

Solid State Notes Part 2

- What holds a crystal together \rightarrow exchange energy, Van der Waals force, covalent bonds
- [Principle types of crystalline bonding] \rightarrow
- a) neutral atom w/ closed electron shells; bound together by van der Waals force (fluctuation in charge)
 - b) ions Cl^- , Na^+ held together by attractive electrostatic forces between positive & negative ions
 - c) covalently neutral atoms are bound together by overlapping of charged distributions, ex; diamond

Cohesive energy: energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation, w/ same energy

\hookrightarrow Lattice energy: ion crystals, energy to separate its component ions into free ions at rest, infinite separation

Kinetic gas crystals are weakly bound, * carbon, Si, etc... intermediate, * are very strong

Consider 2 harmonic oscillators

$$H_0 = \frac{1}{2m_s} P_s^2 + \frac{1}{2} m \omega_s^2 X_s^2 + \frac{1}{2m} P_e^2 + \frac{1}{2} m \omega_e^2 X_e^2, \text{ kinetic energy + potential energy}$$

$\begin{matrix} X_e \\ \downarrow \\ +\text{elec} -\text{elec} \end{matrix} \quad R \quad \begin{matrix} +\text{elec} -\text{elec} \\ \downarrow \\ X_e \end{matrix}$

$$H_1 = \frac{\text{(attractive interaction energy)}}{\text{(between the nuclei)}} = \frac{\text{All (combos)}}{\text{of the nuclei}} = \frac{e^2}{R} + \frac{e^2}{R+X_e} - \frac{e^2}{R-X_e} + \frac{e^2}{R-X_e+X_e}$$

w/ $(X_1, X_2) \ll R$ we can expand $H_1 = -\frac{2e^2 X_1 X_2}{R^3}$

$$H = H_0 + H_1 = \frac{1}{2m_s} P_s^2 + \frac{1}{2} m \omega_s^2 X_s^2 + \frac{1}{2m} P_e^2 + \frac{1}{2} m \omega_e^2 X_e^2 - \frac{2e^2 X_1 X_2}{R^3}$$

(normal modes so freq can read off)

Transform to coordinates w/ form $= \frac{1}{2m} \vec{P}^2 + \frac{1}{2} \omega_{new}^2 \vec{X}^2 + \frac{1}{2m} \vec{P}_a^2 + \frac{1}{2} \omega_{new}^2 \vec{X}_a^2$

$$\hookrightarrow X_1 = \frac{1}{\sqrt{2}}(X_s + X_a), X_2 = \frac{1}{\sqrt{2}}(X_s - X_a), P_1 = \frac{1}{\sqrt{2}}(P_s + P_a), P_2 = \frac{1}{\sqrt{2}}(P_s - P_a)$$

$$H = \left[\frac{1}{2m} P_s^2 + \frac{1}{2} \left(m \omega_s^2 - \frac{2e^2}{R^3} \right) X_s^2 \right] + \left[\frac{1}{2m} P_a^2 + \frac{1}{2} \left(m \omega_a^2 + \frac{2e^2}{R^3} \right) X_a^2 \right]$$

$m \omega_{new}^2 = m \omega_a^2$

$$\omega_{\pm} = \sqrt{\frac{m \omega_s^2 \pm \frac{2e^2}{R^3}}{m}} = \sqrt{\omega_s^2 \pm \frac{2e^2}{m R^3}} = \omega_0 \left(1 \pm \frac{1}{2} \left(\frac{2e^2}{m \omega_s^2 R^3} \right) - \frac{1}{8} \left(\frac{2e^2}{m \omega_s^2 R^3} \right)^2 + \dots \right)$$

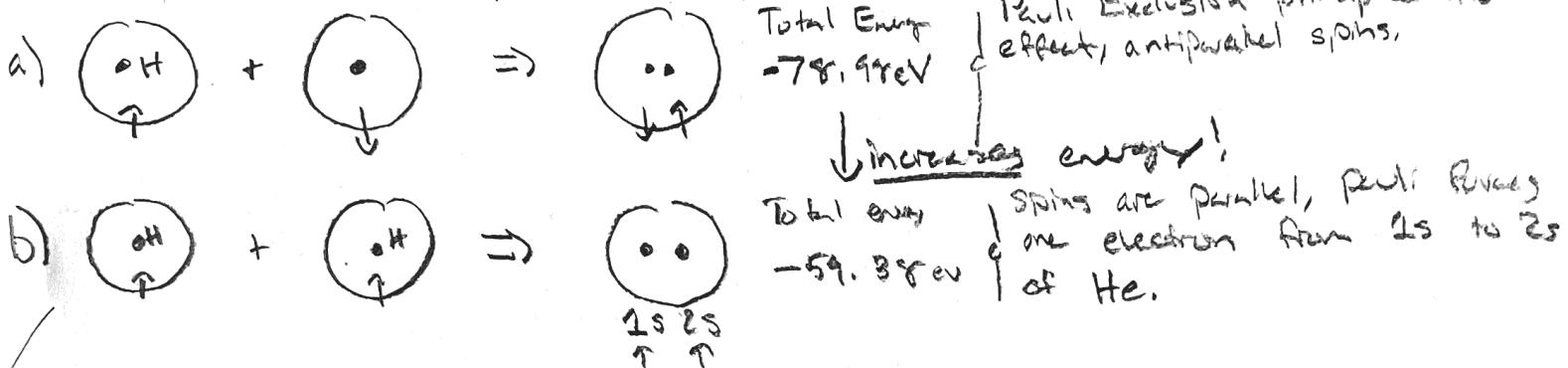
$$U = U_{coupled} + U_{uncoupled} = \frac{1}{2} k \omega_s + \frac{1}{2} k \omega_a = 2 \frac{1}{2} k \omega_0 - \frac{2k \omega_0}{2} \frac{1}{8} \left(\frac{2e^2}{m \omega_s^2 R^3} \right)^2$$

thus $U_{coupled} = -A/R$

Repulsive Interaction

- as two atoms are brought together their charge distributions overlap & repel each other. This increases electrostatic energy (remember it's ~~the whole configuration!~~)
- at sufficiently close separations, they overlap + is repulsive
- ↳ Pauli Exclusion Principle
- ↳ When charge distributions of two atoms overlap there is a tendency for e⁻ from atom B to occupy states of atom A & vice versa.

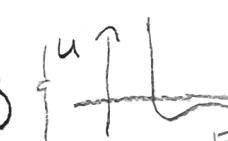
Pauli Exclusion Principle + Rooth



↳ So Pauli has increased repulsion by 19.6 eV

This repulsion is fitted well to a potential $\frac{B}{R^{12}}$

$$U(R) = 4E \left(\left(\frac{\sigma}{R}\right)^1 - \left(\frac{\sigma}{R}\right)^6 \right), \quad 4E\sigma = A, \quad 4E\sigma^2 = B$$



$\frac{\sigma}{R}$ repulsive
Pauli
(repels)
 $\frac{1}{R^6}$ attractive
dipole
(attracts)

Energy in lattice

Forces in a crystal: (force between $\bar{e} + \rho^+$)
 attractive
 Cohesive energy of a crystal = $\left[\begin{array}{l} \text{energy in} = + \\ \text{energy to remove an electron} \end{array} \right] + \left[\begin{array}{l} \text{energy out} = - \\ \text{energy of giving an electron} \end{array} \right] + \left[\begin{array}{l} \text{energy in} = + \\ \text{electro static energy} \end{array} \right] + \left[\begin{array}{l} \text{energy out} = - \\ \text{repulsive energy} \end{array} \right]$

Vander Waals \rightarrow fluctuations in electrons, cause induced dipoles
 (if considered as $\frac{R}{\text{dipole-dipole}}$) $\rightarrow U_{\text{VdW}} = -\frac{A}{R^6}$ [repulsive force due to Pauli exclusion] \rightarrow electrons have higher energies, thus adding energy

Net Potential: $U(R) = 4E \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$, $4E\sigma^6 = A$, $4E\sigma^{12} = B$ for $U_{\text{tot}} = \frac{A}{R^6} - \frac{B}{R^{12}}$
 --- experimentally obtained, $P = \text{range of interaction}$

Other forms $\rightarrow U(R) = \lambda e^{-R/p} = 4E \frac{\sigma^6}{R^6}$, $p = \text{range of interaction}$
 Neglecting Vander Waals $1/R^6$, finding main contributor to binding

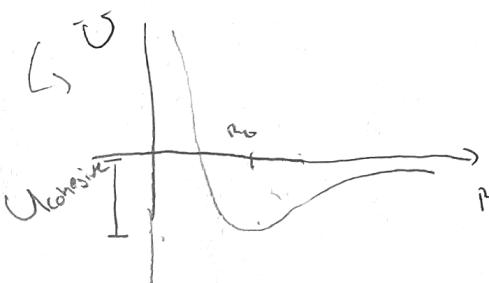
(energy of a crystal)
 Interaction between two atoms of charge $\rightarrow U_{ij} = \begin{cases} \lambda e^{-R/p} - \frac{q^2}{R} & (\text{nearest neighbors}) \\ \pm \frac{q^2}{p_j R} & \text{otherwise} \end{cases}$ $\xrightarrow{\text{be overlap in charge, have Pauli exclusion}}$

Total energy $\rightarrow U_{\text{tot}} = N \left(\sum_{\text{neighbors}} \lambda e^{-R/p} - \frac{\alpha q^2}{R} \right)$, where $\alpha = \sum \frac{1}{p_j} \equiv \text{Molding constant}$
 long range coulomb energy

Since α is summing over long range coulomb interaction make sure you choose sign right w.r.t reference atom, attraction = +, repulsion = -

w/ this:

$$U_{\text{cohesive}} = \frac{-q^2}{4\pi\epsilon_0 r} + \lambda e^{-r/p} + E_{\text{vibr}} - E_{\text{affin}} \quad (\text{for molecule})$$



For a crystal:
 Taking derivative of U_{tot} , $\frac{dU_{\text{tot}}}{dR} = 0 \rightarrow \text{find } R_0 = \text{equilibrium dist}$
 $\rightarrow U_{\text{tot}} = -N \frac{\alpha q^2}{R_0} \left(1 - \frac{R}{R_0} \right)$

\rightarrow lattice energy - energy that must be added to the crystal to separate its components ions into free ions infinitely far

cohesive energy = $\frac{[\text{lattice energy}] + [\text{neutral}]}{[\text{lattice energy}]}$

Long range interaction between ions

• $\pm \frac{q^2}{r}$ For ions like NaCl so $2N$ atoms

↳ Madelung Energy: main contribution to binding energy of atomic cores

U_{ij} = interaction energy between 2 atoms

$$U_i = \sum_{j \neq i} U_{ij} \text{ all interactions for the ion}$$

Guess: $U_{ij} = \underbrace{\lambda e^{-\frac{R_{ij}}{R}}}_{\substack{\text{charge} \\ \text{from } \frac{1}{R^2}}} \pm \underbrace{\frac{q^2}{R_{ij}}}_{\substack{\text{coulomb} \\ \text{potential}}}$

repulsive term, each ion
resists overlap w/ electric
distributions of neighboring
ions

2N atoms become NaCl
again c nearest neighbor
spread

$$U_{tot} = N U_i \quad \text{let } R_{ij} \in P_{ij} R$$

$$U_{ij} = \begin{cases} \lambda e^{-\frac{R_{ij}}{R}} - \frac{q^2}{R} & \rightarrow (\text{nearest : just count in unit of lattice constant}) \\ \pm \frac{1}{P_{ij}} \frac{q^2}{R} & \rightarrow \text{just coulomb otherwise, they care for enough} \end{cases}$$

$$U_{tot} = N U_i = N \left(z \lambda e^{-\frac{R_{ij}}{R}} - \frac{q^2}{R} \right)$$

$$\alpha = \sum_j \frac{\pm}{P_{ij}} = \text{Madelung constant}$$

$$\frac{dU_{tot}}{dR} = N \frac{dU_i}{dR} = -Nz\lambda \frac{e^{-\frac{R_{ij}}{R}}}{R} + \frac{Nq^2}{R^2}$$

$$\hookrightarrow R_0^2 e^{-\frac{R_0}{R}} = \frac{P_{ij} q^2}{2z}$$

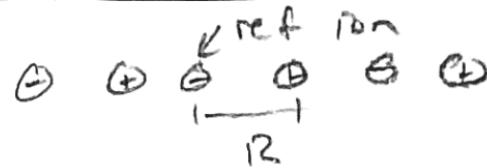
$$U_{tot} = -\frac{Nq^2}{R_0} \left(1 - \frac{R}{R_0} \right)$$

madelung energy

c total energy
in terms
of R_0

$\approx 0.1 R_0$
repulsive
interaction \rightarrow
very short
range

Evaluation of Madelung



$$\frac{\alpha}{R} = \sum \frac{(\pm)}{r_j}, \quad r_j = \text{distance of } j^{\text{th}} \text{ ion from reference ion}$$

For that we'll if

$$\frac{\alpha}{R} = \sum_{j=1}^{\infty} \left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \dots \right] \rightarrow \alpha = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]$$

(as its
symmetric)

$$\hookrightarrow \alpha = 2 \ln(2) \quad \text{bec } \ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

Getting Lattice Constant

$$U_{tot} = \frac{1}{2} N^2 4\epsilon \left(\sum_{j \neq i} \left(\frac{\sigma}{r_{ij} R} \right)^{12} - \sum_{j \neq i} \left(\frac{\sigma}{r_{ij} R} \right)^6 \right)$$

counting twice
 total No. of atoms
~~total atom pair count~~
~~count each pair twice~~
~~So want sum~~
~~of all pairs~~
~~Nearest neighbor count!~~

$r_{ij} R =$ distance between reference atom i and any other atom j

* Same logic of double counting in Griffiths 93

↳ so cont $r_{ij} + r_{ji}$

$$\hookrightarrow W = \frac{1}{2} \sum_{i=1}^N 4\epsilon \left(\sum_{j \neq i} \left(\frac{\sigma}{r_{ij} R} \right)^{12} - \left(\frac{\sigma}{r_{ij} R} \right)^6 \right)$$

→ $N?$

Now find eq. posns we $\frac{dU_{tot}}{dR} = 0 = -2N\epsilon \left[(12)(12,13) \frac{\sigma^{12}}{R^{13}} - (6)(14,15) \frac{\sigma^6}{R^7} \right]$

$$\hookrightarrow \frac{R_0}{\sigma} = 1.09 \quad \text{when} \quad \sum_j r_{ij}^{-12} = 12.13, \quad \sum_j r_{ij}^{-6} = 14.15$$

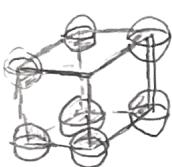
≈ right but there's quantum corrections that change it $30\% \xrightarrow{\text{between}}$ 10%

sum energy for all pairs of atoms in a crystal, R is nearest neighbor distance

Condensed notes

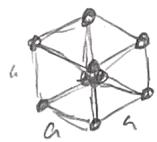
• lattice: how to repeat \rightarrow translational symmetry

↳ unit cell: repeating unit in a crystal



- 8 total atoms
- 1/8 in unit cell
- only 1 full atom per unit cell

BCC packing frac



expand radius's out
hit right from center
atom $d = a\sqrt{3}$
 $r = \frac{d}{4} = \frac{a\sqrt{3}}{4}$

$$\text{Packing fraction} = \frac{\frac{4}{3}\pi \left(\frac{a\sqrt{3}}{4}\right)^3}{a^3} \cdot \frac{\text{number of spheres in cell}}{\text{unit cell vol}}$$

$$\text{PF} = \frac{\frac{4}{3}\pi \left(\frac{a\sqrt{3}}{4}\right)^3}{a^3} \cdot \frac{1}{2} = \frac{\pi\sqrt{3}}{8}$$

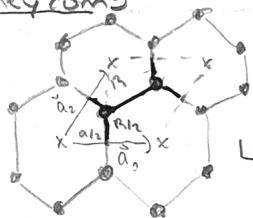
Note

$$\text{Volume of tetrahedron} = \frac{s^3}{6\sqrt{2}} = \frac{1}{8} A h$$

* do h.c.p packing frac
* do diamond packin

DEFINING LATTICE BASIS VECTORS

Honeycomb



$\vec{a}_1 = a\hat{x}$

$\vec{a}_2 = \frac{a}{2}\hat{x} + h\hat{y}$

$R = R + \frac{R}{2} = \frac{3}{2}R$

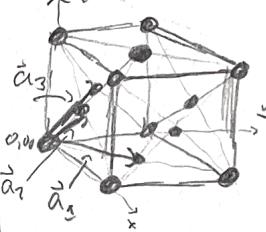
$[R \text{ in terms of } a] \Rightarrow R^2 = \frac{R^2}{4} + \frac{a^2}{4}$

$R = a\sqrt{3}$

SO! $\vec{a}_1 = a\hat{x}, \vec{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$

DEFINING LATTICE BASIS VECTORS

FCC



$\vec{a}_1 = \begin{bmatrix} a/2 \\ a/2 \\ 0 \end{bmatrix}$

$\vec{a}_2 = \begin{bmatrix} a/2 \\ 0 \\ a/2 \end{bmatrix}$

$\vec{a}_3 = \begin{bmatrix} 0 \\ a/2 \\ a/2 \end{bmatrix}$

The translation vector

$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$

* can get to every point w/ right n's

Diffraction

[given $\vec{T} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$] $\rightarrow n(\vec{r}) = n(\vec{r} + \vec{T})$ good for Fourier exp
and the electron number density]

$n(\vec{r}) = n_0 + \sum \epsilon_i e^{i\vec{G}_i \cdot \vec{r}} + S(\vec{r})$

↓ point in reciprocal space

$\vec{G} = \frac{2\pi}{a} \vec{G}_i \times \vec{G}_j \times \vec{G}_k$

* find set of vectors such that $n(\vec{r})$ is invariant

$n(\vec{r}) = n(\vec{r} + \vec{T}) \rightarrow \vec{e}^{i\vec{G} \cdot \vec{T}} = 1$

$\vec{G} = \frac{2\pi}{a} \vec{a}_1 \times \vec{a}_2 \times \vec{a}_3$

$b_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}, b_2 = 2\pi \frac{\vec{a}_1 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}, b_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$

In 3D we now have $\rightarrow n(\vec{r}) = \sum n_0 \epsilon^{i\vec{G} \cdot \vec{r}}, n_0 = \frac{1}{V} \int dV n(\vec{r}) e^{i\vec{G} \cdot \vec{r}}$

(because of this $\rightarrow n(\vec{r}) = n(\vec{r} + \vec{T}) \rightarrow \vec{e}^{i\vec{G} \cdot \vec{T}} = 1$)

$\rightarrow \vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3, \vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}, \vec{b}_2 = 2\pi \frac{\vec{a}_1 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}, \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$

$\rightarrow n(\vec{r} + \vec{T}) = \sum n_0 \epsilon^{i\vec{G} \cdot \vec{r}} e^{i\vec{G} \cdot \vec{T}} = \sum n_0 \epsilon^{i\vec{G} \cdot \vec{r}} = n(\vec{r})$, use $e^{i2\pi n} = 1$

Scattering Amplitude \rightarrow define $\Delta \vec{k} = \vec{k}' - \vec{k} = \text{out} - \text{in}$

Scattering amplitude $\rightarrow F = \sum \int dV n_0 \epsilon^{i(\vec{G} - \Delta \vec{k}) \cdot \vec{r}}$

If $\vec{G} = \Delta \vec{k}$ then there is diffraction, TF

$|k| = |k'|$

$\Delta \vec{k} = \vec{G} \rightarrow \vec{k} + \vec{G} = \vec{k}' \rightarrow (\vec{k} + \vec{G})^2 = \vec{k}'^2$

\rightarrow Diffraction Cond.

$$2\vec{k} \cdot \vec{G} + \vec{G}^2 = 0$$

Brillouin Zone: primitive cell in reciprocal space constructed like Wigner-Seitz cell in real space

Definitions

$$F = \int n(\vec{r}) e^{i\Delta \vec{k} \cdot \vec{r}} dV \rightarrow S_G = \int_{\text{cell}} dV n(\vec{r}) e^{i(\vec{G} \cdot \vec{r})} \quad \left(\begin{array}{l} \text{if non-zero then} \\ \text{there will be diffraction} \end{array} \right)$$

$$S_G = \sum_j \int_{\text{atom}} dV n_j(\vec{r} - \vec{r}_j) e^{-i(\vec{G} \cdot \vec{r})}, \quad f_j = \int dV n_j(\vec{r}) e^{-i(\vec{G} \cdot \vec{r})}$$

↳ $S_G = \sum_j f_j e^{-i(\vec{G} \cdot \vec{r}_j)}$, $\vec{r}_j = x_j \vec{a}_1 + y_j \vec{a}_2 + z_j \vec{a}_3$ (for atom j)
 w/ $\vec{b}_i \cdot \vec{a}_j = 2\pi S_{ij}$ $\rightarrow \vec{G} \cdot \vec{r}_j = 2\pi (h x_j + k y_j + l z_j)$

Example: pick vectors = # of lattice points + forms basis

↳ have \vec{r}_j be in simple cartesian basis

2 atoms: $\vec{r}_1 = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$ and $\vec{r}_2 = a \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix}$, same atom so
 $S_G = f e^0 + f e^{-i(\vec{G} \cdot a \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix})} = f + f e^{-2\pi i (\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l)}$

↳ $S_G = f \left(1 + e^{-i\pi(h+k+l)} \right)$ $\rightarrow h+k+l = \text{odd} \rightarrow S_G = 0 \rightarrow \text{no diffraction}$
 $\rightarrow h+k+l = \text{even} \rightarrow S_G = 2f \rightarrow \text{diffraction}$

↳ let's also define for $\vec{G} = h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3$

Miller Indices: From this, $(h k l)$ represent primitive lattice vector

* family of lattice planes correspond to directions of reciprocal lattice vectors \vec{G}
 ↳ to which they are normal

↳ [Separation between planes is this] $\rightarrow [d = \frac{2\pi}{|\vec{G}|}]$

Selection Rules for Miller Indices

$$h = \frac{1}{x_1}, \quad k = \frac{1}{x_2}, \quad l = \frac{1}{x_3}$$

$$x_1 = 2, \quad x_2 = 2, \quad x_3 = 3$$

smallest number to make all integer values of h, k, l positive in reciprocal space

$$n = \frac{1}{2} \cdot 6$$

$$\begin{aligned} h &= \frac{1}{2} \cdot 6 \\ k &= \frac{1}{2} \cdot 6 \\ l &= \frac{1}{3} \cdot 6 \end{aligned} \quad \begin{array}{l} \text{Miller index} \\ (3, 3, 2) \end{array}$$

$$d_{(h k l)} = \frac{2\pi}{|\vec{G}|} = \sqrt{\frac{2\pi}{h^2 b_1^2 + k^2 b_2^2 + l^2 b_3^2}}$$

If orthogonal basis $|b_i| = \frac{2\pi}{L_i}$

Cumulative Review
Midterm #2
Solid State Physics

Thermal Conductivity:

$$j = -k \frac{\partial T}{\partial x}, \quad k = \frac{1}{3} C_v V l$$

High temp: C_v is constant, thermal conductivity \propto $\frac{1}{l}$
mean free path of phonon

metals:
 e^- & phonon
conductors
phonon only

Free Electron Theory:

[A free electron gas]

Free e^- approx: metallic ions only serve as source of collision
+ no effect on motion of e^- between collisions
valence e^- become conduction e^- +
travel freely throughout the crystal
ind e^- approx: $e^- e^-$ interactions are ignored
Relaxation Time approx: outcome of collision doesn't depend on momentum
at e^- at collision.

[Fermi Surfaces]

$$1D \quad k_F = \frac{N}{2} \cdot \frac{2\pi}{L} \rightarrow N = \frac{1}{\pi} k_F L$$

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

$$dE = \frac{\hbar^2 \pi^2}{2m} 2n dm, n = \frac{N}{L}$$

$$g(E) = \frac{dn}{dE} = \frac{m}{\hbar^2 \pi^2} \frac{1}{N}$$

$$2D \quad n = \frac{N}{V} = \frac{N}{L^2}$$

$$\frac{1}{4} \pi k_F^2 = \frac{N}{2} \left(\frac{\pi}{L}\right)^2 \rightarrow k_F^2 = \frac{2\pi^2 N}{V}$$

$$E_F = \frac{\hbar^2}{2m} k_F^2$$

$$dE = \frac{\hbar^2}{2m} 2\pi dm \rightarrow \frac{dn}{dE} = \frac{m}{\hbar^2 \pi^2}$$

$(\frac{1}{4} \pi k_F^2)$: area in 1-sphere, # of states

$(\frac{N}{2})$: 1 state $(\frac{\pi}{L})^2$: area in 1 state

$$3D \quad n = \frac{N}{V} = \frac{N}{L^3}$$

$$\frac{1}{8} \frac{4}{3} \pi k_F^3 = \frac{N}{2} \left(\frac{\pi}{L}\right)^3 \rightarrow k_F^3 = \frac{3\pi^2 N}{V}$$

$$E_F = \frac{\hbar^2}{2m} k_F^2 \rightarrow \text{use to get } N, E$$

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{2/3}, \quad N(E) = \frac{V}{3\pi^2} \left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

$$\text{tip! } \frac{N}{V} = \frac{\text{# atoms}}{\text{vol of unit cell}}$$

$$\left. \text{other equations: } E_F = k_B T_F, \quad V_F = \frac{\hbar k_F}{m}, \quad V_F = \frac{E_F}{2}, \quad N = \int_0^{\infty} D(E) f(E) dE, \quad C_V = \frac{1}{2} \pi^2 N k_B T_F \right] \leftarrow$$

[Electronic Specific Heat]

$$\Delta U = U(T) - U(0) = \int_0^{\infty} E D(E) f(E) dE - \int_0^{E_F} E D(E) f(E) dE = \left(S_0 + \int_{E_F}^{\infty} E f(E) D(E) dE\right) F_F$$

$\hookrightarrow \Delta U = \int_{E_F}^{\infty} (E - E_F) f(E) D(E) dE - \int_0^{E_F} (E - E_F) (1 - f(E)) D(E) dE$, do $\frac{dU_{el}}{dT} = C_V$

thermally excited states unfilled states below E_F electron phonon
(state after) - (state before) at low temp ($= \sqrt{T} + \beta T^3$)

[Drude Theory]

How electrons move in metals

$$\frac{dp}{dt} = F - \frac{e}{c} \vec{v} \rightarrow \vec{F} = -e \vec{v}$$

$$\rightarrow \text{In electric field} \rightarrow \frac{dp}{dt} = -e \vec{E} - \frac{e}{m} \vec{v} \rightarrow j = -en\vec{v}$$

$$\rightarrow \text{Assume steady state, } \frac{dv}{dt} = 0 \rightarrow m\vec{v} = -e \vec{E}$$

$$\rightarrow j = +\frac{e^2 n}{m} \vec{E} = \sigma \vec{E}, \quad \sigma = \frac{e^2 n}{m}$$

Ohms law: $I = \sigma A V$
(current density j)

Hall Effect: $\frac{dp}{dt} = -\frac{e}{c} \vec{v} - e(\vec{E} + \frac{B}{m} \vec{v} \times \vec{B})$, $\vec{B} = B\hat{z}$ → solve steady state so $\frac{dp}{dt} \approx 0$

$$\Omega_x = -\frac{B}{c} - eF_x + e\frac{p_y}{m} B \rightarrow \text{mult by } \frac{m}{m} \rightarrow \Omega_x = -j_x + \frac{eB}{m} \tau j_y$$

$$\Omega_y = -\frac{B}{c} - eE_y - e\frac{p_x}{m} B \rightarrow \Omega_y = -j_y - \frac{eB}{m} \tau j_x$$

$$R_H = -\frac{e}{m} \frac{1}{\Omega_x} = -\frac{1}{ne}$$

* For other Drude Theory problem IN HOMEWORK

fill a table sheet \rightarrow resistance and σ conductivity!

Periodic Potential

* Electrons are now in a potential well $U(\vec{r}) = U(\vec{r} + \vec{T})$

* Bloch Theorem: $\Psi_k(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_k(\vec{r})$, $u_k(\vec{r} + \vec{T}) = u_k(\vec{r})$

(Represent Ψ as superposition of plane waves solutions)

$$\Psi_i(r) = \sum C(k) e^{ik \cdot r}, \quad [Fourier Expans]$$

$$U(r) = \sum_G U_G e^{iG \cdot r}$$

Plug into Schrödinger eq: $\left(-\frac{\hbar^2}{2m} \nabla^2 + U(r)\right) \Psi = E \Psi \rightarrow$ bunch of math trick & lattice stuff
 [Central Equation] $\rightarrow \left(\frac{\hbar^2 k^2}{2m} - E\right) C_k + \sum_G C_{k+G} U_G = 0$ * Do HW on deriving & Bloch theorem

[Nearly free Electron model] assume the crystal potential is so weak that electron behaves like a free electron, only have to consider interaction between adjacent bands!
 Just following slides do HW #7, P3

$$(\epsilon_0(k) - E) C(k) + C(k-G) U_G = 0$$

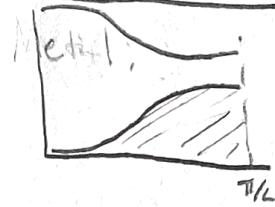
$$(\epsilon_0(k-G) - E) C(k-G) + U_G C(k) = 0 \rightarrow \begin{pmatrix} \epsilon_0(k) - E & U_G \\ U_G & \epsilon_0(k-G) - E \end{pmatrix} \begin{pmatrix} C(k) \\ C(k-G) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

* Do determinant & solve for E *

$$E = \frac{1}{2} (\epsilon_0(k) + \epsilon_0(k-G)) \pm \sqrt{\left(\frac{\epsilon_0(k) - \epsilon_0(k-G)}{2}\right)^2 + |U_G|^2}$$

$$\# \text{ of states } N = \frac{2\pi}{a} / \frac{2\pi}{L} = \frac{L}{a}, \quad L = \text{height between states}$$

Metals, Insulators, Semiconductors, Semi-Metals



insulator, because one full band, no free electrons in conduction band



metal, partially filled band, electrons are free to move



metal or semi-metal, if overlap is small it's a semi-metal

Alkali Metal

$$h = \frac{2}{a^3} = \frac{1c^3}{3\pi^2} / \Gamma N = 0.707 \frac{2\pi}{a}$$

Suppose a sphere, lies in 1st BZ
has free electron

Noble Metals

Still in first BZ, but gets close to free

Dirac metals

2e per primitive cell
lasts most completely filled
1st BZ, big gap

Trivalent 1st zone Alkal

Forms surface in 2nd, 3rd zone
deletes it

[EOM of Electron in Energy Band]

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

$$\vec{F} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon}{\partial k^2} \vec{F}, \quad m^* = \frac{\hbar^2}{\partial k^2}$$

$$\vec{F} = \hbar \frac{dk}{dt}$$

Period calculation, in magnetic field

$$\hbar \frac{dk}{dt} = eV\vec{B} \rightarrow dt = \frac{\hbar dk}{eV\vec{B}}$$

$$T = \oint \frac{\hbar}{eV\vec{B}} \frac{dk}{\sqrt{\epsilon(k)}} \rightarrow V(k) = \frac{\partial \epsilon}{\partial k}$$

insulators, metals, semiconductors, semi-metals

of k-states in a single Brillouin zone] [If each unit cell has exactly 1 free e^-
 is equal to # of unit cells in entire sys.] [that would be exactly enough e^- to fill
 the band if there were only 1 spin state,

↳ [But there's two spin states
 of the e^- , then band is $\frac{1}{2}$ full]

Proof for square lattice: let system be N_x by N_y unit cells,
 with periodic boundary cond. the value of k_x is quantized in
 units of $2\pi/L_x = \frac{2\pi}{N_x \cdot a}$ & for y $2\pi/L_y = 2\pi/(N_y a)$

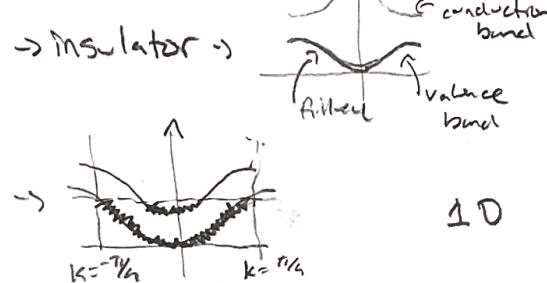
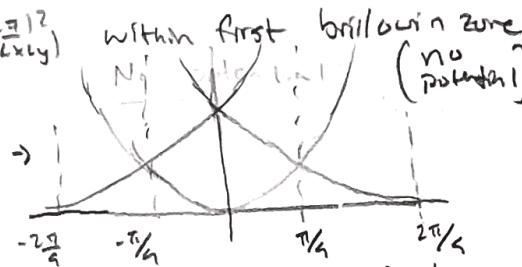
$$\text{Proof onto } N_x = \frac{2\pi/a}{2\pi/L_x}, N_y = \frac{2\pi/a}{2\pi/L_y} / \text{total size of brillouin zone} = \left(\frac{2\pi/a}{L_x}\right)^2 \rightarrow N_x N_y = \frac{\left(\frac{2\pi/a}{L_x}\right)^2}{\left(\frac{2\pi/a}{L_x} \times \frac{2\pi/a}{L_y}\right)} = \text{is exactly # of unit cells in whole system}$$

↳ thus # of k-states (of area $\frac{2\pi}{L_x L_y}$)

Recall from the central
 equation there were gaps
 in energy bands

If there are 2 e^- per
 unit cell, then we precisely
 have enough e^- to fill band

↳ could be metallic if
 you have overlap bands



thick region shows half-filled band.
 If band gap < 4eV
 ↳ Semiconductor

Now in multiple dimensions?

Consider a square lattice
 each w/ 1 free electron

↳ mathematically $\rightarrow k_F = \frac{1}{a} (2\pi N)^{1/3} = \frac{\sqrt[3]{2\pi}}{a} \cdot \frac{2\pi}{a^2} \frac{1}{\sqrt[3]{\pi}}$

In absence of or
 periodic potential \rightarrow just a circle

Brillouin zone
 is a square

Exactly enough
 e^- to fill half
 of Brillouin zone

$$\frac{2\pi}{a} \left(\frac{2\pi}{a} \right)^2 \frac{1}{\sqrt[3]{\pi}} \leftarrow \begin{array}{l} \text{length} \\ \text{(is the radius)} \end{array} \leftarrow \begin{array}{l} \text{height} \\ \text{(needed to} \\ \text{half fill circle)} \end{array}$$



further away
 zone boundary
 close to
 zone boundary

Add a periodic potential \rightarrow gaps open up at the
 zone boundaries

States have to go somewhere
 states close to zone boundary get moved down
 in energy
 closer to zone boundary, more they get moved

↳ As a result: states close to the boundary get filled up, preferentially at expense of
 states further away

took those states, & put them

here, since states near
 zone boundary get filled
 up more!



Free Electron Model

- A free electron gas; valence electrons become conduction electrons & travel freely throughout the crystal \rightarrow ~~feel no~~
- \hookrightarrow Jellly model: positive charges are uniformly distributed throughout the crystal
- * satisfy Pauli exclusion

Free electron theory

* free electron apprx: metallic ions only serve as a source of collisions and has no effect on the motion of an electron between collision

* independent electron apprx: e^-e^- interactions are ignored

* relaxation time apprx: outcome of a collision doesn't depend on momentum of electrons at the moment of collision

Free Electron Gas: 3D Schrödinger eq $\rightarrow \frac{-\hbar^2}{2m} \nabla^2 \psi = E \psi \rightarrow$ use separation of variables to get soln in X, Y, Z

let $k_x = \frac{1}{\lambda} \sqrt{2mE_x}$, $k_y = \sqrt{\frac{2mE_y}{\lambda}}$, $k_z = \sqrt{\frac{2mE_z}{\lambda}}$ \rightarrow get general soln, apply B.C.

$$\left. \begin{array}{l} k_x l_x = n_x \pi \\ k_y l_y = n_y \pi \\ k_z l_z = n_z \pi \end{array} \right\} \psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi x}{l_x}\right) \sin\left(\frac{n_y \pi y}{l_y}\right) \sin\left(\frac{n_z \pi z}{l_z}\right)$$

$$\vec{k} = \begin{bmatrix} k_x \\ k_y \\ k_z \end{bmatrix} = \begin{bmatrix} n_x \pi / l_x \\ n_y \pi / l_y \\ n_z \pi / l_z \end{bmatrix}$$

Ans!

$$E = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right), \text{ let: } |\vec{k}|^2 = \frac{n_x^2 \pi^2}{l_x^2} + \frac{n_y^2 \pi^2}{l_y^2} + \frac{n_z^2 \pi^2}{l_z^2}$$

$$E = \frac{\hbar^2 k^2}{2m} \rightarrow \text{Volume in k-space} = k_x \cdot k_y \cdot k_z = \frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V} \text{ Volume}$$

Each $\{\psi\}$ corresponds to a state ψ and occupies a volume $\frac{\pi^3}{V}$ in k-space.

$$\left(\frac{N \cdot d}{V} \right) \cdot \frac{\pi^3}{V} = \left(\frac{\# \text{ of pairs}}{\# \text{ of electrons}} \right) \cdot \left(\frac{\text{Volume each}}{\text{k-space}} \right) = \left(\frac{\text{Total volume held}}{\text{in k-space}} \right) = \frac{1}{8} \left(\frac{4}{3} \pi^3 k_F^3 \right)$$

$$\text{And } E_F = \frac{\hbar^2 k_F^2}{2m} \rightarrow k_F = \left(\frac{3\pi^2 N d}{V} \right)^{1/3}, \text{ just call } N d = \# \text{ of } e^- = N$$

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \rightarrow N(E) = \frac{V}{3\pi^2} \left(\frac{2mE}{\hbar^2} \right)^{3/2} \rightarrow \frac{dN}{dE} = D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

$$E_F = k_B T_F^{\text{Fermi temp}}, \quad \frac{1}{2} m V_F^2 = \frac{\hbar^2 k_F^2}{2m} \rightarrow V_F = \frac{\hbar k_F}{m} \quad \left| \begin{array}{l} \text{at zero km} \\ N = \int_0^{E_F} D(E) dE \end{array} \right.$$

for finite temp:

$$N = \int_0^\infty D(E) f(E) dE$$

fermi dirac distribution

Heat capacity of electron gas

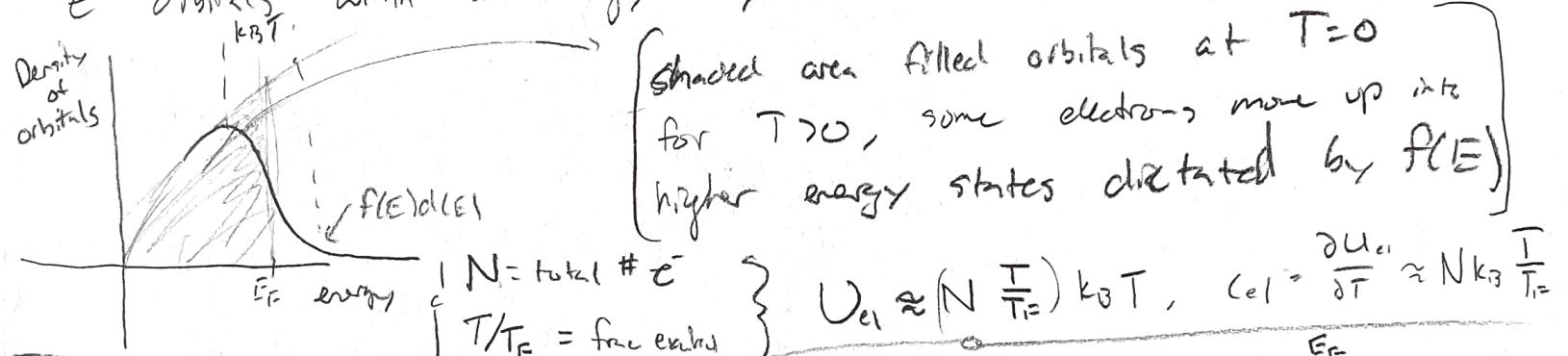
classically statistical mech predicts $C_V = \frac{3}{2} N k_B$ → $E = \frac{3}{2} k_B T$ → $C_V = \frac{\partial E}{\partial T}$ at constant V

↳ Total $C_V = \frac{3}{2} N k_B$ → observed value at room temp is < 0.01 of this value

How can e^- participate in electrical conduction processes → as if they were mobile → But not contributing to the heat capacity.

Answer: Pauli Exclusion principle.

* when heating a specimen from abs 0, not every e^- gets $\approx k_B T$, but only e^- orbitals within an energy range $k_B T$ of the Fermi level are excited.



Quantitative Expression for C_V increase intotal energy from 0+T

Value of $f(E) \ll E_F \rightarrow \Delta U = U(T) - U(0) = \int_0^\infty E D(E) f(E) dE - \int_0^\infty E D(E) dE$

where $f(E, T, \mu) = 1 / \exp((E - \mu) / k_B T + 1)$, note $E_F N = \int_0^\infty E_F f(E) D(E) dE = \int_0^{E_F} E_F D(E) dE$

↳ $(\int_0^{E_F} + \int_{E_F}^\infty) D(E) f(E) D(E) = \int_0^{E_F} E_F D(E) dE$

↳ $\Delta U = \int_{E_F}^\infty (E - E_F) f(E) D(E) dE + \int_0^{E_F} (E_F - E) (1 - f(E)) D(E) dE$

thermally excited states above E_F ↳ Unfilled states below E_F

$C_{el} = \frac{dU_{el}}{dT} = \int_0^\infty (E - E_F) D(E) \frac{df(E, T)}{dT} dE$, non- T term don't go away, f is only temp dep

$$T = k_B T \rightarrow \frac{df}{dT} = \frac{E - E_F}{T^2} \cdot \frac{C}{(e^{(E-E_F)/T} + 1)^2}, \text{ let } X = (E - E_F)/T$$

$$C_{el} = D(E_F) \int_0^\infty (E - E_F) \frac{df}{dT} dE, \quad \hookrightarrow C_{el} = k_B^2 T D(E_F) \int_{E_F/2}^\infty dx \frac{x^2 e^x}{(e^{x+1})^2} \text{ set } x = -\infty \text{ integral } = \pi^2/3$$

Kittel page 143, good approx. $\rightarrow = E_F$

$$\hookrightarrow C_{el} = \frac{1}{3} \pi^2 D(E_F) k_B^2 T = \frac{1}{2} \pi^2 N k_B \frac{T}{E_F} \quad \text{and } D(E_F) = \frac{3N}{2E_F}$$

Total Heat Capacity κ at low temp $\xrightarrow{\text{Debye temp and Fermi}} \propto$ Debye $\propto T^3$ at low temp

$$C_{\text{of metals}} = \text{electron contribution} + \text{phonon contribution} = \frac{\gamma T}{\text{electron part}} + \frac{AT^3}{\text{lattice pm}}$$

$$\frac{C}{T} = \gamma + AT^2 \quad \text{more for plotting or something}$$

[How electrons move in metals Drude Theory]

Assumptions: Electrons have scattering time, τ , probability $\frac{dt}{\tau}$ of scattering occurs assume $\vec{p} = 0$; electrons respond to external $\vec{E} + \vec{B}$

(on average true)

$$\vec{p}(t+dt) - \vec{p}(t) = -\frac{dt}{\tau} \vec{p}(t) + \vec{F}(t) dt + O(dt)^2$$

$$\frac{d\vec{p}}{dt} = -\frac{\vec{p}(t)}{\tau} + \vec{F}(t), \quad \vec{F} = -e(\vec{E} + \frac{\vec{p}}{m} \times \vec{B})$$

[Another way to look at it] $\langle \vec{p}(t+dt) \rangle = \left(1 - \frac{dt}{\tau}\right) \langle \vec{p}(t) + \vec{F} dt \rangle + O \frac{dt}{\tau}$

Probability it doesn't scatter $\left\{ \begin{array}{l} \text{if it doesn't scatter it follows EOM} \\ \text{if it scatters it follows EOM} \end{array} \right.$

$I = \frac{dp}{dt}$

$\frac{d\vec{p}}{dt} = \vec{F} - \frac{\vec{p}}{\tau}$

like a drag force

In Electric Field: $\frac{d\vec{p}}{dt} = -e\vec{E} - \frac{\vec{p}}{\tau}$

(Steady state) $\rightarrow m\vec{v} = -e\tau\vec{E}$

current density, $\vec{j} = -e n \vec{v}$, n = electron density, e = charge density

length $\vec{k} = \vec{v}/\tau$, here $\vec{k} = \vec{j}$ and $\theta = -en$

$\rightarrow \vec{j} = \frac{e^2 \tau n}{m} \vec{E} \rightarrow \sigma = \text{conductivity} = \frac{e^2 \tau n}{m}$ (drude conductivity)

Ohms law is $\vec{j} = \sigma \vec{E}$

(Ex) conductive properties of thin film, sheet resistance R_s

mean free path = thickness of sheet, $R_s = \rho/d$

(Calculate sheet resistance), assume e here $k_F = \text{surface!}$

$\sigma = \frac{e^2 \tau n}{m}, \quad k_F = (3\pi^2 n)^{1/3}, \quad \tau = \frac{1}{V_F}, \quad V_F = \frac{n k_F}{m}$

so: $\sigma = \frac{k_F^3}{3\pi^2} \frac{e^2}{m} \frac{1}{n k_F / m}$ and $R_s = \frac{2\pi}{2k_F^3 e^2} \frac{h}{e^2}$

$R_s = \frac{1}{\sigma d}$ $\rho = \text{resistivity} = \frac{1}{\sigma} *$

In magnetic Field

Drude Theory \rightarrow How electrons move in metals!

\hookrightarrow have scattering time τ , probability $\frac{dt}{\tau}$

\hookrightarrow since $\vec{p} = 0$ on average scattering

$$\frac{d\vec{p}}{dt} = \vec{F} - \frac{\vec{p}\omega}{\tau} \quad \text{equation of motion}$$

In Griffiths $\vec{E} = \sigma \vec{V}$
 \downarrow
 \downarrow
 \downarrow -en

$$\left[\begin{array}{l} \text{In Electric field} \\ \text{so } \frac{d\vec{p}}{dt} = -e\vec{E} - \frac{\vec{p}\omega}{\tau} \end{array} \right]$$

Assume
Steady state

$$\rightarrow m\vec{v} = -e\tau\vec{E}, \text{ current density } \vec{j} = e\vec{v}n \vec{v}$$

electron density

$$\hookrightarrow \left(\text{multiplied by } -en \right) \rightarrow \vec{j} = \frac{e^2 \tau n}{m} \vec{E} \quad \text{and Ohms law } \vec{j} = \frac{\sigma}{\text{conductivity}} \vec{E}$$

$$\sigma_{\text{conductivity}} = \frac{e^2 \tau n}{m}$$

ex sheet resistance $R_D = \rho/d$ ∞ thickness of sheet
 mean free path $= d$, \vec{E} on surface hance k_F

$$\hookrightarrow \rho = \frac{e^2 n}{m} \tau, \tau = \frac{d}{V_F}, V_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} (3\pi^2 n)^{1/3}$$

Solve for $\tau \rightarrow$ know $\sigma \rightarrow$ get $\rho \rightarrow$ arrive at R_D

Hall effect

$$\frac{d\vec{p}}{dt} = -\frac{\vec{p}}{\tau} - e(\vec{E} + \frac{\vec{p}}{m} \times \vec{B}) \rightarrow \vec{B} = B\hat{z} \rightarrow = -enV_x$$

Solve steady state

$$\left. \begin{array}{l} \sigma = -\frac{p_x}{\tau} - eE_x - \frac{eB}{m} p_y \\ \sigma = -\frac{p_y}{\tau} - eE_y + \frac{eB}{m} p_x \end{array} \right\} \text{mult by } \frac{neci}{m}$$

$$\hookrightarrow \sigma_0 E_x = \frac{eB}{m} \tau j_y + j_x \quad * \text{ if } j_y = 0 * \quad \rightarrow j_x = \sigma_0 E_x \quad (\text{Ohms law})$$

$$\sigma_0 E_y = -\frac{eB}{m} \tau j_x + j_y \quad \hookrightarrow E_y = -\frac{eB}{m} \frac{\tau}{\sigma_0} j_x = -\frac{B}{ne} j_x$$

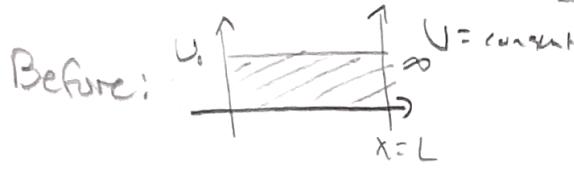
$$\hookrightarrow \text{define } R_H = \frac{E_y}{j_x B} = -\frac{1}{ne} \quad \left. \begin{array}{l} \text{nice but not completely true result} \\ \text{periodic potential for better desc.} \end{array} \right\} !$$

* redo HW 6

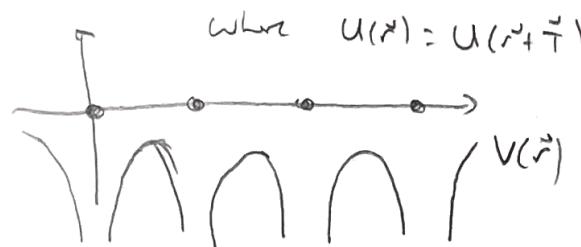
for complete \rightarrow other prob

understanding x

Electrons in a periodic Potential



Real lattice
(Periodic Potential)



[More Bloch]
Theorem

$$U_k(\vec{r}) = \sum_{\vec{G}} \hat{U}_{\vec{G}, \vec{k}} e^{i \vec{G} \cdot \vec{r}}$$

T same as

↳ Thus $\Phi_k(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}, \vec{k}} e^{i (\vec{G} + \vec{k}) \cdot \vec{r}}$

Moreover: $\Phi_k(\vec{r}) = e^{i \vec{k} \cdot \vec{r}} U_k(\vec{r})$, $U_k(\vec{r} + \vec{T}) = U_k(\vec{r})$

$$\Phi_k(\vec{r} + \vec{T}) = e^{i \vec{k} \cdot (\vec{r} + \vec{T})} U_k(\vec{r} + \vec{T}) = e^{i \vec{k} \cdot \vec{T}} \Phi_k(\vec{r})$$

By symmetry $e^{i \vec{k} \cdot \vec{T}} = 1 \rightarrow \vec{k} \cdot \vec{T} = 2\pi m$

This theorem tells us that even though the potential that the electron feels from each atom is extremely strong, still behaves almost as if they don't see the atoms at all. Still almost plane wave eigenstate

↳ [Refresher from before "free electron model of metals"]

[Free Electron Model of Metals]

↳ * metallic ions only serve as a source of collisions & no effect on motion of an electron between

→ thermal conductivity

→ Drude theory tells us how electrons move in metals $\rightarrow \frac{d\vec{p}}{dt} = \vec{F} - \frac{\vec{p}}{\tau}$

→ [specific heat] $\rightarrow C_V = \frac{1}{2} \tau^2 N k_B \frac{T}{\pi^2} \frac{V}{\text{cell}}$, $C_{\text{dusty}} = A T^3$
(for phonon at low T)

Note! Need band theory to describe insulators, semiconductors, metals,

↳ Have to consider bound electrons instead of as electrons just moving freely (where free space wave comes from) in metal

[Fourier Expansion Recap] Periodicity leads itself well to Fourier expansion & some inter For a general function $n(x) = n_0 + \sum_{\vec{G}} A \cos\left(\frac{2\pi m}{a} x\right) + B \sin\left(\frac{2\pi m}{a} x\right)$, $\frac{2\pi m}{a}$ = point on reciprocal lattice

[Using Euler formula &
generalizing to 3D]

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} e^{i \vec{G} \cdot \vec{r}}, \quad n_{\vec{G}} = \frac{1}{V} \int_{\text{cell}} dV n(\vec{r}) e^{-i \vec{G} \cdot \vec{r}}$$

For our particle in Periodic Potential, we represent its ψ as superposition of plane waves

think as basic quantum, solution is superposition of all waves.

$$\Psi(\vec{r}) = \sum_{k=1}^L c_k e^{ik\vec{k}\cdot\vec{r}}, \quad k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}$$

$\rightarrow \Psi(x_1, 0) = \sum_{n=1}^L c_n \psi_{n,k=0}$ & here n is L different states

Expand potential Energy: $U(\vec{r}) = \sum_G U_G e^{iG\cdot\vec{r}}$, $U_G = \frac{1}{\text{volume}} \int e^{-iG\cdot\vec{r}} U(\vec{r}) d\vec{r}$

Schrodinger Equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \right) \Psi_k(\vec{r}) = E \Psi_k(\vec{r}), \quad \text{now substitute!}$$

only radial dependence. tells why the

$$\frac{\hbar^2}{2m} \sum_k k^2 c_k e^{ik\vec{k}\cdot\vec{r}} + \sum_k \sum_G U_G c_k e^{i(k+G)\cdot\vec{r}} = E \sum_k c_k e^{ik\vec{k}\cdot\vec{r}}$$

(Tricky to simplify)
(the equation) $\rightarrow \int_0^L e^{-ik\vec{k}\cdot\vec{r}} e^{i(k+G)\cdot\vec{r}} dr = L S_{k, k'}$, k, k' are diff. wave vectors

* otherwise you get an integral over the period or some sides & comes = 0,
↳ so $k' = k$ is only way to get non-zero, integrate both sides by $e^{ik\vec{k}\cdot\vec{r}}$
w/ $k' = k$ otherwise its 0.

$$\int \left[\sum_k \frac{\hbar^2 k^2}{2m} c_k e^{ik\vec{k}\cdot\vec{r}} e^{-ik\vec{k}\cdot\vec{r}} + \sum_k \sum_G c_k U_G e^{i(k+G)\cdot\vec{r}} e^{-ik\vec{k}\cdot\vec{r}} - E \sum_k c_k e^{ik\vec{k}\cdot\vec{r}} e^{-ik\vec{k}\cdot\vec{r}} \right] dr = 0$$

w/ $k = k'$

$$\int \left[\sum_k \frac{\hbar^2 k^2}{2m} c_k + \sum_k \sum_G c_k U_G e^{iG\cdot\vec{r}} - E \sum_k c_k \right] dr = 0 \quad \begin{cases} k' = k - G \\ G = k - k' = 0 \end{cases}$$

otherwise diffraction const. otherwise 0, see dephasing part argument, for explanation in this case

$$\int \sum_k c_k \left(\frac{\hbar^2 k^2}{2m} - E \right) + \sum_{k'} \sum_G c_{k'} U_G e^{iG\cdot\vec{r}} dr = 0$$

(Drop sum + integral) since $k' = k$ we can choose which one is true as k or k'

$$\boxed{\left(\frac{\hbar^2 k^2}{2m} - E \right) c_k + \sum_G c_{k-G} U_G = 0}$$

central eq for
any periodic
potential w/
 $\Psi = \sum_k c_k e^{ik\vec{k}\cdot\vec{r}}$

Central Equation

$$\left(\frac{\hbar^2 k^2}{2m} - \varepsilon \right) c_k + \sum_G c_{k+G} U_G = 0$$

We only care about our original k point + k points shifted by $\pm G$ for 2D crystal

$$\psi_k = \sum_k c_k e^{ik \cdot r} \rightarrow \psi_{k'} = \sum_G c_{k-G} e^{i(k-G) \cdot r}$$

$k' = k - G$
 $k = k'$
 $e^{iG \cdot r} = 1$

↳ Define $u_k(r) = \sum_G c_{k-G} e^{-iG \cdot r} \rightarrow u_k(r+T) = \sum_G c_{k-G} e^{-iG(r+T)} = u_k e^{-ik \cdot T}$

↳ $\boxed{\psi_{k'} = e^{ik \cdot r} u_k}$ — restatement of block them

Application

• [wave function] $\rightarrow \psi_k(r+T) = e^{ik \cdot T} e^{ik \cdot r} u_k(r+T) = e^{ik \cdot T} \psi_k(r)$

translated
↳ Thus: $\boxed{\psi_k(r+T) = e^{ik \cdot T} \psi_k(r)}$ "free electron soln"

• If lattice potential is 0 $\rightarrow \frac{\hbar^2 k^2}{2m} - \varepsilon = 0 \rightarrow u_k = \text{constant} \rightarrow \psi_k = e^{ik \cdot r}$

• [Central Equation] $\rightarrow \left(\frac{\hbar^2 k^2}{2m} - \varepsilon \right) c_k + \sum_G c_{k+G} U_G = 0 \rightarrow \boxed{(E_0(k) - \varepsilon) c_k + \sum_G c_{k+G} U_G = 0}$

* note $U_G = U_{-G}$, represents

* a system of equations for 5 terms

$$\begin{bmatrix} E_0(k-2G) - \varepsilon & U_G & 0 & 0 & 0 \\ U_G & E_0(k-G) - \varepsilon & U_G & 0 & 0 \\ 0 & 0 & E_0(k) - \varepsilon & U_G & 0 \\ 0 & 0 & U_G & E_0(k+G) - \varepsilon & U_G \\ 0 & 0 & 0 & U_G & E_0(k+2G) - \varepsilon \end{bmatrix} \begin{bmatrix} c_{k-2G} \\ c_{k-G} \\ c_k \\ c_{k+G} \\ c_{k+2G} \end{bmatrix} = 0$$

Since C_k were the coefficients on our wave function, a solution to or eq for them gets us our general solution.
 $\hookrightarrow \Psi = \sum C_k e^{ik \cdot r}$ get C_k 's from central equation

$$[\text{Central Eq}] \rightarrow \left(\frac{k^2 \hbar^2}{2m} + \epsilon \right) C_k + \sum_G U_G C_{k+G} = 0$$

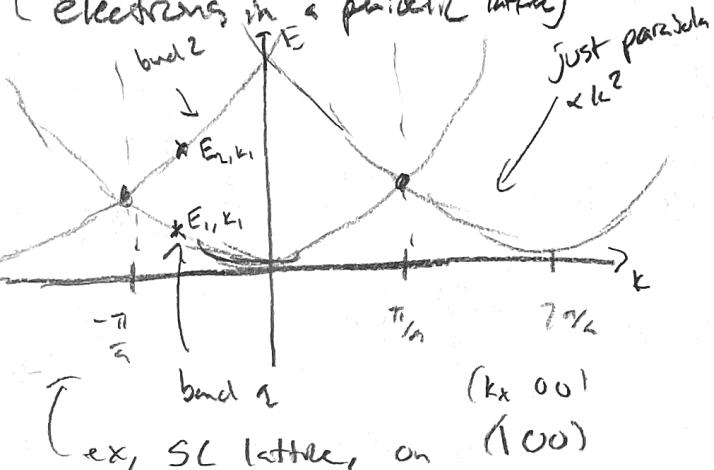
- Even though this is for all lattice vectors in the lattice
- We only need solutions in the first Brillouin zone

"Proof"

For the full infinite matrix, making k just separated by G , yields same info matrix

(Just showing the solution)

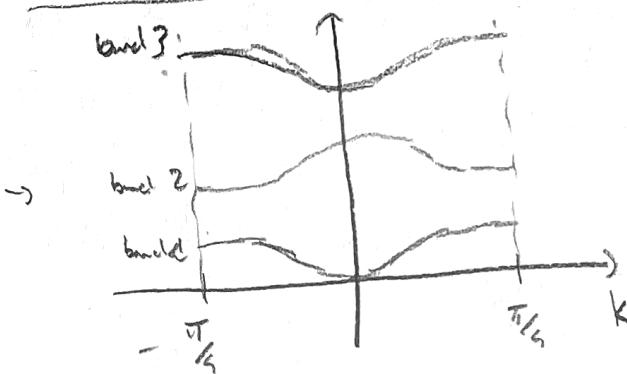
No potential, just free electrons in a periodic lattice



means that the eigenvalues & eigenvectors are periodic in G . $E_{k+G} = E_k$ (to be distinct need n , for diff engys bands)

\hookrightarrow choose k 's restricted to first Brillouin zone
 b/c we can just shift by G to get there!

Potential added: ϵ



Equation of Motion
of an electron
in an energy band

and effective mass m^*

looking at motion in an applied electric field

$$\nu_F = \frac{d\omega}{dk} \quad \text{and} \quad \omega = \frac{E}{k}$$

$$\hookrightarrow V = \frac{1}{\hbar} \frac{dE}{dk} \quad \text{or} \quad \vec{V} = \frac{1}{\hbar} \vec{\nabla}_k E(k)$$

Imagine applying a force to an electron, $\vec{F} = -e\vec{E}$, then equate work done on the electron to its change in energy.

\hookrightarrow start w/ electron in momentum state k , $\vec{p} = \hbar\vec{k}$

$$\hookrightarrow \text{group velocity: } \vec{V} = \frac{1}{\hbar} \vec{\nabla}_k E(k) \quad (\text{if } k \text{ is real})$$

$$\frac{dW}{dt} = \vec{F} \cdot \vec{V} = \frac{1}{\hbar} \vec{F} \cdot \vec{\nabla}_k E(k) \quad \text{and} \quad \frac{dE}{dt} = \frac{\hbar k^2}{2m} \rightarrow \frac{dE}{dt} = \frac{\hbar k}{m} \frac{dk}{dt}, \quad \frac{\partial E}{\partial k} = \frac{\hbar k}{m}$$

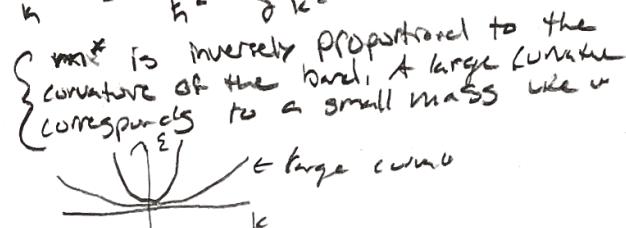
$$\hookrightarrow \text{so} \quad \frac{dE}{dt} = \frac{\partial E}{\partial k} \frac{dk}{dt} \Rightarrow \frac{dE}{dt} = \frac{dk}{dt} \cdot \vec{\nabla}_k E(k) \stackrel{\substack{\text{set equal to} \\ \frac{dW}{dt}}}{=} \frac{1}{\hbar} \vec{F} \cdot \vec{\nabla}_k E(k)$$

in a crystal, $\frac{dk}{dt}$ is equal to the external force on the e^-

$$\hookrightarrow \vec{F} = \hbar \frac{d\vec{k}}{dt} = \frac{d\vec{p}}{dt} \quad \text{get Newton's second law}$$

$$\hookrightarrow \vec{a} = \frac{d\vec{v}}{dt} = \frac{d\vec{v}}{dk} \frac{dk}{dt} = \frac{1}{\hbar} \frac{d\vec{v}}{dk} \frac{\vec{F}}{\hbar} = \frac{d}{dk} \left(\frac{1}{\hbar} \frac{\partial E}{\partial k} \right) \frac{\vec{F}}{\hbar} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \vec{F}$$

$$\text{Thus: effective mass is } \frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}} = m^*$$

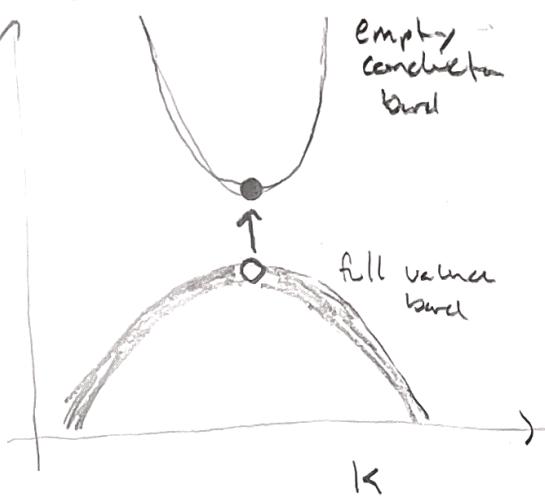


$$m_e^* = \frac{\hbar^2}{\frac{\partial^2 E_e}{\partial k^2}}, \quad M_{\text{hole}}^* = \frac{\hbar^2}{\frac{\partial^2 E_{\text{hole}}}{\partial k^2}}$$

$$M_{\text{hole}}^* = \frac{\hbar^2}{\frac{\partial^2 E_{\text{hole}}}{\partial k^2}}$$

Electrons and Holes

The idea: Start w/ insulator or semiconductor, excite one electron from the valence band to the empty conduction band.



↳ leaves absence of e^- behind (HOLE)
 ↳ since completely filled band is inert, it is convenient to keep only track of the HOLE in the valence band
 ↳ treat HOLE as individual empty particle
 * e^- can fall back into empty state (HOLE)
 & emit a photon (similar to annihilation)
 e^- = negative charge HOLE = positive charge

[Energy conversion of electrons + Holes]

$E(\text{absence of } e^- \text{ in state } k) = -E(\text{electron in state } k)$
 its weird to think ↳ think of it like pushing a balloon under water
 ↳ k as minimum energy but ↳ lowest energy config is w/ electron at lowest energy
 ↳ and hole at highest energy possible is lowest energy config

$$V_{\text{hole}} = \frac{\nabla_{k_{\text{hole}}} E_{\text{hole}}}{m}, \quad k_{\text{hole}} = -k_e$$

Crystal doesn't weigh anything if effective mass is smaller, important concept is that electron in periodic potential is accelerated relative to the lattice in an applied E or B field as if the mass of e^- were equal to an effective mass.

kittel pg 199 } for what effective mass means + sign
 220 pdf } in terms of momentum transfer