.p.)

Ca, Sr, Ba: cubic system

Two s electrons in outer shell, s band has overlap with neighboring higher empty energy band.

Fermi surface is quite different from a sphere.

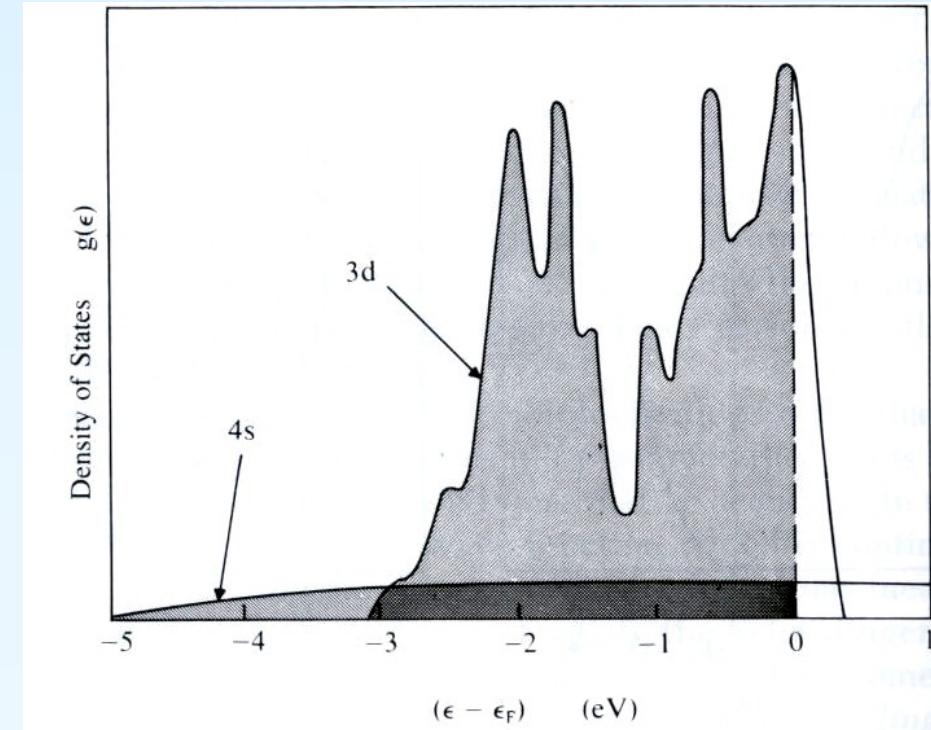




### III. Transition Metal

It contains partially filled *d* shell.

- ✓ *d* band is quite narrow, has large DOS, and share overlap with *s* band.
- ✓ Fermi energy is within *d* band, quite different from those of simple metals, and can not be obtained by perturbative modification of free electron Fermi sphere.





## 8.7 Achievement & Limitation of Band Theory

### I. Main conclusion of energy band theory

- (i) Crystal electron wavefunction is in a form of Bloch function
- (ii) Electron energy levels in crystal consist of a series of quasi-contineous levels, each of which is called a energy band. Between two neigboring bands there might exist energy gap (forbidden band).
- (iii) Each energy band contains  $N$  quantum states, which equals the number of primitive cells. If spin degree of freedom is taken into consideration, there are  $2N$  states.



(iv) Crystal electrons fill bands from lowest level to higher ones.

The bands include: **full band, partially filled band, and empty band.**

(v) Different band can share some overlap, and the gap disappears.

## II. Main achievements of energy band theory

(a) Explained the difference between conductor, insulator, and semiconductor, providing a uniform framework for studying the very *diverse* properties of solid state materials.

(b) With the concept of hole, energy band theory can explain the appearance of **positive** Hall coefficient.



(c) Based on energy band theory, one can explain the light absorption and emmision, various *transport* and *scattering* processes of electrons in external fields (electric, magnetic, impurity potential, etc.)

### III. Limitation of energy band theory

Energy band theory is built on the basis of single electron approximation, electron-electron and electron-lattice correlations are *ignored*.

- (1) Cannot explain conductivity of **transition metal compounds**.
- (2) Cannot explain the **metal-insulator** transition for several metals when the lattice constant increases.

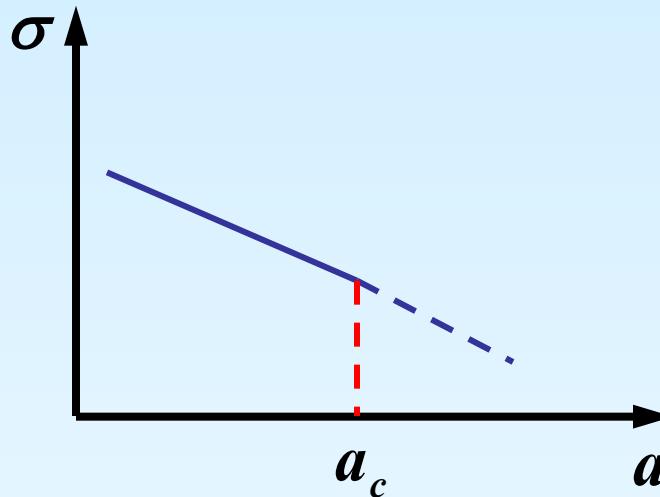


- (3) Cannot explain problems concerning electron-electron or electron-phonon interactions, for instance, **superconductivity**; and collective excitations in solids, like plasmon in metals.
- (4) Cannot be applied to incomplete solid, **solid state surface**, or **amorphous metal**.

### Example: metal-insulator transition

During metal dilation, the lattice constant enhances.

According to energy band theory, the metal should remain to be conductor all along, which, however is not true.



**Dilation of sodium:** when  $a$  increases to  $a_c$ , electric conductivity decreases to **zero**, becoming a **insulator**.

Bloch electrons exist in the whole crystal, and thus are non-local. Electron-electron interactions on average is very small and can be ignored.

When  $a$  increases, the band width decreases; when  $a$  is large enough, the band width is so narrow such that band theory no longer works.



When  $a$  is very large, crystal electrons are no longer in a Bloch form, but in a localized form.

Strong electron-electron correlation should not be ignored.

Even though the energy levels are still in a band form, and the band is still “half filled”, the metal becomes an insulator due to strong electron-electron correlation.

Strongly correlated electronic systems! => True many-body problem!