Ch 6

Free e^- model

→ metals

col I → 1 valence e^-
monovalent

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s

recall how to write e^- config.

classical free e^- has problems -
- heat capacity
- mag susceptibility
- straight, unimpeded e^- paths.

10^8

because
- condn e^- not deflect by ion core in pdic structure → wave propagates freely in pdic lattice.
- condn e^- deflected only occasionaly by other cond. e^- _ Pauli

free e^- Fermi gas – cloud of e^- subj. to Pauli Excl Principle

Energy Levels

free e^-
mass m
$\psi_n(x)$ = wave fn of e^-

Schrödinger Eqn (SE) $\mathcal{H}\psi_n = E\psi$

$\overset{\uparrow}{KE}$

$$\mathcal{H} = \frac{p^2}{2m} \qquad p = \text{momentum operator}$$
$$= j\hbar \frac{d}{dx}$$
$$= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

SE: $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n = E_n \psi_n \rightarrow$ sinusoid

$\psi_n(0) = 0$
$\psi_n(L) = 0$

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

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2$$

In general $\rightarrow N e^-$

Pauli $\rightarrow$ no $2e^-$ have all same quantum #s
(each orbital has only one e^-)

quantum # of conduction e^-: n, m_s
$\uparrow$ spin $\pm\frac{1}{2}$

Ex: $N = \boxed{6e^-}$

n	1		2		3	
m_s	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
	↑	↓	↑	↓	↑	↓

start filling @ bottom ($n=1$)
to top ($n = n_F$)
$$2n_F = N$$

Note: more than one orbital can have
same Energy : degeneracy

Fermi Energy $= E_F =$ energy of n_F topmost filled level

from SE: $E_F = \frac{\hbar^2}{2m}\left(\frac{n_F \pi}{L}\right)^2$

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

ground state @ $T = 0K$.

as $T\uparrow$, $KE\uparrow$ — higher energy levels become occupied.

$F(E)$ = probability an orbital @ energy E is occupied.

Fermi Dirac

$$= \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

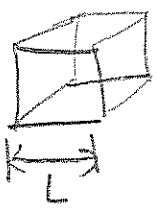
μ = chemical pot'l

@ $T = 0K$: $\mu = E_F$

K_B = Boltzmann constant

See App D.

Free e^- gas in 3D



(cube)

$$\frac{d^2}{dx^2} = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} = \nabla^2$$

$x \rightarrow \vec{r}$

$n \rightarrow \vec{k} = (n_x, n_y, n_z)$

SE: $-\frac{\hbar}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_k(\vec{r}) = E_k \psi_k(\vec{r})$

$\psi_k(\vec{r}) = A \sin\left(\frac{\pi n_x}{L} x\right) \sin\left(\frac{\pi n_y}{L} y\right) \sin\left(\frac{\pi n_z}{L} z\right)$

General soln of S.E.

pdic w/ pd L

$\psi_{\vec{k}}(\vec{r}) = e^{j(\vec{k}\cdot\vec{r})}$ → travelling plane wave

$\vec{k}$ = wave vector

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

↳ quantum #s

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_k(r) = E_k \psi_k(r)$$

$$\psi_k(r) = e^{j(\vec{k}\cdot\vec{r})}$$

$$\Rightarrow E_k = \frac{\hbar^2 k^2}{2m} \quad \omega \quad |k| = \frac{2\pi}{\lambda}$$

since $\vec{p} = -j\hbar\nabla$

$$\vec{p}\,\psi_k(r) = -j\hbar\nabla\psi_k(r)$$

$$\psi_k(r) = e^{-j(k\cdot r)}$$

$$-j\hbar\nabla\psi_k(r) = -j\hbar(-j\vec{k})e^{-j(\vec{k}\cdot\vec{r})}$$

$$= \hbar\vec{k}\underbrace{e^{-j(\vec{k}\cdot\vec{r})}}_{\psi_k(\vec{r})}$$

∴ $\psi_k(\vec{r})$ is eigenvector of $\vec{p}$

$$\vec{p} = \hbar\vec{k} = m\vec{v} \Rightarrow \boxed{\vec{v} = \frac{\hbar\vec{k}}{m}}$$

Now consider system of N e^- in ground state

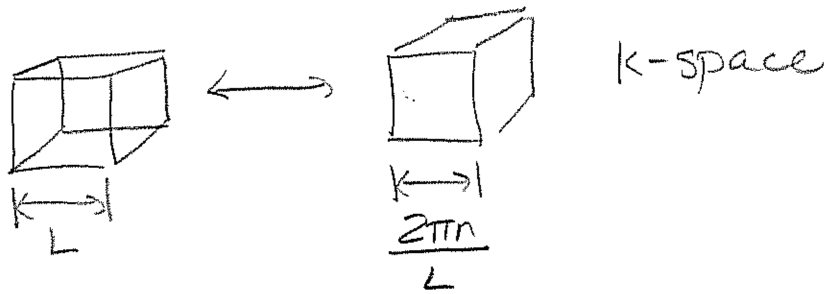
$\Rightarrow$ model orbitals as spheres in k-space

$$Vol = \frac{4\pi}{3} k^3$$

energy on surface = Fermi energy

$$E \to E_F \qquad E_F = \frac{\hbar^2 k_F^2}{2m}$$
$$k \to k_F$$

recall $k_{x,y,z} = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \ldots$



min vol cube in k-space $\left(\frac{2\pi}{L}\right)^3$

$$\left(\frac{V_{sphere}}{V_{cube}}\right) \underset{\uparrow \text{spin}}{2} = N = \# \text{ orbitals}/e^-$$

$$k_F, E_F \longleftrightarrow N$$

$$2\left(\frac{4\pi/3\ k_F^3}{(2\pi/L)^3}\right) = N$$

$$\frac{8\pi/3\ k_F^3}{8\pi^3/L^3} = \frac{\overset{V}{L^3}\, k_F^3}{3\pi^2} = N$$

$$K_F = \left(\frac{3\pi^2 N}{L^3}\right)^{1/3}$$

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

<u>e^- concentration</u> $= \frac{N}{V} = \frac{N}{L^3}$

$$E_F \propto \left(\frac{N}{L^3}\right)^{2/3}$$

e^- velocity @ Fermi surface

$$p = mv = \hbar k$$

$$\vec{v} = \frac{\hbar \vec{k}}{m} \Rightarrow \vec{v} \propto \left(\frac{N}{L^3}\right)^{1/3}$$

<u>Density of States</u> - # orbitals / unit energy

$$D(E) \equiv \frac{dN}{dE} = \frac{L^3}{2\pi^2}\left(\frac{2m}{\hbar}\right)^{3/2}\sqrt{E} \quad \leftarrow \text{derive}$$

$$= \frac{3N}{2E}$$

$$\Rightarrow \sim \frac{N}{E}$$

<u>HEAT CAPACITY</u>

classical : $U = \frac{3}{2} K_B T$

$$\& \ C = \frac{dU}{dT} = \frac{3}{2} K_B$$

N atoms (Ne^-) $\Rightarrow \frac{3}{2} N K_B = C_{TOTAL}$

@ $T = 0K \rightarrow C = 0$

as $T\uparrow$: only e^- around E_F

are thermally excited

E_F ———— $\updownarrow K_B T$

Total thermal KE

$$U = N\underbrace{\left(\frac{T}{T_F}\right)} k_B T$$

$$C = \frac{dU}{dT} = 2Nk_B\frac{T}{T_F}$$

Refined (quantitative) answer:

small T $(k_B T << E_F)$

$$\Delta U = U(T) - U(0)$$

for Ne^-:

$$\Delta U = \int_0^\infty E\underbrace{(D(E))}_{\substack{\#\text{ orb.}/\#e^- \\ \text{unit Energy}}}\overbrace{f(E)}^{\substack{\text{prob. that} \\ e^- @ E}}dE - \int_0^{E_F} E(D(E))\,dE$$

$$D(E) \equiv \frac{dN}{dE}$$

N = total # of orbitals w/ $E < E_F$ (inside sphere)

$$N = \int_0^{E_F} D(E)\,dE = \int_0^\infty D(E)\underbrace{f(E)}\,dE$$

$$NE_F = \int_0^\infty E_F D(E) f(E)\,dE$$

$$= \int_0^{E_F} E_F D(E) f(E)\,dE + \underbrace{\int_{E_F}^\infty E_F D(E) f(E)\,d}_{\int_0^{E_F} E_F (D(E))(1-f)\,dE}$$

$$= \int_0^{E_F} E_F D(E)\,dE$$

prob. in $E_F \to \infty$

= prob. not in $0 \to E_F$

$$\Delta U = \int_{E_F}^{\infty} (E-E_F) \overbrace{F(E) D(E) dE}^{\#e^- \text{ raised to orbitals in range } dE}$$

$$+ \int_0^{E_F} (E_F - E) \underbrace{[1 - F(E)] D(E) dE}_{\#e^- \text{ removed from orbital } E}$$

$$C_{el} \equiv \frac{dU}{dT}$$

$$F(E) = \frac{1}{\exp[(E-\mu)/k_B T] + 1}$$

$$C_{el} = \int_0^{\infty} (E-E_F) \frac{dF}{dt} D(E) dE$$

$$C_{el} = \underbrace{\frac{1}{2}\pi^2 N k_B}\frac{T}{T_F}$$

Electrical Conductivity + Ohms Law

$$\vec{p} = m\vec{v} = \hbar\vec{k}$$

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

$$\vec{F} = \frac{d\vec{p}}{dt} = m\frac{d\vec{v}}{dt} = \hbar\frac{d\vec{k}}{dt}$$

assume Fermi sphere w/ no collisions in const. $\vec{E}$ field

assume $B = 0$

$$\hbar\frac{d\vec{k}}{dt} = -eE \rightarrow \hbar d\vec{k} = -eE dt$$

$$\int_0^t \Rightarrow \hbar\underbrace{(\vec{k}(t) - \vec{k}(0))}_{\text{sphere displacement} \rightarrow \delta\vec{k}} = -e\vec{E}t$$

$$m\vec{v} = \hbar\vec{k}$$

$$\vec{v} = \frac{\hbar\vec{k}}{m} \Rightarrow \vec{v} = \frac{\hbar\,\delta\vec{k}}{m} = -\frac{e\vec{E}t}{m}$$

const. $\vec{E}$ field w/ n e^-

$\Rightarrow$ current density $\vec{J} = -ne\vec{v}$

$$= \frac{ne^2\tau}{m}\vec{E}$$

τ = mean collision free time

$\vec{J} = \sigma\vec{E}$: Ohm's Law

σ = conductivity

$$= \frac{ne^2\tau}{m}$$

$$\rho = \frac{1}{\sigma}$$

Motion in magnetic fields

$$\vec{F} = \underbrace{\frac{d}{dt}(m\vec{v})}_{m\left(\frac{d\vec{v}}{dt} + \frac{\vec{v}}{\tau}\right)} = \frac{d}{dt}(\hbar\vec{k}) = -e(\vec{E} + \vec{v}\times\vec{B})$$

$$= \hbar \left[\frac{d\,\delta\vec{k}}{dt} + \frac{\delta\vec{k}}{\tau}\right]$$

$$m\left(\frac{d\vec{v}}{dt} + \frac{\vec{v}}{\tau}\right) = -e(\vec{E} + \vec{v}\times\vec{B})$$

suppose $\vec{B}$ is along z-axis

$$\vec{v}\times\vec{B} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ v_x & v_y & v_z \\ 0 & 0 & B \end{vmatrix} = \hat{x}(v_y B) - \hat{y}(v_x B) \cancel{+ \hat{z}(0)}$$

assume steady state, static $\vec{E}$

$$x: \quad m\left(\cancel{\frac{dv_x}{dt}} + \frac{v_x}{\tau}\right) = -e\left(E_x + v_y B\right)$$

$$m v_x = -e\tau\left(E_x + v_y B\right)$$

$$v_x = -\frac{e\tau}{m} E_x - \frac{e\tau B}{m} v_y$$

$$\omega_c = \frac{eB}{m}$$

↳ cyclotron freq.

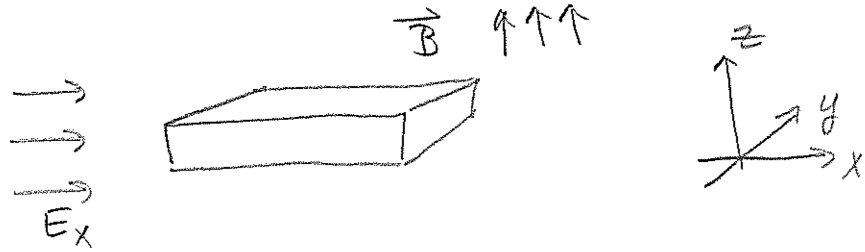
$$v_x = -\frac{e\tau}{m} E_x - \omega_c \tau v_y$$

$$v_y = -\frac{e\tau}{m} E_y + \omega_c \tau v_x$$

$$v_z = -\frac{e\tau}{m} E_z$$

HALL EFFECT

Hall field = E field across two faces of conductor in direction $\vec{J} \times \vec{B}$



$$\delta v_y = 0 \Rightarrow (v_y = 0)$$

$$\frac{e\tau E_y}{m} = \omega_c \tau v_x$$

$$v_x = -\frac{e\tau}{m} E_x$$

$$\frac{e\tau E_y}{m} = \omega_c \tau \left(\frac{-e\tau}{m}\right) E_x$$

$$E_y = -\omega_c \tau E_x$$

$$= -\frac{eB}{m}\tau E_x$$

Hall coeff $= R_H = \dfrac{E_y}{(J \times B)_y}$ ← y-comp.

$$J \times B = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ J_x & J_y & J_z \\ 0 & 0 & B \end{vmatrix}$$

$$= \hat{x}(J_y B) - \hat{y}\underline{(J_x B)} + \hat{z}(0)$$

$$R_H = \frac{E_y}{J_x B}$$

recall: $\vec{J} = \dfrac{ne^2\tau}{m} \vec{E}$

$$J_x = \frac{ne^2\tau}{m} E_x$$

$$E_y = -\frac{eB\tau}{m} E_x$$

$$R_H = \frac{-(eB\tau/m) E_x}{(ne^2\tau/m) E_x B} = \boxed{\frac{-1}{ne}}$$