Jan/22/2008
(class: Jan/23)

Chapter 1

Crystal Structure and Interatomic Forces

→) Solid – composed of discrete basic units – atoms

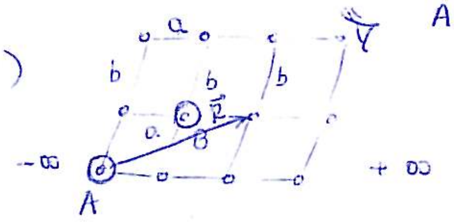
- atoms are arranged in order ⟶ crystal

- atoms appear to be randomly arranged ⟶ amorphous solid

→) Crystal structures
- dep. interatomic force
- experimental determination – x-rays (Ch. 2)
- properties

→) perfect crystal ⟶ atoms are arranged so that their positions are exactly periodic

(Fig 1.1)



in A, B, C equivalent

⇓

crystal is the same

⇓

crystal possesses

$\boxed{\text{translational symmetry}}$

crystal is $\boxed{\text{invariant under translation}}$ → $\vec{R}$

→) imperfections exist

- ∘) not (∞) → surface (atoms at) → see ≠ environment
- ∘) T ≠ 0 → vibrations → deformations
- ∘) impurities → foreign atoms

↓

imptt topic

↓

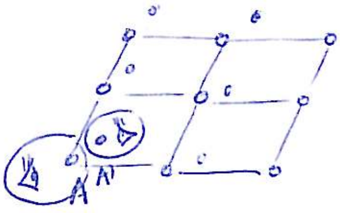
here start with an ideal perfect crystal

→) Definitions

∘) geometrical pattern, atoms – points } crystal lattice

∘) Bravais lattice → all points are equivalent
↳ atoms of the same kind

∘) non-Bravais lattice → some points are non-equivalent
(even if the atoms are of the same kind)

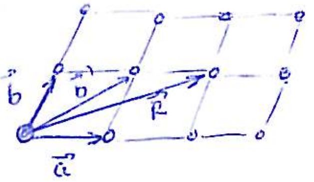


A and A' – non equivalent
2 interpenetrating Bravais lattice (2 or more)
AA' – basis

→) Basis vectors

•) origin

•) position of any lattice point determined by vector $\vec{R}_n$



$$\underset{\substack{\uparrow \\ \text{dep. on} \\ \text{basis vectors} \\ \text{chosen}}}{\vec{R}_n} = n_1\vec{a} + n_2\vec{b} \qquad (\text{lattice vectors})$$

$$\boxed{\vec{R} = 2\vec{a} + \vec{b}}$$

Bravais
•) lattice is invariant under translation given by $\vec{R}_n$

•) (n_1, n_2) pair of integers

•) $\vec{a}, \vec{b}$ non colinear

•) $\vec{a}, \vec{b}$ not unique, check $\vec{a}, \vec{b}'$ $\boxed{\vec{R} = 2\vec{a} + 2\vec{b}'}$

→) Unit cell

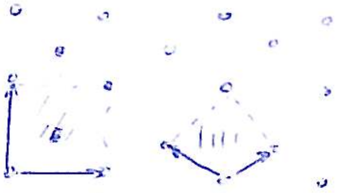
area of ▱ (parallelogram) whose sides are the basis vectors $\vec{a}, \vec{b}$

•) translate it → can cover the area of whole lattice

•) if area of unit cell is the smallest area to cover lattice → primitive cell

•) primitive cell vs. non primitive

(Fig 1.4)



•) all primitive cells have the same area $S = |\vec{a}\times\vec{b}| \overset{=}{\longleftrightarrow} S = |\vec{a}\times \overset{(\vec{a}+\vec{b})}{\overset{\uparrow}{\vec{b}'}}|$

→) Symmetry

∘) inversion center

cell has inversion center if there is point where $\vec{r} \to -\vec{r}$ ⇒ cell remains invariant

All Bravais

because $\vec{R}_n \to -\vec{R}_n$ ⇒ cell invariant

∘) reflection plane

plane in cell – mirror reflect ⇒ cell remains invariant

~~triclinic~~ (no)   monoclinic (yes)

∘) rotation axis

axis – rotate → cell remains invariant

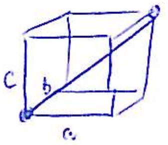
(2π)

→) Directions and Crystal Planes

to describe phenomena in crystals $\left\{ \begin{array}{l} \text{directions} \\ \text{plane} \end{array} \right.$

◦) crystal direction

$$\vec{R} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$



$$[1\ 1\ 1]$$

because of rotation^l symmetry – non// directions may be equivalent

$$[1\,0\,0]\ ,\ [0\ 1\ 0]\ ,\ [0, 0, 1] \quad [\bar{1}\,0\,0]\ [0\,\bar{1}\,0]\ [0\,0\,\bar{1}]$$

$$\langle 1\,0\,0 \rangle$$

◦) crystal plane   Kittel – $\left\{ \begin{array}{l} \text{Fig 13} \\ \text{Fig 14} \end{array} \right\}$ page 12

↓

Specified by

Miller indices

$$x, y, z \longrightarrow \underbrace{\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c} \right)}_{\text{fractional triplet}} \xrightarrow{\text{invert}} \left(\frac{a}{x}, \frac{b}{y}, \frac{c}{z} \right) \xrightarrow[\text{to smallest integers}]{\text{reduce}}$$

(multiply by common factor)

Fig. 13 Kittel $x = 3a$, $y = 2b$, $z = 2c$ $(3, 2, 2) \longrightarrow \left(\frac{1}{3}, \frac{1}{2}, \frac{1}{2} \right) \longrightarrow (2, 3, 3)$

Fig 1.11 $x = 2a$, $y = 1b$, $z = 1c$ $(2\ 1\ 1) \longrightarrow \left(\frac{1}{2}, 1, 1 \right) \longrightarrow (1, 2, 2)$

↓

◦) infinite set of equivalent planes all with the same Miller indices procedure for miller indices ⟶ ·) all equivalent planes — same indices

·) reciprocal lattice

Fig. 1.11 (b)   (120) planes

because of rotational symmetry — non// planes are equivalent

(100), (010), (001) ⟶ ~~@~~ {100}

($\bar{1}$00), (0$\bar{1}$0), (00$\bar{1}$)

·) spacing between planes ~~ex~~ of the same Miller indices

a

Fig 1.11 (d)

(h k l) $d_{hkl} = x\cos\alpha = y\cos\beta = z\cos\gamma \Rightarrow \cos\beta = \frac{x}{y}\cos\alpha \qquad \cos\gamma = \frac{x}{z}\cos\alpha$

$\swarrow$

$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$

$\cos^2\alpha + \frac{x^2}{y^2}\cos^2\alpha + \frac{x^2}{z^2}\cos^2\alpha = 1$

$$\cos^2\alpha = \frac{1}{1+\frac{x^2}{y^2}+\frac{x^2}{z^2}}$$

$$d_{hkl} = \frac{x}{\sqrt{1+\frac{x^2}{y^2}+\frac{x^2}{z^2}}} \qquad \boxed{d_{hkl} = 1\Big/\sqrt{\frac{1}{x^2}+\frac{1}{y^2}+\frac{1}{z^2}}}\,//$$

$$h = \frac{na}{x} \qquad k = \frac{nb}{y} \qquad l = \frac{nc}{z} \Rightarrow \boxed{d_{hkl} = \frac{n}{\sqrt{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}}}$$

SC and (111) planes

$\Downarrow$

$d = \frac{na}{\sqrt{3}}$

1-28 ①

Jan/28/2008

[redacted]

{ Diamond → insulator
{ pure silicon crystal ↗ but impurities (P) → semiconductor
(phosphorus)

www.play-hookey.com/semiconductors/basic_structure.html

http://enpub.fulton.asu.edu/widebandgap/NewPages/SCbasics.html

Amorphous Solids and Liquids

Ex.) window glass {
- silicon oxide
- no crystal structure
- Si, O – distributed at a what APPEARS to be random fashion

) liquid {
- no crystal structure
- atoms appear to have a random distribution

liquids similar to amorphous solids ← instantaneous pictures (look the same)
but fixed atoms, no drift
↓
called supercooled liquids

liquid state: average number of NN, NNN remains ~ the same ⇒ liquid has a structure
order restricted to few shells

↳ has short-range order and long-range is absent

↳ intratomic forces remain operative but ⊕ thermal kinetic energy

spherical
shell:

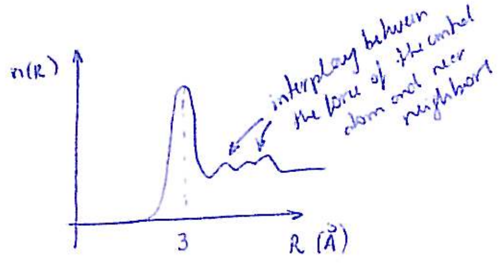
concentration

$$\Delta N(R) = n(R)\, 4\pi R^2 \Delta R$$

(liquid is isotropic)

number of atoms in this shell

structural properties contained here



result of attractive interatomic force

$R \lesssim 2.2\,\text{Å} \Rightarrow n(R)=0$ · atoms approach central one to strong repulsive forces

↓

~ diameter of the atom

R large : $n(R) \sim n_0$ — average concentration in the system

└ dist. is completely random, indep. of R

pair distribution function : $g(R) = \dfrac{n(R)}{n_0}$ — relative density

1-28-③

Interatomic Forces

Solids are stable structures

$\boxed{\text{crystal}}$ of NaCl more stable than $\boxed{\text{free}}$ Na and Cl atoms

↑ energy is lower than →

attractive interatomic force - holds the atom together

Energy of crystal is lower than that of free atoms

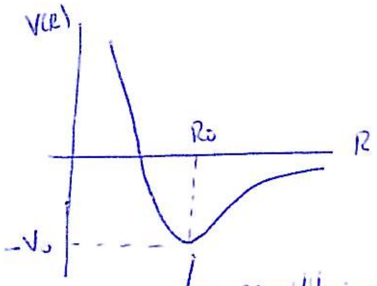
↓

amount = energy required to pull the crystal apart

↓

binding energy

potential energy representing interaction between atoms varies with R



↳ equilibrium position R_0

binding energy $-V_0$

$V_0 < 0 \Rightarrow$ stable, energy < than when they are apart at $R \to \infty$

$R_0 \sim$ Å → short-range force

decay of the |potential| is very fast, 10, 15 Å — force may be disregarded

gases ≅ free atoms

↑

distance is large

$$F(R) = -\frac{\partial V(R)}{\partial R} \quad \left\{ \begin{array}{l} R > R_0 :\ F(R) < 0 \text{ - attractive} \\ R < R_0 :\ F(R) > 0 \text{ - repulsive} \end{array} \right\} \text{ these forces cancel at } R = R_0$$

Types of Bonding

Attractive intratomic forces ⇒ bonding of atoms

these forces form bonds between atoms

⇓

stability of the crystal

→) ionic bond

Ex: NaCl
(sodium chloride)

Na loses single valence electron to Cl

⇓

ionic crystal

Na^+ surrounded by six Cl^- ions

⇓

attractive electrostatic Coulomb force

repulsive force

⇓

ions overlap - e^- repel: repulsive electrostatic Coulomb force

- Pauli exclusion principle (orbits of e^- overlap can't occupy orbit already occupied)

ionic bond is strong

binding energy ~ 5eV

⇓

high melting temperatures { NaCl ~ 801°C.
while Na ~97.8°C
metals: K ~ 63°C

eV energy gained by an electron in potential of 1V

$$1eV = 1.6 \times 10^{-19}\ C \left(\frac{J}{C}\right)$$

→) <u>covalent bond</u>

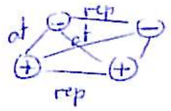
<u>Ex</u> diamond : C   all atoms are identical → no transfer of e^- between atoms

each atom has ④ valence e^- and forms ④ bonds with NN

bond: <u>composed of two</u> e^-, one from each atom

covalent bond   (each C now has 8 e^- ⇒ complete shell structure (p shell))

(think of H_2 molecule)



} by adjusting orbitals e^- can hold p together

covalent bond is strong

hard - diamond

high melting point >3000°C

few eV per bond
binding energy

Si, Ge, Sn

GaAs : both ionic and covalent bonds

→) <u>metallic bond</u>

metals - high electrical conductivity and mechanical strength
ductile (can be shaped)

<u>Ex</u> Na

Na has a single valence e^-

↳ can't be ionic
can't be covalent } bond → (why?)
→ equal
→ bind with many

Crystal formed : valence e^- detaches from atom, becomes ~ free
↳ moves through crystal

<u>valence</u> or <u>conduction</u> electrons

Na^+ in bcc lattice immersed in gas of free electrons

energy lower than free atoms

because ◦) for free Na atoms in gas : valence e^- confined to atomic volumes
↳ large K (Heisenberg principle small $x \rightarrow$ large p)

◦) in crystal e^- move throughout volume of the crystal
↳ decrease in K
↳ diminution of total energy

(free e^- hold positive ions together)

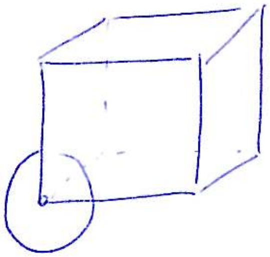
metallic bond is $\boxed{\text{weak}}$; melting point for Na ~ 97.8°C

high <u>electrical</u> conductivity - valence e^- can move easily
thermal "

<u>ductility</u> - deformation - e^- can easily adapt

→) Hint for HW

4) packing fraction / packing ratio for $\boxed{sc}$



distance between NN = a

$r = a/2$

each corner gives 1/8 of a sphere to the unit cell

$\Rightarrow \underset{\text{corners}}{8} \times \frac{1}{8} = 1$ sphere per unit cell

$$\text{density} = \frac{\text{volume of spheres}}{\text{volume of unit cell}} = 1\ \frac{4/3\,\pi r^3}{a^3}$$

$$= \frac{4}{3}\frac{\pi}{a^3}\frac{a^3}{8} = \boxed{\frac{\pi}{6}}$$

diamond

fcc = (4 + 4)

½ of bcc → $r = \sqrt{3}/8$

$\Rightarrow$ density $\frac{8 \times \text{vol}}{\text{vol}}$

corners: $8 \times \frac{1}{8} = 1$

face: $6 \times \frac{1}{2} = 3$

$\boxed{fcc}$ $$\frac{(4)\times\left(4/3\,\pi\,\frac{a^3}{2^3 (2)^{3/2}}\right)}{a^3} = \frac{2\pi}{3\ 2\sqrt{2}}$$

(1 + 3)

$$\sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2} = \frac{a}{\sqrt{2}}$$

$$r = \frac{a}{2\sqrt{2}}$$

3) NN

sc: 6

fcc: 12

bcc: 8

diamond: 4

$\boxed{bcc}$

diagonal
distance between 2 ~~diagonals~~ extreme atoms

base $\sqrt{a^2 + a^2} = \sqrt{2}\,a$

diagonal $\sqrt{(\sqrt{2}\,a)^2 + a^2} = \sqrt{3}\,a$

½ is where bcc atom is

$\sqrt{3}\,a/2$

$\Rightarrow$ $\boxed{r = \sqrt{3}\,a/4}$ of sphere

corners = $8 \times 1/8 = 1$

center = 1

density = $\frac{(1+1)\text{ vol}}{\text{vol.}}$

[illegible]

2) bcc – yes

$\vec{a} = \frac{a}{2}(\vec{i} + \vec{j})$

$\vec{b} = \frac{a}{2}(\vec{i} - \vec{j})$

$\vec{c} = a\vec{k}$

scc – no

$\Rightarrow$ 3 sc lattices

(0 0 0) (0 ½ ½) (½ 0 ½)

X- Ray Diffraction

to determine the structure of a crystal } study diffraction pattern of a beam of radiation incident on the crystal

λ of X-rays ~ 1 Å → of the same order of magnitude as the lattice constants of crystals

$$E = h\nu = 6.6\times10^{-27}\,\text{erg}\cdot\text{s}\;(c/\lambda) \simeq 10^4\,\text{eV}$$

$c = \lambda\nu$

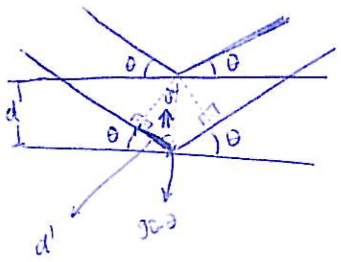
e^- accelerated ——→ impinge on a metallic target
(cathode tube - large potential)
~~(synchro~~

↓ bursts of x-rays are emitted

Bragg's law

Monochromatic x-ray beam incident on the surface of crystal
↳ reflect depending on angle of incidence
↓
values depend on
$\underline{\lambda}$ and <u>lattice constant</u>

Incident beam is partially reflected by the atomic planes
↓
all collected at a distant detector



$\sin\theta = d'/d$

path difference: $\Delta = 2d' = \underline{2d\sin\theta}$

assumption: reflection is <u>specular</u>

∡ of incidence = ∡ of reflection

interference is constructive if

$\Delta = n\lambda \qquad n = 1, 2, 3 \ldots$

$$\boxed{2d\sin\theta = n\lambda}$$ Bragg's law

↳ only angles for reflection

λ is known, θ measured from experiment ⇒ can obtain interplanar distance d

actually (2θ)

Notice: we need $\underline{\lambda < 2d}$ ⇒ x-rays

treating atomic planes as reflecting mirrors $\overset{\text{is}}{\Rightarrow}$ simplification

<u>scattering</u> of x-rays is caused by <u>discrete</u> atoms

↓

let us now

consider all discrete atoms in the

lattice and see that

Bragg's law is recovered

1-28-⑪

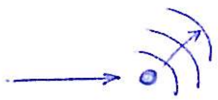
Scattering from an atom

x-ray : plane-wave field $u = A e^{i(\vec{K_0}\cdot\vec{r} - \omega t)}$

is incident on e^-, which absorbs energy and scatters it in all directions

scattered field is an outgoing spherical wave

[see Griffiths - EM page 398]

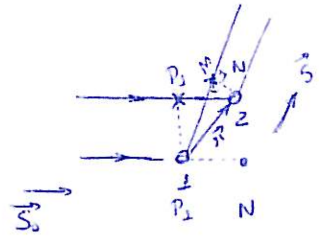


$$u' = \boxed{f_e}\ \frac{A}{\boxed{D}}\ e^{i(KD - \omega t)}$$

$|K| = |K_0|$ (because λ doesn't change)

f_e → scattering length

D → radial distance from e^- to point the field is evaluated → amplitude decreases as $1/D$



scattered field observed at a distant point

(neglect ωt for the moment)

$$u' = f_e \frac{A}{D}\left[e^{iKD} + e^{i(KD + \delta)} \right]$$

δ → phase lag of wave from e^- ①

$$\delta = \left(\overline{P_1M} - \overline{P_1N}\right) k$$

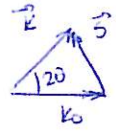
incident on ① travels $\overline{P_1M}$ and during this time incident on 2 travels P_1N

$\overline{P_1M} = \vec{r}\cdot\vec{S}$ (since $\overline{P_1M}$ is projection of $\vec{r}$ on $\vec{S}$)

$\overline{P_1N} = \vec{r}\cdot\vec{S_0}$

$$\vec{S} = K(\vec{S} - S_0) = \vec{K} - \vec{K_0}$$

$\vec{S}$ → scattering vector



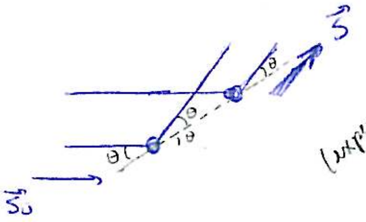
Can we get Bragg's law from discrete units? ← scattering

relation between interplanar distance d with θ and λ

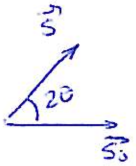
Scattering from 2 e^-

$$u' = f_e \frac{A}{D}\left[e^{iKD} + e^{i(KD+\delta)}\right] e^{-i\omega t}$$

D is large, so that it is ~ the same for both e^-



(experiment gets 2θ)



mention **DIAMOND**
- covalent bound
- impurities

phase lag $\delta = \vec{S}\cdot\vec{r}$

↑

scattering vector $\vec{S} = K(\vec{s} - \vec{s}_0) = \vec{K} - \vec{K}_0$

$$u' = f_e \frac{A}{D} e^{iKD}\left[1 + e^{i\vec{S}\cdot\vec{r}}\right] e^{-i\omega t}$$

← e^- ① is the origin

arbitrary origin:

$$u' = f_e \frac{A}{D} e^{iKD}\left[e^{i\vec{S}\cdot\vec{r}_1} + e^{i\vec{S}\cdot\vec{r}_2}\right] e^{-i\omega t}$$

Scattering from arbitrary number of scatterers

$$u' = f_e \frac{A}{D} e^{iKD} \sum_l e^{i\vec{S}\cdot\vec{r}_l}\; e^{-i\omega t}$$

comparing to single electron:

$$u' = \underbrace{(f_e)}_{\text{scattering length of the electron}} \frac{A}{D} e^{iKD} e^{-i\omega t}$$

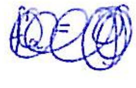
$$\boxed{u' = (f)\frac{A}{D} e^{iKD} e^{-i\omega t}}$$

scattering length of the whole system: $f = f_e \sum_l e^{i\vec{S}\cdot\vec{r}_l}$

Single free atom

$$f = f_e \sum_e e^{i\vec{s}\cdot\vec{r}_e}$$

e^-s spread in a cloud around the nucleus

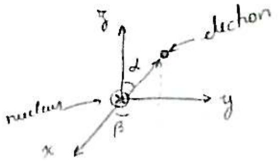


$$f \rightarrow \underbrace{f_e \int \rho(\vec{r})\, e^{i\vec{s}\cdot\vec{r}}\, d^3r}$$

f_a – atomic scattering factor

if

$\rho(\vec{r})$ – spherically symmetric



$$f_a = \int \rho(\vec{r})\, e^{i\vec{s}\cdot\vec{r}}\, d^3r = \int_0^R \int_0^{2\pi} \int_0^{\pi} \sin\alpha\, d\alpha\, d\beta\, r^2 dr\, \rho(r)\, e^{isr\cos\alpha}$$

$$\int_0^{\pi} \sin\alpha\, e^{isr\cos\alpha}\, d\alpha = \int_1^{-1} (-du)\, e^{isru} = \frac{e^{isr} - e^{-isr}}{isr} = \frac{2\sin sr}{sr}$$

$u = \cos\alpha$

$du = -\sin\alpha\, d\alpha$

$$\int_0^{2\pi} d\beta = 2\pi$$

$$\boxed{f_a = \int_0^R 4\pi r^2 \rho(r) \frac{\sin sr}{sr}\, dr}$$

particular behavior of f_a
depends on the electron
density $\rho(\vec{r})$ of the atom in question

Scattering from a crystal

sum over all electrons in the crystal

$$f_{cr} = \sum_{l} e^{i\vec{S}\cdot\vec{r}_l}$$

fcr: crystal scattering factor

has the sum of all electrons in each atom

$$= \sum_{l} f_{a_l}\, e^{i\vec{S}\cdot\vec{R}_l}$$

sum over all atoms

$\vec{R}_l$: position of the lth atom

relative position of jth atom

position of lth cell

$$= \underbrace{\left(\sum_{j} f_{aj}\, e^{i\vec{S}\cdot\vec{\delta}_j}\right)}_{\text{geometrical structure factor } F} \underbrace{\left(\sum_{l} e^{i\vec{S}\cdot\vec{R}_l^{(c)}}\right)}_{\text{lattice structure factor } S}$$

sum over the unit cell

all e^- in atom

each atom

sum over all unit cells

geometrical structure factor F

lattice structure factor S

depends on geometrical shape and contents of the unit cell

depends only on the crystal system involved, on the structural properties of the lattice

for simple lattice, unit cell contains just one atom

$$\Downarrow$$

$$\boxed{F = f_a}$$

this is the part from where Bragg's law is extracted

Example

has four corners (4)
but each atom
is shared with four (1/4)
unit cells

$\Rightarrow 4 \times \frac{1}{4} = ①$ atom per unit cell

→) <u>3 D</u>

$\vec{a}, \vec{b}, \vec{c}$ noncoplanar / not unique

$\vec{R}_n = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$ parallelepiped – unit cell

all primitive cells – same volume

→) <u>Bravais Lattice</u>

(Only 14) in 3D

↓

because of translational-symmetry condition

→) 2D

→ can't construct Bravais lattice

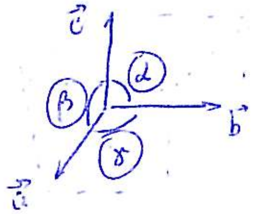
∘) non-Bravais → 230 → also finite

(Fig. 1.7)

↙

⑭ Bravais lattices

grouped into ⑦ crystal systems



in all nonsimple lattices → unit cells are nonprimitive

Lattice structure factor

$$S = \sum_{l} e^{i\vec{s}\cdot\vec{R}_l^{(c)}}$$

$\vec{a}$: basis vector of the lattice

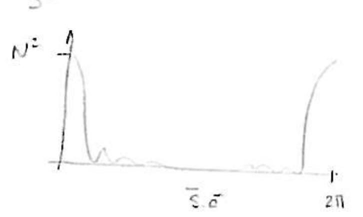
$$\Rightarrow \quad S = \sum_{l=1}^{N} e^{i\vec{s}\cdot l\vec{a}}$$

(geometric progression)

students

$$S = \frac{\sin\left[(1/2)\,N\,\vec{s}\cdot\vec{a}\right]}{\sin\left[(1/2)\,\vec{s}\cdot\vec{a}\right]} \qquad S^2 = \frac{\sin^2\left[(1/2)\,N\,\vec{s}\cdot\vec{a}\right]}{\sin^2\left[(1/2)\,\vec{s}\cdot\vec{a}\right]}$$

$$\left.\begin{array}{l} \vec{s}\,\vec{a} \to 0 \Rightarrow S^2 \to N^2 \\ \vec{s}\,\vec{a} \to 2\pi \Rightarrow S^2 \to N^2 \end{array}\right\} \text{maxima at } \vec{s}\cdot\vec{a} = 0 \text{ and } 2\pi$$



$N \to \infty$

$\hookrightarrow S^2 \neq 0$ only at $\boxed{\vec{s}\cdot\vec{a} = 2\pi h}$ $\quad h$ = any integer

$\boxed{S = N}$

directions $\left\{\begin{array}{l}\text{where } S \neq 0 \\ \text{where diffraction takes place}\end{array}\right.$

3D

$$\vec{R}^{(c)} = l_1\vec{a} + l_2\vec{b} + l_3\vec{c}$$

$$S = \sum_{l_1,l_2,l_3} e^{i\vec{s}\cdot(l_1\vec{a} + l_2\vec{b} + l_3\vec{c})} = \Big(\sum_{l_1}\quad\Big)\Big(\sum_{l_2}\quad\Big)\Big(\sum_{l_3}\quad\Big)$$

$\Rightarrow$ condition for constructive interference

$$\boxed{\begin{array}{l} \vec{s}\cdot\vec{a} = h\,2\pi \\ \vec{s}\cdot\vec{b} = k\,2\pi \\ \vec{s}\cdot\vec{c} = l\,2\pi \end{array}}$$

Laue equations

$\Longrightarrow$ WHAT VALUES of $\vec{s}$ (scattering vector) SATISFY this condition?

Reciprocal Lattice

⟶ NEED primitive cell to obtain reciprocal lattice

for primitive lattice

lattice basis vectors: $\vec{a}, \vec{b}, \vec{c}$

Reciprocal basis vectors

define new set of basis vectors: $\boxed{\vec{a}^*, \vec{b}^*, \vec{c}^*}$

$$\vec{a}^* = \frac{2\pi}{\Omega_c}(\vec{b}\times\vec{c}) \qquad \vec{b}^* = \frac{2\pi}{\Omega_c}(\vec{c}\times\vec{a}) \qquad \vec{c}^* = \frac{2\pi}{\Omega_c}(\vec{a}\times\vec{b})$$

$\Omega_c = \vec{a}\cdot(\vec{b}\times\vec{c})$: volume of a unit cell

basis for new lattice whose vectors are

$$\vec{G}_n = n_1\vec{a}^* + n_2\vec{b}^* + n_3\vec{c}^*$$

RECIPROCAL lattice

$\vec{a}^*\cdot\vec{a} = 2\pi$

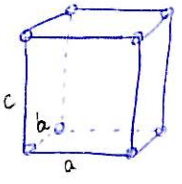
$\vec{a}^*\cdot\vec{b} = 0$ etc

Examples

○) 1D

$a^* = 2\pi/a$

○) SC



$\vec{a} = a\hat{i}$

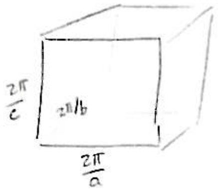
$\vec{b} = b\hat{j}$

$\vec{c} = c\hat{k}$

$$\vec{a}^* = \frac{2\pi\, bc\, \overset{\hat{i}}{(\hat{j}\times\hat{k})}}{abc\,(\hat{i}\cdot(\hat{j}\times\hat{k}))} = \frac{2\pi}{a}\hat{i}$$

$$\vec{b}^* = \frac{2\pi}{b}\hat{j}$$

$$\vec{c}^* = \frac{2\pi}{c}\hat{k}$$



○) reciprocal lattice to bcc is fcc

2-04
~~1-30~~-⑥

→ lattice structure factor

$$S = \sum_{l=1}^{N} e^{i\vec{s}\cdot\vec{R}_l^{(c)}}$$

↓

S vanishes for every value of $\vec{s}$, except when $\boxed{\vec{s} = \vec{G}_{hkl}}$

↑
reciprocal lattice vector

$$\vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

$$\vec{s}\cdot\vec{R}_l^{(c)} = \vec{G}_{hkl}\cdot\vec{R}_l^{(c)} = (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*)\cdot(l_1\vec{a} + l_2\vec{b} + l_3\vec{c})$$

$$= (hl_1 + kl_2 + ll_3)\,2\pi = \boxed{m\,2\pi}\,//$$

◦) Condition for refraction: $\Bigg\{$ scattering vector $\vec{s}$ is equal to a reciprocal lattice vector

◦) The vectors of the reciprocal lattice are related to the crystal planes of the direct lattice.

consider

$\text{planes} \quad \underbrace{(h\ k\ l)}_{\text{Miller indices}} \quad \text{and} \quad \vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$

$$h = n\frac{a}{x} \qquad k = n\frac{b}{y} \qquad l = n\frac{c}{z}$$

point where the plane crosses x-axis

Ex: $x = 3a$

2-04
~~1-30~~ - ①

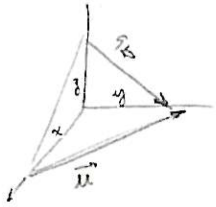
want to show

(i) $\vec{G}_{hkl} \perp (hkl)$

(ii) $d_{hkl} = 2\pi / G_{hkl}$

↑
interplanar
distance

(i) need to show that $\vec{G}_{hkl}$ is ⊥ to two vectors in the plane



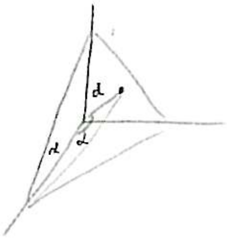
$$\begin{cases} \vec{u} = -\frac{x}{a}\vec{a} + \frac{y}{b}\vec{b} \\ \vec{v} = \frac{y}{b}\vec{b} - \frac{z}{c}\vec{c} \end{cases}$$

$$\vec{u} \cdot \vec{G}_{hkl} = \left(-\frac{x\vec{a}}{a} + \frac{y\vec{b}}{b}\right) \cdot \left(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\right) = -2\pi\frac{x}{a}h + 2\pi\frac{y}{b}k$$

$$= -2\pi\left(\frac{x}{a}h - \frac{y}{b}k\right) = -2\pi n\left(\frac{\cancel{x}}{a}\frac{a}{\cancel{x}} - \frac{\cancel{y}}{b}\frac{b}{\cancel{y}}\right) = \boxed{0}$$ ✓

$$\vec{v} \cdot \vec{G}_{hkl} = \boxed{0}$$ ✓

(ii) direction normal to (hkl) $\quad \hat{G}_{hkl} = \frac{\vec{G}_{hkl}}{|G_{hkl}|}$



$$d_{hkl} = \left(\frac{x}{a}\underbrace{\vec{a} \cdot \hat{G}_{hkl}}_{2\pi h}\right) \Big/ G_{hkl} = \left(2\pi \underset{\underset{x}{\simeq}}{h} \frac{x}{a}\right) \Big/ G_{hkl} = \boxed{2\pi / G_{hkl}} \;//$$

$$\cos\alpha = \frac{d_{hkl}}{x}$$

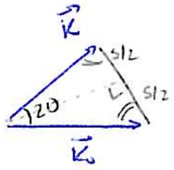
$$\left.\begin{array}{l} d_{hkl} = x\cos\alpha \\ \text{direction of } d_{hkl} \text{ is } \frac{\vec{G}_{hkl}}{|G_{hkl}|} \end{array}\right\} \Rightarrow x\cos\alpha = \frac{x\vec{a}}{a} \cdot \frac{\vec{G}_{hkl}}{|G_{hkl}|}$$

$$\vec{a} \cdot \vec{G}_{hkl} = \vec{a} \cdot \frac{2\pi h\,(\vec{b} \times \vec{c})}{\vec{a} \cdot (\vec{b} \times \vec{c})} = 2\pi h$$

2-04
~~1-30~~-⑧

⟶) $\boxed{\vec{S} = \vec{G}_{hkl}}$ ← condition of diffraction

$$\vec{S} = \vec{K} - \vec{K}_0 = K(\vec{s} - \vec{s}_0)$$



$$|\vec{K}| = |\vec{K}_0|$$

$$\Longrightarrow \frac{S}{2} = \sin\theta \; K$$

⟶) $\boxed{S = 2K\sin\theta}$

wave vector: $K = 2\pi/\lambda$

⟶) $\boxed{d_{hkl} = \frac{2\pi}{G_{hkl}}}$

put all together. $d_{hkl} = \dfrac{\cancel{2\pi}}{2\left(\frac{2\pi}{\lambda}\right)\sin\theta}$

$$\boxed{2\, d_{hkl} \sin\theta = \lambda}$$ //

Bragg's law

derived from scattering theory

Therefore, if $\vec{s} = \vec{G}_{hkl}$ the lattice structure factor is nonzero and

$$\overline{\underline{S_{hkl} = N}}$$

$$f_{cr_{hkl}} = N F_{hkl} \longrightarrow I_{hkl} \sim |F_{hkl}|^2$$

Bragg condition satisfied: incident beam is diffracted and recorded at detector

rotations – identify ≠ planes

<u>However</u>,

diffraction from certain planes may be missing

$\underline{F_{hkl} \text{ may be zero}}$

Example: <u>bcc</u>

$$F_{hkl} = f_a \sum_j e^{i\vec{s}\cdot\vec{\delta}_j}$$

$$\vec{\delta}_j = u_j\vec{a} + v_j\vec{b} + w_j\vec{c}$$

$$\vec{s} = \vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

$$F_{hkl} = f_a \sum_j e^{i2\pi(hu_j + kv_j + lw_j)} \underset{\substack{\uparrow \\ \text{for} \\ \text{bcc}}}{=} f_a\left(1 + e^{i\pi(h+k+l)}\right)$$

basis
(0,0,0) – (1/2, 1/2, 1/2)

if $(h+k+l)$ is even $\Rightarrow F_{hkl} = 2f_a$

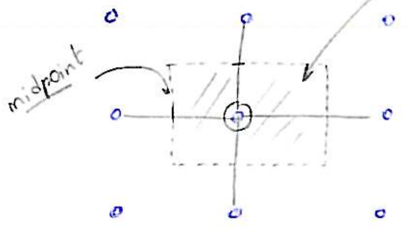
is odd $\Rightarrow \boxed{F_{hkl} = 0}$

<u>fcc</u>
in homework

For the direct lattice

↳ another way to choose the primitive cell

Wigner-Seitz cell



it is also a primitive cell
but it has an atom in
the middle

The same procedure for
the reciprocal lattice ⟹ $\boxed{\text{first Brillouin zone}}$

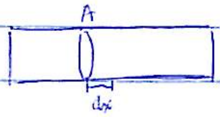
translate it with $\vec{G}_n$ and whole
reciprocal lattice space is covered

(will be impt in the next chapter)

for 3D
the lattice vectors are bisected
in the midpoint by planes

Feb/06 - ①

Ch. 3 - Lattice Vibrations



long bar: L

1) vibrations ⇒ wave, λ is long ⇒ disregard the atomic nature of the crystal
⇒ treat the solid as a continuous medium

want to find eq. describing wave (longitudinal wave - sound wave)

some definitions: STRAIN $e = \frac{du}{dx}$

elastic const (Young modulus)

STRESS $S = \frac{F}{A} = Ye$

Newton's 2nd law: $F = ma$

$\downarrow$ $F = SA$

$$\rho A dx \frac{\partial^2 u}{\partial t^2} = \underbrace{\left(S(x+dx) - S(x)\right)}_{\frac{\partial S}{\partial x} dx} A$$

(short segment dx)

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{\partial S}{\partial x} = Y \frac{\partial^2 u}{\partial x^2}$$

$$\boxed{\frac{\partial^2 u}{\partial x^2} - \frac{\rho}{Y} \frac{\partial^2 u}{\partial t^2} = 0} \leftarrow \text{wave equation}$$

relation
(dispersion law)

speed of sound: $v_s = \lambda f = \frac{2\pi}{q} \frac{\omega}{2\pi} \longrightarrow v_s = \frac{\omega}{q} \Rightarrow \boxed{\omega = v_s q}$

$q = \frac{2\pi}{\lambda}$

$\omega = 2\pi f$

want v_s in terms of properties of the medium: ρ, Y

02-06 ②

solution for wave eq.

plane wave : $u = A\, e^{i(qx-\omega t)}$

$$\frac{\partial^2 u}{\partial x^2} - \frac{\rho}{Y}\frac{\partial^2 u}{\partial t^2} = 0$$

$$-q^2 + \frac{\rho}{Y}\omega^2 = 0 \Rightarrow \omega = \sqrt{\frac{Y}{\rho}}\, q \Rightarrow \boxed{v_s = \sqrt{\frac{Y}{\rho}}}$$

discuss : tension, inertia

linear relation : $\boxed{\omega = v_s\, q}$

- solid
- liquid
- gas
- optical waves ⇒ ⓒ

deviations appear when the discrete atomic nature of solid is taken into account, that is, when $\lambda <$ atomic distance

sound wave → elastic const.
shear wave → shear elastic const
} isotropic

anisotropic solid → more consts / planes

02-06-63)

Boundary Conditions ⟷ Density of States

$u = Ae^{iqx}$ $\left(e^{-i\omega t}\right)$ ⟵ $\boxed{1D}$

periodic boundary conditions ↑ (ring)

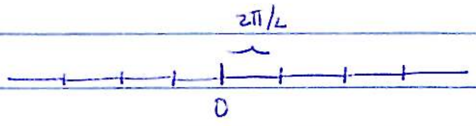
$u(x=0) = u(x=L)$

$e^{iqL} = 1$

$\boxed{q = n\frac{2\pi}{L}}$

↑ allowed λ, f

in q-space



⇒ continuous when L → 0

each $\boxed{q\text{-value}}$ ⟶ one $\boxed{\text{MODE}}$ of vibration

number of modes in interval dq

1 mode ⟶ 2π/L
x ⟶ dq

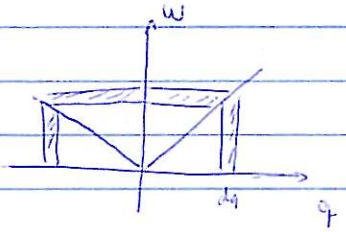
$\boxed{\frac{L}{2\pi}\, dq}$ //

Definition

$g(\omega)\, d\omega$ = number of modes in $d\omega$
↑ freq. range

$g(\omega)$ ⟶ (density of states)

$g(\omega)\, d\omega = \frac{L}{2\pi}\, dq \; (\times 2)$ ⟶ because



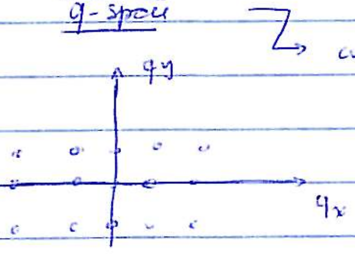
$g(\omega) = \frac{L}{\pi} \frac{dq}{d\omega}$ ⇒ $\boxed{g(\omega) = \frac{L}{\pi} \frac{1}{v_s}}$ // ⟵ const in $\boxed{1D}$ //

$\omega = v_s q$

$\boxed{3D}$

$$u = e^{i\vec{q}\cdot\vec{r}} = e^{i(q_x x + q_y y + q_z z)}$$

$$\begin{cases} q_x = n\frac{2\pi}{L} \\ q_y = m\frac{2\pi}{L} \\ q_z = l\frac{2\pi}{L} \end{cases}$$



$\rightarrow$ cube of volume $\left(\frac{2\pi}{L}\right)^3$

each $\left(\frac{2\pi}{L}\right)^3 \Rightarrow$ one $\underline{\underline{\text{allowed}}}$ $\vec{q}$

one allowed $\underline{\underline{\text{MODE}}}$

how many modes in spherical shell

$$4\pi q^2 dq$$

$$1 \text{ mode} \longrightarrow (2\pi/L)^3$$
$$x \longrightarrow 4\pi q^2 dq$$

$$\left(\frac{L}{2\pi}\right)^3 4\pi q^2 dq \qquad L^3 = V \quad \text{volume of the sample}$$

$$\hookrightarrow \frac{V}{2\pi^2} q^2 dq$$

density of states

$$g(\omega)\, d\omega = \frac{V}{2\pi^2} q^2 dq$$

in 3D $\underline{\text{NOT}}$ const.

$$g(\omega)\cancel{d\omega} = \frac{V}{2\pi^2}\frac{\omega^2}{v_s^2}\frac{d\omega}{v_s} \Rightarrow \boxed{g(\omega) = \frac{V}{2\pi^2}\frac{\omega^2}{v_s^3}}$$

$\uparrow$

$\omega = v_s q$

$d\omega = v_s dq$

in 3D each $\vec{q}$ has 3 modes 1 longitudinal
and 2 transverse

they have ≠ dispersion relations
but simplifying - assume common velocity

$$\boxed{g(\omega) = ③ \frac{V}{2\pi^2} \frac{\omega^2}{v_s^3}}$$

⇒) V can be omitted by taking into = to unity

⇒) when $\lambda \ll$ dimensions of sample
⇒ $g(\omega)$ is indep. of boundary conditions
└ periodic - assumed for convenience.

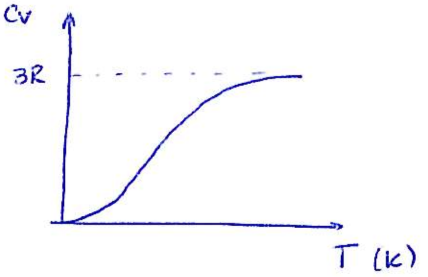
Specific Heat

$$\underset{\substack{\downarrow \\ \text{per} \\ \text{mole}}}{C} = \frac{\Delta Q}{\Delta T}$$

heat ΔQ required to raise temperature of one mole by ΔT

process at const V $\Rightarrow$ $\Delta Q = \Delta E$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$



becomes const 3R at $\boxed{\text{high temp.}}$
$\Rightarrow$ same $\overset{\Delta E}{\Delta Q}$ for ΔT for any substance
$\Rightarrow$ $C_V \sim 3R$ for any substance
} Dulong-Petit law

at $\boxed{\text{low temp}}$ $C_V \propto T^3$

classical theory: each atom = harmonic oscillator

$$\left.\begin{aligned} \bar{E}_{\substack{\text{one harm} \\ \text{1D}}} &= kT \\ \bar{E}_{\text{atom}} &= 3kT \end{aligned}\right\} \quad E = 3\underset{\substack{\uparrow \\ \text{amount of atoms / molecules} \\ \text{in 1 mole}}}{N_A} kT = 3\overset{\text{universal const.}}{R}T \Rightarrow \boxed{C_V = 3R}$$

explains high temp. behavior

NOT low temp.

↳ need QM

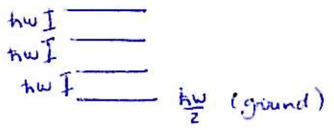
02-06-(07)

Einstein Model

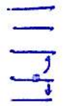
$$E_n = (n + 1/2)\hbar\omega$$

↗

closed
system



open
system exchages energy with the surrounding thermal bath



in
equilibrium $$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n e^{-E_n/kT}}{\sum_{n=0}^{\infty} e^{-E_n/kT}}$$ ← normalization

discuss
probability $\boxed{e^{-E_n/kT}}$ ← Boltzmann factor

T small ⇒ E_n small
T large ⇒ more E_n available

$$\bar{E} = \frac{(\hbar\omega/2)\, e^{-\hbar\omega/2kT} + (3\hbar\omega/2)\, e^{-3\hbar\omega/2kT} + (5\hbar\omega/2)\, e^{-5\hbar\omega/2kT} + \ldots}{e^{-\hbar\omega/2kT} + e^{-3\hbar\omega/2kT} + e^{-5\hbar\omega/2kT} + \ldots}$$

infinite
geom
series

$$e^{-\hbar\omega/2kT}\left(1 + e^{-\hbar\omega/kT} + e^{-2\hbar\omega/kT} + \ldots\right) \underset{\substack{\uparrow \\ \text{ratio } e^{-\hbar\omega/kT}}}{=} \frac{e^{-\hbar\omega/2kT}}{1 - e^{-\hbar\omega/kT}}$$

$$\frac{\hbar\omega}{2} e^{-\hbar\omega/2kT}\left(1 + 3e^{-\hbar\omega/kT} + 5e^{-2\hbar\omega/kT} + \ldots\right) =$$

$$= \frac{\hbar\omega}{2} e^{-\hbar\omega/2kT}\left[\left(1 + e^{-\hbar\omega/kT} + e^{-2\hbar\omega/kT}\right) + 2e^{-\hbar\omega/kT}\left(1 + e^{-\hbar\omega/kT} + \ldots\right) + 2e^{-2\hbar\omega/kT}\left(1 + e^{-2\hbar\omega/kT} + \ldots\right) + \ldots\right]$$

$$= \frac{\hbar\omega}{2} e^{-\hbar\omega/2kT}\left[\frac{1}{1 - e^{-\hbar\omega/kT}} + \frac{2e^{-\hbar\omega/kT}}{1 - e^{-\hbar\omega/kT}}\left(1 + e^{-\hbar\omega/kT} + \ldots\right)\right]$$

$$= \frac{(\hbar\omega/2)\, e^{-\hbar\omega/2kT}}{(1-e^{-\hbar\omega/kT})}\left[1+\frac{2\,e^{-\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}}\right]$$

$$\bar{\epsilon} = \frac{(\hbar\omega/2)\, \cancel{e^{-\hbar\omega/2kT}}}{\cancel{(1-e^{-\hbar\omega/kT})}}\left[1+\frac{2\,e^{-\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}}\right]\frac{\cancel{(1-e^{-\hbar\omega/kT})}}{\cancel{e^{-\hbar\omega/2kT}}}$$

$$\boxed{\bar{\epsilon} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}} \quad //$$

◦) $T \to \infty$ $\quad (kT \gg \hbar\omega)$

$$\bar{\epsilon} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\cancel{1}+\frac{\hbar\omega}{kT}+\dots\cancel{-1}} \simeq \frac{\hbar\omega}{2} + kT \sim \boxed{kT} \quad //$$

◦) $T \to 0$ $\quad (kT < \hbar\omega)$

$$\bar{\epsilon} \approx \frac{\hbar\omega}{2} + \hbar\omega\, e^{-\hbar\omega/kT} \longrightarrow \boxed{\frac{\hbar\omega}{2}} \quad //$$

$$\boxed{\bar{\epsilon} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}} \quad \leftarrow \text{one oscillator}$$

each atom = 3 oscillators

1 mol = N_A of atoms

$$\boxed{E = 3N_A\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right)}$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N_A \frac{\hbar\omega}{\left(e^{\hbar\omega/KT}-1\right)^2} \frac{\hbar\omega}{KT^2} e^{\hbar\omega/KT}$$

$$= 3\,\overset{R}{\left(N_A K\right)} \left(\frac{\hbar\omega}{KT}\right)^2 \frac{e^{\hbar\omega/KT}}{\left(e^{\hbar\omega/KT}-1\right)^2}$$

$$\boxed{C_V = 3R\left(\frac{\hbar\omega_E}{KT}\right)^2 \frac{e^{\hbar\omega_E/KT}}{\left(e^{\hbar\omega_E/KT}-1\right)^2}}$$

ω_E : Einstein frequency

θ_E : Einstein temperature → $K\theta_E = \hbar\omega_E$

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}$$

- $T \to \infty$ $\quad C_V \to 3R\left(\frac{\hbar\omega_E}{KT}\right)^2\left(\frac{KT}{\hbar\omega_E}\right)^2 \Rightarrow \boxed{C_V \to 3R}$

- $T \to 0$ $\quad C_V \to 3R\left(\frac{\hbar\omega_E}{KT}\right)^2 e^{-\hbar\omega_E/KT}$ decays exponentially with temperature

Einstein model does not apply at very low temperature, where it was experimentally seen that $C_V \propto T^3$

02-11-(00)

SUMMARY

Vibrations → elastic waves / elastic sound waves

∘) λ long → linear dispersion relation

∘) some allowed ω = mode
↑
boundary conditions

∘) periodic

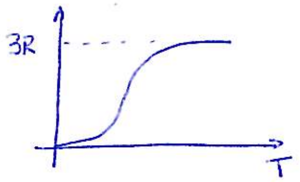
1D – const

DENSITY of STATES (modes in ω, ω+dω)

3D → $$\boxed{g(\omega) = \frac{3V}{2\pi^2}\frac{\omega^2}{v_s^3}}$$ //

∘) specific heat

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$



high temp

classical theory: each direction of vibration of atom — harm. oscillator

$$\bar{E}_{atom} = 3kT$$

$$E_{lattice} = 3\overset{R}{(kN_A)}T \rightarrow \underline{C_V = 3R}$$

low temp

QM - Einstein Model

$$\bar{E}_{h.o.} = (n+1/2)\hbar\omega$$

in equilibrium: $$\bar{E} = \frac{\sum E_n e^{-E_n/kT}}{\sum e^{-E_n/kT}} \overset{\text{quant. harm. os.}}{=} \boxed{\frac{\hbar\omega}{e^{\hbar\omega/kT}-1} + \frac{\hbar\omega}{2}}$$ //

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}$$

→ high temp → 3R

→ intermediate → fine

→ low temp → $\underbrace{B(T)\,e^{-\theta_E/T}}_{\text{PROBLEM !!}}$

Debye model

↳ to describe C_v at low temperatures

↳ need to consider also $\boxed{\text{interaction}}$ between atoms

(in Einstein model: oscillators are independent)

need to consider solid as a whole / motion of one atom affects the others

example of collective modes } sound waves { atoms do not oscillate independently / have same amplitude

Debye assumed lattice modes obey dispersion relation

$$\boxed{\omega = v_s q}$$

{ Einstein lattice vibration: only one frequency ω
Debye ω varies with q

holds if discreteness of the lattice is ignored
long λ

each mode — one harmonic oscillator

Total energy

$$E = \int \bar{E}(\omega)\, g(\omega)\, d\omega$$

$g(\omega)\,d\omega$ → number of modes in $(\omega, \omega + d\omega)$

↑ integration over all allowed frequencies

(modes are indep. but for each mode ⇒ collective motion of atoms)

$$E = \frac{\text{③}V}{2\pi^2 v_s^3}\int \omega^2 \left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{(e^{\hbar\omega/kT}-1)}\right) d\omega$$

Limits for the integration

minimum $= 0$

maximum $\Longleftrightarrow$ $\underbrace{\int_0^{\omega_D} g(\omega)\, d\omega}_{\text{total number of modes}} = \underbrace{3N_A}_{\text{number of degrees of freedom for the entire solid}}$

$\Rightarrow$ upper cutoff frequency

$\omega_D =$ Debye frequency

$$\int_0^{\omega_D} \frac{3V}{2\pi^2} \frac{\omega^2}{v_s^3}\, d\omega = \frac{3V}{2\pi^2} \frac{\omega_D^3}{\cancel{3} v_s^3} = 3N_A$$

$$\omega_D = \left(6\pi^2 \frac{N_A}{V} v_s^3\right)^{1/3}$$

$$\boxed{\omega_D = (6\pi^2 n)^{1/3} v_s}$$

where $n = \frac{N_A}{V}$ } concentration of atoms in the solid

02-11-③

$$E = \frac{3V}{2\pi^2 v_s^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{\left(e^{\hbar\omega/kT}-1\right)}\, d\omega$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

$$\boxed{C_V = \frac{3V}{2\pi^2 v_s^3}\,\frac{\hbar^2}{kT^2} \int_0^{\omega_D} \frac{\omega^4\, e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}\, d\omega}$$

$x = \hbar\omega/kT$, $k\theta_D = \hbar\omega_D$, $\omega_D = v_s\,(6\pi^2 n)^{1/3}$, $n = N_A/V$

θ_D → Debye temperature

$$C_V = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2}\, dx$$

θ_D obtained experimentally to fit the curve

a) $\overset{T \gg \theta_D}{T \to \infty} \Rightarrow C_V \to 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4}{x^2}\, dx$

$C_V \to 9R\left(\frac{T}{\theta_D}\right)^3 \left(\frac{\theta_D}{T}\right)^3 \frac{1}{3}$ $\quad \boxed{C_V \to 3R}$

dependence on material is expected since $\theta_D \sim \omega_D \sim v_s$

b) $\overset{T \ll \theta_D}{T \to 0} \Rightarrow \int_0^{\infty} \Longrightarrow \boxed{C_V = \frac{12\pi^4}{5} R\,(T/\theta_D)^3} \longleftarrow \int_0^{\infty} \frac{x^4}{(e^x-1)^2}\, dx = \frac{4\pi^4}{15}$

Fig. 3.3
Table 3.1

[redacted]

Note: $\theta_D \sim \omega_D \sim v_s\, n^{1/3}$

$\theta_D \sim \sqrt{\frac{Y}{\rho}}\, n^{1/3}$

↓

stiff crystal (like carbon) ⇒ large θ_D

[redacted]

Debye model – very successful, but also an approximation

The Phonon

elastic waves $\Leftarrow$ collective motion of atoms, collective vibration

$\downarrow$

determined, characterized by a specific ω, lattice ω

each elastic wave – a mode of lattice vibration

$\downarrow$

each mode is equivalent to a single harmonic oscillator of energy $\hbar\omega$

energy of each mode is quantized ($\hbar\omega$)

↳ = quantization of the energy of sound waves

$\Big\{$ electromagnetic field $\longleftrightarrow$ corpuscular nature characterized represented by photon

elastic field $\longleftrightarrow$ phonon

| particle that carries the unit energy of the elastic field in a particular mode

phonon $\begin{cases} E = \hbar\omega \\ p = h/\lambda \longrightarrow \lambda = \dfrac{2\pi}{q} \longrightarrow \vec{p} = \hbar \vec{q} \leftarrow \text{wave vector} \end{cases}$

$\downarrow$

carries energy and momentum of the elastic wave

$\Big\{$ electromag. wave = stream of photons

elastic sound wave = stream of phonons

speed of phonon $= v_s$ in the medium

in thermal equilibrium

$$\bar{\epsilon} = \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}$$

energy per phonon = $\hbar\omega$ $\Longrightarrow$ $\boxed{\bar{n} = \frac{1}{e^{\hbar\omega/kT}-1}}$ average number of phonons in the mode

depends on temperature

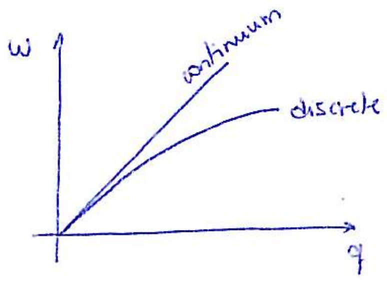
$\left\{ \begin{array}{l} \bar{n}=0 \text{ for } T=0 \\ \bar{n} \sim \frac{kT}{\hbar\omega} \text{ for high } T \end{array} \right\}$ different from other particles, such e^-, p^+ where the number is conserved

Lattice waves

{ consider discreteness of solid
how the dispersion relation $\omega = \omega(q)$ changes

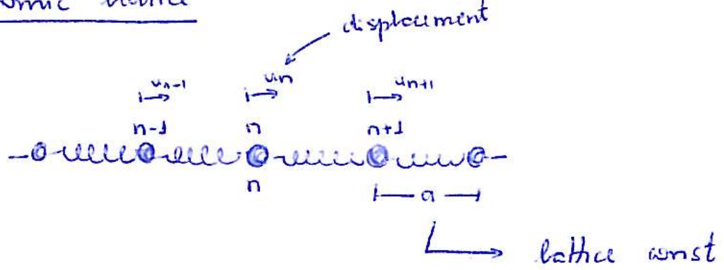
•) $\boxed{\omega = v_s q}$ for $q \to 0$, λ long } medium treated as continuum

•) q increases, λ decreases } discreteness becomes imptt., atoms scatter the wave
⇓
impede propagation
velocity of the wave decreases



2-11-(06)

1D monatomic lattice



→ consider nth atom

- α - interatomic force const
- F ∝ u : harmonic approx. (like Hooke's law)
- only NN consider

interaction with n+1 ⇒ ⊕ $\alpha(u_{n+1}-u_n)$

interaction with n-1 ⇒ ⊖ $\alpha(u_n-u_{n-1})$

restoring

→ Newton's 2nd law

$$M\frac{d^2u_n}{dt^2} = +\alpha(u_{n+1}-u_n)+\alpha(u_{n-1}-u_n) = -\alpha(2u_n-u_{n+1}-u_{n-1})$$

atom mass

we need an equation like this to each atom in the lattice

↳ Ⓝ coupled differential equations to be solved simultaneously

Let us now attempt a solution to $M\frac{d^2u_n}{dt^2}=\dots$ of the form

$$\boxed{u_n = A e^{i(qx_n-\omega t)}}\quad , \text{ where } \overline{x_n = na}$$

all atoms oscillate with ω, A

phases of atoms are interlocked and increases qa from one atom to the next one

→ this solution possible because: translational symmetry, i.e. equal masses at regular intervals

- masses with random values ⇒ attenuation or even no propagation
- mode of vibration where all atoms with same ω ⇒ $\boxed{\text{NORMAL MODE}}$ → propagating wave in the lattice

2-11-(07)

$$M(-\omega^2) A u_n = -\alpha\left[2u_n - e^{iqa}u_n - e^{-iqa}u_n\right]$$

$$\cancel{-}\omega^2 M = \cancel{-}\alpha\,(2 - e^{iqa} - e^{-iqa})$$

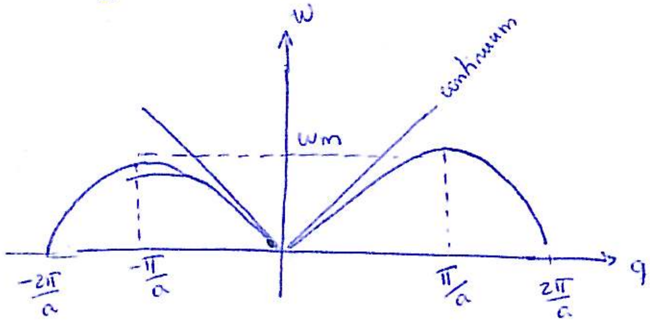
$$\omega^2 M = \alpha\left(e^{iqa/2}\underbrace{\left(e^{-iqa/2} - e^{iqa/2}\right)}_{-\sin(qa/2)(2i)} + e^{-iqa/2}\underbrace{\left(e^{iqa/2} - e^{-iqa/2}\right)}_{\sin(qa/2)(2i)}\right)$$

$$\omega^2 M = \alpha\, 2i\sin(qa/2)\,(-2i)\,\sin(qa/2)$$

$$\omega^2 M = 4\alpha\sin^2(qa/2)$$

$$\boxed{\omega = \omega_m\,|\sin(qa/2)|} \qquad \text{where} \qquad \boxed{\omega_m = \left(\frac{4\alpha}{M}\right)^{1/2}}$$

ω is ⊕



dispersion relation

Sinusoid with period $\frac{2\pi}{a}$

and max. frequency ω_m

Study of the dispersion relation

i) Long-wavelength limit

in range $0 < q < \pi/a$ → $\underbrace{\text{frequencies } 0 < \omega < \omega_m}$

only these frequencies correspond to transmitted waves, others ⇒ strongly attenuated

lattice is a low-pass mechanical filter

∘) long λ : $q \to 0$

$$\Rightarrow \omega \sim \omega_m \frac{qa}{2}$$

$$\boxed{\omega = \left(\frac{\omega_m a}{2}\right) q}$$ <u>linear</u> relation

$$v_s = \frac{\omega_m a}{2} = \sqrt{\frac{Y}{\rho}}$$

$$\left(\frac{4\alpha}{M}\right)^{1/2} \frac{a}{2} = \left(\frac{Y}{\rho}\right)^{1/2}$$

$$\alpha = \frac{M}{a^2} \frac{Y}{\rho} = \frac{\cancel{M}}{\cancel{a^2}} \frac{Y}{\cancel{M}} a^{\cancel{3}}$$

$$\boxed{\alpha = aY}$$

interatomic force const

elastic const.

∘) as q increases – curve deviates

at $q = \frac{\pi}{a}$ it <u>saturates</u> $\underbrace{\omega = \omega_m = (4\alpha/M)^{1/2}}_{}$

dependence as in harmonic oscillators

$$\left(\begin{array}{l} \frac{1}{2} K A^2 = \frac{1}{2} m v_{max}^2 = \frac{1}{2} m \frac{(2\pi)^2 A^2}{T^2} \\ \omega = \frac{2\pi}{T} \Rightarrow \omega = \sqrt{K/m} \end{array}\right)$$

Therefore

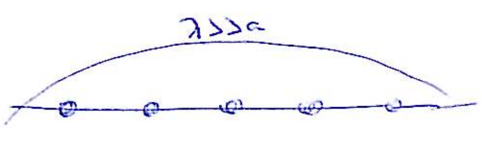
$q \to 0 \Rightarrow \lambda \gg a \Rightarrow$ atoms move $\boxed{\text{in phase}}$

from eq. $\boxed{\omega \to 0}$

$\Downarrow$

due to neighbors } restoring force is small $\Rightarrow \boxed{\omega \to 0}$

qualitative argument

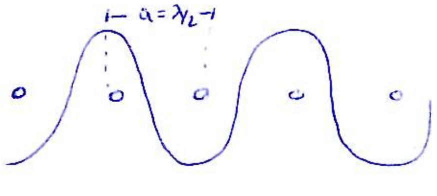


$q = \pi/a$
[illegible] $\Rightarrow \lambda = \frac{2\pi}{q} = 2a \Rightarrow$ neighbors are $\boxed{\text{out of phase}}$

ω largest

$\Downarrow$

restoring force is max. $\Rightarrow \omega$ is max



2-13-(02)

~~we~~ Note that

$$\underbrace{M\frac{d^2 u_n}{dt^2}}_{F} = -\underbrace{\left[4\alpha \sin^2(qa/2)\right]}\, u_n$$

force depends on q (λ) because motions of atoms are connected.

corresponds to a harmonic oscillator of force constant

$$\alpha(q) = 4\alpha\sin^2(qa/2)$$

Hooke's law

$$\begin{cases} F = -Kx \\ V(x) = \frac{1}{2} m\omega^2 x^2 \\ F = -m\omega^2 x \end{cases}$$

$\Downarrow$

frequency of the oscillator

$$\boxed{\omega = \sqrt{\alpha(q)/M}}$$

which is the dispersion relation

ii) Phase and group velocity

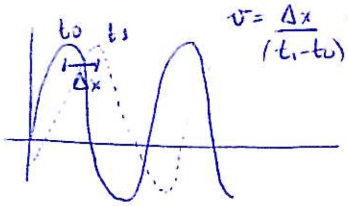
For any dispersion relation

phase veloc. $\boxed{v_p = \frac{\omega}{q}}$ — velocity of pure / single wave

group veloc. $\boxed{v_g = \frac{\partial\omega}{\partial q}}$ — velocity of wave created by combination of 2 or more

Example:

one wave: $A\cos(qx-\omega t)$



$$v = \frac{\Delta x}{(t_1-t_0)} \Rightarrow v_p = \frac{\lambda}{T}$$

$$\Downarrow$$

$$v_p = \frac{2\pi}{q}\frac{\omega}{2\pi}$$

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

two waves: $A\cos\left((q-\Delta q)x + (\omega-\Delta\omega)t\right)$

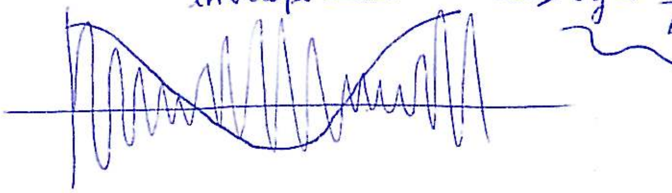
$A\cos\left((q+\Delta q)x + (\omega+\Delta\omega)t\right)$

$$A\cos\left[(qx-\omega t) - (\Delta q x - \Delta\omega t)\right] + A\cos\left[(q\ldots) + (\quad)\right]$$

$$\cos(a+b) + \cos(a-b) = \cos a\cos b - \sin a\sin b + \cos a\cos b + \sin a \sin b$$

$$\underbrace{2A\cos(\Delta q x - \Delta\omega t)}_{\text{envelope}}\cos(qx-\omega t)$$

envelope $\Longrightarrow$ $\boxed{v_g = \frac{\Delta\omega}{\Delta q}}$

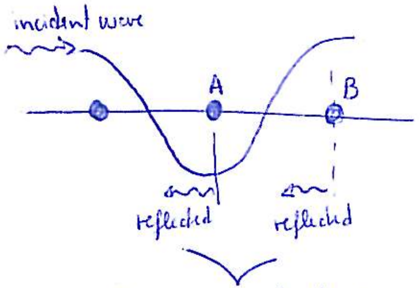


Study group velocity

∘) λ long $\rightarrow \omega = v_s q \rightarrow \boxed{v_g = v_p = v_s}$

no dispersion takes place
lattice as a continuum

∘) λ short $= \boxed{2a}$
$\boxed{q = \pi/a} \rightarrow \omega = \omega_m = \text{const} \rightarrow \boxed{v_g = 0}$



like in Bragg's law

they are out of phase, but since $\boxed{d_{AB} = \lambda/2}$
by the time $\overset{\text{wavelet}}{B}$ reaches $\overset{\text{wavelet}}{A}$ they are in phase
and interfere constructively

at $q = \pi/a$, all scattered wavelets interfere constructively → max. reflection

↳ ~~[illegible]~~

reflected wave combines with incident $\Rightarrow$ standing wave $\Rightarrow \boxed{v_g = 0}$

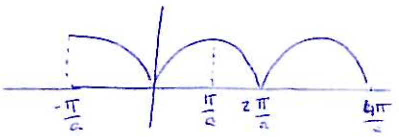
doesn't appear to move

think of incident waves as pulses

2-13-(04)

Symmetry in q-space: the 1st Brillouin zone

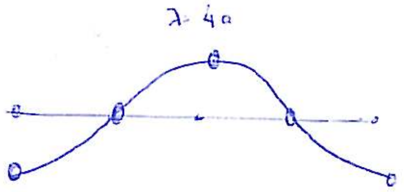
dispersion curve: periodic in q-space

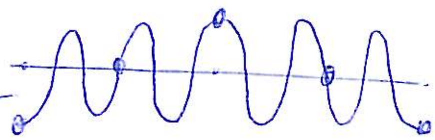


$\omega(q+2\pi/a) = \omega(q)$

consider $\begin{cases} q = \pi/2a \longrightarrow \lambda = 4a \\ q' = \underbrace{q + 2\pi/a}_{\frac{5\pi}{2a}} \longrightarrow \lambda = \frac{4a}{5} \end{cases}$

Fig 3.21a





represent same physical motion of atoms

both modes = frequency

this has more oscillations, but we only see atoms

in discrete lattice

λ, for a certain wave is not unique, ≠ λ lead to same ω by translation in q-space

For unique representation, choose interval in q-space of length $2\pi/a$

$\boxed{-\frac{\pi}{a} < q < \pi/a}$ ⇒ then specify wave by a unique q and λ

↳ λ is the largest possible for set of atomic displacements

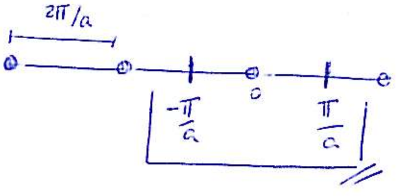
all λ's corresponding to additional oscillations are eliminated

this is the $\boxed{\text{1st Brillouin zone}}$

real lattice

reciprocal ⟹

$\vec{a}^* = \frac{2\pi(\vec{b}\times\vec{c})}{\vec{a}\cdot(\vec{b}\times\vec{c})}$



↳ we may confine our consideration of q-space to the $\boxed{\text{1st zone}}$

Note: $q = \frac{\pi}{a} \Rightarrow \lambda = 2a \Rightarrow$ distance between atoms $= \boxed{\frac{\lambda}{2}} \rightarrow$ Bragg's condition

2-13-05

symmetry: $\omega(-q) = \omega(q)$

wave traveling to the left with same λ

wave traveling to the right

Number of modes in the first zone

periodic boundary conditions

$$u_n = A e^{i(qx_n - \omega t)}$$

$$u_0 = u_L \Rightarrow 1 = e^{iqL} \qquad \Rightarrow \boxed{q = n\frac{2\pi}{L}}$$

total number of points inside the first zone

$$\left.\begin{array}{l} 1 \rightarrow 2\pi/L \\ x \rightarrow \frac{2\pi}{a} \end{array}\right\} \quad \left(\frac{2\pi}{a}\right)\frac{L}{2\pi} = \frac{L}{a} = \boxed{N}$$

total number of atoms (or unit cells) in the lattice

values of q inside 1st zone describes all possible vibration modes of the lattice

↳ must be equal to the total number of degrees of freedom, i.e. Ⓝ

Specific Heat : Exact Theory

$$E = \int \bar{\epsilon}(\omega)\, g(\omega)\, d\omega$$

$$C_v = \int \frac{\partial \bar{\epsilon}(\omega)}{\partial T} \boxed{g(\omega)}\, d\omega$$

use density of states obtained by considering discreteness of the lattice

Example : 1D monatomic lattice

$$\omega(q) = \omega_m \left|\sin(qa/2)\right|$$

$$\underbrace{\text{number of modes in } (\omega, \omega + d\omega)}_{g(\omega)\, d\omega} = ② \times \underbrace{\text{number of modes in } (q, q+dq)}$$

periodic boundaries: $1 = e^{iqL} \Rightarrow q = \frac{2\pi}{L} n$

$$\left.\begin{matrix} 1 \text{ mode} \rightarrow 2\pi/L \\ x \rightarrow dq \end{matrix}\right\} \Rightarrow \boxed{dq\, \frac{L}{2\pi}}$$

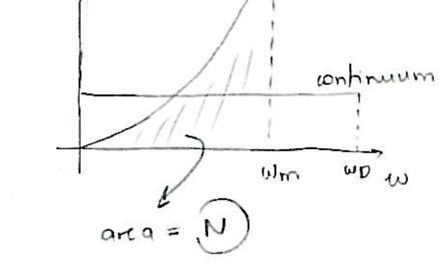
$$\Rightarrow g(\omega)\, d\omega = \frac{L}{\pi}\, dq \Rightarrow g(\omega) = \frac{L}{\pi} \frac{1}{d\omega/dq}$$

$$g(\omega) = \frac{L}{\pi} \frac{2}{\omega_m a} \frac{1}{\cos(qa/2)}$$

$$\boxed{g(\omega) = \frac{2L}{\pi a \omega_m} \left[\cos(qa/2)\right]^{-1}}$$

$$\left\{\begin{matrix} \underset{\omega \to 0}{q \to 0} \Rightarrow g(\omega) = \frac{2L}{\pi a \omega_m} \\ \underset{\omega = \omega_m}{q = \pi/a} \Rightarrow g(\omega) \to \infty \end{matrix}\right.$$

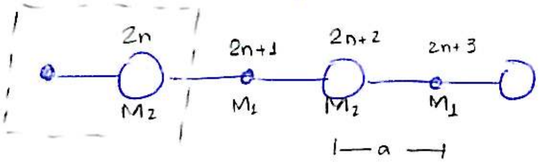
↳ nothing above out of BZ



2-25-②

1D diatomic lattice

1 unit cell: has length 2a



there are N unit cells
2N atoms
N of each kind

coupled eqs.

$$\begin{cases} M_1 \dfrac{d^2 u_{2n+1}}{dt^2} = -\alpha\,(2u_{2n+1} - u_{2n+2} - u_{2n}) \\ M_2 \dfrac{d^2 u_{2n+2}}{dt^2} = -\alpha\,(2u_{2n+2} - u_{2n+3} - u_{2n+1}) \end{cases}$$

there are 2N coupled equations

$$\begin{pmatrix} u_{2n+1} \\ u_{2n+2} \end{pmatrix} = \begin{pmatrix} A_1 e^{iqX_{2n+1}} \\ A_2 e^{iqX_{2n+2}} \end{pmatrix} e^{-i\omega t}$$

$$\begin{cases} M_1 A_1 (-\omega^2)\, e^{iq\cancel{X_{2n+1}}} = -\alpha\,(2A_1 e^{iq\cancel{X_{2n+1}}} - A_2 e^{iq\cancel{X_{2n+1}}} e^{iqa} - A_2 e^{iq\cancel{X_{2n+1}}} e^{-iqa}) \\ M_2 A_2 (-\omega^2)\, e^{iqX_{2n+2}} = \end{cases}$$

HW

$$\begin{cases} -M_1 A_1 \omega^2 + 2\alpha A_1 = 2\alpha \cos(qa)\, A_2 \\ \end{cases}$$

$$\begin{pmatrix} 2\alpha - M_1\omega^2 & -2\alpha\cos(qa) \\ -2\alpha\cos(qa) & 2\alpha - M_2\omega^2 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = 0$$

solutions comes from
det = 0

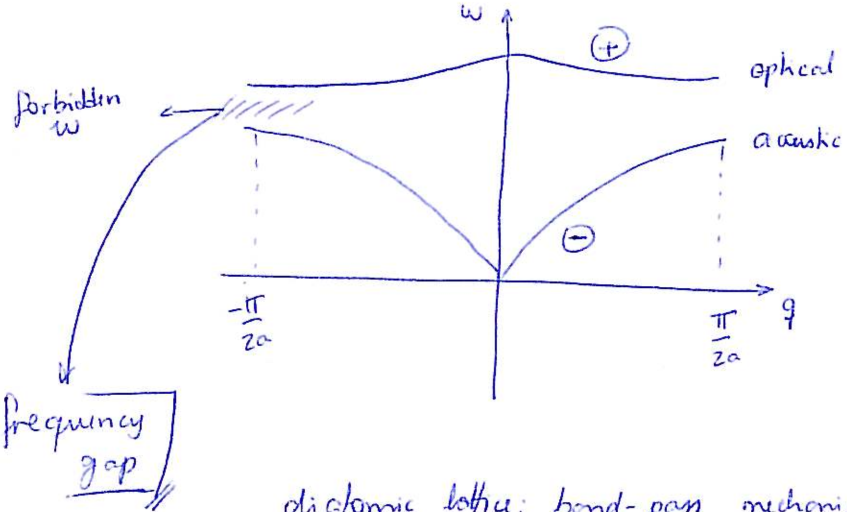
or $\begin{cases} ax + by = 0 \\ bx + cy = 0 \end{cases}$ $\begin{cases} -ab\cancel{x} - b^2 y = 0 \\ +abx + acy = 0 \end{cases}$

$$\underbrace{(ac - b^2)}_{\text{det}}\, y = 0$$

HW

$$w^2 = \alpha\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \alpha\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2(qa)}{M_1M_2}}$$

two dispersion relations
two branches



diatomic lattice: band-pass mechanical filter

Acoustic

$q \to 0$ $\boxed{w \to 0}$ sin → 0

$\lambda \to \infty$

$\boxed{M_2 > M_1}$

$q = \pi/2a$ $$w^2 = \alpha\frac{(M_2+M_1)}{M_1M_2} - \frac{\alpha\sqrt{(M_2+M_1)^2 - 4M_1M_2}}{M_1M_2} = \frac{\alpha(\cancel{M_2}+M_1) - \alpha(\cancel{M_2}-M_1)}{M_1M_2}$$

$\boxed{w = \sqrt{\frac{2\alpha}{M_2}}}$ ← $\boxed{\text{MAX}}$

Optical

$q \to 0$

$\lambda \to \infty$

$$w = \sqrt{2\alpha\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}$$

↗ MAX

$q = \pi/2a$

$\boxed{w = \sqrt{\frac{2\alpha}{M_1}}}$

$\boxed{q=0 \quad \lambda \to \infty}$

Acoustic

$\underline{\omega = 0}$

$2\alpha A_1 - 2\alpha A_2 = 0 \Rightarrow \boxed{A_1 = A_2}$ same amplitude

they are in phase

CM moves back and forth

cell oscillates as rigid body

Optical (frequency in IR region)

$$\omega = \sqrt{2\alpha\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}$$

HW

$$\boxed{M_1 A_1 = -M_2 A_2}$$

$$\frac{A_2}{A_1} = -\frac{M_1}{M_2}$$

they are out of phase

HW: present ③D

Thermal Conductivity

$T_2 > T_1$

heat flows / diffuses
down the gradient temperature

thermal conductivity

$\oplus$

$$\boxed{j} = -\boxed{K}\frac{dT}{dx}$$

flux of thermal energy } = energy transmitted across unit area per unit time

this is a diffusive process, carriers suffer frequent collision (there is a mean free path)

⇒ gradient

if there was no deflection, flux would depend on ΔT not on gradient
(ballistic transport)

Carriers of heat ?

metal { free e^-
phonons

insulator { phonons

phonon gas (like molecules in ordinary gas)

└ but

$\overline{v}_{\text{atoms in lattice}} \propto T^{1/2}$ but $v_{\text{phonons}} = \boxed{v_s}$ → depends only on the material

at T_2 ⇒ more phonons (atoms displace faster)
at T_1 ⇒ few phonons

} phonons/energy flows from more to less concentration

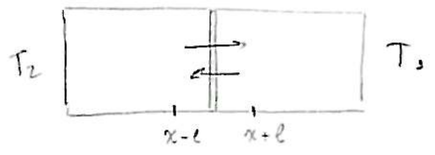
From Kinetic theory

$$K = \frac{1}{3}\, C\, \bar{v}\, l$$

↳ mean free path

↳ average particle velocity
here: phonon velocity

↳ heat capacity per unit volume



$n = \frac{N}{V}$ concentration of phonons

$\frac{1}{3} n$ have velocities along the x direction

$\frac{1}{6} n$ $(+x)$ and $\frac{1}{6}$ $(-x)$

·) how many phonons cross plane per unit time per unit area?
on the average there are $\frac{1}{6} n \bar{v}$ phonons per unit time per unit area

$$\frac{1}{6} n \bar{v} = \frac{1}{6} \frac{N}{V} \frac{l_x}{t} = \frac{1}{6} \frac{N}{A t}$$

·) how much energy do they carry?

$\frac{1}{6} n \bar{v} \bar{E}(x-l)$ mean energy transported by unit time per unit area across plane in $(+x)$

$\frac{1}{6} n \bar{v} \bar{E}(x+l)$; " to $(-x)$

$$\underbrace{\left(n \frac{\partial \bar{E}}{\partial T}\right)}_{C} \frac{\partial T}{\partial x}$$

$$J = \frac{1}{6} n \bar{v} \bar{E}(x-l) - \frac{1}{6} n \bar{v} \bar{E}(x+l)$$

$$= \frac{1}{6} n \bar{v} \left[\bar{E}(\cancel{x}) - l \frac{\partial \bar{E}}{\partial x} - \bar{E}(\cancel{x}) - l \frac{\partial \bar{E}}{\partial x} \right] = \frac{1}{3} \left(n \frac{\partial \bar{E}}{\partial x} \right) \bar{v}\, l$$

$$\boxed{= \frac{1}{3} C \bar{v} l \frac{dT}{dx}}$$

$$K = \frac{1}{3} C \bar{v} \, \ell$$

$\bar{v}$ ↓ no dependence on T

C → $\begin{cases} \boxed{\text{const}} & \text{at T large} \\ \propto \boxed{T^3} & \text{at T small} \end{cases}$

$\underline{\underline{\ell}}$: average distance phonon travels between collisions

$\left\{ \begin{array}{l} \text{phonon - phonon} \\ \text{phonon - impurity} \\ \text{phonon - boundaries} \end{array} \right.$ $\left. \begin{array}{l} \\ \\ \end{array} \right\}$ concentration increases with T ⇒ $\ell \propto 1/T$

dominant process at high T

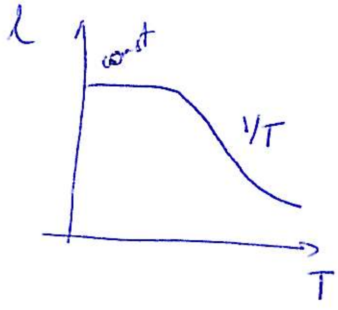
$\boxed{\ell \sim 1/T}$

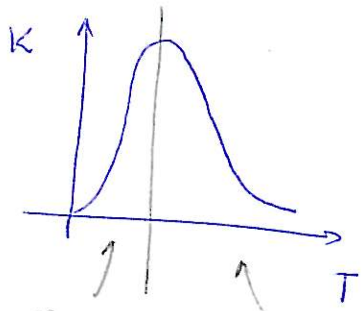
at low T – number of phonons decrease and they have long λ (short ω)

↳ can't be scattered by impurities only by boundaries

↳ geometrical effects

$\boxed{\ell \sim D}$





low T

$\left. \begin{array}{l} \ell \sim D \\ C \sim T^3 \end{array} \right\}$ $\boxed{K \sim T^3}$ //

high T

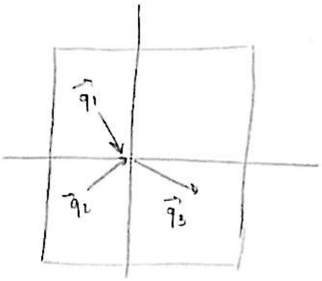
$\left. \begin{array}{l} \ell \sim 1/T \\ C - \text{const} \end{array} \right\}$ $\boxed{K \sim 1/T}$ //

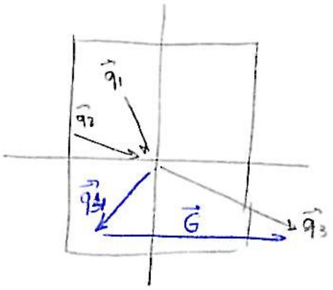
Phonon- phonon collision

$\vec{q_1} + \vec{q_2} = \vec{q_3}$ two phonons collide and produce a 3rd one

if $\vec{q_3}$ is inside Brillouin zone: normal process

if $\vec{q_3}$ is out : umKlapp process - dominant process for thermal resistivity } $\vec{q_4}$ is almost opposite to original phonons





$\vec{q_3} = \vec{q_4} + \vec{G}$
reciprocal lattice vector

coming from discussion on 1st BZ

$\omega(q+2\pi/a) = \omega(q)$ 2 waves are physically identical

$$\boxed{q' = q + \underbrace{\frac{2\pi}{a} n}_{\vec{G}}}$$

Metals

$\underbrace{\text{valence } e^-}_{\text{becomes conduction } e^-}$ loosely bound – each belongs to the whole crystal

Na, K, Cu, ... (monovalent) number of conduction e^- = atoms

Be, Mg, Zn.... (divalent) number of conduc. e^- is twice the atoms

ρ_m : density of the substance $\qquad \rho_m = \frac{M}{V}$

$$\text{atom concentration} = \frac{N}{V} = \frac{N}{M}\rho_m = N_A \, \rho_m \underbrace{\boxed{\frac{N}{N_A M}}}_{\frac{n_{moles}}{M} = \frac{1}{M'} \text{ atomic weight}}$$

$$= N_A \frac{\rho_m}{M'}$$

$$e^- \text{ concentration} = \boxed{\underbrace{Z_v}_{\text{atomic valence}} \frac{\rho_m N_A}{M'}}$$

Free e^- gas

simplified model: e^- are free, no collisions among them, just reflection from the surface and collisions with phonons and impurities

like molecules in ideal gas

↳ but { have charges (~ plasma)
large concentration

works because interaction with ion is small and e^-s repel each other

Electrical Conductivity

$$V = R\,I \qquad\qquad I = \frac{V}{R}$$

(Ohm's law)

potential difference

resistance of the wire

current

from a microscopic perspective...

some definitions $J = \frac{I}{A}$ $\qquad \mathcal{E} = \frac{V}{L}$ $\qquad R = \frac{L\rho}{A}$

current density

cross section of wire

electric field

length of wire

electrical resistivity

$$I = \frac{V}{R} \Rightarrow JA = \frac{\mathcal{E}\cancel{L}A}{\cancel{L}\rho} \Rightarrow J = \frac{1}{\rho}\mathcal{E} \Rightarrow \boxed{J = \sigma\,\mathcal{E}}$$

conductivity

current is due to the motion of conduction e^- under the field

one e: force exerted by field: $-e\mathcal{E}$

friction force due to collisions: $-m^*\frac{v}{\tau}$

m^* - effective mass different from free e^- because of interaction with lattice

τ - collision time or relaxation time

Newton's law

$$m^*\frac{dv}{dt} = -e\mathcal{E} - m^*\frac{v}{\tau}$$

•) if $\mathcal{E} = 0$, collisions ⇒ relaxation

$$m^*\frac{dv}{dt} = -m^*\frac{v}{\tau} \Rightarrow v(t) = v_0\,e^{-t/\tau}$$

approaches zero exp. in time with characteristic time τ

•) $\mathcal{E} \neq 0$ keeps flow

steady state: $\frac{dv}{dt} = 0 \Rightarrow \boxed{v = -\frac{e\tau}{m^*}\mathcal{E}}$

drift velocity

$$\overset{v_d}{\text{drift velocity}} \neq \overset{v_r}{\text{random velocity}}$$

$\uparrow$ caused by field

$\uparrow$ random motion in the absence of field

$$\overline{\underline{v_r >> v_d}}$$

$$J = \left(-\frac{N}{V} e\right) v_d \qquad \text{because} \qquad \frac{Ne}{V} v_d = \frac{Ne}{V} \frac{l}{t} = \frac{Ne}{At}$$

$J \downarrow$ charge crossing per unit area per unit time

$$J = -\frac{N}{V} e \, v_d = -\frac{N}{V} e \left(-\frac{e\tau\mathcal{E}}{m^*}\right) = \boxed{\frac{N}{V}\frac{e^2\tau}{m^*}}\mathcal{E}$$

$$\boxed{\sigma = \frac{N}{V}\frac{e^2\tau}{m^*}}$$

increases with $\frac{N}{V}$

∟ more current carriers

decreases with m^*

∟ more inertia

increase with τ

∟ time between 2 collisions

↙

<u>mean free lifetime</u>

larger τ – more e^- can accelerate

Electrical resistivity vs. temperature

$$\sigma = \frac{1}{\rho} = n_e \frac{e^2 \tau}{m^*} \qquad n_e = N/V$$

$$\rho = \frac{m^*}{n_e e^2} \frac{1}{\tau}$$

frequency of collisions

$$\frac{1}{\tau} = \frac{1}{\tau_i} + \frac{1}{\tau_{ph}}$$

coll. with impurities

coll with phonons

$$\rho = \frac{m^*}{n_e e^2} \frac{1}{\tau_i} + \frac{m^*}{n_e e^2} \frac{1}{\tau_{ph}}$$

do not dep. on T only on concentration of impurities

dip. on T

$$\boxed{\rho = \rho_i + \rho_{ph}}$$

→) $\tau_i = \frac{l_i}{v_F}$ → mean free path for collision with impurities

σ_i l_i

$$n_i = \frac{N_i}{V} = \frac{1}{l_i \sigma_i}$$ → cross section of impurities

$$l_i = \frac{1}{\sigma_i n_i} \longrightarrow \frac{1}{\tau_i} = \underline{\sigma_i n_i v_F}$$

→) $\tau_{ph} = \frac{l_{ph}}{v_F}$ $\qquad l_{ph} = \frac{1}{n_{ion} \sigma_{ion}}$ → area of displacement / vibration of ions

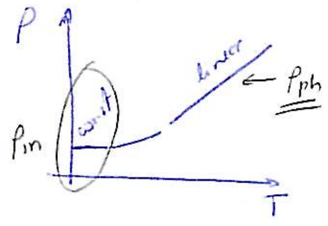
$$\sigma_{ion} \simeq \pi \langle x^2 \rangle \longrightarrow \frac{1}{2} \left(\frac{1}{2} \alpha \langle x^2 \rangle \right) = \frac{\hbar \omega}{e^{\hbar\omega/kT} - 1}$$

total energy of harm. oscillator

on the average ½ of it goes to potential energy

$$\frac{1}{\tau_{ph}} \propto v_F \, n_{ion} \frac{\hbar \omega}{e^{\hbar\omega/kT} - 1}$$

↳ $\rho_{ph} \sim T$ when T is large



when T is small → get $\underbrace{e^{-\hbar\omega/kT}}_{\text{Einstein}}$ although it is $\underbrace{T^5}_{\text{Debye}}$

Heat Capacity

free - e^- model $\Rightarrow$ free particles obey classical laws of mech.

from kinetic theory of gases: free particle in equilibrium at T has average energy $\frac{3}{2}kT$

$$\hookrightarrow \langle E \rangle = N_A\left(\frac{3}{2}kT\right) = \frac{3}{2}RT$$

energy per mole

$$C_e = \frac{\partial E}{\partial T} = \boxed{\frac{3}{2}R}$$

e^- heat capacity per mol

total heat capacity in $\boxed{\text{metals}}$: e^- + phonons

$$C = C_{ph} + C_e$$

$$= 3R + \frac{3}{2}R = \boxed{\frac{9}{2}R}$$

but experiments show that $C \approx 3R$ at high T as for insulators

$\swarrow$

Energy of e^- in metal is quantized. Each energy level can have at most ② e^- $\leftarrow$ Pauli exclusion principle

one with spin ↑ one with spin ↓

The energy of the highest occupied level is called Fermi energy or Fermi level

$\Rightarrow$ even at the lowest possible temperatures, electron system has considerable amount of energy.

Ex: E_F for 1D $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \epsilon_n\psi_i$ $\psi = A\sin\left(\frac{n\pi x}{L}\right)$ $\epsilon_n = \frac{\hbar^2}{2m^2}\left(\frac{n\pi}{L}\right)^2$

N even - number of electrons $\Rightarrow$ $\boxed{\epsilon_F = \frac{\hbar^2}{2m^2}\left(\frac{N}{2}\frac{\pi}{L}\right)^2}$

in 3D

$$E_F = \frac{\hbar^2}{2m}\,\frac{\pi^2}{L^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{\hbar^2}{2m}\,\frac{\pi^2}{L^2}\,n_F^2$$

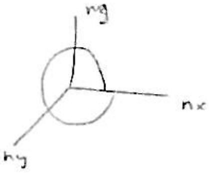
sphere of radius nF

number of states with energy < E_F

$$N = 2 \times \frac{1}{8} \times \frac{4}{3}\pi n_F^3$$

$\frac{1}{8}$ of sphere

for n_x, n_y, n_z positive



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

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

$$\boxed{L^2 = V^{2/3}}$$

$$\frac{\hbar^2\,\pi^{6/3}}{2m\,L^2}\,\frac{(3N)^{2/3}}{\pi^{2/3}} \longrightarrow \pi^{4/3}$$

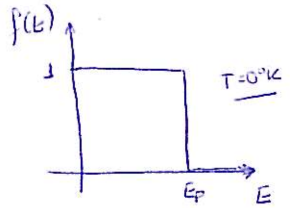
$$\boxed{E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}}$$

Distribution function: dist. of e^- among the levels

$f(E)$: prob. that level E is occupied by an e^-

at $T = 0°K$

$$f(E) = \begin{cases} 1 & E < E_F \\ 0 & E > E_F \end{cases}$$



for $T > 0°K$

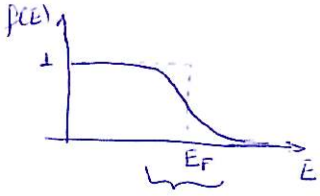
thermal energy excites the e^-s

but e^- well below E_F cannot absorb energy, because higher levels are already occupied

only e^- close to E_F can be excited

↳ dist. function:

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



only close to E_F
some variation from $T = 0°K$

fraction $\frac{KT}{E_F}$ of e^- is affected and absorbs energy KT

number of e^- excited per mole: $N_A \left(\frac{KT}{E_F}\right)$

Note
($KT \sim 0.025$ eV at room Temp
$E_F \sim 5$ eV in metals)

$$\bar{E} = N_A \left(\frac{(KT)^2}{E_F}\right)$$

$$C_e = 2R \left(\frac{KT}{E_F}\right)$$

↑ reduced by this amount – in agreement with experiment

Fermi temperature

$$E_F = K T_F \Rightarrow \boxed{C_e = 2R \frac{T}{T_F}} \,//$$

exact evaluation: $\boxed{C_e = \frac{\pi^2}{2} R \frac{KT}{E_F}} \,//$

linear function of temperature ≠ lattice heat capacity

Fermi surface

$$E = \frac{1}{2} m^* v^2$$

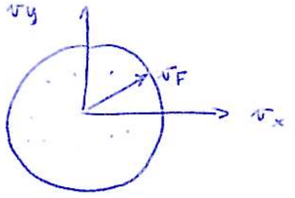
$$\boxed{E_F = \frac{1}{2} m^* v_F^2}$$

maximum energy — maximum velocity

of conduction electrons

v_F : Fermi speed

In velocity space



→ no points out of $\boxed{\text{Fermi}}$ sphere

When T is raised some few e^- are excited to the outside of the $\boxed{\text{Fermi}}$ surface

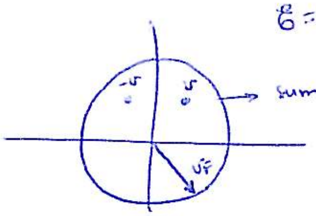
Fermi surface
also
Fermi ~~velocity~~ speed
} are indep. of temperature

$$E_F = 5\,eV \Rightarrow \underset{\text{very high}}{v_F} = \left(\frac{2E_F}{m^*}\right)^{1/2} \simeq \left(\frac{2 \times 5 \times 1.6 \times 10^{-9}}{9 \times 10^{-31}}\right)^{1/2} \simeq \underbrace{10^6\, m/s}_{\frac{1}{100} \text{ of } c}$$

Fermi surface — very imptt in solid-state studies, such as transport

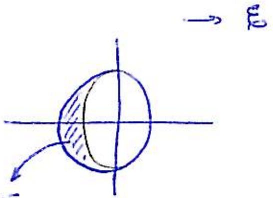
Electrical Conductivity: effects of Fermi surface (FS)

$\mathcal{E} = 0$



→ sum of their currents = zero

$\mathcal{E} \neq 0 \rightarrow v_d = -\frac{e\tau}{m^*}\mathcal{E} \Rightarrow$



these e^- produce the observed current

fraction $\boxed{\frac{v_d}{v_F}}$

$$J = (-n_e e)\frac{v_d}{v_F} \cdot v_F$$

$J = (-n_e e)\, v_d$ ← old result but different interpretation

small fraction $\frac{v_d}{v_F}$ with high speed v_F

$$\sigma = \frac{n_e e^2 \boxed{\tau_F}}{m^*}$$ ↖ collision time of an e^- in the FS

Current is transported by e^- lying close to the Fermi surface

inner e^- are irrelevant for conduction.

Thermal Conductivity

$$J = -K \frac{dT}{dx}$$

$$K = \underset{\substack{\downarrow \\ \text{negligible} \\ \text{in metals}}}{K_{ph}} + K_e \qquad K_e = \frac{1}{3} \overset{\nearrow \text{ heat capacity per volume}}{C} \, v \, l$$

$$K_e = \frac{1}{3}\left(\frac{\pi^2 n_e K^2 T}{2 E_F}\right) \overbrace{v_F \; l_F}^{e^- \text{ in the Fermi surface}}$$

$$E_F = \frac{1}{2} m^* v_F^2$$

$$K_e = \frac{1}{3} \, \frac{\pi^2 n_e K^2 T \; \cancel{v_F} \; l_F}{m^* \, v_F^{\cancel{2}}} \rightarrow \tau_F \qquad v_F = \frac{l_F}{\tau_F}$$

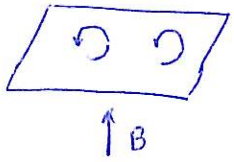
$$\boxed{K_e = \frac{\pi^2 n_e K^2 T \, \tau_F}{3 m^*}} \qquad \sigma = \frac{n_e e^2 \tau_F}{m^*}$$

$$\frac{K_e}{\sigma T} = \frac{1}{3}\left(\frac{\pi K}{e}\right)^2 \longrightarrow \text{Lorenz number} \sim \text{same for all metals}$$

electrical and thermal conductivities are related

Effects arising from the conduction e^- in magnetic field

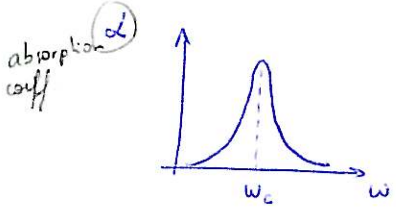
•) Cyclotron resonance



$$w_c = \frac{eB}{m^*}$$

} signal
(electromagnetic signal)

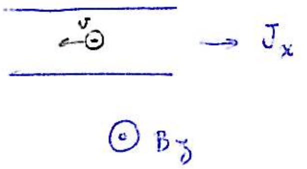
will be absorbed
$w_S \sim w_c$
(e^- and wave are in phase)



cyclotron resonance: used to measure e^- effective mass

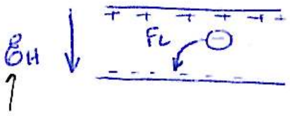
find w_c from absorption curve
know B
} m^*

•) Hall effect



Lorentz force

$$\vec{F}_L = e\,(\vec{v} \times \vec{B}) \rightarrow (y)$$



additional electric field appears (Hall field) ⇒ new force opposite to F_L appears → F_H

$$F_H = F_L$$

$$e\,\mathcal{E}_H = e\,v\,B \Rightarrow \boxed{\mathcal{E}_H = v_x B}$$

in terms of measurable quantities

$$J = (-n_e e)\,v_x \Rightarrow \mathcal{E}_H = \frac{J}{(-n_e e)} B \Rightarrow \frac{\mathcal{E}_H}{JB} \rightarrow \text{can measure } n_e$$

→ Hall const

in magnetic field current is not influenced by field
it still flows in the x direction

AC conductivity

$$\mathcal{E} = \mathcal{E}_0 \, e^{-i\omega t} \longrightarrow v = v_0 \, e^{-i\omega t}$$

$$m^* \frac{dv}{dt} = -e\mathcal{E} - \frac{m^* v}{\tau}$$

$$\left(m^* v_0 (-i\omega) + \frac{m^* v_0}{\tau} = -e\mathcal{E} \right) \cancel{e^{-i\omega t}}$$

$$m^* v_0 (1 - i\omega\tau) = -e\tau\mathcal{E}$$

$$v = -\frac{e\tau}{m^*} \frac{1}{(1-i\omega\tau)} \mathcal{E}$$

$$\boxed{\tilde{\sigma} = \frac{\sigma_0}{1-i\omega\tau}} \longrightarrow \tilde{\sigma} = \frac{\sigma_0}{(1-i\omega\tau)} \frac{(1+i\omega\tau)}{(1+i\omega\tau)} = \underbrace{\overbrace{\frac{\sigma_0}{(1+\omega^2\tau^2)}}^{\text{Re}}}_{\text{predominant when } \omega\tau \ll 1} + i \underbrace{\overbrace{\frac{\omega\tau\sigma_0}{(1+\omega^2\tau^2)}}^{\text{Im}}}_{\text{predominant when } \omega\tau \gg 1}$$

Exercise : in 3D

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

The atom He^3 has spin 1/2 and is a fermion. The density of liquid He^3 is 0.081 g/cm³ near absolute zero. Calculate the Fermi energy E_F and the Fermi temperature T_F

$$\rho = \frac{81\times10^{-3}}{cm^3}\, g \quad \Rightarrow \quad \frac{n_{moles}}{cm^3} = \frac{81\times10^{-3}}{③} = 27\times10^{-3}$$

atomic mass of $He^{③}$

$$\Downarrow$$

$$\text{concentration: } \frac{N}{V} = n_{He} = N_A\ 27\times10^{-3}/cm^3 = (6.02\times10^{23})(27\times10^{-3}) = \boxed{16\times10^{21}\ \frac{atoms}{cm^3}}$$

$N_A = 6.02\times10^{23}$ /mol

$$m_{He^3} = (3.017)\times(1.66\times10^{-24}\, g) = \boxed{5.01\times10^{-24}\, g}$$

$1\, u = 1.661\times10^{-24}\, g$
(atomic unit mass)

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{2/3} \simeq \boxed{7\times10^{-16}\ erg}$$

$\hbar = 1.054\times10^{-34}\times10^{7}$ erg.s

NOTE

where does $w = \frac{e\,B}{m^*}$ in cyclotron resonance comes from ?

Lorentz force :

$$\vec{F} = e\,(\vec{v} \times \vec{B})$$

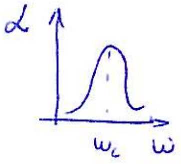
$$F = ma \xrightarrow{} \text{centripetal acceleration} = m\,\frac{v^2}{r}$$

$$e\,v\,B = m\,\frac{v^2}{r} \Rightarrow v = \frac{eBr}{m}$$

$$v = \frac{2\pi r}{T} \Rightarrow \frac{eB\cancel{r}}{m} = \boxed{2\pi\,\cancel{r}\,f} = \omega\,\cancel{r}$$

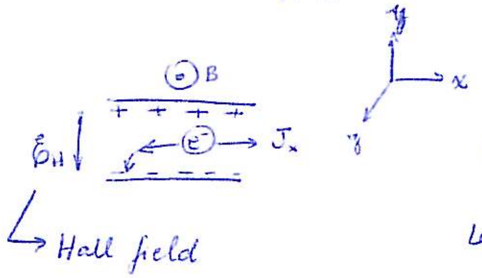
$$\Rightarrow \boxed{\omega_c = \frac{eB}{m^*}}$$

→) signal : greatest absorption when $w = w_c$



→) measure m^* (effective mass)

Hall effect



negative in y

$F_L = (-) e v_x B$

Lorentz force

field opposes F_L, accumulation until $F_H = F_L$

$$-e\mathcal{E}_H = -e v_x B \Rightarrow \mathcal{E}_H = v_x B$$

$$J_x = (-ne)\, v_x$$

$$J_x = (-ne)\frac{\mathcal{E}_H}{B} \Rightarrow \boxed{\mathcal{E}_H = -\frac{1}{ne} J_x B}$$

→) $R_H = \dfrac{\mathcal{E}_H}{J_x B} = \boxed{-\dfrac{1}{ne}}$ Hall constant

→) $\mathcal{E}_H$, J_x, B measurable quantities ⇒ use R_H to find ⓝ
electron concentration

⇒ to find signs of current carriers

→) after equilibrium
current is not influenced by field

- **Test** Ch3 (section 3.6 on) [Monday 24]
  Ch 4
  Ch. 5 - up to what is covered on Monday
  (assignment ↑ given on Wednesday)

- give assignment, discuss solutions

- Start Ch. 5

→) The He^3 atom has spin 1/2 and is a fermion. The density of liquid He^3 is 0.081 g/cm^3 near absolute zero. Calculate the Fermi energy E_F and the Fermi temperature T_F

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

$m_p = 1.6\times10^{-24}$ g
$N_A = 6\times10^{23}$/~~atoms~~ mol
$\hbar$, K_B

$\rho = 0.081$ g/cm^3

$$\frac{\#\,\text{moles}}{cm^3} = \frac{\rho}{③} \Rightarrow n = \left(\frac{\rho}{3}\right) \times N_A$$

$m_{He} = 3\,m_p$

⑥ → use Table 4.1, need K in eV/K

⑦ fraction ~ KT/E_F (page 153)

→) conductivity for AC field $\underline{\mathcal{E} = \mathcal{E}_0 e^{-i\omega t}}$

$$m^* \frac{dv}{dt} = -e\mathcal{E} - m^*\frac{v}{\tau} \qquad v = v_0 e^{-i\omega t}$$

$$m^* v_0(-i\omega) = -e\mathcal{E}_0 - m^*\frac{v_0}{\tau} \rightarrow \frac{m^*}{\tau}(1-i\omega)v_0 = -e\mathcal{E}_0 \rightarrow v_0 = -\frac{e\tau}{m^*}\frac{1}{(1-i\omega)}\mathcal{E}_0$$

$$J = (-n_e e)v = \boxed{\frac{n_e e^2\tau}{m^*}}\,\mathcal{E}\frac{1}{(1-i\omega)} \rightarrow \boxed{\sigma = \frac{\sigma_0}{(1-i\omega)}}$$

has real and imaginary part

Ch 5 : (Metals : energy bands in solids)

Failure of the free e^- model

-) doesn't explain ⊕ Hall const / doesn't predict holes
-) Fermi surface - usually not a sphere

↓

prob. is it doesn't take into account crystal potentials caused by ions

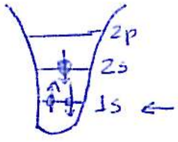
Energy spectra in atoms, molecules, and solids

Atomic levels

one Li atom (3 e^-)

e^- moves in its potential

Schröd. eq. - discrete energy levels (like H atom)



← Pauli exclusion principle

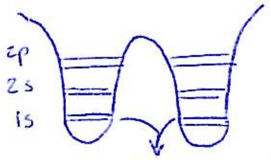
(1s shell is complete)

Molecular levels [Rood A.7]

two Li atoms - form Li molecule (Li_2)

double potential is seen by e^-

energy spectrum: discrete doublet



degeneracy lift by atom interaction

eigenstates of e^- : superpositions $\psi_1 + \psi_2$, $\psi_1 - \psi_2$ } molecular orbitals

(6 e^- : 4 in the 1s molecular doublet
2 in lower level of the 2s doublet)

splitting deps. { on the internuclear distance : closer, stronger perturbation, larger splitting
on the atomic orbital : 1s radius is small, tightly bound
2s larger radius, loosely bound, larger splitting

polyatomic molecules : 3 atoms → triplet
4 atoms → quadruplet

solid → { like a gigantic molecule, splitting : N close sublevels → energy bands
+ gaps of forbidden energy

crystal orbitals

ψ - extend throughout the solid - DELOCALIZED

while atomic orbitals are localized

Bloch function

behavior of e^- in solid described by Schröd. eq.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

$\downarrow$

e - atom
e - e interactions

$V(\vec{r}) = V(\vec{r}+\vec{R})$: potential is $\left\{\begin{array}{l}\text{periodic / same}\\ \text{symmetry of lattice}\end{array}\right.$

$\downarrow$

lattice vector

$\swarrow$ wave vector : $\vec{p} = \hbar\vec{k}$

.) If e^- was free : $\psi(\vec{r}) \propto e^{i\vec{k}.\vec{r}}$

but potential $\Rightarrow$ $\boxed{\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}.\vec{r}}\,\underbrace{u_{\vec{k}}(\vec{r})}}$ $\longleftarrow$ Bloch function

Bloch theorem

$\underbrace{u_{\vec{k}}(\vec{r})}$ modulates the wave, amplitude oscillates periodically from 1 cell to the other

$\downarrow$

same symmetry as lattice

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})$$

because V is periodic, all observables associated with e must be periodic $\rightarrow$ $|\psi(\vec{r})|^2 = |\psi(\vec{r}+\vec{R})|^2$

Bloch function is delocalized throughout the solid like free e, but it also has new properties

Energy bands

energy spectrum results from solving Schröd. eq.

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}u_{\vec{k}}(\vec{r}) \rightarrow \nabla\psi = i\vec{k}\,e^{i\vec{k}.\vec{r}}u(\vec{r}) + e^{i\vec{k}.\vec{r}}\nabla u$$

$$\nabla^2\psi = \left((i\vec{k})^2 + (i\vec{k})\nabla u + (i\vec{k})\nabla u + \nabla^2 u\right)e^{i\vec{k}.\vec{r}}$$

$$(\vec{\nabla}+i\vec{k})^2 u(\vec{r})$$

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

Note: eigenfunctions and eigenvalues dep. on $\vec{k}$

for each $\vec{k}$: a set of discrete energies $E_{1\vec{k}}, E_{2\vec{k}}, \dots$

each **band** $\textcircled{n}$ ~~has~~ covers continuous $\left.\begin{array}{l}\text{energy range}\\ \text{determined}\\ \text{by } \vec{k}\end{array}\right\}$ eigenvalue $E_n(\vec{k})$)

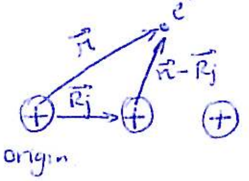
↑ band index

Crystal potential

potential acting on e^- $\Big\}$ $V(\vec{r}) = \underset{\substack{\downarrow\\ \text{interaction}\\ \text{with}\\ \text{ion core}}}{V_i(\vec{r})} + \underset{\substack{\downarrow\\ \text{int. with}\\ \text{other}\\ \text{Bloch } e^-}}{V_e(\vec{r})}$

$$V_i(\vec{r}) = \underset{j}{\sum{}'}\, \underbrace{v_j(\vec{r} - \vec{R}_j)}_{\substack{\text{potential of an}\\ \text{ion located at}\\ \text{lattice vector } \vec{R}_j}}$$

↙ sum over all ions



$V_e(\vec{r})$: e-e int. is very difficult

◦) need state of all e^-

◦) V_e not strictly periodic, e^- are in motion $\Big\}$ many-body problem

Approximation: e-e int is weak (Pauli exclusion, Coulomb repulsion)

↙ they distribute around ions and screen them from other e^-

e-ion int is also weak

$$\hookrightarrow V(\vec{r}) = \underset{j}{\sum{}'}\, \underbrace{v_s(\vec{r} - \vec{R}_j)}_{\text{potential of screened ion}}$$

it is periodic

◦) but how about oscillations of atoms in solid?

↳ smaller than interatomic distance

so atoms at rest is a good approximation below melting point

Band Symmetry

◦) Brillouin zones

find reciprocal basis vectors

$$\vec{a}^* = \frac{2\pi}{\Omega_c}(\vec{b}\times\vec{c})$$

$\vec{b}^*$

$\vec{c}^*$

find reciprocal lattice

$$\vec{G} = n_1\vec{a}^* + n_2\vec{b}^* + n_3\vec{c}^*$$

(lattice vector)

$\perp$ lines to vectors at their midpoints

connect origin to neighboring lattice points

↳ 1 BZ

see Fig. 5.7

in square lattice $\vec{G}_1, \vec{G}_2, -\vec{G}_1, -\vec{G}_2$

2 BZ $\perp$ line to $\vec{G}_1+\vec{G}_2$, $\vec{G}_1-\vec{G}_2$, ... at midpoints

3 BZ $\perp$ line to $(\vec{G}_1+\vec{G}_2)+(\vec{G}_1-\vec{G}_2)$, $(\vec{G}_1+\vec{G}_2)+(-\vec{G}_1-\vec{G}_2)$ ... at midpoints

◦) Symmetry properties

$E_n(\vec{k}+\vec{G}) = E_n(\vec{k})$

$E_n(-\vec{k}) = E_n(\vec{k})$

$E_n(\vec{k})$ has the same rotational symmetry as the real lattice

↳ make it easier to find energies

See Fig. 5.9

(†) <u>Proof</u>

∘) $\psi_{\vec{k}+\vec{G}}$ } has the same form as { $\psi_{\vec{k}}$ $\Rightarrow$ $E_n(\vec{k}+\vec{G}) = E_n(\vec{k})$

because

$$\psi_{\vec{k}+\vec{G}} = e^{i(\vec{k}+\vec{G})\vec{r}}\, u_{\vec{k}+\vec{G}} = e^{i\vec{k}\cdot\vec{r}} \underbrace{\left(e^{i\vec{G}\cdot\vec{r}}\, u_{\vec{k}+\vec{G}}\right)}_{v(\vec{r})}$$

$\swarrow$

but $v(\vec{r}+\vec{R}) = e^{i\vec{G}\cdot(\vec{r}+\vec{R})}\, u_{\vec{k}+\vec{G}}(\vec{r}+\vec{R}) =$

$= e^{i\vec{G}\cdot\vec{r}}\, u_{\vec{k}+\vec{G}}(\vec{r}) = v(\vec{r})$

$v(\vec{r})$ behaves like $u_k(\vec{r})$

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

equivalent to

$\left[\frac{-\hbar^2}{2m}(\nabla + ik)^2 + V\right]^* u_k^* = E_{n}^*(k)\, u_k^*$

} $\Rightarrow$ $E_n(-k) = \underbrace{E_n^*(k)}$

$E_n^*(k) = E_n(k)$ (real

∘) potential has lattice symmetry $\Rightarrow$ so does $E_n(\vec{k})$

One of the few examples of ANALYTICALLY solvable many-body systems

$$H = \sum_n J \left[\sigma_z^n \sigma_z^{n+1} + \sigma_x^n \sigma_x^{n+1} + \sigma_y^n \sigma_y^{n+1} \right]$$

(studied in quantum computing)

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ +i & 0 \end{pmatrix}$$

Pauli matrices describe spin direction

Heisenberg model of spins-1/2 on a chain with N sites

question for Andy

$$\underset{1}{\lfloor \uparrow \rfloor} \quad \underset{2}{\lfloor \downarrow \rfloor} \quad \underset{3}{\lfloor \downarrow \rfloor} \quad \underset{4}{\lfloor \uparrow \rfloor} \quad \ldots$$

interaction described by H (NN int.)

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

eigenstate of σ_z

$$|+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

eigenstate of σ_x

$$\boxed{\begin{aligned} \sigma_z |\uparrow\rangle &= +1\,|\uparrow\rangle \\ \sigma_z |\downarrow\rangle &= -1\,|\downarrow\rangle \end{aligned}}$$

$$\begin{cases} \sigma_+ = \sigma_x + i\sigma_y = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \\ \sigma_- = \sigma_x - i\sigma_y = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} \end{cases}$$

$$\sum_n \sigma_z^n \sigma_z^{n+1} = \underbrace{\sigma_z^1 \otimes \sigma_z^2}_{} + \sigma_z^2 \otimes \sigma_z^3 + \ldots$$

$$\sigma_z^1 \otimes \sigma_z^2 \otimes \mathbb{1}^3 \otimes \mathbb{1}^4 \otimes \ldots$$

$$H = \sum_n J \left[\sigma_z^n \sigma_z^{n+1} + \frac{1}{2} \left(\underbrace{\sigma_+^n \sigma_-^{n+1}}_{} + \sigma_+^{n+1} \sigma_-^n \right) \right]$$

$$\ldots \mathbb{1}^{n-1}\, \sigma_+^n \sigma_-^{n+1}\, \mathbb{1}^{n+2} \ldots \quad |\ldots \downarrow_n \uparrow_{n+1} \ldots\rangle$$

$$\left.\begin{aligned} \sigma_+^n |\downarrow_n\rangle &= \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \sigma_-^{n+1} |\uparrow_{n+1}\rangle &= \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{aligned}\right\} \quad \sigma_+^n \sigma_-^{n+1} |\downarrow\uparrow\rangle \rightarrow 4\, |\uparrow\downarrow\rangle$$

(hopping)

leads to superposition of all basis vectors / spreading

DELOCALIZATION

[illegible]

$|1100\rangle$ couples to $|1010\rangle$
but not to $|1110\rangle$
} syst conserves total spin in the z-direction
↓
solve the problem for each sector

sector size increases with number of excitations

① $|10000\rangle$

(N=4)
$|11000\rangle$
$|10100\rangle$
$|10010\rangle$
$|10001\rangle$

$\binom{N}{2} = 20$
$|11100\rangle$

$\binom{N}{N/2}$ is the largest size

each sector is a band when $N \to \infty$

Sector with one excitation

Bethe ansatz

30's

[illegible]

$$|\psi\rangle = \sum_{n=1}^{N} a(n)|\phi(n)\rangle$$

$$\left.\begin{aligned}
|\phi(1)\rangle &= |11000\ldots\rangle \\
|\phi(2)\rangle &= |10100\ldots\rangle \\
|\phi(3)\rangle &= |10010\ldots\rangle \\
&\vdots \\
|\phi(N)\rangle &= |100\ldots1\rangle
\end{aligned}\right\}\ \text{basis}$$

$$\begin{array}{ccc}
100\ldots & 010\ldots & \\
\varepsilon & J & 0 \\
J & \varepsilon & J \\
0 & J &
\end{array}$$

tridiagonal matrix

could diagonalize numerically

but let's try ANALYTICALLY

Effect of H on $\phi(n)$

$\longrightarrow)\ H\phi(1)$

<u>diagonal</u>

$$J\Big(\underbrace{\sigma_z^1\sigma_z^2}_{} + \sigma_z^2\sigma_z^3 + \sigma_z^3\sigma_z^4 + \dots\Big)|1000\dots\rangle = \underbrace{\Big(\boxed{-1+1} + 1 + \dots\Big)}_{J(N-2)\,|1000\dots\rangle}|1000\dots\rangle$$

$\sigma_z^1 \otimes \sigma_z^{②} \otimes \mathbb{1}^3 \otimes \mathbb{1}^4 \otimes \dots$

$\sigma_z^N \sigma_z^{①}$

PERIODIC $\longrightarrow$ $\boxed{\text{RING}}$

<u>off diagonal</u> (it depends on boundary conditions)

<u>PERIODIC</u>

$$\frac{J}{2}\Big(\sigma_+^1\sigma_-^2 + \sigma_+^2\sigma_-^3 + \dots \sigma_+^2\sigma_-^1 + \sigma_+^3\sigma_-^2 + \dots \; + \sigma_+^N\sigma_-^{①} + \sigma_+^{①}\sigma_-^N\Big)|100\dots\rangle = \begin{cases} 2J|00\dots1\rangle \\ 2J|010\dots\rangle \end{cases}$$

periodic $\longrightarrow$ $+\sigma_+^N\sigma_-^{①}$ $\leftarrow N+1$

$$\begin{cases} H\phi(1) = J(N-2)\,\phi(1) + 2J\big[\phi(N) + \phi(2)\big] \\ H\phi(n) = J(N-2)\,\phi(n) + 2J\big[\phi(n-1) + \phi(n+1)\big] \\ H\phi(N) = J(N-2)\,\phi(N) + 2J\big[\phi(N-1) + \phi(1)\big] \end{cases}$$

substitute this and

$\Psi = \sum a(n)\,\phi(n)$

in

$\boxed{H\Psi = E\Psi}$

electrons
locked in sites

1D chain

↓

spins are free
to move

excitation $|\uparrow\rangle \longrightarrow \sigma_z|\uparrow\rangle = \sigma_z\begin{pmatrix}1\\0\end{pmatrix} = \textcircled{+1}\begin{pmatrix}1\\0\end{pmatrix}$

$|\downarrow\rangle \longrightarrow \sigma_z|\downarrow\rangle = \sigma_z\begin{pmatrix}0\\1\end{pmatrix} = \textcircled{-1}\begin{pmatrix}0\\1\end{pmatrix}$

spin-spin interaction

$$H = \sum J\left(\sigma_n^z\sigma_{n+1}^z + \frac{1}{2}\left(\sigma_n^+\sigma_{n+1}^- + \sigma_n^-\sigma_{n+1}^+\right)\right)$$

write the Hamiltonian in matrix form — needs basis vectors

$$\begin{array}{c|ccccccccc}
 & |\downarrow\downarrow\downarrow..\downarrow\rangle & |\uparrow\downarrow\downarrow...\downarrow\rangle & |\downarrow\uparrow\downarrow...\downarrow\rangle & \dots & |\downarrow\downarrow..\downarrow\uparrow\rangle & |\uparrow\uparrow\downarrow..\downarrow\rangle & \dots & |\uparrow\uparrow..\uparrow\rangle \\
\hline
\langle\downarrow\downarrow..\downarrow| & & & & & & & & \\
\langle\uparrow\downarrow\downarrow..\downarrow| & & & & & & & & \\
\langle\downarrow\uparrow\downarrow..\downarrow| & & & & & & & & \\
\langle\downarrow\downarrow..\downarrow\uparrow| & & & & & & & & \\
\langle\uparrow\uparrow\downarrow..\downarrow| & & & & & & & & \\
\langle\uparrow\uparrow\uparrow..\uparrow| & & & & & & & &
\end{array}$$

simplify notation

$$\begin{array}{c|cccccccc} & |\phi_0\rangle & |\phi(1)\rangle & |\phi(2)\rangle \dots & |\phi(N)\rangle & |\phi(1,2)\rangle & |\phi(1,3)\rangle \dots & |\phi(1,2,\dots N)\rangle \\ \hline \langle\phi_0| & \langle\phi_0|H|\phi_0\rangle & \langle\phi_0|H|\phi(1)\rangle & \langle\phi_0|H|\phi(2)\rangle & & & & \\ \langle\phi(1)| & \langle\phi(1)|H|\phi_0\rangle & & & & & & \\ \langle\phi(2)| & \langle\phi(2)|H|\phi_0\rangle & & & & & & \\ \vdots & & & & & & & \end{array}$$

$$H|\phi_0\rangle = J\begin{pmatrix} \sigma_1^3\sigma_2^3 + \sigma_2^3\sigma_3^3 + \dots + \sigma_{N-1}^3\sigma_N^3 + \overset{\underline{\text{RING}}}{\boxed{\sigma_N^3\sigma_1^3}} \\ (\sigma_1^+\sigma_2^- + \sigma_2^+\sigma_3^- \dots \sigma_{N-1}^+\sigma_N^- + \sigma_N^+\sigma_1^-)/2 \\ (\sigma_1^-\sigma_2^+ \qquad \sigma_N^-\sigma_1^+)/2 \end{pmatrix} |\phi_0\rangle =$$

from $\sigma^3\sigma^3$ (Ising term)

$$= J\left((-1)(-1) + (-1)(-1) + \dots (-1)(-1)\right)|\phi_0\rangle$$

$$= NJ|\phi_0\rangle$$

$\langle\phi|H|\phi_0\rangle = 0$ unless $\langle\phi_0|H|\phi_0\rangle = \boxed{NJ} \leftarrow$ one single element in sector of states with no excitation sector of states with one excitation (= one spin up, all the others are down)

$$H|\phi(1)\rangle = J\begin{pmatrix} \sigma_1^3\sigma_2^3 + \dots & \sigma_N^3\sigma_1^3 \\ (\sigma_1^+\sigma_2^- + \dots & \sigma_N^+\sigma_1^-)/2 \\ (\sigma_1^-\sigma_2^+ + \dots & \sigma_N^-\sigma_1^+)/2 \end{pmatrix} |\phi(1)\rangle =$$

$$|\phi(1)\rangle \leftarrow |\uparrow_{①}\downarrow_{②}\downarrow_{③}\dots\downarrow_{Ⓝ}\rangle$$

$$= J\left(\cancel{(+1)(-1)} + \cancel{(-1)(+1)} + (-1)(-1)\dots(-1)(-1)\right)|\phi(1)\rangle$$

$$2\frac{J}{2}\,|\phi(N)\rangle$$

$$\frac{2J}{2}\,|\phi(2)\rangle$$

$$= J(N-2)|\phi(1)\rangle + 2\frac{J}{2}|\phi(2)\rangle + 2\frac{J}{2}|\phi(N)\rangle$$

in general:

$$\longrightarrow H|\phi(n)\rangle = J(N-2)|\phi(n)\rangle + 2\frac{J}{2}|\phi(n-1)\rangle + 2J|\phi(n+1)\rangle$$

"almost" tridiagonal matrix

numerically

or

analytically

$$\boxed{\Psi = \sum_{n=1}^{N} a(n)\,\phi(n)}$$

$\uparrow$

Delocalization

$H\Psi = E\Psi$ $\qquad\qquad$ $\Psi = \sum a(n)\,\phi(n)$

$$a(1)\,\phi(1)\,J(N-2) + a(1)\,2J\left[\phi(N) + \phi(2)\right] +$$

$$+\, a(2)\,\phi(2)\,J(N-2) + a(2)\,2J\left[\phi(1) + \phi(3)\right] +$$

$$\dots$$

$$+\, a(n)\,\phi(n)\,J(N-2) + a(n)\,2J\left[\phi(n-1) + \phi(n+1)\right] +$$

$$\dots$$

$$+\, a(N)\,\phi(N)\,J(N-2) + a(N)\,2J\left[\phi(N-1) + \phi(1)\right] = E\left[a(1)\,\phi(1) + \dots a(n)\,\phi(n) + \dots a(N)\,\phi(N)\right]$$

group all $\phi(n)$'s

$$\left(a(1)\,J(N-2) + a(2)\,2J + a(N)\,2J\right)\phi(1) = E\,a(1)\,\phi(1)$$

in general

$$\begin{cases} E\,a(n) = J(N-2)\,a(n) + 2J\left[a(n-1) + a(n+1)\right] \\ \text{where } \boxed{a(n+N) = a(n)} \end{cases}$$

PERIODIC boundary conditions

Ansatz: $\boxed{a(n) = e^{ink}}$

$$E\,\cancel{e^{ink}} = \left[J(N-2) + 2J\left(e^{-ik} + e^{ik}\right)\right]\cancel{e^{ink}}$$

energy of any basis vector

splitting because of the interaction

$$\boxed{E_k = E_1 + 4J\cos(k)}$$

← this is the band of just one excitation

bandwidth

$$\boxed{\Psi_k = \sum_{n=1}^{N} a_k(n)\,\phi_k(n)}$$

K is determined by $a(n+N) = a(n)$

$$\Rightarrow e^{ikN} = 1 \Rightarrow k = \frac{2\pi j}{N}, \quad \underbrace{j \in \{0, \pm 1, \pm 2, \dots N/2\}}_{N \text{ states in that band}}$$

03/31/05 ①

To explicitly find Ψ and E, need to solve Schröd. eq.

Start with simplified potentials

- nearly-free-electron model
  - e^- is almost a free-particle
  - ↳ crystal potential is a perturbation
  - rough approx. for Na, K, Al
- tight-binding model
  - ↳ atomic potential is so strong that e^- move around single atom and interaction with neighboring atom is a perturbation

TIGHT-BINDING MODEL (TB)

crystal potential / ionic potential - very strong

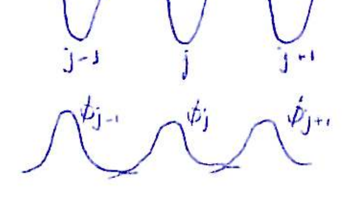
e^- captured by ion - remains for a long time then leaks or tunnels to next ion

⇒ its state is essentially atomic orbital (tightly bound to its own atom)

Choose Bloch function to describe syst.: $\Psi_k(x) = \underbrace{\frac{1}{N^{1/2}}}_{\text{normalization}} \underbrace{\sum_{j=1}^{N}}_{\text{sum over atoms in lattice}} e^{ikX_j} \overbrace{\phi_v(x - X_j)}^{\text{atomic orbital centered around jth atom}}$

X_j: position of jth atom

$\boxed{X_j = j\,a}$



basic assumption of TB [decays rapidly away from X_j

little overlap with neighboring orbitals

03/31/05 -②

Energy of electron

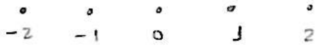
$$E(k) = \langle \psi_k | H | \psi_k \rangle$$

$$E(k) = \frac{1}{N} \sum_{j j'} e^{ik(x_j - x_{j'})} \langle \phi_v (x - X_{j'}) | H | \phi_v (x - X_j) \rangle$$

for each j' → sum over j leads to same result
↳ N values

$$\hookrightarrow E(k) = \sum_{j=-N/2}^{(N-1)/2} e^{ikX_j} \langle \phi_v (x) | H | \phi_v (x - X_j) \rangle$$

↳ Ex: N=5



$$\Rightarrow E(k) = \underbrace{\langle \phi_v(x) | H | \phi_v(x) \rangle} + \underbrace{\sum_j{}^{①} e^{ikX_j} \langle \phi_v(x) | H | \phi_v (x - X_j) \rangle}$$

no j = zero

energy of e⁻ if it were entirely localized around atom j=0

delocalization included here

term responsible for band structure

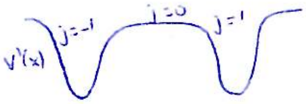
effects of e⁻ tunneling to other atoms appreciable only for nearest neighbors $\boxed{j = 1,\ j = -1}$

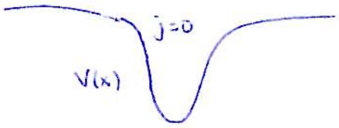
since beyond, overlap of ϕ_v's with ϕ of j=0 are negligible

3-31-08 -③

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \underset{\substack{\uparrow \\ \text{crystal} \\ \text{potential}}}{V(x)}$$

$$V(x) = \overbrace{\sum_j v(x - X_j)}^{\text{sum of atomic potentials}} = \underbrace{v(x)}_{\substack{\text{atomic potential} \\ \text{due to atom at} \\ \text{origin } j=0}} + \underbrace{V'(x)}_{\substack{\text{due to} \\ \text{all other} \\ \text{atoms}}}$$





diagonal

$$\langle \phi_v(x)|H|\phi_v(x)\rangle = \underbrace{\left\langle \phi_v(x) \left| \overbrace{\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + v(x)\right]}^{\text{H for free atom}} \right| \phi_v(x)\right\rangle}_{\substack{\text{atomic energy} \\ E_v}} + \underbrace{\langle \phi_v(x)|V'(x)|\phi_v(x)\rangle}_{\boxed{-\beta}}$$

$\rightarrow$ ⊕ since $V'(x)$ is ⊖

$$\beta = -\int \phi_v^*(x)\, V'(x)\, \phi_v(x)\, dx$$

interaction term $\boxed{j=1}$

$$\langle \phi_v(x)|H|\phi_v(x-X_j)\rangle = \langle \phi_v(x)|H|\phi_v(\overset{\substack{\text{nearest neighbor} \\ \downarrow}}{x-a})\rangle =$$

$$= \underbrace{\left\langle \phi_v(x) \left| -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + v(x-a) \right| \phi_v(x-a)\right\rangle}_{E_v \langle \phi_v(x)|\phi_v(x-a)\rangle} + \underbrace{\langle \phi_v(x)|V'(x-a)|\phi_v(x-a)\rangle}_{\gamma = -\int \phi_v^*(x)\, V'(x-a)\, \phi_v(x-a)\, dx}$$

very small since $\phi_v(x)$ and $\phi_v(x-a)$ don't overlap much

$\uparrow$ overlap integral

$\rightarrow$ $\left.\begin{matrix} V(-a) \\ V(+a) \end{matrix}\right\}$ is appreciable

$\boxed{j=-1}$ → same result, since atomic functions are symmetric

$$\Rightarrow E(k) = E_v - \beta - \gamma \sum_{j=-1}^{1} e^{ikX_j} \Rightarrow \boxed{E(k) = E_v - \beta - 2\gamma \cos ka}$$

→ atomic level E_v broadened into energy band

$\cos 2x = 1 - 2\sin^2 x$ ⟶ $E(k) = E_0 + 4\gamma \sin^2(ka/2)$, $E_0 = E_v - \beta - 2\gamma$

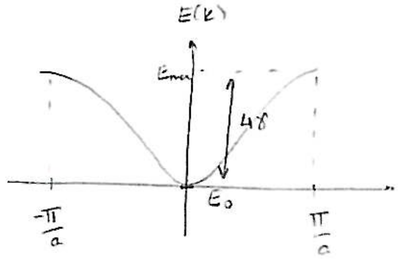
$$E(K) = \underset{\text{atomic energy for free atom}}{E_\nu} - \beta - \underbrace{2\gamma \cos Ka}_{\text{kinetic energy because } e^- \text{ moves}}$$

$E_0 = E_\nu - \beta - 2\gamma$

$E_{max} = E_\nu - \beta + 2\gamma$

bandwidth = 4γ

In the 1st BZ



⇒) K small (bottom of the band)

$$E(K) \simeq E_\nu - \beta - 2\gamma + \frac{2\gamma\,(Ka)^2}{2} \simeq E_0 + \underbrace{\gamma a^2 K^2}_{\text{as free electron}}$$

$$\frac{p^2}{2m^*} = \frac{\hbar^2 K^2}{2m^*} = \gamma a^2 K^2 \Rightarrow \boxed{m^* = \frac{\hbar^2}{2a^2\gamma}}$$

→) larger γ ⇒ larger interaction ⇓ smaller inertia

→) smaller γ ⇒ larger inertia

⇒) K large ~ π/a (top of the band)

$$K' = \pi/a - K \Rightarrow K = \pi/a - K'$$

$$E = E_\nu - \beta - 2\gamma\cos(\pi - K'a) = E_\nu - \beta + 2\gamma\cos(K'a) \simeq \underbrace{E_\nu - \beta + 2\gamma}_{E_{max}} - \gamma a^2 K^2$$

$$\frac{\hbar^2 K'^2}{2m^*} = -\gamma a^2 K^2 \Rightarrow m^* = \frac{(-)\hbar^2}{2a^2\gamma}$$

e^- behaves like a particle of NEGATIVE effective mass

remember from Sec 3.6

K ~ π/a ⇒ small λ ⇒ e^- are scattered by atoms

large

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$\boxed{\text{Dynamical}}$ Effective mass (5.15)

$a = \frac{dv}{dt}$

group velocity

$v = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{\partial E}{\partial k}$

free particle

$mv = p = \hbar k$

$a = \frac{dv}{dk}\frac{dk}{dt}$

$\mathscr{E}$ applied in crystal

$\vec{F} = -e\vec{\mathscr{E}}$

power

$\underbrace{\frac{dE}{dt}} = \vec{F}\,\vec{v} = -e\,\vec{\mathscr{E}}\cdot\vec{v}$

$\boxed{E(k)}$

$\frac{dE}{dk}\frac{dk}{dt} = -e\,\vec{\mathscr{E}}\cdot\vec{v} \Rightarrow \cancel{\frac{\partial E}{\partial k}}\frac{dk}{dt} = -\frac{e\,\mathscr{E}}{\hbar}\cancel{\frac{\partial E}{\partial k}}$

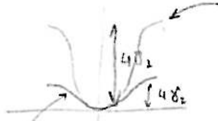
$\hbar\frac{\partial \vec{k}}{\partial t} = \vec{F}$

$a = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}\,F$

$F = m^* a$

m^*

$\rightarrow \boxed{m^* = \frac{\hbar^2}{d^2E/dk^2}} \longrightarrow$ m^* is inversely proportional to the curvature of the band



δ_1 is large, large interaction

↳ large curvature

⇓

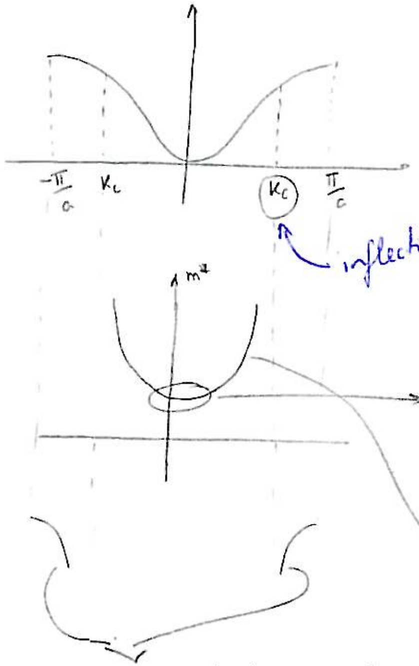
small m^*

small inertia

significant delocalization

δ_2 is small, small interact.

↳ small curvature → large inertia



inflection point

~ const and ⊕ ⟹ $E = \alpha k^2$

bottom of band

⇓

$m^* = \frac{\hbar^2}{2\alpha}$

k increases, m^* no longer const

m^* begins to be a function of k

beyond inflection point

m^* becomes ⊖ → close to the top of the band

a is ⊖, opposite to applied F

lattice exerts strong retarding force on e^- and overcomes applied F ⟸

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Time-independent Perturbation Theory

(Griffiths Ch. 6)

Suppose we know how to solve the time-indep Schröd. eq.

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \Longrightarrow \left\{ \begin{array}{l} \text{complete set of orthon.} \\ \text{eigenfunctions } \psi_n^0 , \quad \langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \\ \text{and} \\ \text{eigenvalues } E_n^0 \end{array} \right.$$

→) perturb potential slightly

$$H = \overset{\text{unperturbed}}{H^0} + \underbrace{\lambda}_{\text{small number}} H' \rightarrow \text{perturbation}$$

We won't solve exactly, but find approximations to solution

$$\boxed{H \psi_n = E_n \psi_n}$$

write ψ_n and E_n as power series in λ (simple perturbation theory)

→ only first few terms need be considered

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots$$

$$E_n = E_n^0 + \lambda \underbrace{E_n^1}_{\text{1st order correction}} + \lambda^2 \underbrace{E_n^2}_{\text{2nd order correction}} + \dots$$

$$H\psi_n = E_n\psi_n$$

$$(H^0 + \lambda H^1)(\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)(\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots)$$

collecting same powers in λ

$$\lambda^0 \longrightarrow H^0\psi_n^0 = E_n^0\psi_n^0$$

$$\lambda^1 \longrightarrow H^0\psi_n^1 + H^1\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

$$\lambda^2 \longrightarrow H^0\psi_n^2 + H^1\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$$

First-order

→) inner product with ψ_n^0 to find E_n^1

(λ^1)

$$\underbrace{\langle\psi_n^0|H^0|\psi_n^1\rangle}_{\underbrace{\langle H^0\psi_n^0|\psi_n^1\rangle}_{\cancel{E_n^0\langle\psi_n^0|\psi_n^1\rangle}}} + \langle\psi_n^0|H^1|\psi_n^0\rangle = \cancel{E_n^0\langle\psi_n^0|\psi_n^1\rangle} + E_n^1\langle\psi_n^0|\psi_n^0\rangle$$

$$\boxed{E_n^1 = \langle\psi_n^0|H^1|\psi_n^0\rangle} //$$

{ 1st order correction is the expectation value of the perturbation in unperturbed state

→) to find ψ_n^1

rewrite Equation for λ^1 $\quad (H^0 - E_n^0)\psi_n^1 = -(H^1 - E_n^1)\psi_n^0$

ψ_n^0 is a complete set, so we can write

$$\psi_n^1 = \sum_{m\neq n} c_m^{(n)}\psi_m^0$$

$m \neq n$ because $\psi_n^1 - c_n^{(n)}\psi_n^0$ in has no effect

$(H^0 - E_n^0)\psi_n^0 = 0$

$$(H^0 - E_n^0) \sum_{m\neq n}' c_m^{(n)} \psi_m^0 = -(H' - E_n') \psi_n^0$$

$$\sum_{m\neq n}' (E_m^0 - E_n^0)\, c_m^{(n)} \psi_m^0 = -(H' - E_n') \psi_n^0$$

inner product with ψ_ℓ^0

$$\sum_{m\neq n}' (E_m^0 - E_n^0)\, c_m^{(n)} \underbrace{\langle \psi_\ell^0 | \psi_m^0 \rangle} = \underbrace{- \langle \psi_\ell^0 | H' | \psi_n^0 \rangle + E_n' \langle \psi_\ell^0 | \psi_n^0 \rangle}$$

if $\underline{\ell = n}$

$\langle \psi_n^0 | \psi_m^0 \rangle = 0$ and we recover $E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$

but if $\underline{\boxed{\ell \neq n}}$

$\langle \psi_\ell^0 | \psi_m^0 \rangle = \delta_{\ell m}$

$\Downarrow$

$\langle \psi_\ell^0 | \psi_n^0 \rangle = 0$

$$(E_\ell^0 - E_n^0)\, c_\ell^{(n)} = - \langle \psi_\ell^0 | H' | \psi_n^0 \rangle$$

$$\boxed{c_m^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}}$$

$$\psi_n^1 = \sum_{m\neq n}' \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0$$

} it applies if there are no degeneracies $E_n^0 \neq E_m^0$

Second - order

→) inner product with ψ_n^0 to find E_n^2

$$\underbrace{\langle \psi_n^0 | H^0 | \psi_n^2 \rangle}_{\cancel{E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle}} + \langle \psi_n^0 | H' | \psi_n^1 \rangle = \cancel{E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle} + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$$

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \underbrace{\langle \psi_n^0 | \psi_n^1 \rangle}_{\sum_{n \neq m} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0}$$

$$\frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}$$

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} \langle \psi_n^0 | H' | c_m^{(n)} \psi_m^0 \rangle$$

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}}$$

Degenerate Perturbation Theory

two-fold degenerate ⟹ $H^0\psi_a^0 = E^0\psi_a^0$ and $H^0\psi_b^0 = E^0\psi_b^0$ $\quad\langle\psi_a^0|\psi_b^0\rangle = 0$

any linear combination: $\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0$ is also eigenstate of H^0 with eigenvalue E^0

$$H^0(\alpha\psi_a^0 + \beta\psi_b^0) = E^0(\alpha\psi_a^0 + \beta\psi_b^0)$$

Perturbation ψ' breaks / lifts the degeneracy, but to apply perturbation theory we don't know from which linear combination to start

"good" → which values for α, β

$H\psi = E\psi$

(λ): $H^0\psi^1 + H^1\psi^0 = E^0\psi^1 + E^1\psi^0$

→ inner product with ψ_a^0

$$\underbrace{\langle\psi_a^0|H^0|\psi^1\rangle}_{E^0\cancel{\langle\psi_a^0|\psi^1\rangle}} + \langle\psi_a^0|H^1|\psi^0\rangle = E^0\cancel{\langle\psi_a^0|\psi^1\rangle} + E^1\langle\psi_a^0|\psi^0\rangle$$

$$\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0$$

$$\alpha\underbrace{\langle\psi_a^0|H^1|\psi_a^0\rangle}_{W_{aa}} + \beta\underbrace{\langle\psi_a^0|H^1|\psi_b^0\rangle}_{W_{ab}} = \alpha E^1 \qquad \boxed{W_{ij} = \langle\psi_i^0|H^1|\psi_j^0\rangle}$$

$$\boxed{\alpha W_{aa} + \beta W_{ab} = \alpha E^1} //$$

→ inner product with ψ_b^0

$$\langle\psi_b^0|H^1|\psi^0\rangle = E^1\langle\psi_b^0|\psi^0\rangle$$

$$\boxed{\alpha W_{ba} + \beta W_{bb} = \beta E^1} //$$

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix}\begin{pmatrix}\alpha \\ \beta\end{pmatrix} = E^1\begin{pmatrix}\alpha \\ \beta\end{pmatrix}$$

↳ diagonalize to find E^1 and also α, β

$$\boxed{E^1_\pm = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2}\right]} //$$

this can be extended to n-fold degeneracy

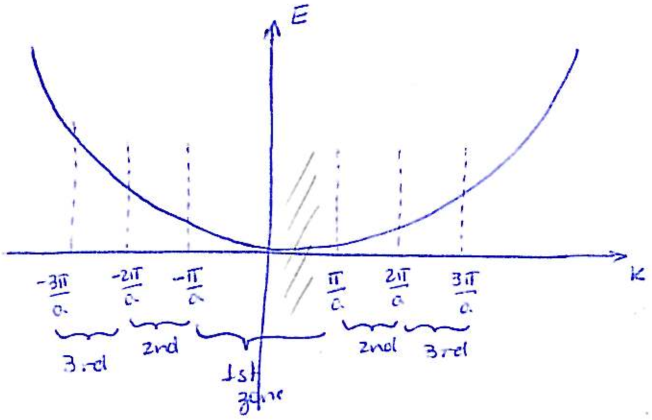
Nearly - free - electron Model

Crystal potential is weak ⇒ treated as a perturbation
e^- are almost free
} good approximation for the valence bands of simple metals Na, K, Al, ...

→ unperturbed states { empty-lattice model : e^- are free, but solutions satisfy (translational symmetry) imposed by the lattice

$$\psi_K^0 = \frac{1}{\sqrt{L}}\, e^{iK\cdot x}$$

$$E_K^0 = \frac{\hbar^2 K^2}{2\,\boxed{m_0}}$$ → mass of free e^-



each zone covers the entire range of K and is associated with a band

Now let's go for perturbation theory $\boxed{H = H^0 + V}$

⟹ first notice that states in the same zone (band) (do not) couple

because

V(x) has translational symmetry ⇒ $V(x) = V(x + R)$ ← lattice vector

V(x) can be expanded as a Fourier series (used to decompose periodic functions with simple functions – cos, sin, e)

$$V(x) = \sum_K{}' V_K\, e^{iKx} \xrightarrow[\text{coefficients}]{\text{Fourier}} V_K = \frac{1}{L}\int_0^L V(x)\, e^{-iKx}\, dx$$

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symmetry $\Rightarrow$ $\sum V_K e^{iKx} = \sum V_K e^{iKx} \boxed{e^{iKR}}$

$\Downarrow$

$K = G$ (reciprocal lattice vector)

$\boxed{G = \frac{2\pi}{a} j}$

[if $K \neq G \Rightarrow V_K = 0$]

Therefore

$$\langle \psi_{①,K'} | V | \psi_{1,K} \rangle = \frac{1}{L}\int_0^L e^{-i(K'-K)x} V(x)\, dx = V_{K'-K}$$

1st zone/band

$\hookrightarrow$ $K' - K$ must be $= G$

but this is impossible if they are in the same zone

$\Downarrow$

so states in the same zone are not coupled

$\hookrightarrow$ so in perturbation theory, even though $E(K) = E(-K)$ we don't use degenerate pert. theory since their 2 states <u>don't couple</u>

$\Rightarrow$ Perturbation theory for the 1st zone (band)

let's focus on <u>$0 \leq K \leq \pi/a$</u>

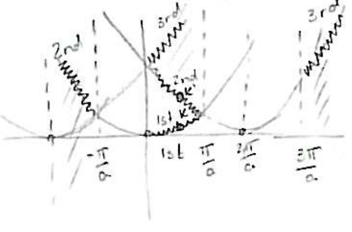
$$E_{①}(K) = E_1^0(K) + \underbrace{\langle \psi_{1,K}^0 | V | \psi_{1,K}^0 \rangle}_{\frac{1}{L}\int_0^L e^{-iKx} V e^{iKx} dx = \text{const}} + \sum_{K,n}^{n \neq 1} \frac{|\langle \psi_{n,K'}^0 | V | \psi_{1,K}^0 \rangle|^2}{E_1^0(K) - E_n^0(K')}$$

1st band

$\hookrightarrow$ increases as n increases, so major effect comes from <u>$n=2$</u>

$$\langle \psi_{2,K'}^0 | V | \psi_{1K}^0 \rangle = \underbrace{\frac{1}{L}\int_0^L e^{-i(K'-K)x} V(x)\, dx}_{V_{-\frac{2\pi}{a}}}$$

$K' = K - \frac{2\pi}{a}$



but $|V_{2\pi/a}|^2$ is very small $\Rightarrow$

$\Rightarrow$

effect of the lattice potential is <u>negligible</u>

EXCEPT at one point in K-space

$\boxed{K = \pi/a}$

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$\boxed{G = \frac{2\pi}{a}}$

$$k' = k - \frac{2\pi}{a} \qquad k'' = k + \frac{2\pi}{a}$$

For $0 \le k \le \pi/a \Rightarrow \underbrace{E_1^0(k) = \frac{\hbar^2 k^2}{2m}}_{\text{1st zone}}, \quad \underbrace{E_2^0(k') = \frac{\hbar^2}{2m}\left(k - \frac{2\pi}{a}\right)^2}_{\text{2nd zone}}, \quad \underbrace{E_3^0(k'') = \frac{\hbar^2}{2m}\left(k + \frac{2\pi}{a}\right)^2}_{\text{3rd zone}}, \ldots$

at $\boxed{k = \frac{\pi}{a}} \Rightarrow E_1^0(k) = E_2^0(k') \Rightarrow$ they are degenerate

↳ here we do need degenerate perturbation theory

$$E_\pm^1(k) = \frac{1}{2}\left[V_{11} + V_{22} \pm \sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2}\right]$$

where $V_{11} = \langle \psi_{1,k}^0 | V | \psi_{1,k}^0 \rangle = \text{const}$

$V_{22} = \langle \psi_{2,k'}^0 | V | \psi_{2,k'}^0 \rangle = \text{const}$

$$\boxed{V_{12} = \langle \psi_{1,k}^0 | V | \psi_{2,k'}^0 \rangle}$$

we then lift the degeneracy and have

in the 1st band: $E_1^0(k) + E_-^1$

while

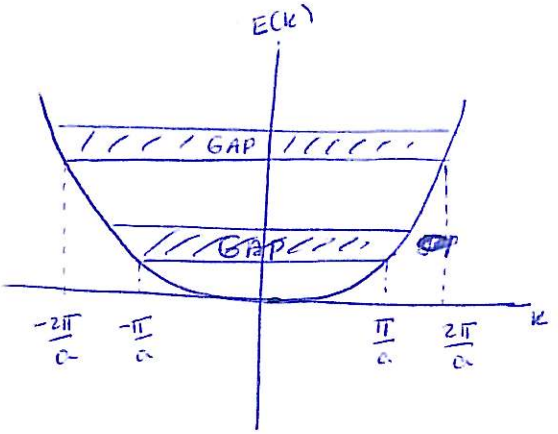
in the 2nd band: $E_2^0(k') + E_+^1$

$\boxed{\text{the energy gap is } 2V_{12}}$ // $\boxed{V_{12} = V_{-\frac{2\pi}{a}}}$

→ the same happens for $E_2^0(k)$ and $E_3^0(k')$ at $k = \frac{2\pi}{a} \Rightarrow$ gap

$k' = k - \frac{4\pi}{a}$

$2V_{-\frac{4\pi}{a}}$



Wave function

$$\psi_{1,k} = \psi^{(0)}_{1,k} + \sum_{n,k'} \frac{\langle \psi^{(0)}_{n,k'} | V | \psi^{(0)}_{1,k} \rangle}{E^{(0)}_1(k) - E^{(0)}_n(k')} \psi^{(0)}_{n,k'}$$

$n = 2, 3, \ldots$

$n = 2 \rightarrow k' = k - \frac{2\pi}{a}$

$$\psi_{1,k} = \psi^{(0)}_{1,k} + \boxed{\frac{V_{-2\pi/a}}{E^{(0)}_1(k) - E^{(0)}_2(k - 2\pi/a)}} \psi^{(0)}_{2,(k-\frac{2\pi}{a})}$$

$\sim e^{ikx}$ (right)

small at center, increases closer to edges of zone

$\sim e^{i(k-\frac{2\pi}{a})x}$ (going left since $0<k<\pi/a$)

$\Downarrow$

potential introduces new left-traveling wave

↳ caused by scattering of e^- by crystal potential

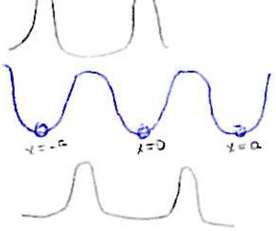
degenerate perturbation

$\psi_{1,\pi/a}$ and $\psi_{2,(\frac{\pi}{a}-\frac{2\pi}{a})}$

$$\psi_\pm = \frac{1}{\sqrt{2L}} \left(e^{i\pi x/a} \pm e^{-i\pi x/a} \right) \leftarrow \text{standing wave} \Rightarrow \boxed{v=0} \rightarrow \text{very different from free } e^-$$

$\psi_+ \sim \cos\frac{\pi x}{a} \longrightarrow |\psi_+|^2 \sim \cos^2 \pi x/a$

$\psi_- \sim \sin\frac{\pi x}{a} \longrightarrow |\psi_-|^2 \sim \sin^2 \pi x/a$



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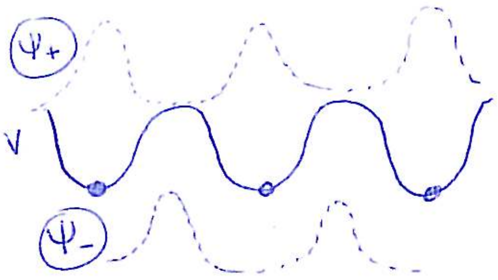
The wavefunction

$\hookrightarrow$ from $\underbrace{\begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}}_{\begin{pmatrix} \text{const} & V_{12} \\ V_{12}^{*} & \text{const} \end{pmatrix}} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^{1} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$ $\Rightarrow \alpha = \beta = \frac{1}{\sqrt{2}}$

$$\psi_{\pm}^{0}(x) = \frac{1}{\sqrt{2}} \left[\psi^{0}_{1,\frac{\pi}{a}}(x) \pm \psi^{0}_{2,-\frac{\pi}{a}}(x) \right] = \frac{1}{\sqrt{2L}} \left(e^{i\pi x/a} \pm e^{-i\pi x/a} \right)$$

$\psi_{+} \sim \cos\left(\frac{\pi x}{a}\right) \longrightarrow e^{-}$ piled at nuclei

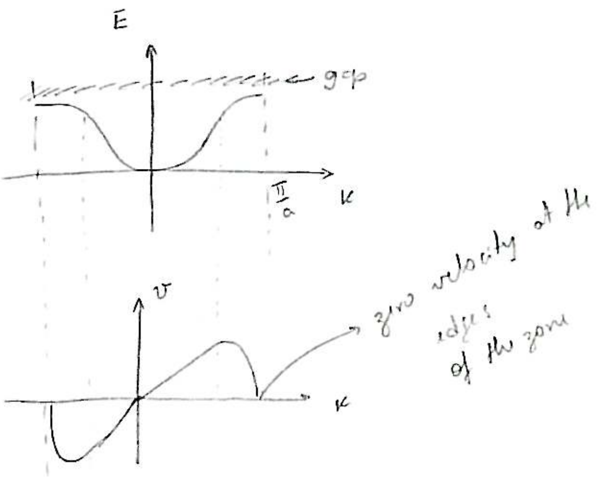


$\psi_{-} \sim \sin\left(\frac{\pi x}{a}\right) \longrightarrow e^{-}$ piled between ion

at $k = \frac{\pi}{a}$ → scattering is so strong that the reflected wave has the same amplitude as the incident wave

$\Rightarrow$ standing wave very ≠ from free e^{-} ← $\boxed{v=0}$

$\hookrightarrow$ e^{-} there has zero velocity



$$v = \frac{1}{\hbar} \frac{\partial E}{\partial k}$$

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Metals vs. Insulators (Sec 5.10 and Sec 5.13)

→ Using energy-band theory

valence band full → $\boxed{\text{NO}}$ current → insulator

valence band partially occupied → current → metal

$\boxed{\text{Sec. 5.4}}$

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

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

but $E(\vec{k}) = E(-\vec{k})$ because in Schröd. eq $\left[-\frac{\hbar^2}{2m}(\vec{\nabla}+i\vec{k})^2 + V(\vec{r})\right]u_{\vec{k}}(\vec{r}) = E_{\vec{k}}\, u_{\vec{k}}(\vec{r})$

$-\vec{k}$ correspond to complex conjugate of Schröd eq → $\left[-\frac{\hbar^2}{2m}(\vec{\nabla}-i\vec{k})^2 + V^*(\vec{r})\right]u_{\vec{k}}(\vec{r}) = E^*(\vec{k})\, u_{\vec{k}}(\vec{r})$

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

$\Rightarrow E^*(\vec{k}) = E(-\vec{k})$

since energy is a real number $E^*(\vec{k}) = E(\vec{k})$

$\Rightarrow E(\vec{k}) = E(-\vec{k})$

$$\Downarrow$$

$$\boxed{\vec{v}(-\vec{k}) = -\vec{v}(\vec{k})}\ //$$

The current density due to all e^- in the band is

$$\boxed{\vec{J} = \frac{(-e)}{V}\sum_{\vec{k}} \vec{v}(\vec{k})}$$

↓

if the band is full, since $\vec{v}(-\vec{k}) = -\vec{v}(\vec{k})$

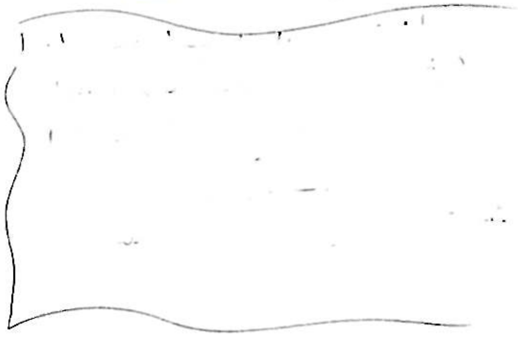
$\boxed{\text{insulator}}$ // ⇐ $\boxed{\vec{J} = 0}$

semiconductors: gap between the valence (full) band and band above is small, then e^- can be thermally excited from former to the latter band (incident light, high electric field)

4-09-01

Holes

A hole appears in a band completely filled but with one vacant state



hole located at k_1

$$J = -\frac{e}{V} \sum_{k}{}^{'(1)} v_e(k)$$

since $-\frac{e}{V} \sum_{k}{}' v_e(k) - \frac{e}{V} v_e(k_1) = 0$

$\Rightarrow$

$$J_h = \frac{e}{V} v_e(k_1)$$

} easier to focus on the motion of vacant site than motion of large number of e^-

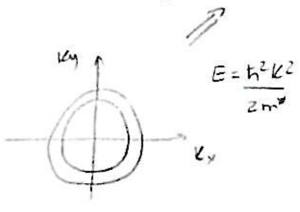
---

Density of states

1D 1 k in each $2\pi/L$ $\leftarrow$ $e^{ikL} = 1$

3D 1 k in each $(2\pi)^3/L^3$

number of states per unit volume in $k, k+dk$ } $\frac{4\pi k^2 dk}{(2\pi)^3} \frac{L^3}{V}$



$E = \frac{\hbar^2 k^2}{2m^*}$

in terms of E

$$k^2 = \frac{2m^* E}{\hbar^2} \qquad k = \frac{\sqrt{2m^* E}}{\hbar} \Rightarrow \frac{dk}{dE} = \frac{1}{2\hbar} \frac{2m^*}{\sqrt{2m^* E}}$$

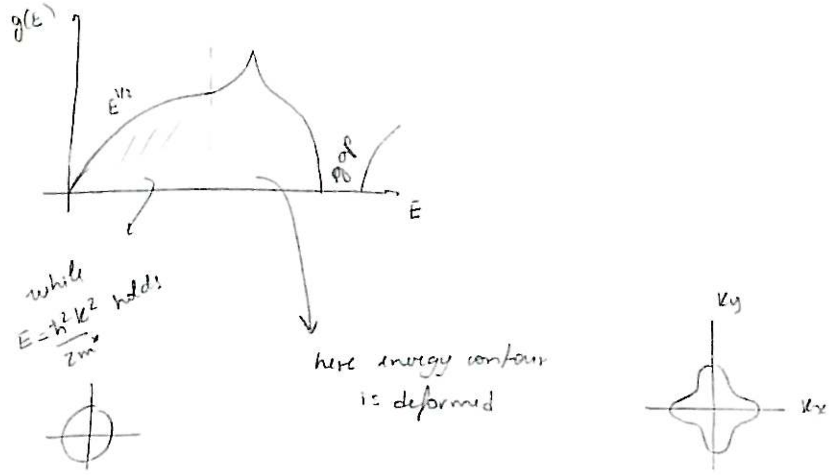
$$\frac{4\pi k^2 dk}{(2\pi)^3} = \frac{1}{2\pi^2} \frac{2m^* E}{\hbar^2} \frac{1}{\hbar} \frac{m^*}{\sqrt{2m^* E}} dE = \frac{1}{4\pi^2} \frac{1}{\hbar^3} (2m^*)^{3/2} E^{1/2} dE = \underbrace{g(E)\, dE}_{\text{number of states per unit volume in } (E,\, E+dE)}$$

$$g(E) = \frac{2}{4\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}$$

each $\vec{k}$ can accomodate 2 spins

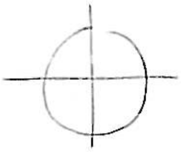
$$\boxed{g(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}}$$

4-09-02

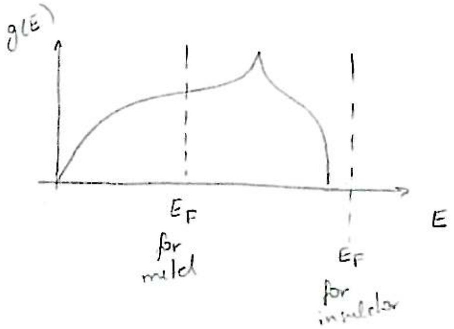


energy contour translates into <u>Fermi surface</u>

For metals



For insulators — shape is deformed



Fermi energy for metals

$$\int_0^{E_F} g(E)\, dE = n \quad \Rightarrow \quad \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \int_0^{E_F} E^{1/2}\, dE = \frac{1}{\cancel{2}\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \frac{\cancel{2}}{3} E_F^{3/2}$$

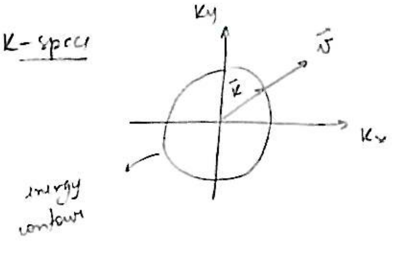
$$\Rightarrow \quad E_F = (3\pi^2 n)^{2/3} \frac{\hbar^2}{2m^*}$$

$$\boxed{E_F = \frac{\hbar^2}{2m^*} (3\pi^2 n)^{2/3}} \; //$$

4-09-03

Velocity of the Bloch electron

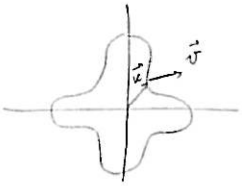
- For the free electron : $m_0 \vec{v} = \hbar \vec{k}$



$\Rightarrow \vec{v}$ is // to $\vec{k}$

- For Bloch electron
(e⁻ that feels crystal potential)

$$\underbrace{\boxed{\vec{v} = \frac{1}{\hbar} \nabla_{\vec{k}} E(\vec{k})}}_{\text{perpendicular to the energy contour}}$$



Apply external field
$$a = \frac{dv}{dt} = \underbrace{\frac{dv}{dk}}_{\frac{1}{\hbar}\frac{d^2E}{dk^2}} \underbrace{\frac{dk}{dt}}_{\frac{1}{\hbar} F_{ext}} = \overset{1/m^*}{\frac{d^2E/dk^2}{\hbar^2}} F_{ext}$$

$$\rightarrow \frac{dE}{dt} = \overset{\hbar v}{\frac{dE}{dk}} \underbrace{\frac{dk}{dt}}_{\frac{dk}{dt} = -\frac{e\mathcal{E}}{\hbar}} = -e\mathcal{E}v$$

Physical origin of m^*

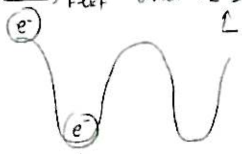
$$\frac{dv}{dt} = \frac{F_{ext}}{m^*}$$

$\boxed{m_0 \vec{v}}$ → real momentum of electron

$$m_0 \frac{dv}{dt} = (F_{ext} + F_L) = m_0 \frac{F_{ext}}{m^*} \Rightarrow \boxed{m^* = \frac{m_0 F_{ext}}{(F_{ext} + \underset{\text{responsible for } m^* \neq m_0}{F_L})}}$$

$F_L = 0 \Rightarrow m^* = m_0$

→ F_{ext} and $F_L > 0$ $\Rightarrow \boxed{m^* < m_0}$
↳ helps motion



↳ $F_L < 0$ $\Rightarrow \boxed{m^* > m_0}$ → F_L can even lead to $\boxed{m^* < 0}$ if $|F_L| > |F_{ext}|$
contrary to motion

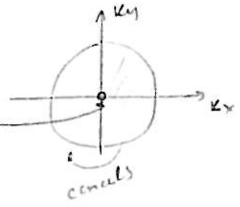
4-07-04

Electrical Conductivity

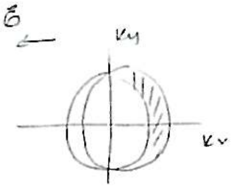
free-electron model: $\sigma = \frac{n e^2 \tau_F}{m^*}$

→) No electric field → Fermi surface centered at origin

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



→) Electric field displaces FS



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

$$\delta k_x = -\frac{e\mathcal{E}}{\hbar}\,\tau$$

displacement

collision time

$$J_x = -e\, v_{F,x} \underbrace{g(E_F)\, \delta E}_{\text{concentration of uncompensated electrons}} = -e\, v_{F,x}\, g(E_F) \left(\frac{\partial E}{\partial k_x}\right)_{E_F} \delta k_x$$

$\hbar v_{F,x}$

$$J_x = e^2 v_{F,x}^2 \tau_F\, g(E_F)\, \mathcal{E}$$

$$v_{F,x}^2 = \frac{1}{3} v_F^2$$

$$\boxed{\sigma = \frac{1}{3} e^2 v_F^2 \tau_F\, g(E_F)}$$

→ more general than for free e⁻ which ~ (n)

$\sigma = \frac{n e^2 \tau}{m^*}$ is recovered for metal

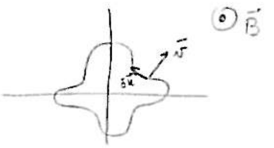
$$\begin{cases} g(E_F) = \frac{1}{2\pi^2}\left(2m^*/\hbar^2\right)^{3/2} E_F^{1/2} \\ E_F = \frac{1}{2} m^* v_F^2 \\ E_F = \frac{\hbar^2}{2m^*}\left(3\pi^2 n\right)^{2/3} \end{cases}$$

4-09-05

Cyclotron Resonance

for Bloch electron

$$\vec{F}_{ext} = \hbar \frac{d\vec{K}}{dt} = -e \left[\vec{v}(\vec{K}) \times \vec{B} \right]$$



$$\delta \vec{K} = -\frac{e}{\hbar} \left[\vec{v} \times \vec{B} \right] \delta t$$

($\delta\vec{K}$ lies along contour
e^- rotates around energy contours $\perp$ to $\vec{B}$)

motion of e^- in K-space is cyclic

$$T = \oint \delta t = \frac{\hbar}{eB} \oint \frac{dK}{v(\vec{K})} \qquad T = \frac{2\pi}{\omega_c}$$

$$\boxed{\omega_c = \frac{2\pi e B}{\hbar} \frac{1}{\oint \frac{dK}{v(\vec{K})}}}$$ → cyclotron frequency of Bloch electron

for free electron we recover $\omega_c = eB/m^*$

because $E = \frac{\hbar^2 K^2}{2m^*} \rightarrow m^* v = \hbar K \rightarrow v = \frac{\hbar K}{m^*}$ → is a contour around this contour

$$\omega_c = \frac{\cancel{2\pi} e B}{\cancel{\hbar}} \frac{\cancel{\hbar} K}{m^*} \frac{1}{\oint dK} \xrightarrow{} \frac{1}{2\pi K} \Rightarrow \boxed{\omega_c = \frac{eB}{m^*}}$$

Hall effect

$$R_e = -\frac{1}{n_e e} \qquad R_h = \frac{1}{n_h e}$$

$$R = \frac{R_e \sigma_e^2 + R_h \sigma_h^2}{(\sigma_e + \sigma_h)^2}$$

Semiconductors

↳ main application: transistors
(computers, electronic devices)
(switches, signal amplifiers)

∘) group IV : C, Si, Ge, Sn (tin) — diamond structure (fcc
basis atoms at 000 1/4 1/4 1/4)
↓
(equal)

each atom has 4 valence e^-

each atom { surrounded by 4 equal atoms forming tetrahedron
has 4 bonds
↓
each composed of 2 e^- of opposite spin
↓
one from each atom

$\underbrace{\text{each composed of 2 } e^- \text{ of opposite spin, one from each atom}}_{\text{covalent bond (strong)}}$

covalent crystal: + ion cores occupy
lattice sites
total charge on each atom is zero

covalent bond (strong)

∘) group III - V compounds : one element III, one V — zincblende structure
↓
like diamond
but basis formed of
2 different atoms

$\boxed{\text{GaAs}}$, $\boxed{\text{InSb}}$, GaP, InAs, GaSb

GaAs → Gallium Arsenide

InSb → Indium Antimony

- each atom surrounded by 4 of different kind
- bonding: primarily covalent 3 e^- from III and 5 e^- from V

but distribution of e^- — not symmetric, one of the atoms has net electric charge

heteropolar bond (elemental semiconductors IV — homopolar bond)

⇓

lattice can be polarized by $\vec{E}$

∘) II - VI semiconductors: CdS, ZnS — zincblende structure ⟹ bonding primarily covalent

polar character even stronger

∘) IV - VI compounds : PbTe

Band Structure

↳ valence (VB) band (highest occupied energy band) is full at $T = 0°K$

but gap to $\underbrace{\text{next band}}_{\text{(conduction (CB) band)}}$ is small

⇓

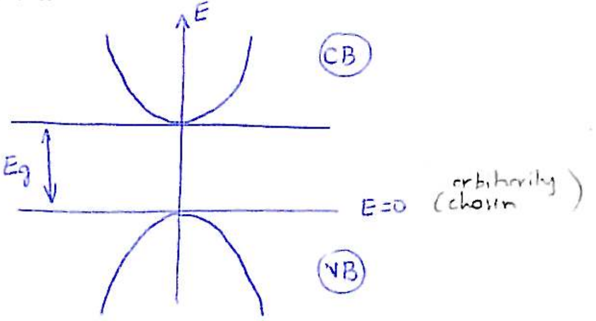
number of excited e^- is appreciable when $E_g < 2\,eV$ ⟹ semiconductor

Obs: for metals, valence and conduction bands are the same

e^- excited ⟹ { CB populated by e^- / VB by holes } both bands are partially full ⟹ carry current if $\vec{E}$ is applied

Energy of CB: $E_c(\vec{k}) = E_g + \dfrac{\hbar^2 k^2}{2m_e^*}$ → holds true near the bottom of the band

Energy of VB: $E_v(\vec{k}) = -\dfrac{\hbar^2 k^2}{2m_h^*}$



See Table 6.1 → notice big gap for C

Carrier concentration; intrinsic semiconductors

e^-, holes } free carriers. Number of carriers determines electrical conductivity

Fermi-Dirac distribution { particles whose Ψ is antisymmetric obey Pauli exclusion princ. and F-D dist. They are called fermions - have odd half-integral spin ($1/2$, $3/2$, etc) }

↓

[like electrons spin $= 1/2$]

protons, positrons, neutrons (constituents of matter)

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

↓

probability that energy level E is occupied by an e^- when syst is at T

Obs { particles whose Ψ is symmetric obey Bose-Einstein distribution

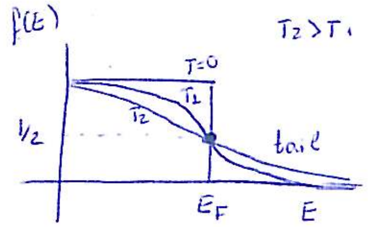
$$f(E) = \frac{1}{e^{(E-E_F)/k_BT} \ominus 1}$$

They are called bosons and have zero or integer spin }

↓

mediators of forces

photon, W, Z bosons [illegible], gluons, phonons, Cooper pairs



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

as T increases more e^- have $E > E_F$

in semiconductors: tail is of interest, that's where conducting e^- are

$\hookrightarrow E - E_F > k_BT$

$\hookrightarrow \underbrace{f(E) = e^{E_F/k_BT}\, e^{-E/k_BT}}_{\text{enough for our discussions}}$ } Maxwell-Boltzmann dist.

⟶) concentration of e^- in CB

$g_e(E)\,dE$ = number of states in $(E, E+dE)$

states have occupation prob. $f(E)$

} $f(E)\, g_e(E)\, dE$ = concentration of e^- in range $(E, E+dE)$

$$n = \int_{E_{c_1}}^{E_{c_2}} f(E)\, g_e(E)\, dE \qquad g_e(E) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} (E - E_g)^{1/2}$$

because zero-energy level here is at top of VB

$g_e(E) = 0$ if $E < E_g$

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} e^{E_F/k_BT} \int_{E_g}^{\infty} (E - E_g)^{1/2}\, e^{-E/k_BT}\, dE$$

$x = \dfrac{E - E_g}{k_BT}$

$dE = k_BT\, dx$

$$\longrightarrow \underbrace{\int_0^{\infty} x^{1/2}\, e^{-x}}_{\frac{\pi^{1/2}}{2}}\; e^{-E_g/k_BT} (k_BT)^{1/2} (k_BT)$$

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} \frac{\pi^{1/2}}{2} (k_BT)^{3/2}\, e^{E_F/k_BT}\, e^{-E_g/k_BT}$$

$$n = 2\left(\frac{m_e k_B T}{2\pi \hbar^2}\right)^{3/2} e^{E_F/k_BT}\, e^{-E_g/k_BT}$$

→) for holes

$$f_H = 1 - f(E)$$

↳ prob for hole occupation

↳ here energy is lower than E_F, we need Fermi-Dirac

$$f_h = 1 - \frac{1}{e^{(E-E_F)/k_BT}+1} = \frac{e^{(E-E_F)/k_BT}}{e^{(E-E_F)/k_BT}+1} = \frac{1}{1+e^{(E_F-E)/k_BT}} \simeq e^{-E_F/k_BT}\, e^{E/k_BT}$$

since $(E_F - E > k_BT)$

$$g_h = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}(-E)^{1/2}$$

↳ positive because zero-energy level is at top of VB

$$p = \int_{-\infty}^{0} f_h(E)\, g_h(E)\, dE = 2\left(\frac{m_h k_BT}{2\pi\hbar^2}\right)^{3/2} e^{-E_F/k_BT}$$

$$\underline{\overline{n=p}} \Rightarrow \left(\frac{m_e}{m_h}\right)^{3/2} e^{2E_F/k_BT} = e^{E_g/k_BT}$$

$$\frac{2E_F}{k_BT} = \frac{E_g}{k_BT} + \frac{3}{2}\ln\left(\frac{m_h}{m_e}\right)$$

$$\boxed{E_F = \frac{1}{2}E_g + \frac{3}{4}k_BT\ln\left(\frac{m_h}{m_e}\right)} \Rightarrow$$

small compared to E_g

⇓

E_F is close to $E_g/2$
middle of gap

$$n = 2\left(\frac{m_e k_BT}{2\pi\hbar^2}\right)^{3/2} e^{E_g/2k_BT}\, e^{-E_g/k_BT}\left(\frac{m_h}{m_e}\right)^{3/4}$$

$$\boxed{n = 2\left(\frac{k_BT}{2\pi\hbar^2}\right)^{3/2}(m_e m_h)^{3/4}\, e^{-E_g/2k_BT}}$$

→ concentration increases exponentially with T

↑ pure semiconductors (= intrinsic semiconductors) / extrinsic semiconductors: carriers are supplied by impurities $(n \neq p)$

Impurity States

-) pure semiconductor : equal numbers of both types of carriers $\underbrace{e^-, \text{holes}}$
(intrinsic)

created by
interband thermal excitation

-) doped semiconductor
(extrinsic)

↳ doping with appropriate impurities ⇒ samples with only e^- or only holes

DONOR

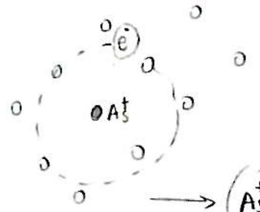
Example: Si doped ~~by~~ with As ⟶ occupy some lattice sites at random

Si ↓ host atoms (4 valence e^-)

As ↓ impurity (5 valence e^-)

↳ 4 participate in bond, one e^- is free (= conduction e^-)
↳ enters CB

(As impurities contribute e^- to CB of the semiconductor
DONORS)



⟶ As^+ attracts free e^- weakly
ionized donor

↓ orbits around at T=0°K

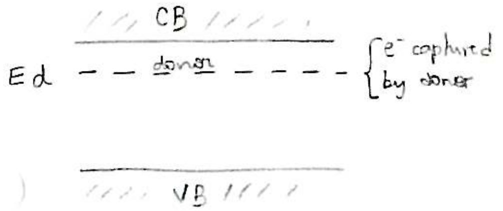
↓ binding energy

Bohr model where
Coulomb interaction is weakened by screening

$$V(r) = -\frac{e^2}{4\pi \epsilon_r \epsilon_0 r}$$

ϵ_r ↓ reduced dielectric const of medium

$$E_d = \frac{1}{\epsilon_r^2}\left(\frac{m_e}{m_0}\right)\underbrace{\left[\frac{e^4 m_0}{2(4\pi\epsilon_0\hbar)^2}\right]}_{\text{Eq. (4.77) in Griffiths (for H = 13.6 eV)}}$$



{ e^- captured by donor

E_d ~ 0.01 eV
while $K_B T \sim 0.025$ eV at room temperature

(concentration of e^- is nearly equal to that of donors)
$n \sim n_d$

ACCEPTOR → one bond remains vacant

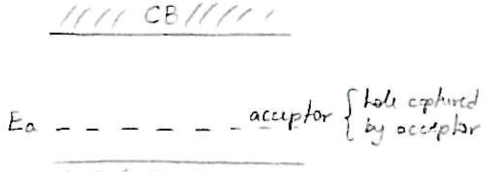
Example Si doped with Ga ↓ (3 valence e^-) ⇒ one bond remains vacant

vacancy may be filled by an e^- from other bond, ...

⇒ hole is free

ionized acceptor is negative

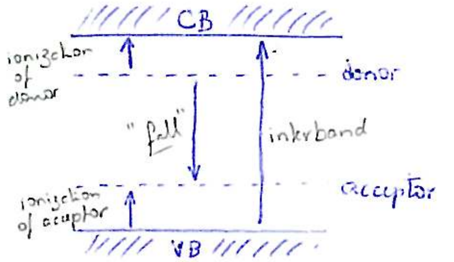
↳ attracts hole → {again binding energy ~ 0.05 eV}



↳ so at room temperature {acceptors are ionized, holes are free}

Semiconductor Statistics

semiconductors usually contain both donors and acceptors



o) e^- in CB created by { interband thermal excitation
or
thermal ionization of donor (e⁻ becomes free - not bound to As^+)

o) holes in VB created by { interband thermal excitation
or
thermal ionization of acceptor (e⁻ from VB goes into acceptor level, hole in VB is free - not bound to Ga^-)

o) also, e⁻ may fall from donor level to acceptor level

Let us treat few special cases in the intrinsic and extrinsic region

o) Intrinsic region

↳ determined primarily by thermally induced interband transitions

$$\boxed{n=p} = 2\left(\frac{K_B T}{2\pi\hbar^2}\right)^{3/2}(m_e m_h)^{3/4}\, e^{-E_g/2K_BT} \qquad n = p = n_i$$

↑ intrinsic concentration

} intrinsic condition more favorable at higher temp
all semiconductors are intrinsic at high temperature

impurity doping is small
semiconductor is ~ pure

$n_i \gg (n_d - n_a)$

Extrinsic region

↳ when contribution of impurities exceeds carriers supplied by interband excitation

→) $n_d \gg n_a$

concentration of e^-

$\boxed{n = n_d}$

still valid: $n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} e^{E_F/k_BT} \, e^{-E_g/k_BT}$ ← come from $n = \cdots\int_{E_g}^{\infty}\cdots$ ← CB

also

$$p = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} e^{-E_F/k_BT}$$

so

$np = 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3} (m_e m_h)^{3/2} e^{-E_g/k_BT}$ ← E_F is gone

$np = n_i^2$ ($n \sim n_d$) $\Rightarrow$ $p = \frac{n_i^2}{n_d} \ll n$ np deps only on T

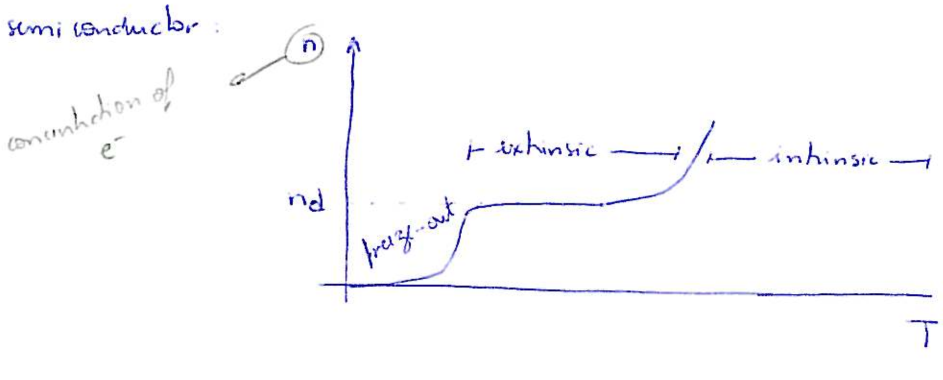
semiconductor where $n \gg p$ ⇒ n-type semiconductor (n from negative)

→) $n_a \gg n_d$

$\boxed{p = n_a}$ → $n = \frac{n_i^2}{n_a}$ ⇒

⇒ $p \gg n$ ⇒ p-type semiconductor

n-type semiconductor:



Electrical Conductivity

→) n-type (free-electron model)

$$\sigma_e = \frac{n e^2 \tau_e}{m_e}$$

order of magnitude $n = 10^{15}\ \mathrm{cm}^{-3} = 10^{21}\ \mathrm{m}^{-3}$ $\tau_e = 10^{-12}\ \mathrm{s}$ $m_e = 0.1\ m_0$

$\Rightarrow$ $\underline{\sigma \sim 1\ (\Omega\,\mathrm{m})^{-1}}$ electrical conductivity typical of semiconductors

$[\sigma \sim 10^{7}\ (\Omega\,\mathrm{m})^{-1}$ for metals$]$

units

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

$$\left[\frac{A}{m^2}\right] = \sigma \left[\frac{V}{m}\right]$$

$$\sigma = \left[\frac{A}{V}\frac{1}{m}\right] = \frac{1}{\Omega m}$$

mobility

Eq(4.7) → $v_e = -\underbrace{\left(\frac{e\tau_e}{m_e}\right)}_{\mu_e} \mathcal{E}$

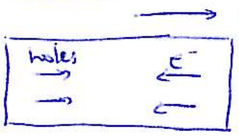
$$\underbrace{\mu_e = \frac{v_e}{\mathcal{E}}}_{\text{sign is disregarded}}$$

(Table 6.3)

$$\sigma_e = n e \mu_e$$

→) p-type

$$\sigma_h = p \frac{e^2 \tau_h}{m_h} = p e \mu_h$$



$$\boxed{\sigma = \sigma_e + \sigma_h = n e \mu_e + p e \mu_h} \leftarrow \text{general}$$

intrinsic: $\overline{\underline{\sigma = n e(\mu_e + \mu_h)}}$ since $n = p$

Dependence on temperature

$n \propto e^{-E_g/2k_BT}$

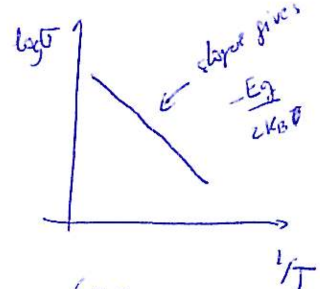
intrinsic

$\sigma = ne(\mu_e + \mu_h) \longrightarrow \sigma = f(T)\, e^{-E_g/2k_BT}$

↓ increases exp with T

used to determine Eg

$\log\sigma = \log f(T) - \frac{E_g}{2k_BT}$



(f(T) is neglected)

[redacted]

extrinsic (n-type)

$\sigma_e = ne\mu_e$

↑ T

$n \sim n_d$ ← (fixed)

↑ at room T all impurities give e⁻

raising T cannot increase number of free e⁻ anymore

but T has effect on mobility

Mobility vs. T

$\mu_e = \frac{e\,\tau_e}{m_e}$ → varies with T ⇒ μ_e deps on T

decrease as T rises

$\bar{\tau}_e = \frac{l_e}{\bar{v}_n}$

average lifetime

l_e → mean free path of e⁻

$\bar{v}_n$ → average random velocity

↓ e⁻ have different speed depending on location in the band

$\mu_e = \frac{e\,l_e}{m_e \bar{v}_n}$

from kinetic theory

$\frac{1}{2} m_e \bar{v}_n^2 = \frac{3}{2} k_B T$

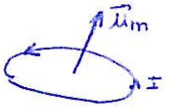
$\mu_e = \frac{e\,l_e}{(m_e 3k_BT)^{1/2}}$ → also deps on T → $\underbrace{l_e \sim T^{-1}}_{\text{at high T}}$ ⇒ $\mu_e \sim T^{-3/2}$

collision with phonon is dominant

Magnetism (Ch. 9)

∘) electric current → magnetic dipole moment

$$\mu_m = IA$$



$$\vec{\mu}_m = \underbrace{\boxed{-\frac{e}{2m}}}_{\text{gyromagnetic ratio}} \underbrace{\vec{L}}_{\text{angular momentum of the } e^-}$$

(orbital rotation)

∘) spin

$$\vec{\mu}_m = -\frac{e}{m}\vec{S}$$

In an external magnetic field $\vec{B}$, dipole experiences a torque

$$\vec{\tau} = \vec{\mu}_m \times \vec{B}$$

that wants to align it with the field. For a time it **precesses** with the Larmor frequency, but due to collisions it eventually lines up (relaxation)

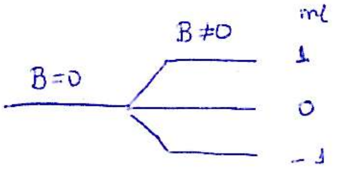
∘) potential energy of dipole in an external field $\boxed{V = -\vec{\mu}\cdot\vec{B}}$

→) orbit

take $\vec{B}$ in z direction

$$E = +\frac{e}{2m}\underset{\substack{\uparrow \\ \text{quantized}}}{L_z} B \xrightarrow{L_z = \hbar m_\ell} E = \underbrace{\boxed{\left(\frac{e\hbar}{2m}\right)}}_{\text{Bohr magneton : } \mu_B} B\, m_\ell$$

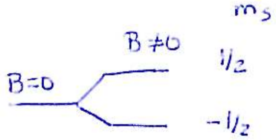
$\ell = 1$



} splitting of an atomic level by a magnetic field

(ZEEMAN EFFECT)

→) spin 1/2 (electron)



$E = 2\mu_B B\, m_s$

Zeeman splitting

in 3 direction

$$H = \frac{\varepsilon}{2}\sigma_z \quad \begin{cases} \begin{pmatrix}1\\0\end{pmatrix} \to +\varepsilon/2 \\ \begin{pmatrix}0\\1\end{pmatrix} \to -\varepsilon/2 \end{cases}$$

$\varepsilon = 2\mu_B B$

---

spin-orbit coupling $H = -\underset{\substack{\vec{S}\\ \text{electron}}}{\vec{\mu}} \cdot \underset{\substack{\vec{L}\\ \text{proton}}}{\vec{B}} = (\text{const})\, \vec{S}\cdot\vec{L}$

caused by torque exerted on mag. dip. moment of the spinning e^- by mag field of the proton → fine structure

---

Susceptibility

magnetic induction: $\vec{B}$

magnetic field intensity $\vec{\mathcal{H}}$

} related in vacuum by $\vec{B} = \mu_0 \vec{\mathcal{H}}$

↓ permeability in free space

in a medium

magnetic induction: $\vec{B} = \mu_0 \vec{\mathcal{H}} + \mu_0 \vec{M}$

↳ magnetization vector (dipole moment per unit volume)

Magnetization is induced by field:

$$\vec{M} = \underset{\uparrow}{\boxed{\chi}}\,\vec{\mathcal{H}}$$

magnetic susceptibility

↓

materials are grouped according to the sign and magnitude of the susceptibility

paramagnetic

χ ⊕

ions of transition

rare-earth ions

(incomplete atomic shells)

have a permanent magnetic moment

diamagnetic

χ ⊖

ionic and covalent crystals

(complete shells)

only occur in the presence of external magnetic field

paramagnetism | **diamagnetism**

paramag. materials are attracted to mag. fields | diamag. materials are repelled to mag. fields

- **Ferromagnetism**: materials can $\boxed{\text{retain}}$ magnetic properties for a period even after the field is removed

(usual magnet)

all magnetic moments aligned with field ↑↑↑↑

- **Antiferromagnetism** another kind of magnetic ordering

anti-align ⇒ zero net magnetization

Above critical temperature: both become paramagnet
- Ferromag.: **Curie** temp
- Antif.: **Néel** temp

Heisenberg interaction
$$\begin{cases} \underline{\text{insulator}} \rightarrow e^- \text{ localized in lattice site} \\ H = \boxed{J} \sum \vec{s}_n \cdot \vec{s}_{n+1} \qquad \vec{s} = \vec{\sigma}/2 \end{cases}$$

(exchange coupling parameter)

Ferromag: $H = -J\,\vec{s}_1 \cdot \vec{s}_2$

$= -\frac{J}{4}\,\vec{\sigma}_1 \cdot \vec{\sigma}_2$

$$\begin{array}{cccc} |\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\downarrow\downarrow\rangle \\ \end{array}$$
$$\begin{pmatrix} -J/4 & 0 & 0 & 0 \\ 0 & +J/4 & -J/2 & 0 \\ 0 & -J/2 & +J/4 & 0 \\ 0 & 0 & 0 & -J/4 \end{pmatrix}$$

$(J/4-\lambda)^2 - J^2/4 = 0$

$\lambda^2 - \frac{J}{2}\lambda - \frac{3J^2}{16} = 0$

$$\lambda = \frac{\frac{J}{2} \pm \sqrt{J^2/4 + 3J^2/4}}{2} \begin{cases} 3J/4 \\ -J/4 \end{cases}$$

$|\uparrow\uparrow\rangle : -J/4$ m = 1

$|\downarrow\downarrow\rangle : -J/4$ m = −1

$3J/4$: $\frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}}$

$-J/4$: $\frac{\uparrow\downarrow + \downarrow\uparrow}{\sqrt{2}}$ m = 0

triplet
s = 1

Antiferromag: $H = +J\,\vec{s}_1 \cdot \vec{s}_2$

$= +\frac{J}{4}\,\vec{\sigma}_1 \cdot \vec{\sigma}_2$

$$\begin{pmatrix} J/4 & 0 & 0 & 0 \\ 0 & -J/4 & J/2 & 0 \\ 0 & J/2 & -J/4 & 0 \\ 0 & 0 & 0 & J/4 \end{pmatrix}$$

$$\left.\begin{array}{l} |\uparrow\uparrow\rangle \\ \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} \\ |\downarrow\downarrow\rangle \end{array}\right\} J/4$$

ground state

$\boxed{\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}}$ $-\frac{3J}{4}$

↳ ext. $\vec{B}$ ⇒ splitting / also Zeeman for each spin $H = \frac{\varepsilon}{2}\sigma_n^3$