

UEEP2024 Solid State Physics

Topic 3 Free Electron in Metals

Drude's classical theory of Electrical Conduction

- Drude assumed that a metal is composed of ions, which are stationary, and valence electrons, which are free to move.
- If no voltage applied to the metal then at each collision the electron is deflected in a different direction so that the overall motion is quite random.
- The valence electrons appears to be similar to the molecules in an idea gas.
- The velocity of the electrons with mass m at temperature T is given by the equation

$$\frac{1}{2}mv^2 = \frac{3}{2}K_B T$$

where K_B is the Boltzmann's constant.

Drude's classical theory of Electrical Conduction

- The mean free path λ is the average distance that an electron travels between collisions.
- The relaxation time τ is the average time duration between collisions.
- The mean speed of the electron $v = \frac{\lambda}{\tau}$.
- The speed of electron at room temperature is about 10^5 ms^{-1} .
- The mean free path is about 1 nm and the relaxation time about 10^{-14} s .

Drude's classical theory of Electrical Conduction

- When we apply an electric field to a sample, the electrons are attracted towards the positive end of the sample, a net flow of electrons in this direction.
- If the electric field is E , then the force on each electron is eE .
- Acceleration on each electron is $a = \frac{eE}{m_e}$.
- Change in velocity $\Delta v = a\tau = \frac{eE\tau}{m_e}$.
- This quantity is called the drift velocity.

Drude's classical theory of Electrical Conduction

- Electron mobility $\mu = e\tau/m$.
- The current density $J = \frac{I}{A} = n\mu eE$.

where n is the number of valence electrons per unit volume,

- Conductivity of the metal is given by $\sigma = n\mu e$.
- Drude's model is
 - a) consistent with ohm's law.
 - b) Explain the phenomenon of electrical resistance.
 - c) Gives good values of conductivity.

Failures of Classical model

- Conductivity should be directly proportional to the valence electron concentration, not in good agreement with experimental data.
- Electrical properties of alloys should be intermediate between the values of corresponding pure materials. However many alloys have resistivity which are considerably larger than those of either of the pure constituents.
- The dependence of resistivity on temperature:
Drude's model predicted resistivity should be proportional to $T^{1/2}$, experimental measurement show that resistivity is actually proportional to T over a wide range of temperature.
- Drude's model predict the molar specific heat capacity for monovalent metal of $9R/2$, $6R$ for divalent metal and $15R/2$ for trivalent metal. However, experiment results show that the molar specific heat capacity at room temperature is approximately $3R$, regardless of the valency of the metal.

Example

Estimate the typical conductivity of a metal at 295 K assuming that the mean free path is about 1 nm and the number of valency electrons is about 10^{29} m^{-3} .

Solution

- Thermal velocity

$$v = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23})(295)}{9.11 \times 10^{-31}}} = 1.16 \times 10^5 \text{ m s}^{-1}$$

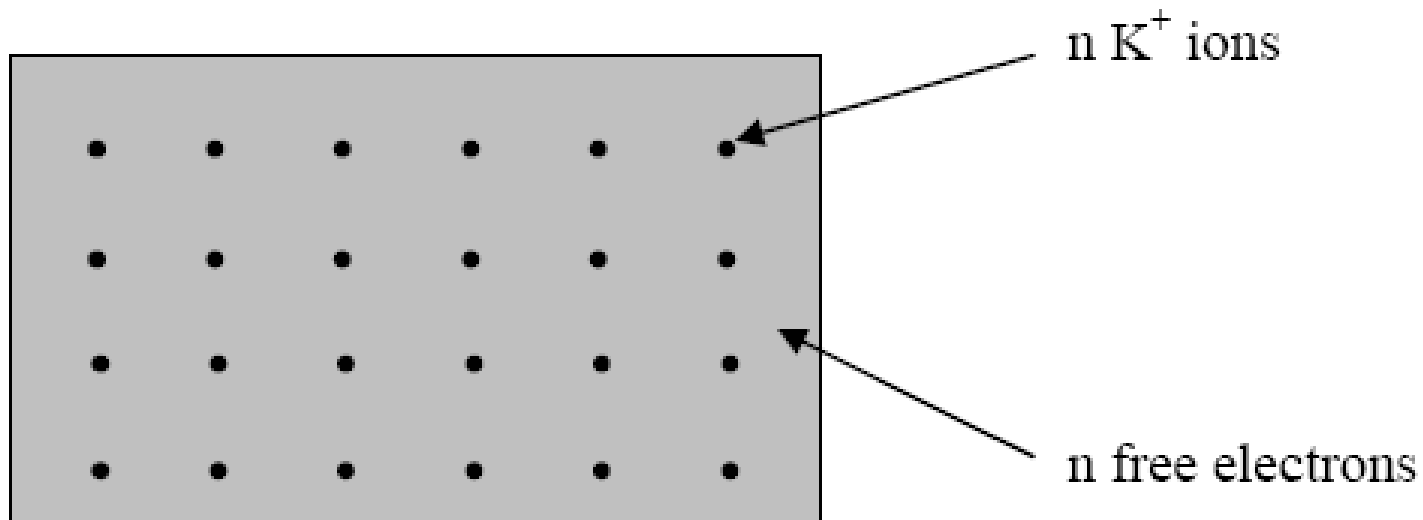
- Relaxation time $\tau = \frac{\lambda}{v} = \frac{1 \times 10^{-9}}{1.16 \times 10^5} = 8.62 \times 10^{-15} \text{ s}$

- Conductivity

$$\begin{aligned} \sigma &= \frac{ne^2 \tau}{m} = \frac{(10^{29})(1.6 \times 10^{-19})^2 (8.62 \times 10^{-15})}{9.11 \times 10^{-31}} \\ &= 2.42 \times 10^7 \Omega^{-1} \text{ m}^{-1} \end{aligned}$$

Free Electron Fermi Gas

- Atoms bounded by “free electrons”. Good example is alkali metals (Li, K, Na, etc.)



Electron in a metal can move freely in a straight path over many atomic distances, undeflected by collisions with other conduction electron or by collisions with the atom cores

Free Electron Fermi Gas

1. A conduction electron is not deflected by ion cores arranged on a periodic lattice
2. A conduction electron is scattered only infrequently by other conduction electrons

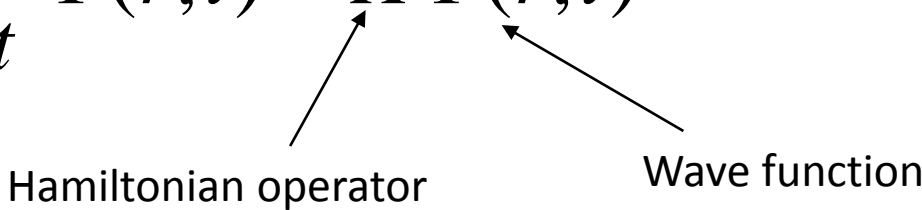


Consequence of the Pauli exclusion principle

Free electron Fermi gas – A gas of free electrons subject to the Pauli principle

Free Electron Fermi Gas

For a general quantum system

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) = \hat{H} \Psi(r, t) \quad (1)$$


Hamiltonian operator

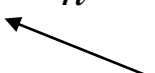
Wave function

For a single particle in three dimensions

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + V(r) \Psi(r, t) \quad (2)$$

Free Electron Fermi Gas (1-D)

Consider a free electron gas in 1-D (electron of mass m is confined to a length L by infinite barriers), (2) can be expressed as

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi_n}{dx^2} = E_n \Psi_n \quad (3)$$


Energy of the electron

With boundary conditions

$$\Psi_n(0) = 0 \quad \Psi_n(L) = 0$$

Free Electron Fermi Gas (1-D)

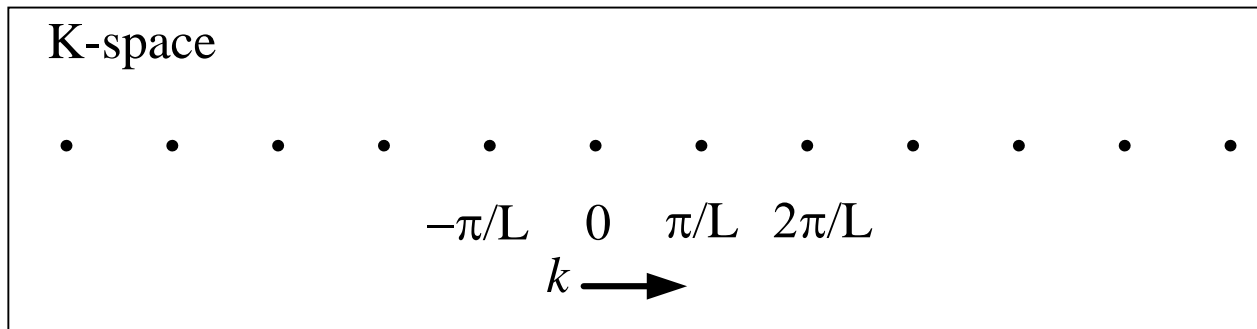
The solution of (3)

$$\Psi_n = A \sin\left(\frac{2\pi}{\lambda_n} x\right) \quad \text{where} \quad \frac{1}{2} n \lambda_n = L$$

Energy E_n is given by

$$E_n = \frac{\hbar^2 k_n^2}{2m} \quad \text{where} \quad k_n = \frac{n\pi}{L}$$

wavevector
↙



Free Electron Fermi Gas

3-D

Consider a free electron gas in 3-D (electron of mass m is confined to a cube of edge L), (2) can be expressed as

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi_k(r) = E_k \Psi_k(r) \quad (4)$$

With boundary conditions

$$\Psi_k(x=0) = 0 \quad \Psi_k(x=L) = 0$$

$$\Psi_k(y=0) = 0 \quad \Psi_k(y=L) = 0$$

$$\Psi_k(z=0) = 0 \quad \Psi_k(z=L) = 0$$

Free Electron Fermi Gas (3-D)

The solution of (4)

$$\Psi_k = A \sin\left(\frac{2\pi}{\lambda_x} x\right) \sin\left(\frac{2\pi}{\lambda_y} y\right) \sin\left(\frac{2\pi}{\lambda_z} z\right) \quad (5)$$

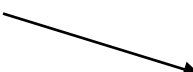
where

$$\frac{1}{2} n_x \lambda_x = L, \quad \frac{1}{2} n_y \lambda_y = L, \quad \frac{1}{2} n_z \lambda_z = L$$

Free Electron Fermi Gas

(3-D, periodic boundary conditions)

- 3-D system
- periodic boundary conditions


$$\begin{aligned}\Psi_k(x+L, y, z) &= \Psi_k(x, y, z) \\ \Psi_k(x, y+L, z) &= \Psi_k(x, y, z) \\ \Psi_k(x, y, z+L) &= \Psi_k(x, y, z)\end{aligned}$$

The solution of (4)

$$\Psi_k(r) = A \exp(ik \cdot r) \quad \text{the components of } k \text{ satisfy}$$

$$k_x, k_y, k_z = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \pm \frac{6\pi}{L}, \pm \frac{8\pi}{L}, \dots$$

One allowed value of k per volume $(2\pi/L)^3$

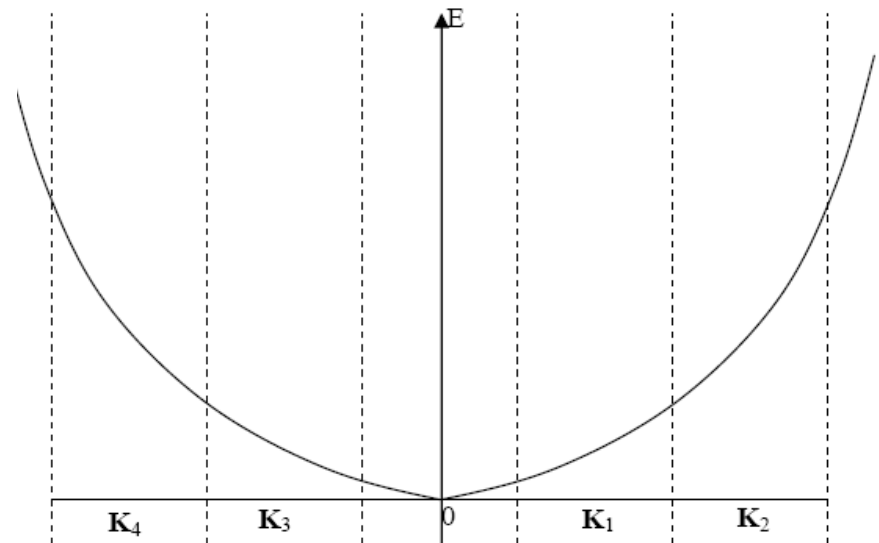
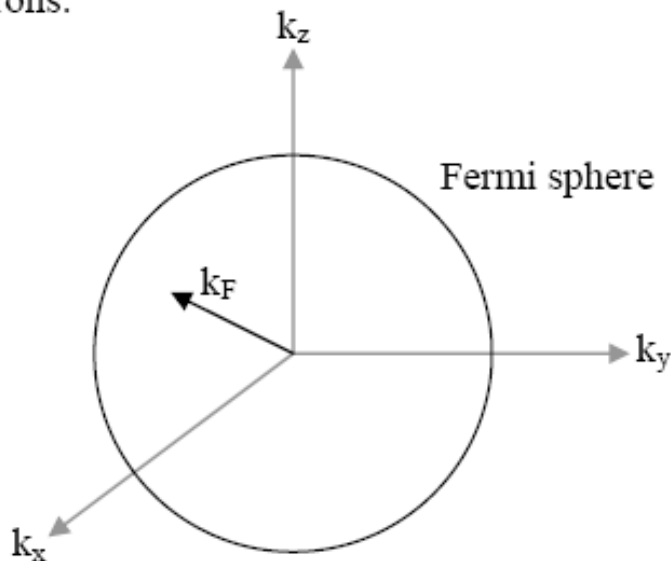
Free Electron Fermi Gas (3-D, periodic boundary conditions)

Energy E_k is given by

$$E_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \quad (6)$$

For free electrons:

K space



Free Electron Fermi Gas (density of state)

total number of allowed energy state

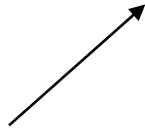
$$N = 2 \cdot \frac{4\pi k^3 / 3}{(2\pi / L)^3} = \frac{L^3}{3\pi^2} \left(\frac{2mE}{\hbar^2} \right)^{3/2} \quad (7)$$

Density of states – number of allowed energy state per unit energy range

$$D(E) = \frac{dN}{dE} = \frac{L^3}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \cdot E^{1/2} \quad (8)$$

Free Electron Fermi Gas (Fermi energy)

The **Fermi energy** is defined as the energy of the **topmost** filled level in the ground state of the N electron system.



The state of the N electron system at absolute zero

From (7), we get

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{L^3} \right)^{2/3}$$

For N electron system

Free Electron Fermi Gas (Fermi-Dirac distribution)

- The Fermi-Dirac distribution gives the probability that an energy state with energy E is occupied by an electron

$$f(E) = \frac{1}{\exp\left[\frac{E - \mu}{kT}\right] + 1}$$

Fermi level – the energy at which the probability of occupation is 1/2

The electron density is given by

$$n = \int D(E) f(E) dE$$

Example

Show that the probability for an electron state at the Fermi energy is equal to 0.5 for all finite temperature.

Solution

- When $E = E_F$,

$$\begin{aligned} f(E) &= \frac{1}{e^{(E-E_F)/K_B T} + 1} = \frac{1}{e^{(E_F-E_F)/K_B T} + 1} \\ &= \frac{1}{e^0 + 1} = \frac{1}{1+1} = \frac{1}{2}. \end{aligned}$$

Example

Using the Fermi-Dirac distribution, determine the values of energy corresponding to $f = 0.9$ and $f = 0.1$ at a temperature of 300 K.

Solution

$$f(E) = \frac{1}{e^{(E-E_F)/K_B T} + 1} = 0.9$$

$$e^{(E-E_F)/K_B T} + 1 = \frac{1}{0.9}$$

$$e^{(E-E_F)/K_B T} = 1.111 - 1 = 0.111$$

$$(E - E_F) / K_B T = \ln(0.111)$$

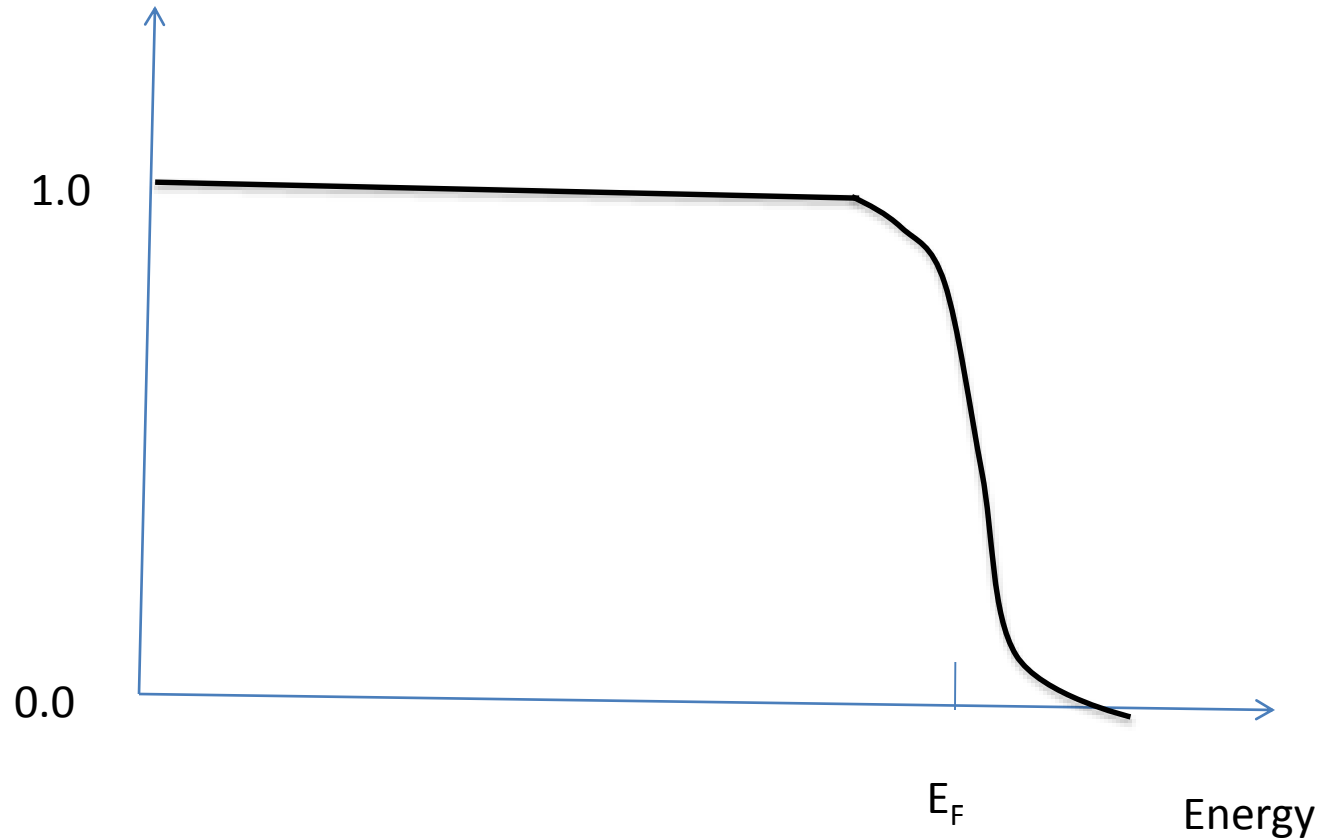
$$E_F - E = 2.20 K_B T$$

$$E = E_F - 2.20 K_B T$$

Fermi-Dirac Distribution

Probability of occupation

$f(E)$



Solution

$$f(E) = \frac{1}{e^{(E-E_F)/K_B T} + 1} = 0.1$$

$$e^{(E-E_F)/K_B T} + 1 = \frac{1}{0.1}$$

$$e^{(E-E_F)/K_B T} = 10 - 1 = 9$$

$$(E - E_F) / K_B T = \ln(9)$$

$$E - E_F = 2.20 K_B T$$

$$E = E_F + 2.20 K_B T$$

Ohm's Law

In an electric field ε and magnetic field B , the force on an electron of charge $-q$ is

$$F = -q(\varepsilon + \vec{v} \times \vec{B})$$

If $B = 0$,

$$\text{momentum} = mv = F\tau = -q\varepsilon\tau$$

thus

$$v = -\frac{q\tau}{m}\varepsilon$$

← collision time

Ohm's Law

The electric current density is

$$|J| = qnv = \frac{q^2 n \tau}{m} \mathcal{E}$$

If we define the electrical conductivity as

$$\sigma = \frac{q^2 n \tau}{m}$$

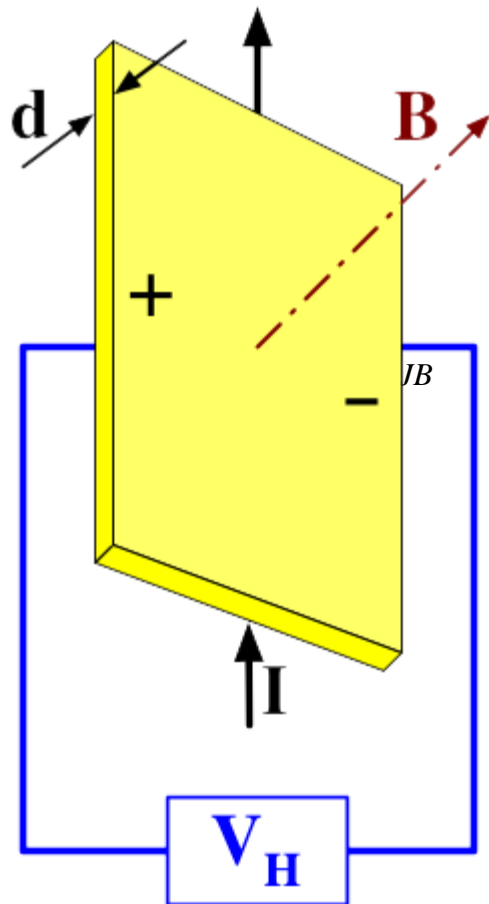
then

$$|J| = \sigma \mathcal{E}$$

← Ohm's Law

Hall Effect

$$B \neq 0$$



$$F = q\varepsilon = qvB$$

$$\varepsilon = -\frac{J}{qn} B = R_H JB$$

Hall coefficient

Quantum Statistics

A single quantum mechanical system consists of N particles constrained to some volume V

assumption

1. weakly interacting particles
2. the particle density is low enough so that the energy of the system can be considered as the sum of the individual particle energies



$$\hat{H}\Psi_i^s = E_i \Psi_i^s$$

← wavefunction of particle s

$$E = \sum_{i=1}^{\infty} n_i E_i$$

← number of particles with energy E_i

Quantum Statistics

- How to determine the most probable distribution of finding n_1 particles out of a total of N with energy E_1 , n_2 with energy E_2 , and so on?



The most probable distribution ($n_1, n_2, \dots, n_s, \dots$) is the one associated with the largest number of microscopically distinguishable arrangements

Thus, the plan of attack would be to derive an expression for P , the total number of microscopically distinct arrangement corresponding to a given arbitrary sequence ($n_1, n_2, \dots, n_s, \dots$) and then find the particular sequence that maximizes P .

Three types of quantum particles

The particles of concern to us fall into one of three categories

1. Identical but distinguishable particles

- harmonic oscillators

2. Identical indistinguishable particles of half-odd integral spin (Fermions)

- electrons
- protons



obey Pauli exclusion principle

3. Identical indistinguishable particles of integral spin (Bosons)

- photons
- phonons



Pauli exclusion principle not apply

N particle system

Our model system is taken to contain N particles, each with a spectrum of allowed energy levels

$$E_1, E_2, \dots, E_s, \dots$$

We divide the single-particle energy spectrum into energy “bins”. Bin s , as an example, represents all the elementary quantum states whose energies lie within some arbitrarily chosen interval ΔE_s centered about E_s . The number of quantum states in bin s is denoted by g_s .

Identical but distinguishable particles

Determine P of N particles such that bin 1 contains n_1 particles, bin 2 n_2 particles, and so on.

For bin 1, the total number of distinguishable choices is

$$P_1 = \frac{g_1^{n_1} N!}{n_1! (N - n_1)!} \quad \text{or} \quad g_1^{n_1} \cdot {}_N C_{n_1}$$

For bin 2, the total number of distinguishable choices is

$$P_2 = \frac{g_2^{n_2} (N - n_1)!}{n_2! (N - n_1 - n_2)!} \quad \text{or} \quad g_2^{n_2} \cdot {}_{N-n_1} C_{n_2}$$

Identical but distinguishable particles

the total number of distinguishable choices in which bin 1 contains n_1 particles, bin 2 n_2 particles, and so on, is

$$\begin{aligned} P(n_1, n_2, \dots, n_s, \dots) &= P_1 P_2 \dots P_s \dots \\ &= N! \prod_{s=1}^{\infty} \frac{g_s^{n_s}}{n_s!} \end{aligned}$$

Identical indistinguishable particles of half-odd integral spin (Fermions)

Determine P of N particles such that bin 1 contains n_1 particles, bin 2 n_2 particles, and so on.

For bin 1, the total number of distinguishable choices is

$$P_1 = \frac{g_1!}{n_1!(g_1 - n_1)!} \quad \text{or} \quad {}_{g_1}C_{n_1}$$

For bin 2, the total number of distinguishable choices is

$$P_2 = \frac{g_2!}{n_2!(g_2 - n_2)!} \quad \text{or} \quad {}_{g_2}C_{n_2}$$

Identical indistinguishable particles of half-odd integral spin (Fermions)

the total number of distinguishable choices in which bin 1 contains n_1 particles, bin 2 n_2 particles, and so on, is

$$P(n_1, n_2, \dots, n_s, \dots) = P_1 P_2 \dots P_s \dots$$
$$= \prod_{s=1}^{\infty} \frac{g_s!}{(g_s - n_s)! n_s!}$$

Identical indistinguishable particles of integral spin (Bosons)

Determine P of N particles such that bin 1 contains n_1 particles, bin 2 n_2 particles, and so on.

For bin 1, the total number of distinguishable choices is

$$P_1 = \frac{(n_1 + g_1 - 1)!}{n_1!(g_1 - 1)!}$$

For bin 2, the total number of distinguishable choices is

$$P_2 = \frac{(n_2 + g_2 - 1)!}{n_2!(g_2 - 1)!}$$

Identical indistinguishable particles of integral spin (Bosons)

the total number of distinguishable choices in which bin 1 contains n_1 particles, bin 2 n_2 particles, and so on, is

$$P(n_1, n_2, \dots, n_s, \dots) = P_1 P_2 \dots P_s \dots$$
$$= \prod_{s=1}^{\infty} \frac{(n_s + g_s - 1)!}{(g_s - 1)! n_s!}$$

Lagrange method

we wish to find the set of n_s for which P is maximized
subjected to conditions :

$$\sum_{s=1}^{\infty} n_s = N = \text{const}$$

$$\sum_{s=1}^{\infty} E_s n_s = E = \text{const}$$

We constrain our solution using [Lagrange multipliers](#)
forming the function:

$$F(n_1, n_2, \dots, n_s, \dots) = \ln(P) + \alpha \left(N - \sum_{s=1}^{\infty} n_s \right) + \beta \left(E - \sum_{s=1}^{\infty} E_s n_s \right)$$

Lagrange method

$$\frac{\partial F}{\partial n_s} = 0 \quad \text{for all } s$$

For Identical but distinguishable particles

$$\ln g_s - \ln n_s - \alpha - \beta E_s = 0$$



$$n_s = \frac{g_s}{\exp(\alpha + \beta E_s)}$$

Maxwell-Boltzmann

Lagrange method

For Identical indistinguishable particles of half-odd integral spin (Fermions)

$$\ln(g_s - n_s) - \ln n_s - \alpha - \beta E_s = 0$$



$$n_s = \frac{g_s}{\exp(\alpha + \beta E_s) + 1} \quad \text{Fermi-Dirac}$$

Lagrange method

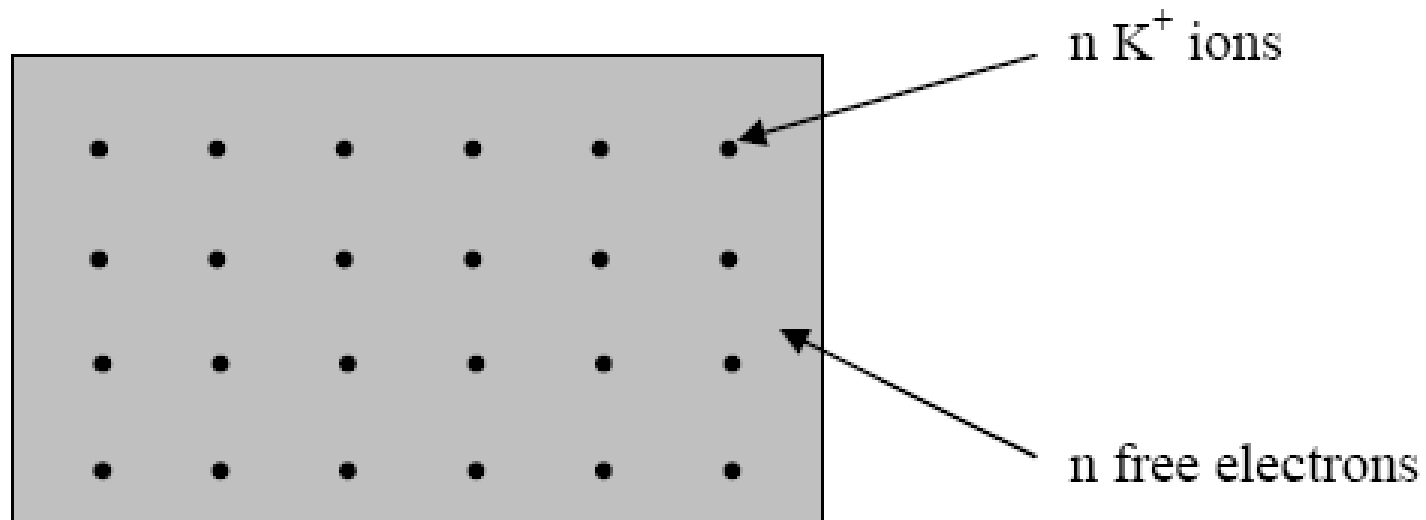
For Identical indistinguishable particles of half-odd integral spin (Fermions)

$$\ln(g_s + n_s) - \ln n_s - \alpha - \beta E_s = 0$$



$$n_s = \frac{g_s}{\exp(\alpha + \beta E_s) - 1} \quad \text{Bose-Einstein}$$

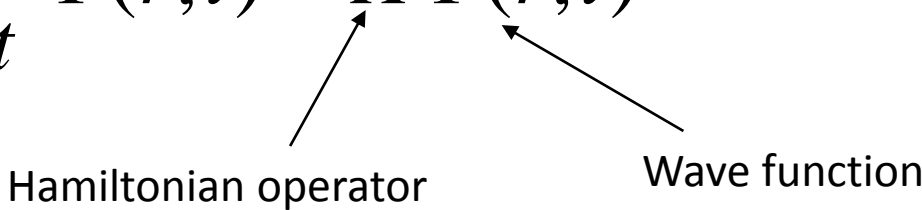
Energy Band



Electron in a metal can move freely in a straight path over many atomic distances, undeflected by collisions with other conduction electron or by collisions with the atom cores

Energy Band

For a general quantum system

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) = \hat{H} \Psi(r, t) \quad (1)$$


Hamiltonian operator

Wave function

For a single particle in three dimensions

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + V(r) \Psi(r, t) \quad (2)$$

Energy Band

free electron gas $\longrightarrow V(r)=0$

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi_n}{dx^2} = E_n \Psi_n \quad (3)$$

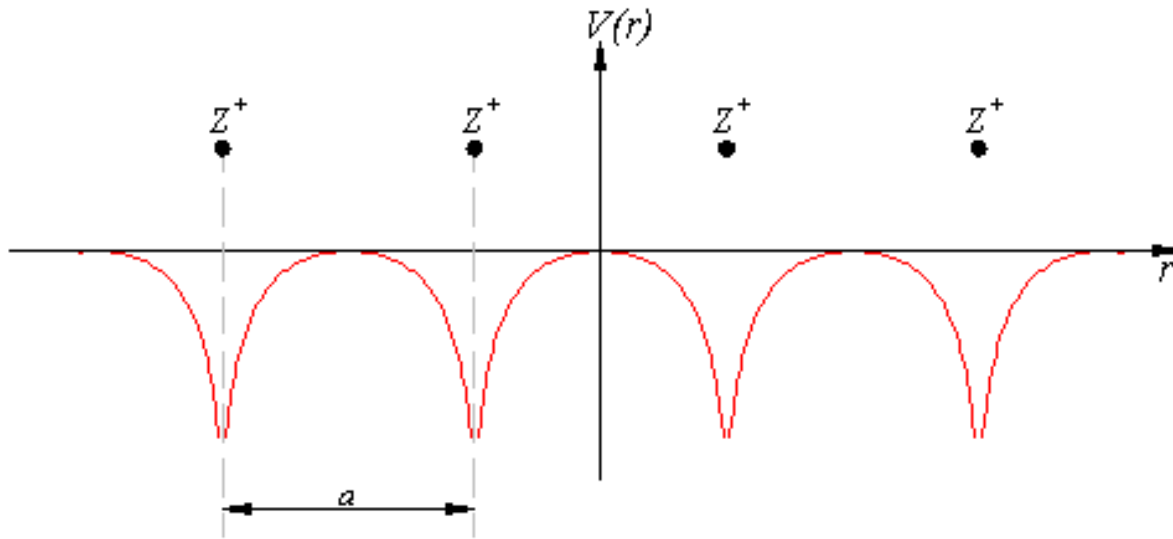
Energy of the electron

Free Electron Model

Energy Band

if $V(r) \neq 0$

Considering a periodic potential, $V(r+T)=V(r)$



(2) can be expressed as

$$E\Psi(r) = -\frac{\hbar^2}{2m}\nabla^2\Psi(r) + V(r)\Psi(r) \quad (4)$$

Energy Band

The periodic potential $V(r)$ may be expanded as a Fourier series in the reciprocal lattice vectors G

$$V(r) = \sum_G U_G e^{iG \cdot r} \quad (5)$$

or

$$V(x) = \sum_G U_G e^{iGx} \quad \text{For 1-D system}$$

Thus, (4) can be rewritten as

$$E\Psi(x) = -\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + \sum_G U_G e^{iGx} \Psi(x) \quad (6)$$

Energy Band

The wavefunction $\Psi(x)$ may be expressed as a Fourier series summed over all values of the wavevector permitted by the boundary conditions

$$\Psi(x) = \sum_k C_k e^{ikx} \quad (7)$$

then

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} = \frac{\hbar^2}{2m} \sum_k k^2 C_k e^{ikx}$$

$$V(x)\Psi(x) = \sum_G \sum_k U_G C_k e^{i(k+G)x}$$

Energy Band

From (6), we get

$$\sum_k \frac{\hbar^2}{2m} k^2 C_k e^{ikx} + \sum_G \sum_k U_G C_k e^{i(k+G)x} = E \sum_k C_k e^{ikx}$$

Each Fourier component must have the same coefficient on both sides of the equation

$$(\lambda_k - E)C_k + \sum_G U_G C_{k-G} = 0 \quad (8)$$

where $\lambda_k = \frac{\hbar^2 k^2}{2m}$

central equation

Energy Band

Once we determine The C_k from central equation, the $\Psi(x)$ is given as

$$\Psi_k(x) = C_k e^{ikx} = \sum_G C_{k-G} e^{i(k-G)x} \quad (9)$$

Rearrange (9), we get

$$\Psi_k(x) = \left(\sum_G C_{k-G} e^{-iGx} \right) e^{ikx} = u_k(x) e^{ikx} \quad (10)$$

$$\text{where } \sum_G C_{k-G} e^{-iGx} \equiv u_k(x)$$

Energy Band (Bloch Theorem)

The solutions of the Schrodinger equation for a periodic potential must be of a special form

$$\Psi_k(r) = u_k(r) \exp(ik \cdot r) \quad (11)$$

$$u_k(r) = u_k(r + T)$$

Translation vector

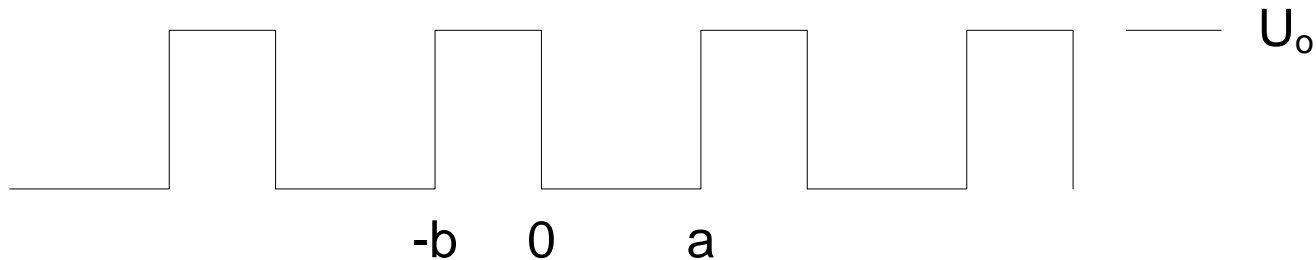
The eigenfunctions of the wave equation for a periodic potential are the product of a plane wave $\exp(ik \cdot r)$ times a function $u_k(r)$ with the periodicity of the crystal lattice



Bloch theorem

Energy Band (Kronig-Penney Model)

If $V(x)$ is



The solutions for (2) are

$$\Psi(x) = \begin{cases} Ae^{iKx} + Be^{-iKx} & 0 < x < a \\ Ce^{Qx} + De^{-Qx} & -b < x < 0 \end{cases}$$

where $U_0 - E = \hbar^2 Q^2 / 2m$ and $E = \frac{\hbar^2 K^2}{2m}$

Energy Band (Kronig-Penney Model)

The constants A,B,C,D are chosen so that Ψ and $d\Psi/dx$ are continuous at $x=0$ and $x=a$

$$\Psi\Big|_{x=0} = \Psi\Big|_{x=0} \Rightarrow A + B = C + D \quad (12)$$

$$\frac{d\Psi}{dx}\Big|_{x=0} = \frac{d\Psi}{dx}\Big|_{x=0} \Rightarrow ik(A - B) = Q(C - D) \quad (13)$$

Bloch theorem

$$\Psi(a < x < a + b) = \Psi(-b < x < 0)e^{ik(a+b)}$$

Energy Band (Kronig-Penney Model)

$$\Psi \Big|_{x=a} = \Psi \Big|_{x=-b} e^{ik(a+b)}$$

\Downarrow

$$Ae^{iKa} + Be^{-iKa} = \left(Ce^{-Qb} + De^{Qb} \right) e^{ik(a+b)} \quad (14)$$

$$\frac{d\Psi}{dx} \Big|_{x=a} = \frac{d\Psi}{dx} \Big|_{x=-b} e^{ik(a+b)}$$

\Downarrow

$$iK \left(Ae^{iKa} - Be^{-iKa} \right) = Q \left(Ce^{-Qb} - De^{Qb} \right) e^{ik(a+b)} \quad (15)$$

Energy Band (Kronig-Penney Model)

From (12)-(15), we can get

$$\frac{Q^2 - K^2}{2QK} \sinh Qb \sin Ka + \cosh Qb \cos Ka = \cos k(a+b) \quad (16)$$

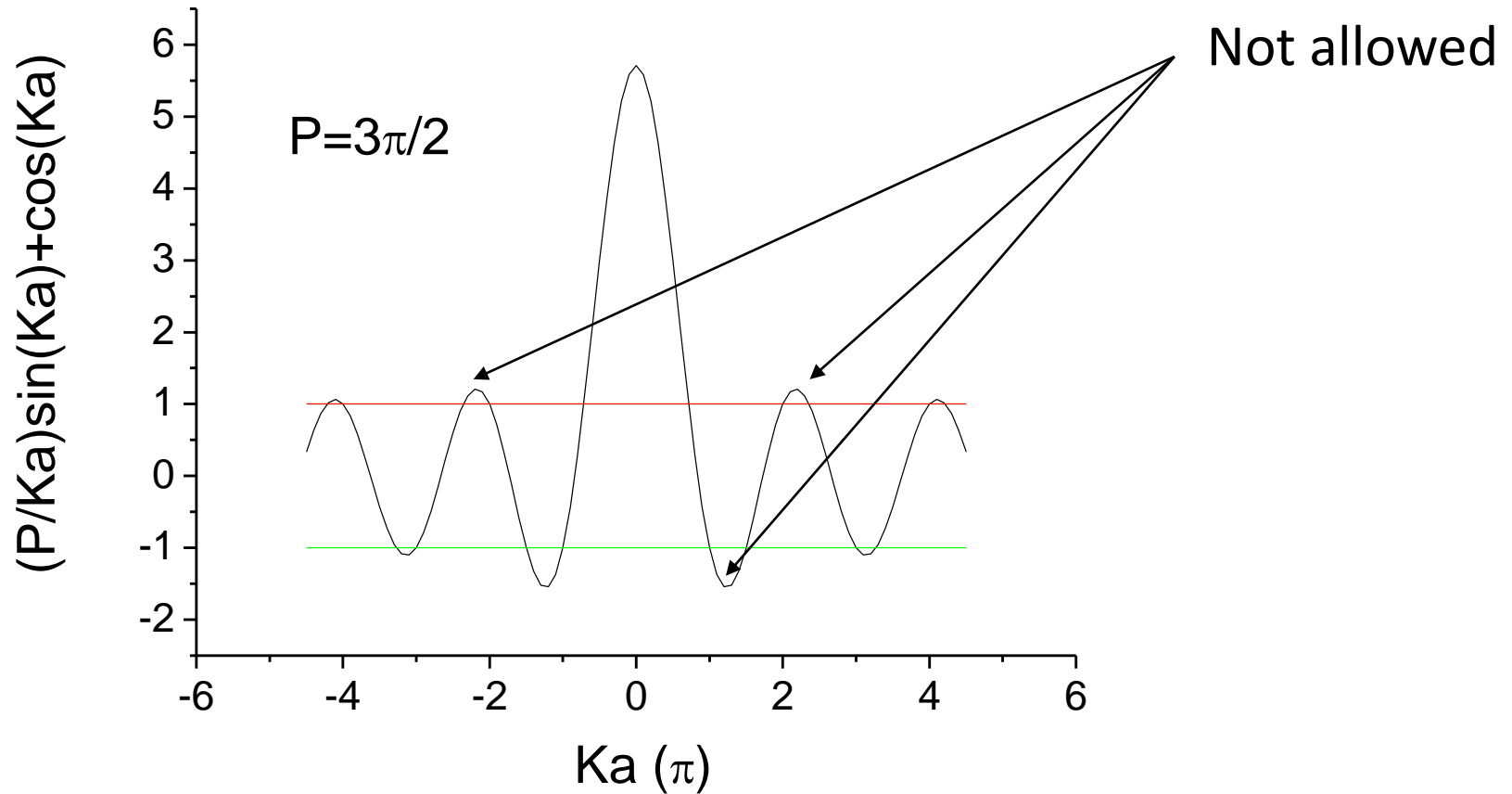
If the potential is a periodic delta function

$$\lim_{b \rightarrow 0} \quad \text{and} \quad \lim_{U_o \rightarrow \infty}$$

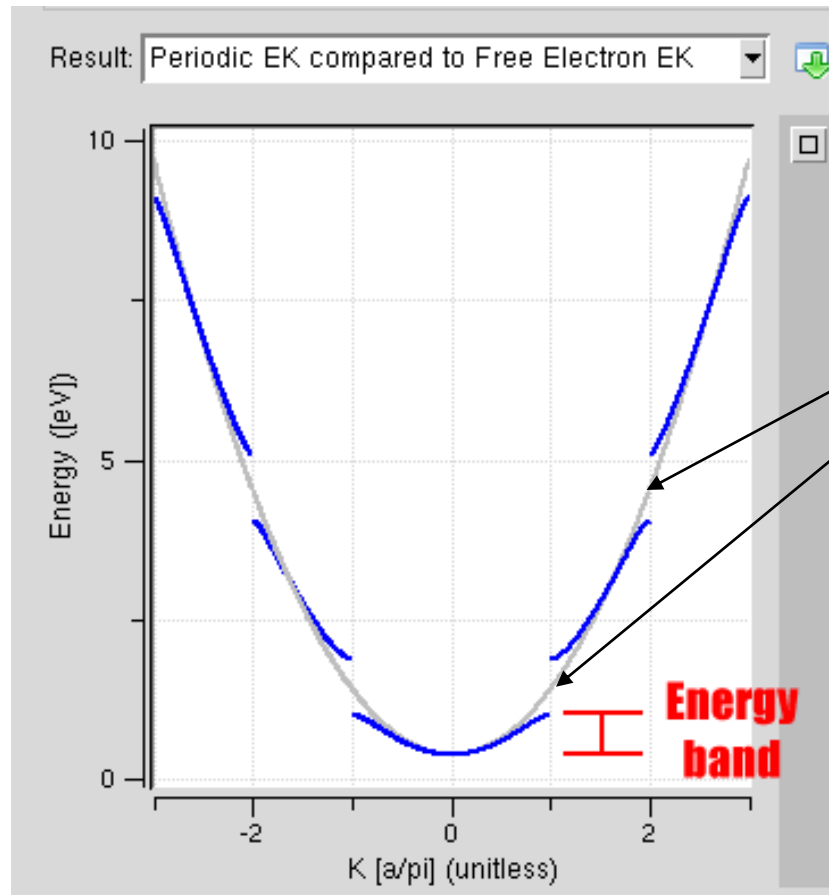
Then, (16) can reduce to $P = Q^2 ba/2$

$$(P/Ka) \sin Ka + \cos Ka = \cos ka \quad (17)$$

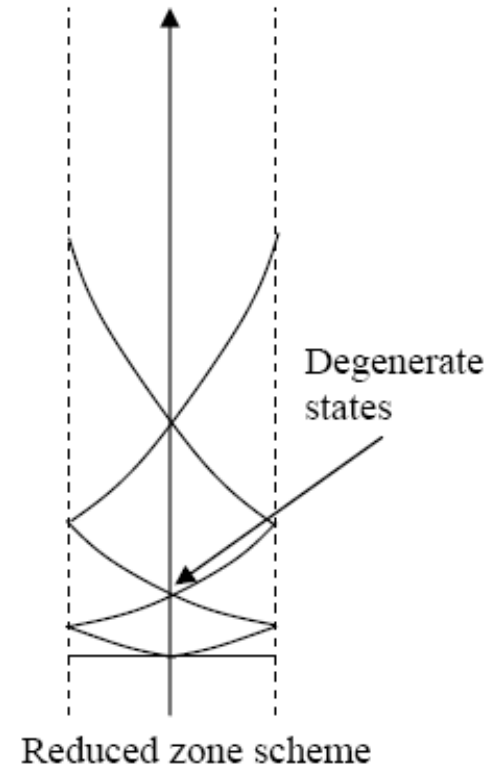
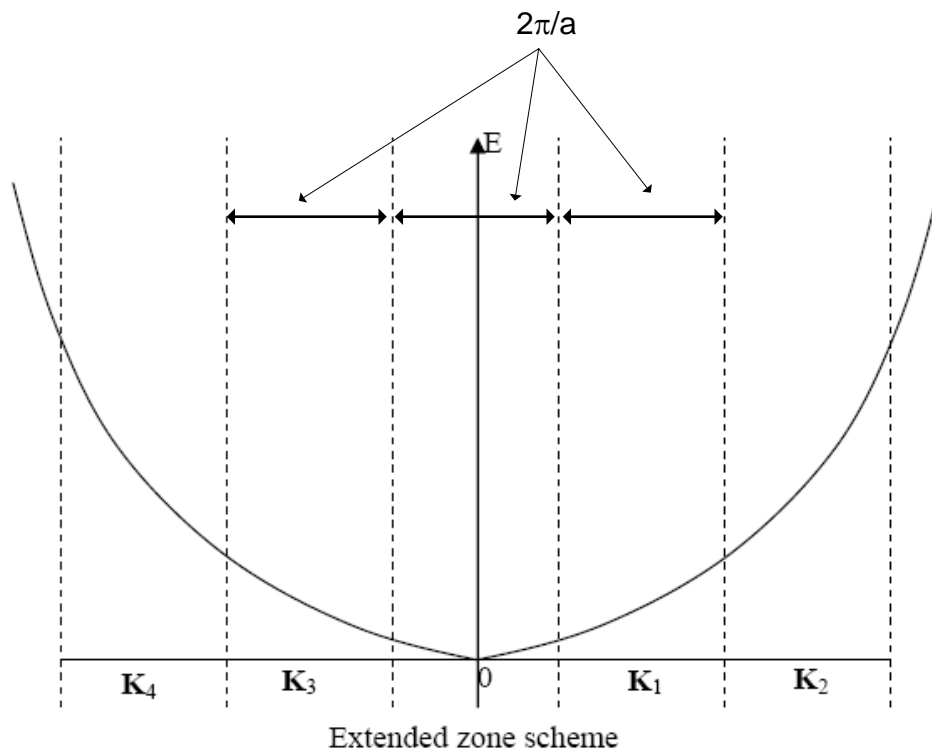
Energy Band (Kronig-Penney Model)



Energy Band (Kronig-Penney Model)



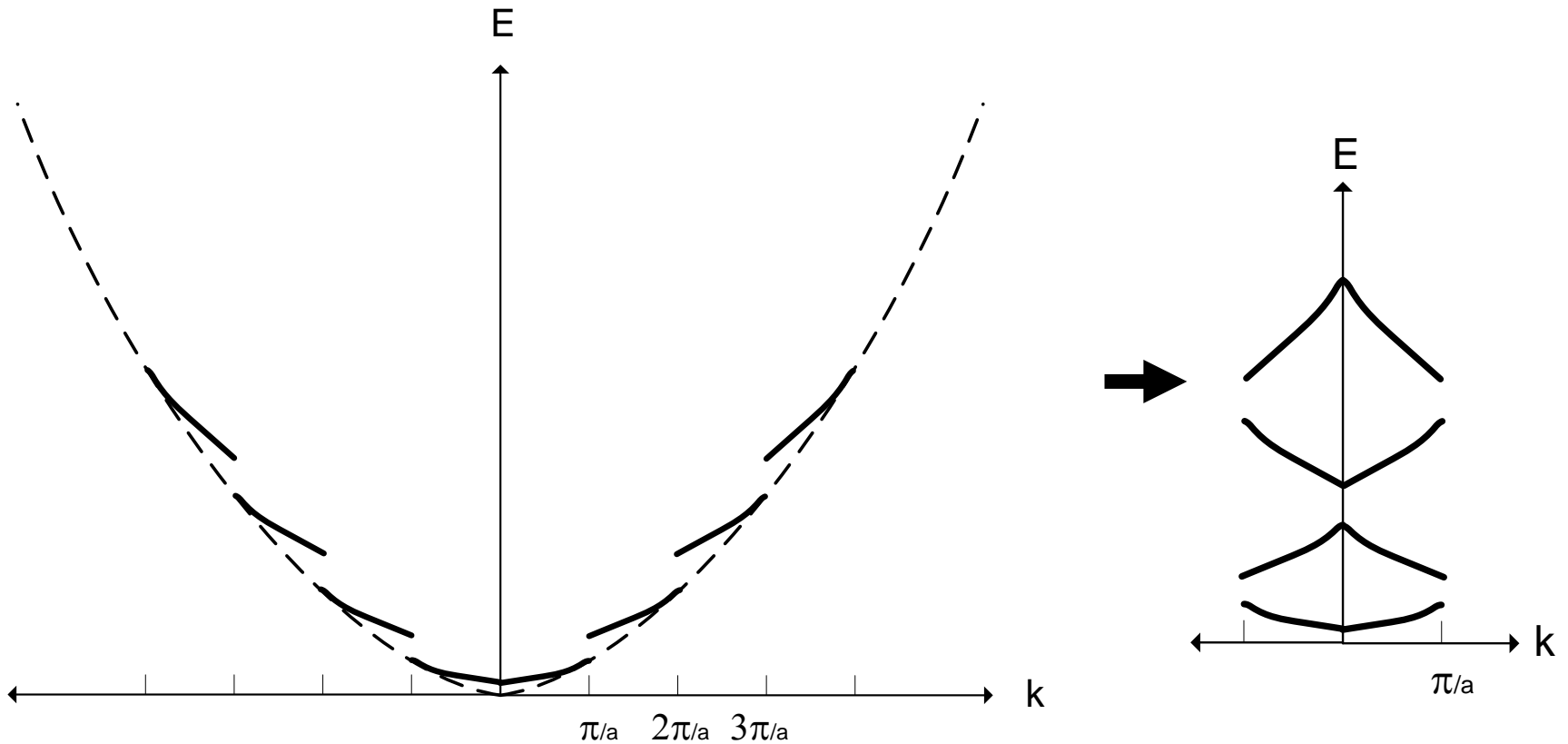
Band Structure



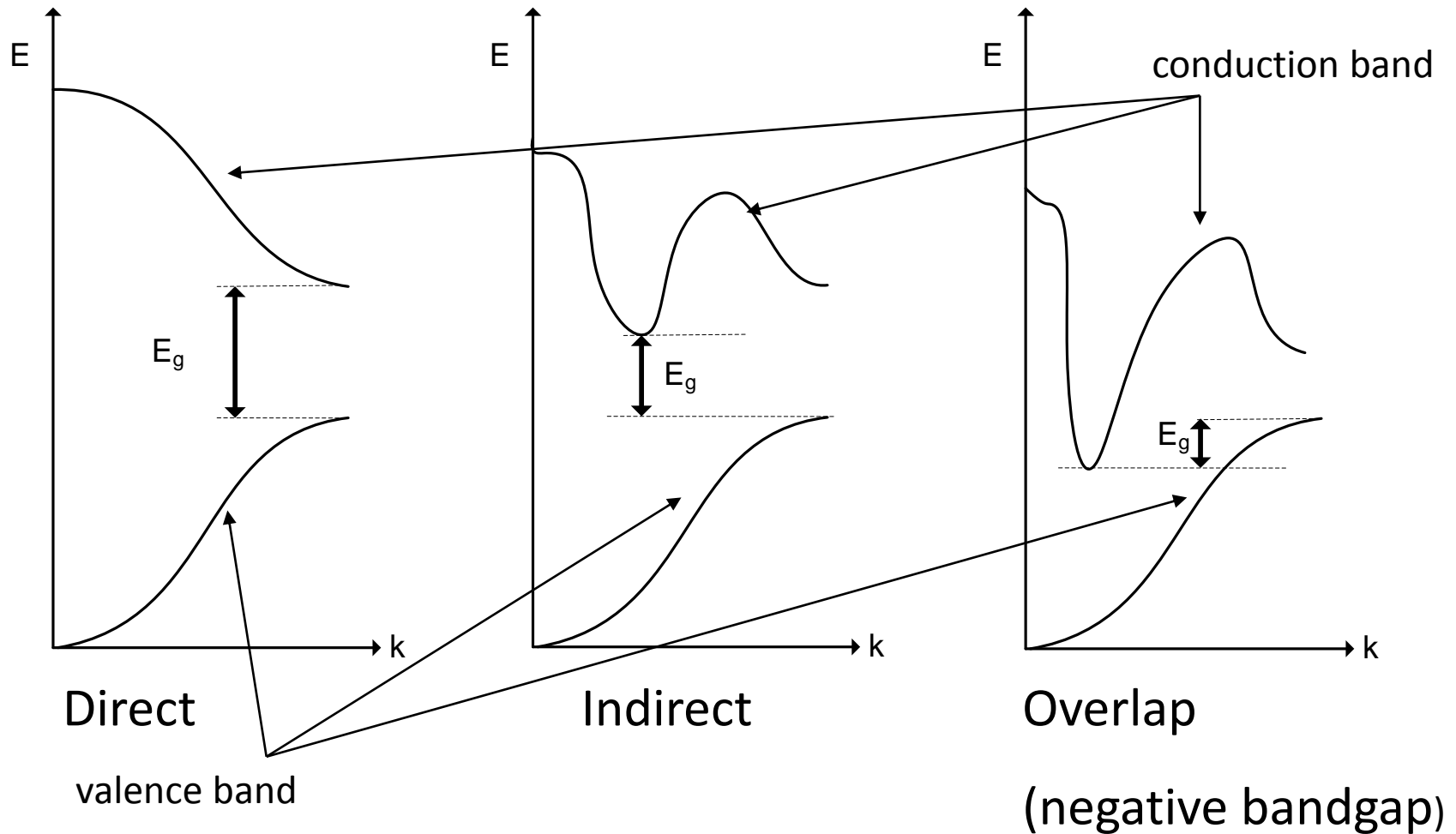
Actual band structures are usually exhibited as plots of energy versus wavevector in the first Brillouin zone. This is helpful in visualization and economical of graph paper.

Band Structure

If the band structure of A is :

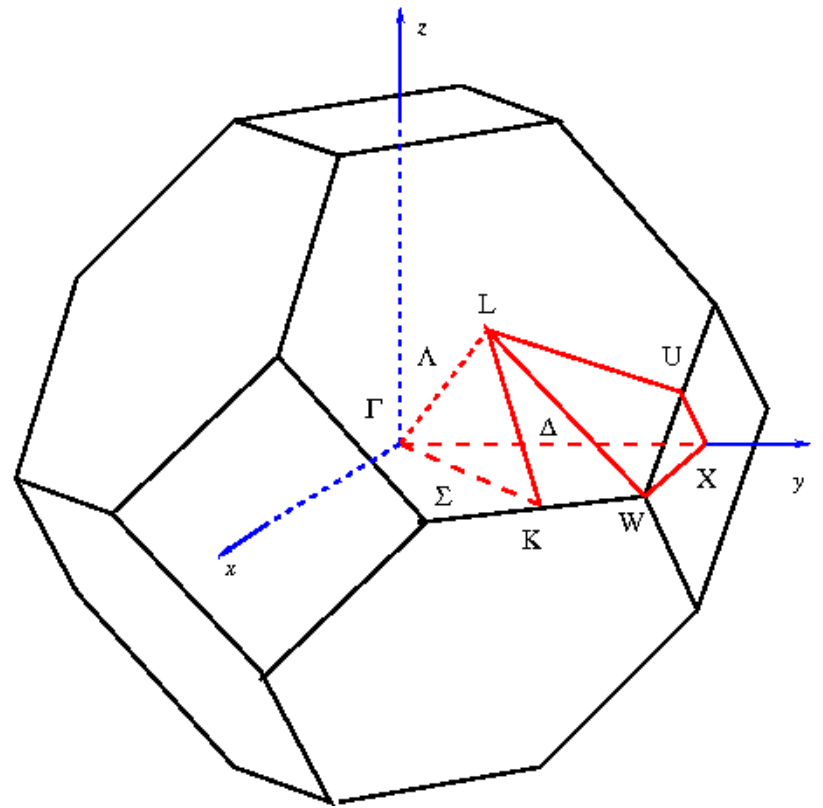
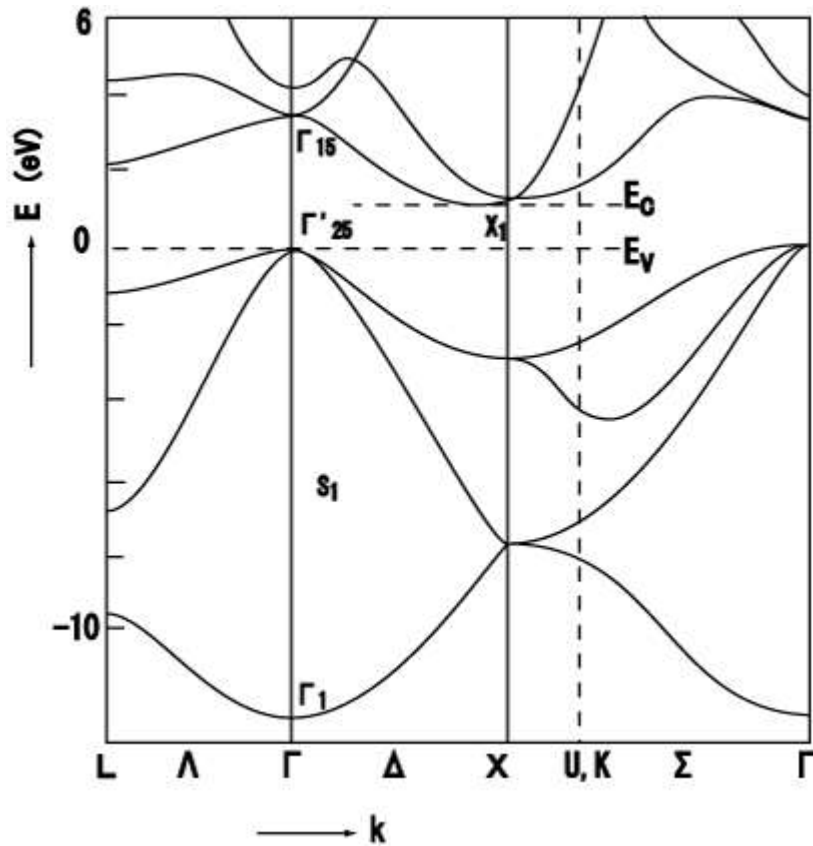


Band Structure



Bandgap – the difference in energy between the lowest point of the conduction band and the highest point of the valence band.

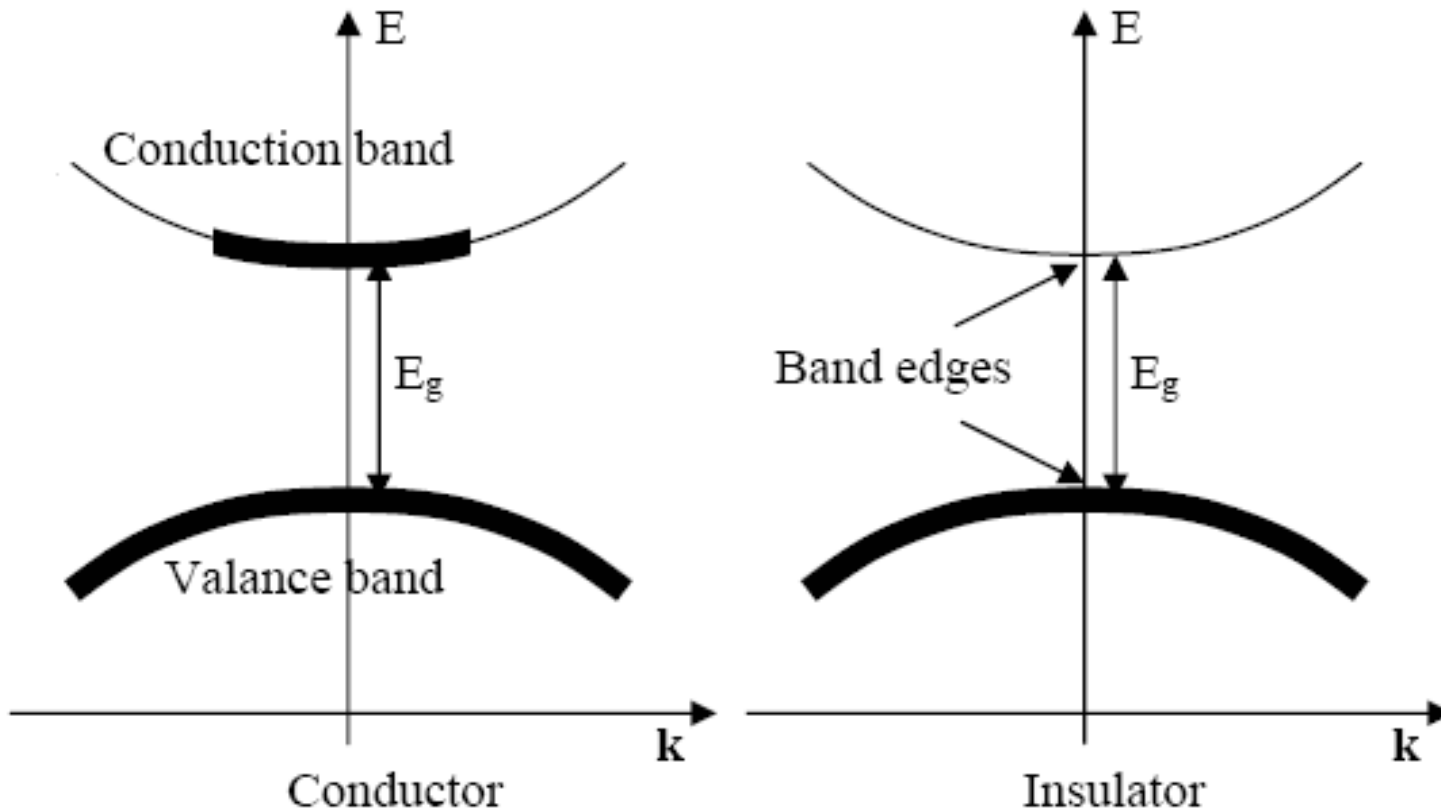
Band Structure



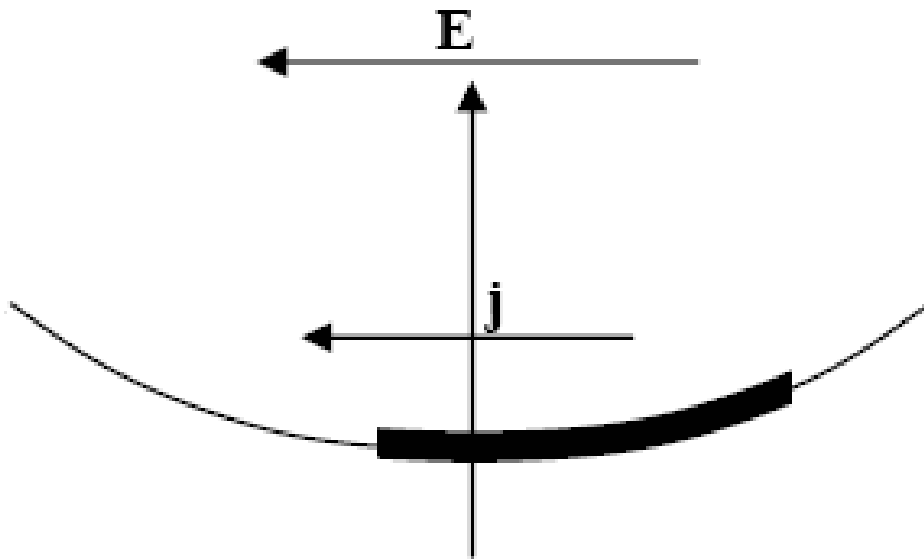
band structure of Si

Energy Band (conductor and insulator)

A band is filled from low energy to high energy



Energy Band (conductor and insulator)



Partially filled band

Only a partially filled band can conduct electricity. The occupied states are not “balance” under an external field. This unbalance causes the current flow.

- A full band cannot conduct electricity. A full band is always a full band no matter what the external field are
- An empty band cannot conduct electricity because it does not have charge carrier.


Energy Band

(Equation of motion and effective mass)

The equation of motion of an electron in an energy band is :

$$F = \hbar \frac{dk}{dt} = q(E + v \times B) \quad (1)$$

From (1), we can get

$$F = \hbar \frac{dk}{dt} = m_e \frac{dv}{dt}$$
$$m_e \frac{dv}{dt} = m_e \frac{d}{dt} \left(\frac{d\omega}{dk} \right) = \frac{m_e}{\hbar} \frac{d^2 E}{dt dk}$$


$$\frac{1}{m_e} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

effective mass

Energy Band

(Equation of motion and effective mass)

Approximate solution near a zone boundary

$$E = E_0 + \frac{\hbar^2 k^2}{2m} (A) \quad (2)$$

Electron rest mass

From (1), we get

$$\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{1}{\hbar^2} \frac{\hbar^2 A}{m} \quad \text{thus} \quad m_e = \frac{m}{A} \quad (3)$$

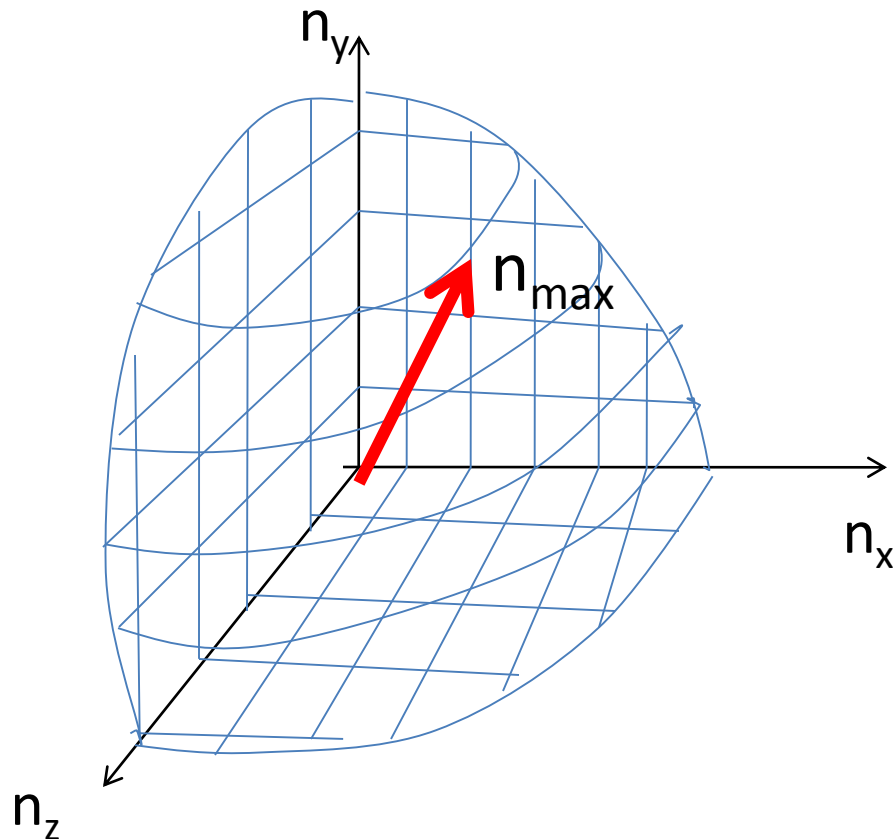
An electron of mass m when put into a crystal respond to applied fields as if the mass were m_e (**effective mass**)

Example

By determine the number of grid points contained beneath the surface of radius n_{max} , show that the Fermi energy (i.e. the energy of the highest occupied state at $T = 0K$) is given by

$$E_F = \frac{\hbar^2}{2m} \left[\frac{3\pi^2 N}{V} \right]^{2/3} .$$

Each allowed quantum state can be represented by a grid point (n_x, n_y, n_z) . Grid points with the same energy are connected by a surface of constant radius. In order to determine the Fermi energy, find the values of the radius n_{\max} , just contains sufficient states to accommodate all the valence electrons in the crystal



Solution

- The volume contained beneath the surface corresponds to one-eighth of a sphere of radius n_{\max} , the volume is $\frac{1}{8} \times \frac{4}{3} \pi n_{\max}^3 = \frac{\pi n_{\max}^3}{6}$
- Each grid point corresponding to a cube of unit volume, this expression also gives the number of grid points beneath the surface.
- As each grid point corresponding to a state which can accommodate two electrons for a crystal containing N electrons we require $N/2$ states.
- $$\frac{N}{2} = \frac{\pi n_{\max}^3}{6} \rightarrow n_{\max} = \left(\frac{3N}{\pi} \right)^{1/3}$$

Solution

- By writing $n_{\max} = \left(n_x^2 + n_y^2 + n_z^2\right)^{1/2}$

- Energy
$$\begin{aligned} E &= \frac{h^2 k^2}{2m} = \frac{h^2}{2m} \left(\frac{\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right) \\ &= \frac{h^2}{2m} \left(\frac{\pi}{L}\right)^2 n_{\max}^2 = \frac{h^2}{2m} \left(\frac{\pi}{L}\right)^2 \left(\frac{3N}{\pi}\right)^{2/3} \\ &= \frac{h^2}{2m} \left(\frac{\pi^3 3N}{L^3 \pi}\right)^{2/3} = \frac{h^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{2/3} \end{aligned}$$

Thermal Conductivity in Metals

- Thermal conductivity of a Fermi gas is

$$K_{el} = \frac{\pi^2}{3} \cdot \frac{nk^2T}{mv_F^2} \cdot v_F \cdot l = \frac{\pi^2 nk^2T\tau}{3m}$$

where n is the electron concentration

k is the Boltzmann constant

T is the temperature

m is the mass of electron

and τ is the collision time.

Thermal Conductivity in Metals

- Do the electrons or phonons carry the greater part of the heat current in a metal?
- In pure metals the electronic contribution is dominant at all temperatures.
- In impure metals or in disordered alloys, the electron mean free path is reduced by collisions with impurities, and phonon contribution may be comparable with the electronic contribution.

Wiedemann-Franz law

- The Wiedemann-Franz law states that for metals at not too low temperatures the ratio of the thermal conductivity to the electrical conductivity is directly proportional to temperature, with the value of the constant of proportionality independent of the particular metal.

$$\frac{K}{\sigma} = \frac{\pi^2 k^2 T n \tau / 3m}{ne^2 \tau / m} = \frac{\pi^2}{3} \left(\frac{k}{e} \right)^2 T$$

Lorenz number L

- The Lorenz number L is defined as

$$L = K / \sigma T$$

- The value of $L = \frac{\pi^2}{3} \left(\frac{k}{e} \right)^2 = 2.45 \times 10^{-8} \text{ watt-ohm/deg}^2$.
- This remarkable result involves neither n nor m.
- Experimental values of L at 0°C and 100°C are in good agreement.

Experimental Lorenz numbers

$L \times 10^8$ watt-ohm/deg²		
Metal	0°C	100°C
Ag	2.31	2.37
Au	2.35	2.40
Cd	2.42	2.43
Cu	2.23	2.33
Mo	2.61	2.79
Pb	2.47	2.56
Pt	2.51	2.60
Su	2.52	2.49
W	3.04	3.20
Zn	2.31	2.33