

PHY-402: SOLID STATE PHYSICS

(1)

- ① Solid State: An introduction, Philip Hoffman
- ② Solid State Basics (Oxford book), Steve H. Simon
- ③ Solid State Physics, Ashcroft & Mermin.
- ④ Intro to Solid State, Charles Kittel.

Instructor: Dr. Yogesh Singh.

Office hours:

Grading: 20% quizzes + 30% midsem + 50% endsem.

Homework? No. Not graded. But yeah, ungraded Psets.

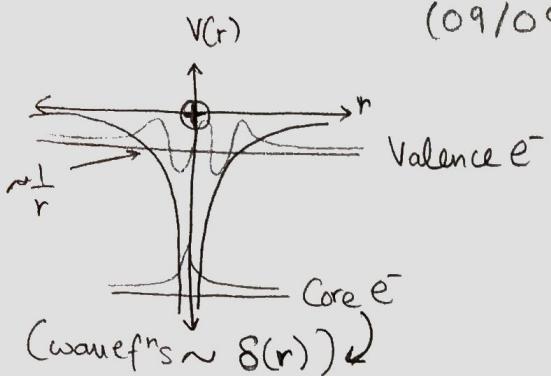
Tutorials? Occasionally. Not weekly.

TOPICS: (Lecture-1)

- Intro
- Why do solids form?
 - Bonding (Ch-6 ②)
- Lattices / Crystals / X-ray diffraction.
- Vibrations in lattices
 - phonons, lattice heat capacity.
- Electrons in Solids / Electronic States in Solids
 - Tight Binding approximation
 - quasi-free electron approximation.
- Conductivity of metals. Metals in fields (\vec{E} , \vec{B})
- Magnetism in Solids, Atomic magnetism, Ferromagnetism, Paramagnetism, anti-ferromagnetism.
- Superconductivity.

Lecture - 2 (PHY402)

(09/09)



core e⁻
↓
Net Nuclear charge Ze - Z_c e

$$V_{\text{eff}} = -\frac{(Z - Z_c)e^2}{4\pi\epsilon_0 r}$$

$$Z_v \equiv Z - Z_c < Z$$

So for a single e⁻ in this system

$$H_i = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + V_{e-e}(r) \quad \text{NOT EXACTLY SOLVABLE}$$

↑ electron-electron interaction

Before discussing bonding, let's consider the case of a two-electron system

$$H^{(n=2)} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2}$$

$\psi(\vec{r}_1, \vec{r}_2)$ itself would need 6 spatial dim's to specify the wavefunction

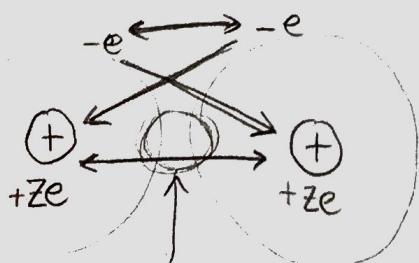
$$\vec{r}_1, \vec{r}_2 \in \mathbb{R}^3$$

∴ just to specify the wavefn of a n-electron system, if we make 100 grids/dim,

$$\Rightarrow 10^{2n} \text{ just to specify } \psi \text{ numbers}$$

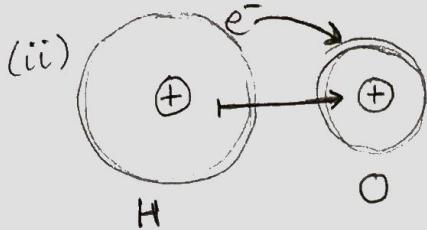
Bonding (Why do solids form?)

(i)



(Ignore e⁻-e⁻ interaction)

accumulation of charge → COVALENT
b/w nuclei BONDING



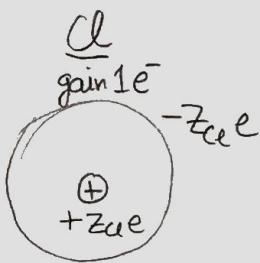
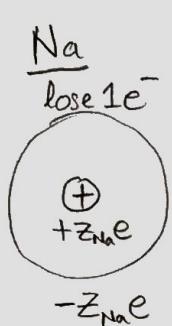
IONIC BONDING

electrons being shared b/w the atoms

Strength of covalent bonds \sim few eV \rightarrow brittle (break easily but don't deform)

Strength of ionic bonds \sim few eV \rightarrow weaker than covalent

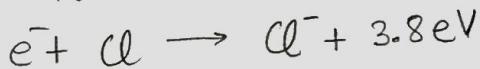
Example H_2O , NaCl



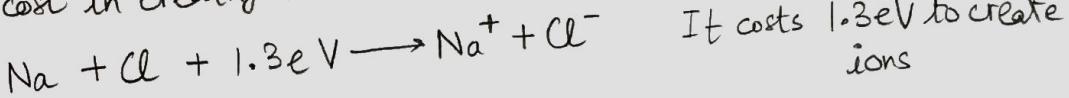
Losing atoms costs energy



However, gaining e^- for Cl gives off energy



\Rightarrow Net cost in creating the two ions is



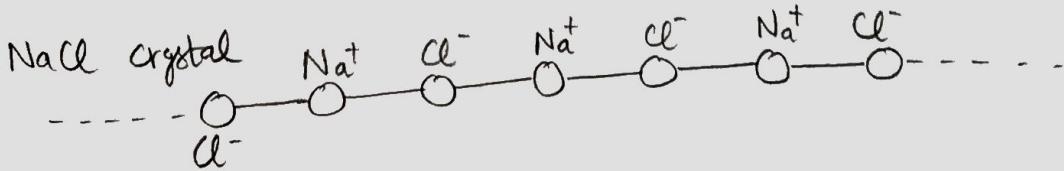
typical distance b/w Na^+ & Cl^- $a \approx 2.5 \text{ \AA}$

in NaCl

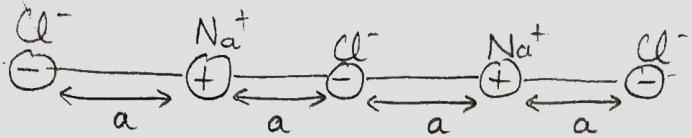
So once the ions bond, $U_{\text{ion}} = -\frac{e^2}{4\pi\epsilon_0 a} \approx -5 \text{ eV}$

Therefore, the net process causes $-5 \text{ eV} + 1.3 \text{ eV} = -3.8 \text{ eV}$ energy to be released (per ion pair) when the final NaCl forms.

Let's now find the energy released in the process of creating a 1D



(3)



Here we shouldn't think of a Na^+ "bonding" with Cl^- . Just think of this as a lattice of ions.

$$U_{\text{Na}^+} = -\frac{e^2}{4\pi\epsilon_0 a} \times 2 + \frac{e^2}{4\pi\epsilon_0 (2a)} \times 2 - \frac{e^2}{4\pi\epsilon_0 (3a)} + \dots$$

(2x because each Na^+ has 2 Cl^- to both sides of it, the 2 Na^+ atoms on both sides & so on)

$$= -\frac{2e^2}{4\pi\epsilon_0 a} \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} \dots \right] = -\frac{2e^2}{4\pi\epsilon_0 a} \ln(2)$$

Interaction energy of a single Na^+ atom

$$\therefore \text{for the entire lattice, } U_{\text{total}} = (U_{\text{Na}^+} + U_{\text{Cl}^-}) N_A = N_A U_{\text{Na}^+}$$

(2) $\approx -780 \text{ eV}$

where did this factor of two come from?

Fixed!

Because we calculate the energy considering the total bonds made.

But while counting bonds for atom ① here



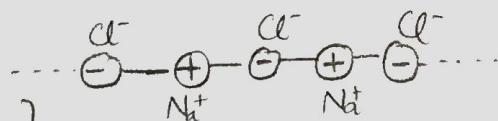
We count 1-2 bond. But it's also counted when we calculate for Cl^-



BUT this isn't a corner atom now. So, I think there's a mistake. Either multiply by 2x in calculation of U_{Na^+} (for single atom) or don't divide by 2 if we are consider Na^+ to be at corner.

Lecture-3

(10/09)



$$U_{Na^+} = \frac{2e^2}{4\pi\epsilon_0 a} \left[-1 + \frac{1}{2} - \frac{1}{3} + \dots \right]$$

$$= -\frac{Md e^2}{4\pi\epsilon_0 a} \quad \text{where } M_d = \text{Madelung constant}$$

Here (for 1-D crystal) , $M_d = 2\ln 2 > 1$

$$\text{So, } U_{Na^+} = -\frac{2\ln(2)}{4\pi\epsilon_0 a} e^2$$

The calculation for Cl^- also runs exactly similarly $\Rightarrow U_{Na^+} = U_{Cl^-}$

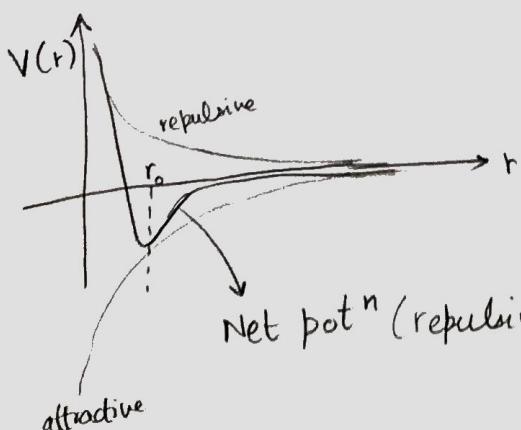
$$\text{So, } U_{\text{total}} = \frac{(U_{Na^+} + U_{Cl^-}) N_A}{2} = \frac{2 U_{Na^+} N_A}{2} = \underline{\underline{U_{Na^+} N_A}}$$

(for 1 mole of NaCl)

2
↓
to factor for
double counting of bonds

COHESIVE ENERGY!

The calculations done here differ by experimental values since the actual interatomic potⁿ looks like



Net potⁿ (repulsive + attractive)

Modelled by something

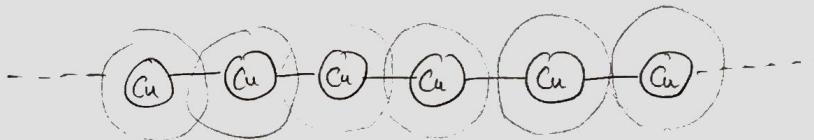
$$\text{like } U(r) = \frac{1}{r^m} - \frac{1}{r^n}$$

repulsion here is modelled
by some "non-electrostatic" interaction.

The point charge picture
fails at close distances.

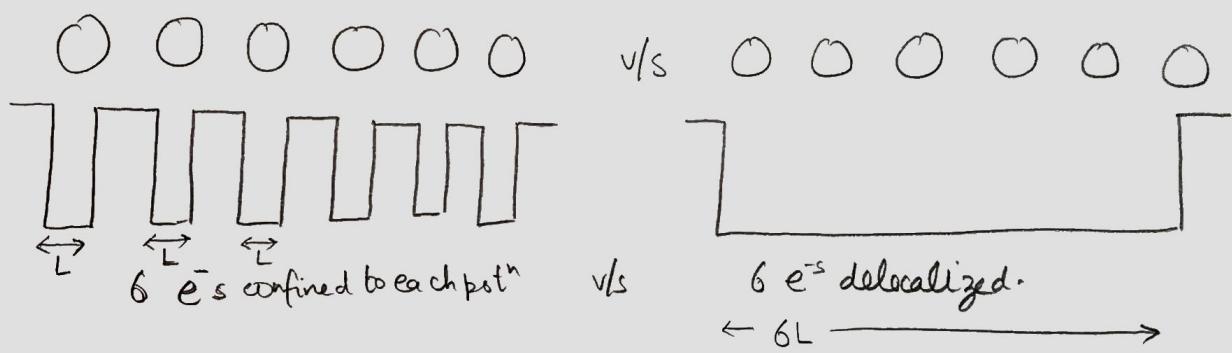
Metallic Bonding.

Say we have a lattice of Cu atoms



The e^- s delocalise over the entire lattice in the absence of ionic/ covalent bonding.

For an e^- confined to the atom (Cu), find the energy relation.
Compare with an e^- delocalised over the entire lattice.



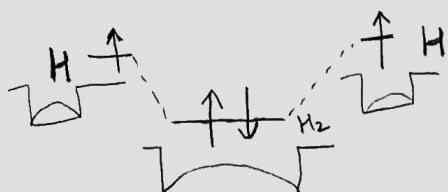
$$E = 6 \cdot \frac{n^2 h^2}{2m L^2}$$

$$E = 6 \cdot \frac{n^2 h^2}{2m (6L)^2}$$

?

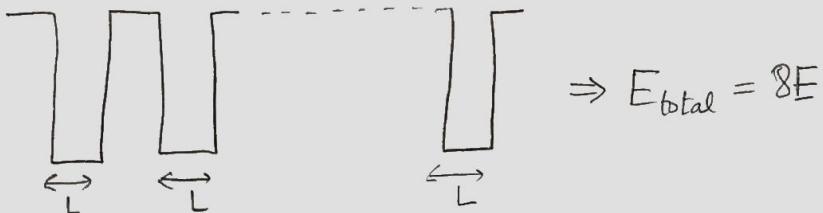
I don't think I understand the question.

The picture of delocalization of e^- to more than one nucleus is what forms covalent bonds. It leads to a reduction in the energy of the overall system. (bonding orbital)

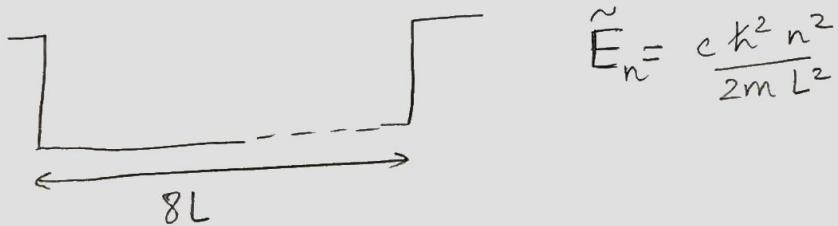


Lecture - 4
(13/09)

(i) If we put the e^- 's in a well of length L (8 Cu atoms & $8e^-$)



(ii) If we however put all the e^- 's in a big well of length $8L$

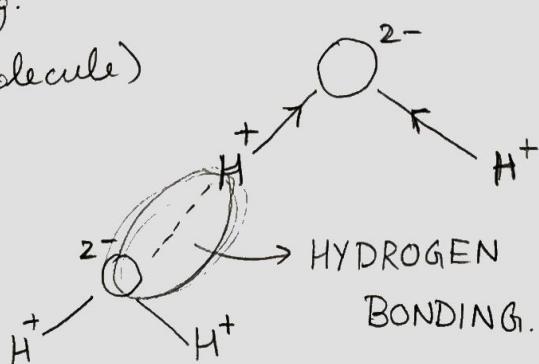


Therefore, let's compare the ground state energies of (i) & (ii)

$$\begin{aligned} E_{(i)}^{(0)} &= \frac{8ck^2}{2mL^2} \\ &= \frac{4ck^2}{mL^2} \\ E_{(ii)}^{(0)} &= 2 \left(\frac{ck^2}{2m(8L)^2} \right) (1^2 + 2^2 + 3^2 + 4^2) \\ &= \frac{2ck^2}{2m(64)L^2} (1+4+9+16) \\ &= \frac{30}{64} \frac{ck^2}{mL^2} \end{aligned} \quad \text{lowering of the energy}$$

Hydrogen Bonding.

H_2O (water molecule)



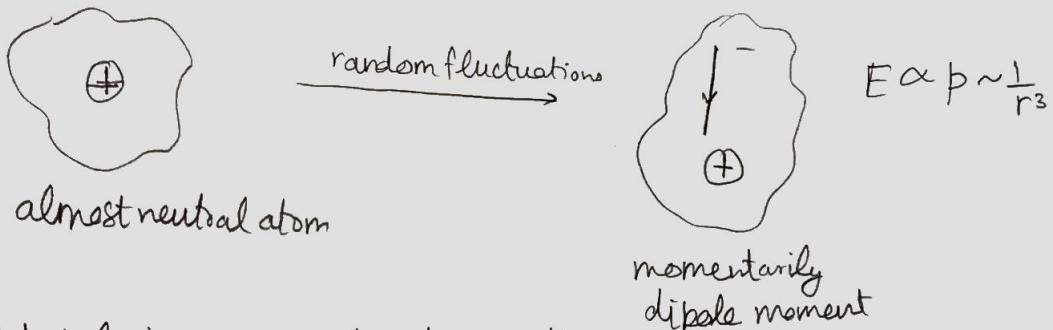
They look like ions to a good approximation.

(2)

Strength of hydrogen bonds, however, is very weak. $\sim (0.1 - 0.2 \text{ eV})$

Van der Waal bonding.

happens b/w neutral atoms, but they're so weak that you have to reduce the thermal energy by a large fraction before we start to see the effects.



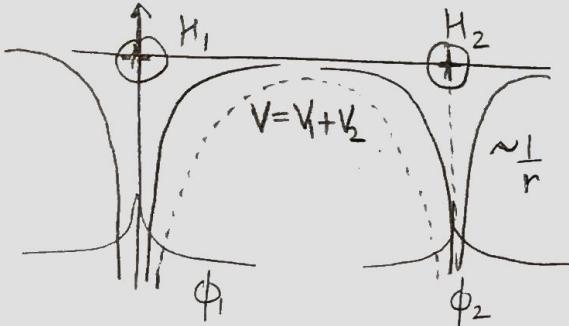
The field polarizes a nearby atom with dipole moment \vec{p} . The two dipole moments as a result, feel an attractive force $F \propto pp' \sim \frac{1}{r^6}$

Strength of Van der Waal bonds $\sim 10 - 20 \text{ meV}$

Lecture-6
(16/09)

Tight bonding model.

LCAO model \rightarrow linear combination of atomic orbitals.



$$H_1 = -\frac{k^2}{2m} \nabla^2 + V_1$$

$$H_2 = -\frac{k^2}{2m} \nabla^2 + V_2$$

$$H_1 \phi_1 = E_0 \phi_1$$

$$H_2 \phi_2 = E_0 \phi_2$$

ϕ_1 & ϕ_2 are 1s states
of hydrogen atoms 1 & 2.

We now have to solve the problem of an e^- in the combined potential $V_1 + V_2$

↓ (we ignore e-e correlation)

$$\Rightarrow H = -\frac{k^2}{2m} \nabla^2 + V_1 + V_2$$

$$H \phi = E \phi \quad \text{what's the new } \phi?$$

LCAO $\rightarrow \underline{\phi \approx a_1 \phi_1 + a_2 \phi_2}$ if overlap b/w ϕ_1 & ϕ_2 isn't much.

$$\left(-\frac{k^2}{2m} \nabla^2 + V_1 + V_2 \right) (a_1 \phi_1 + a_2 \phi_2) = E (a_1 \phi_1 + a_2 \phi_2)$$

$$a_1 (H_1 + V_2) |\phi_1\rangle + a_2 (H_2 + V_1) |\phi_2\rangle = E (a_1 |\phi_1\rangle + a_2 |\phi_2\rangle)$$

$$a_1 H_1 |\phi_1\rangle + a_1 V_2 |\phi_1\rangle + a_2 H_2 |\phi_2\rangle + a_2 V_1 |\phi_2\rangle = E (a_1 |\phi_1\rangle + a_2 |\phi_2\rangle)$$

$$a_1 E_0 |\phi_1\rangle + a_1 V_2 |\phi_1\rangle + a_2 E_0 |\phi_2\rangle + a_2 V_1 |\phi_2\rangle = E (a_1 |\phi_1\rangle + a_2 |\phi_2\rangle)$$

Eqn ①

$$\langle \phi_1 | E_{q^n} | 1 \rangle \Rightarrow a_1 E_0 + a_1 \langle \phi_1 | V_2 | \phi_1 \rangle + a_2 \langle \phi_1 | V_1 | \phi_2 \rangle = a_1 E$$

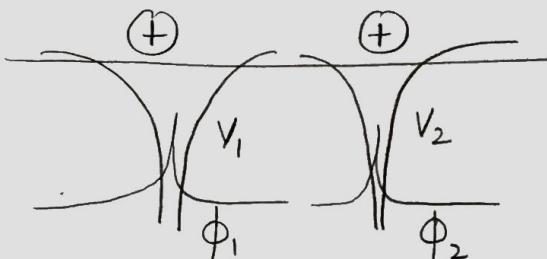
$$\langle \phi_2 | E_{q^n} | 1 \rangle \Rightarrow a_2 E_0 + a_2 \langle \phi_2 | V_2 | \phi_2 \rangle + a_1 \langle \phi_2 | V_1 | \phi_1 \rangle = a_2 E$$

where $\langle \phi_i^* | \phi_j^* \rangle = 1$ and we assume nil overlap $\langle \phi_i^* | \phi_j \rangle \approx 0$
 $i \neq j$

Writing the above in a matrix form,

$$\begin{pmatrix} E_0 + \underbrace{\langle \phi_1 | V_2 | \phi_1 \rangle}_{\Delta E} & \langle \phi_1 | V_1 | \phi_2 \rangle \\ \langle \phi_2 | V_2 | \phi_1 \rangle & E_0 + \underbrace{\langle \phi_2 | V_1 | \phi_2 \rangle}_{\Delta E} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\begin{aligned} \langle \phi_1 | V_2 | \phi_1 \rangle &= \langle \phi_2 | V_1 | \phi_2 \rangle \\ &= \Delta E \quad (\text{by symmetry}) \end{aligned}$$



$$\text{Again, } \langle \phi_1 | V_1 | \phi_2 \rangle = \langle \phi_2 | V_2 | \phi_1 \rangle = t \quad (\text{hopping term})$$

Need to revisit the equivalence of above inner products

$$\begin{pmatrix} E_0 + \Delta E & t \\ t & E_0 + \Delta E \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\det \begin{pmatrix} A - E & B \\ B & A - E \end{pmatrix} = (A - E)^2 - B^2 = 0$$

$$\Rightarrow E_{\pm} = A \pm B$$

$$\underline{E_+ = E_0 + \Delta E + t} \quad \underline{E_- = E_0 + \Delta E - t}$$

Plugging it into eigenvalue eqⁿ

For E_+ $(A - E_+) a_1 + B a_2 = 0$
 $-t a_1 + t a_2 = 0 \Rightarrow \underline{\underline{a_1 = a_2}}$

For E_- $(A - E_-) b_1 + B b_2 = 0 \Rightarrow \underline{\underline{a_1 = -a_2}}$

We also need $|\phi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$ to be normalised so $a^2 + b^2 = 1$

So, $E_+ = E_0 + \Delta E + t$ and $|\phi_+\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle + |\phi_2\rangle)$
 $E_- = E_0 + \Delta E - t$ and $|\phi_-\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle - |\phi_2\rangle)$

Now, how has the energy changed?

$$\text{since } \langle r | \phi_{1,2} \rangle > 0$$

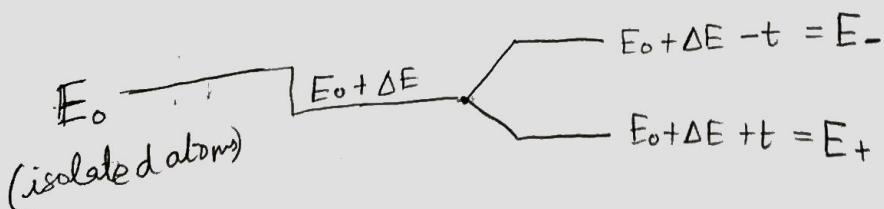
$$\underline{\Delta E = \langle \phi_1 | V_2 | \phi_1 \rangle < 0}$$

$$t = \langle \phi_1 | V_2 | \phi_2 \rangle$$

$$\text{but } V_2 < 0 \Rightarrow \langle \phi_1 | V_2 | \phi_1 \rangle < 0$$

↑ depends on what ϕ_1 & ϕ_2 are.

For the problem we started with however i.e. ground state of Hydrogen atoms will have ϕ_1 & ϕ_2 both as 1s states. So here $t < 0$.



So, what is the total change in energy?

$$\text{total } E_i = 2E_0$$

$$\text{total } E_f = 2E_f = 2E_0 + 2(\Delta E - t)$$

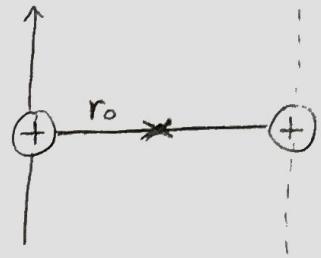
$$\underline{\text{change in energy} = 2(\Delta E - t)}$$

Electron density b/w the two atoms?

$$\text{total } \rho_i(r_0) = |\phi_1|^2 + |\phi_2|^2 = 2|\phi_1|^2$$

$$\text{total } \rho_f(r_0) = 2|\phi_f|^2 = 2 \cdot \frac{1}{2} |\phi_1 + \phi_2|^2 = 4|\phi_1|^2$$

why this defn?



So, the electron density increases. In general, when two atoms decide to share e⁻s such that the e⁻ density increases b/w the atoms, the net energy goes down.

∴ Covalent bonding is stable!

Topics covered:

→ Ionic bonding electronegative & electro-positive atoms turn into ions. Electrostatic forces lower the energy on formation of crystals.

→ Covalent bonding most bonds are covalent. we used QM & LCAO to find lower shared energy. Made by sharing e⁻s.

→ Metallic bonding e⁻s are delocalised throughout the solid. Non-directional bonds in metallic bonding.

→ Hydrogen bonding found in organic materials & water.

→ Van der Waal's bonding. b/w neutral atoms. caused by fluctuating dipole moments.

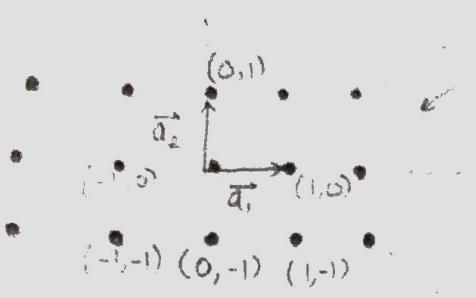
Lecture - 7

(17/09)

Crystal structures

Bravais Lattice - The set of pts given by $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2$

where $n_1, n_2 \in \mathbb{Z}$ and \vec{a}_1, \vec{a}_2 are linearly ind. vectors $\in \mathbb{R}^2$. (for 2D)



square lattice

$$\text{here } |\vec{a}_1| = |\vec{a}_2|$$

$$\vec{a}_1 \cdot \vec{a}_2 = 0$$

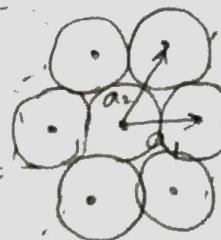
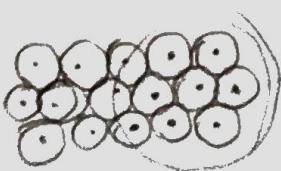
Bravais lattice
 $=$ structurally
 & orientationally
 identical when viewed
 from each lattice
 site.

We can also have rectangular lattice.



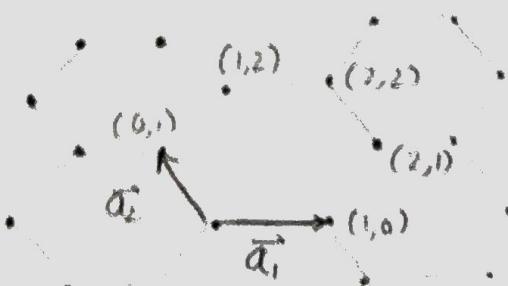
$$|\vec{a}_1| \neq |\vec{a}_2| \quad \vec{a}_1 \cdot \vec{a}_2 = 0$$

Let's now look at packing of spheres in 2D. we get a triangular lattice



In 2D packing of spheres, \vec{a}_1 and \vec{a}_2 s.t. $|\vec{a}_1| = |\vec{a}_2|$ and
 $\vec{a}_1 \cdot \vec{a}_2 = \cos(60^\circ)$

is one of the natural choices

Honeycomb lattice

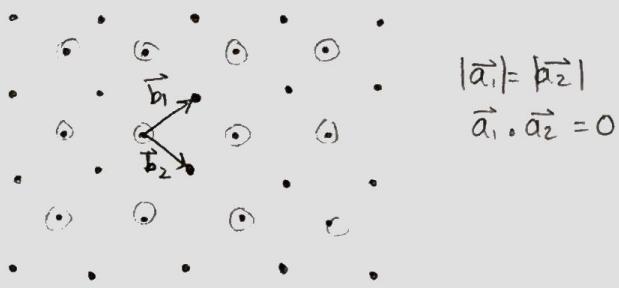
We definitely can generate all the pts. on the Honeycomb lattice using linear combinations of \vec{a}_1 & \vec{a}_2 . However, linear combination like $(1,1)$ \notin Honeycomb lattice. \therefore Not all linear combinations \in Honeycomb lattice. So, it's not a Bravais lattice!

So, the defⁿ of Bravais lattice isn't enough to describe all the lattices found in real solids.

Lattice with a Basis.

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + \{ \vec{b}_i \}$$

$\vec{a}_1, \vec{a}_2 \rightarrow$ primitive vectors
 $n_1, n_2 \in \mathbb{Z}$



\circ \rightarrow Bravais lattice points
 (but we don't need it)

\bullet \rightarrow lattice pts. with a basis.

If $\vec{b}_1, \vec{b}_2 \neq 0$, then the Bravais lattice points don't actually \in Lattice.

Having $\vec{b}_1 = 0$ includes all the B.L. pts in addition to other extra points spanned by \vec{b}_2 (and more \vec{b}_i s).

Honeycomb is NEVER just a Bravais lattice with any primitive vectors \vec{a}_i .

BRAVAIS LATTICE + BASIS = CRYSTAL

Lecture - 8

(20/09)

Quick recap:

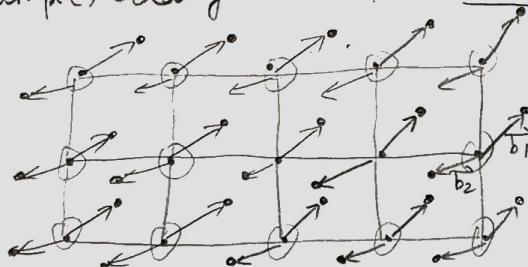
Bravais lattice: $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2$ $n_i \in \mathbb{Z}$
 \vec{a}_1 & linearly ind. vectors

The square, triangular, and rectangular lattices among others are examples of a Bravais lattice.

However, something like a honeycomb lattice isn't a Bravais lattice. Thus we define a crystal structure as

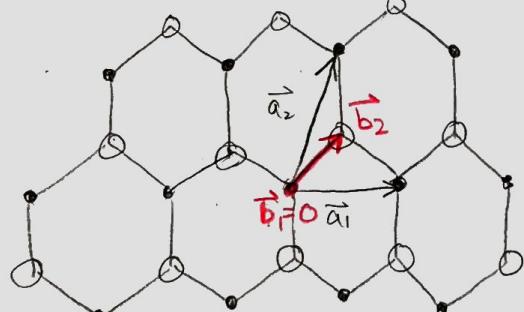
$$\vec{R} = \underbrace{n_1 \vec{a}_1 + n_2 \vec{a}_2}_{\text{B.L.}} + \underbrace{\{b_i\}}_{\text{basis } \vec{v}}$$

For example, adding \vec{b}_1 & \vec{b}_2 to a square lattice would look like



But, we can always translate it s.t. $\vec{b}_1 = 0$.

Honeycomb lattice can't get Q pts. with just the B.L.



$$|\vec{a}_1| = |\vec{a}_2|$$

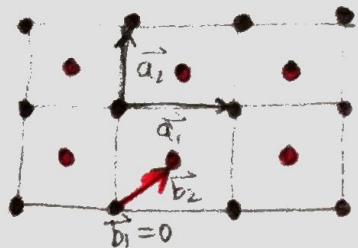
$$\vec{a}_1 \cdot \vec{a}_2 = |\vec{a}_1| |\vec{a}_2| \cos(60^\circ)$$

If we add a basis vector $\vec{b}_1 = 0, \vec{b}_2$ to this B.L., we get all the missing points.

So, Honeycomb = B.L. + basis vectors $\vec{b}_1 = 0, \vec{b}_2 \neq 0$

$(\vec{b}_1 = 0$ includes all B.L. pts & $\vec{b}_2 \neq 0$ spans all the missing pts. of honeycomb)

Now say we have a structure with atoms in centre of the square lattice

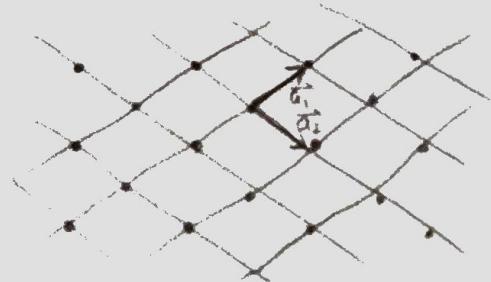


$$\text{Defining } \vec{b}_1 = 0$$

$$\vec{b}_2 = \frac{1}{2} (\vec{a}_1 + \vec{a}_2)$$

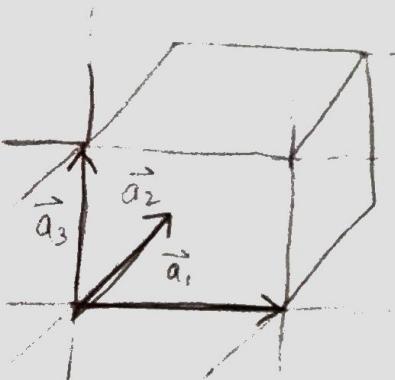
gives all the centre point

However, we could have been a little clever and identified this purely as a Bravais lattice



and $n_1 \vec{a}_1 + n_2 \vec{a}_2$ generates all the points in here

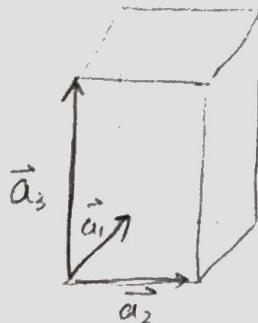
Bravais lattice in 3D



$$|\vec{a}_1| = |\vec{a}_2| = |\vec{a}_3|$$

$$\vec{a}_i \cdot \vec{a}_j = 0$$

Simple cubic.



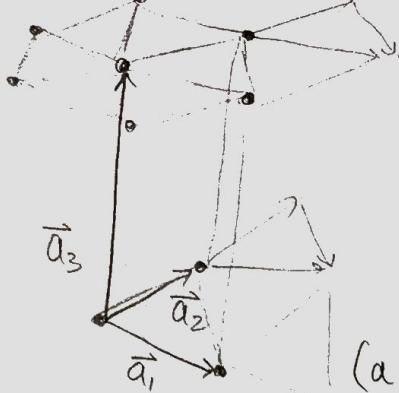
$$|\vec{a}_1| = |\vec{a}_2| \neq |\vec{a}_3|$$

Tetragonal lattice.

$$|\vec{a}_1| \neq |\vec{a}_2| \neq |\vec{a}_3|$$

Orthorhombic lattice

All of the above have orthogonal sides.



Hexagonal lattice

$$|\vec{a}_1| = |\vec{a}_2|$$

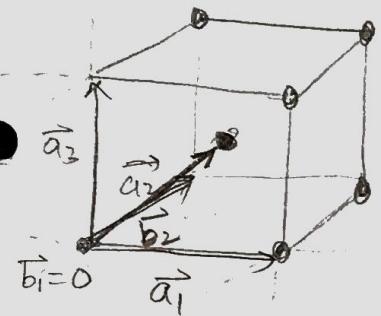
$$\vec{a}_1 \cdot \vec{a}_2 = a_1 a_2 \cos(60^\circ)$$

$$|\vec{a}_3| \neq |\vec{a}_{1,2}|$$

$$\vec{a}_3 \cdot \vec{a}_{1,2} = 0$$

(a mesh of triangular planes.)

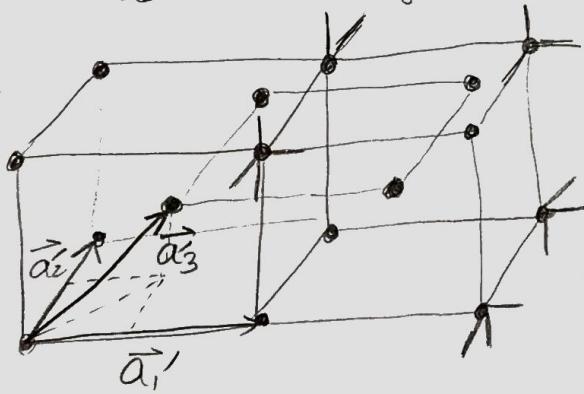
Body centred cubic (b.c.c.)



b.c.c. = simple cubic Bravais lattice

$$+ \{ \vec{b}_1 = 0, \vec{b}_2 = \frac{1}{2}(\vec{a}_1 + \vec{a}_2 + \vec{a}_3) \}$$

However, just like we choose an alternate set of vectors (in the case of square with centre atoms as well) to get a purely B.L. structure instead of B.L. + basis vectors, we can do a similar thing with b.c.c.



However this doesn't have the symmetry of the cube.

But it's a mathematically concise way to describe the lattice.

b.c.c. = (Bravais lattice with $\vec{a}_1' = \vec{a}_1$, $\vec{a}_2' = \vec{a}_2$, $\vec{a}_3' = \vec{b}_2$)

A more symmetric set -

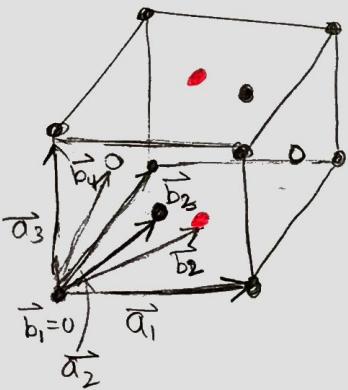
$$\vec{a}_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \quad \vec{a}_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}), \quad \vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})$$

$$\vec{a}_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x})$$

Lecture 9 (contd.)

(21/09)

- For triclinic, $\vec{a}_1, \vec{a}_2, \vec{a}_3$ can be completely arbitrary lattice vectors. (no constraints on magnitude/direction)

Face centred cubic (FCC)

Crystal structure of FCC

$$= \text{simple cubic B.L.} + \underbrace{\{ \vec{b}_1 = 0, \vec{b}_2, \vec{b}_3, \vec{b}_4 \}}_{4 \text{ basis vectors.}}$$

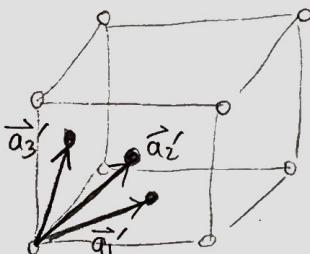
why only four \vec{b}_i ?

because the rest of the points on the face are like the \vec{b}_2, \vec{b}_3 & \vec{b}_4 points of the other cubes attached to this cube.

$$\vec{b}_2 = \frac{1}{2}(\vec{a}_1 + \vec{a}_2) \quad \vec{b}_3 = \frac{1}{2}(\vec{a}_1 + \vec{a}_3) \quad \vec{b}_4 = \frac{1}{2}(\vec{a}_2 + \vec{a}_3) \quad \vec{b}_1 = 0$$

We can again write FCC as just a Bravais lattice by choosing \vec{b}_i as primitive vectors.

$$\text{FCC} = \text{B.L. with primitive } \vec{v} \quad (\vec{a}'_1 = \vec{b}_2, \quad \vec{a}'_2 = \vec{b}_3, \quad \vec{a}'_3 = \vec{b}_4)$$



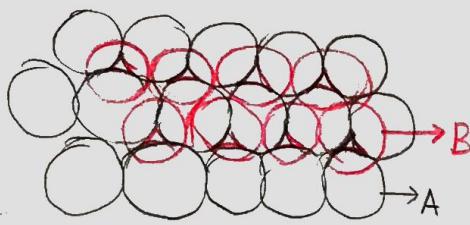
FCC being a common structure \Leftrightarrow problem of packing spheres.

FCC as a symmetric set of primitive vectors

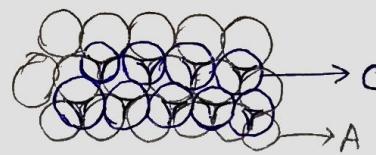
$$\vec{a}'_1 = \frac{a}{2}(\hat{y} + \hat{z}) \quad \vec{a}'_2 = \frac{a}{2}(\hat{z} + \hat{x})$$

$$\vec{a}'_3 = \frac{a}{2}(\hat{x} + \hat{y})$$

Packing of spheres



Spheres on upward triangles Δ
(B)



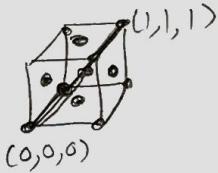
Spheres on downward triangular ∇
(C)

If we put the third layer exactly aligned with the first layer, (or in the downward facing triangles of B, which gives the same alignment), we call the structure ABAB-----.

However, the only other option is putting next layer on upward Δ dips of B, in which case we have ABC-----

But no matter the way of packing, the packing efficiency of these remain same.

Now the interesting is that while looking along $(0,0,0)$ to $(1,1,1)$ diagonal of an fcc, it looks like ABCABC----- structure.



Ti, Al, Fe (high pressure) and many other metals create this structure of ABABAB---- which is called hexagonal closed packing (hcp).

Type
hcp

$$\text{Packing efficiency} \\ \pi/3\sqrt{2} = 0.74 \text{ (ABABAB)}$$

fcc

$$\pi/3\sqrt{2} = 0.74 \text{ (ABCABC)}$$



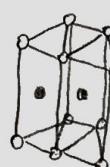
bcc

$$\sqrt{3}\pi/8 = 0.68$$

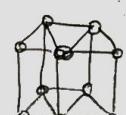


simple hexagonal

$$\pi/3\sqrt{3} = 0.604 \text{ (AAAA)}$$



\rightarrow hcp



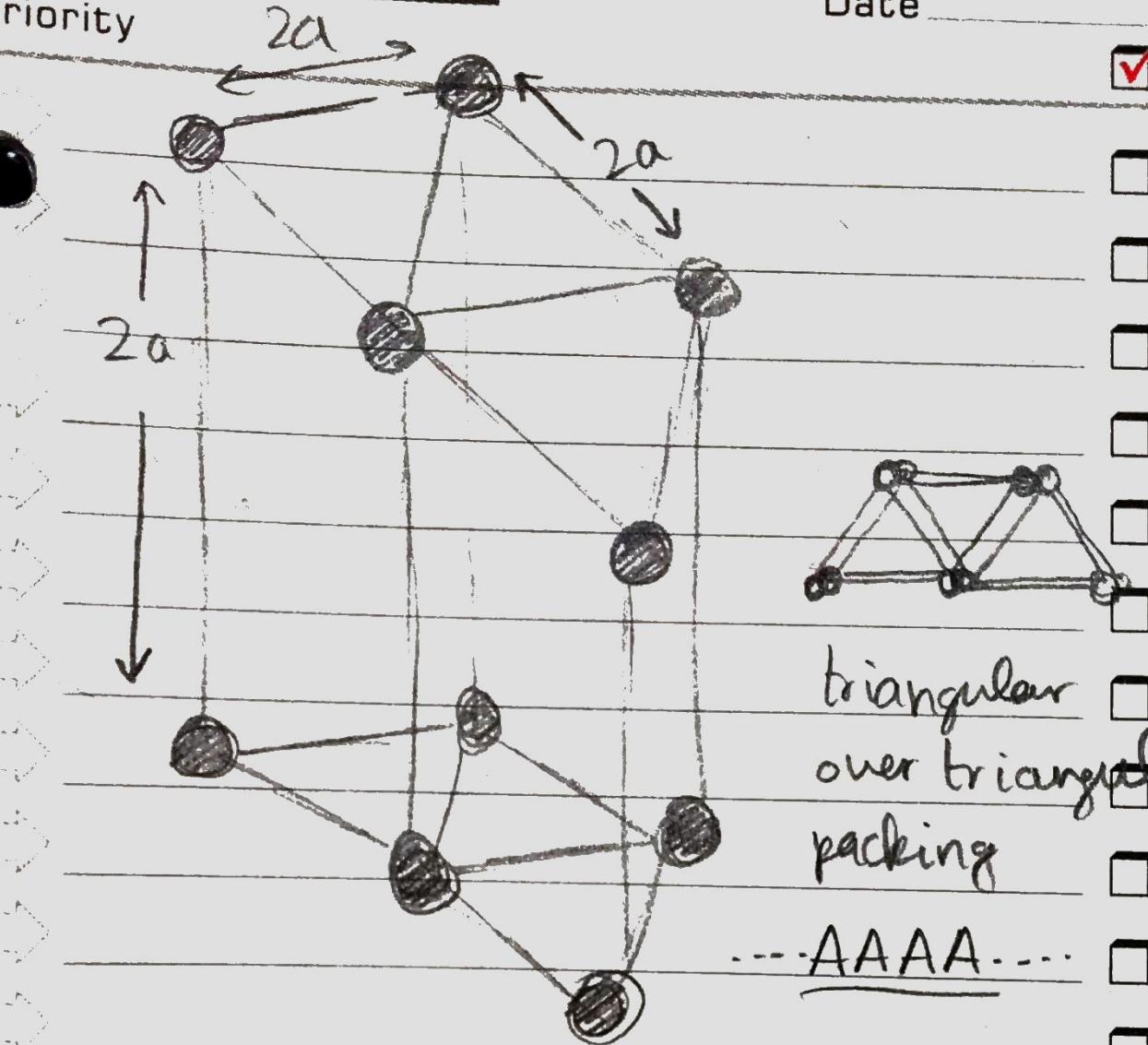
simple hexagonal



THINGS TO DO

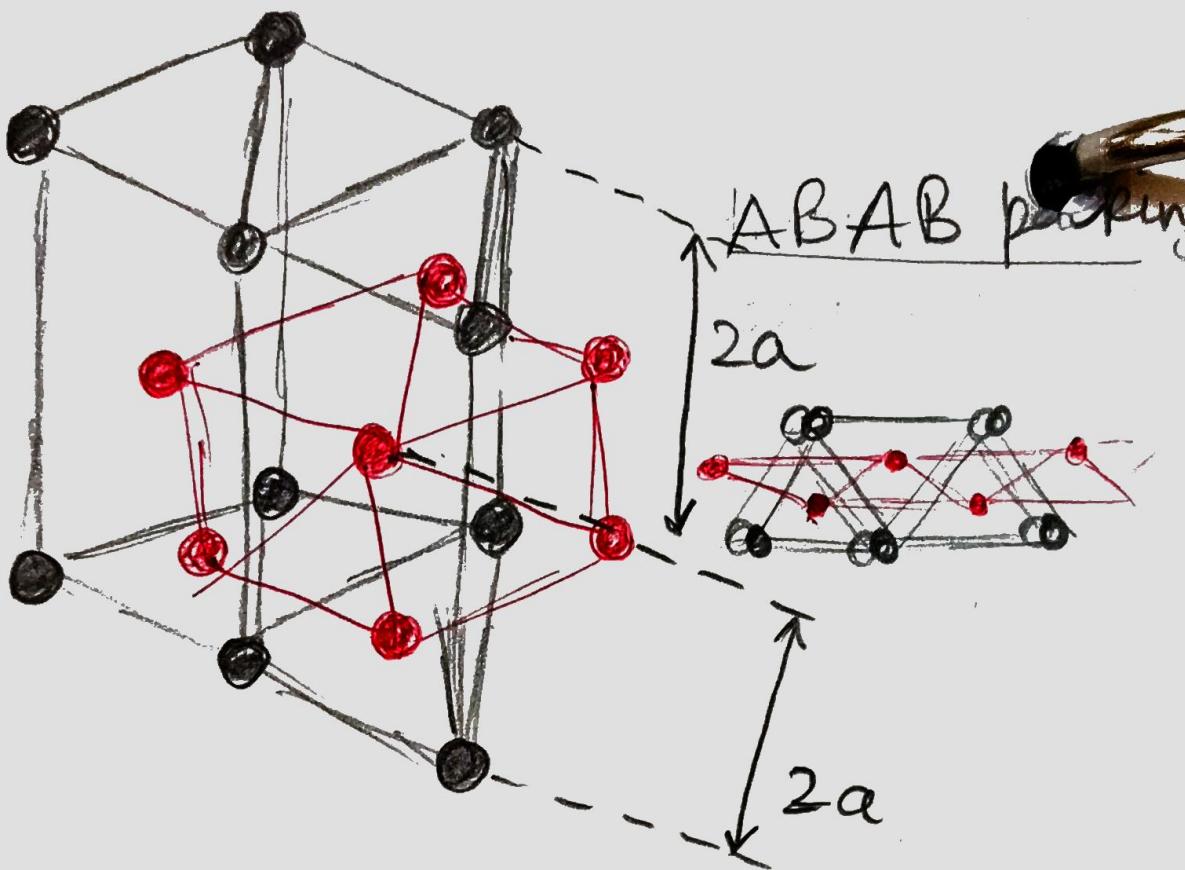
Priority

Date _____



Simple Hexagonal packing.

Day Summary



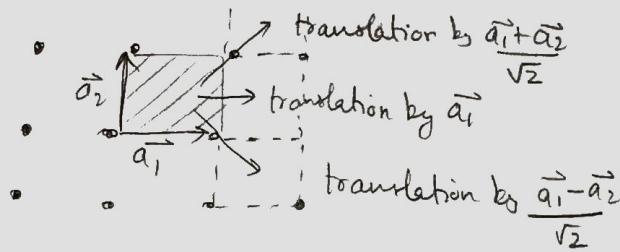
Hexagonal closed packing (hcp)

Simple hexagonal + a basis vector

ABCABCABC packing

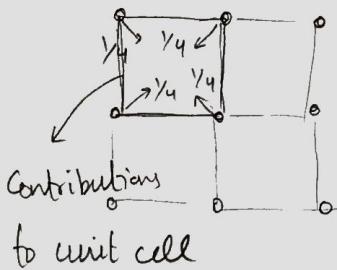
then turns out to be Face centred cubic (fcc)

Unit cell



• unit cell = region of space which when translated by any $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2$ (Bravais lattice vectors)
fills up all space without overlap.

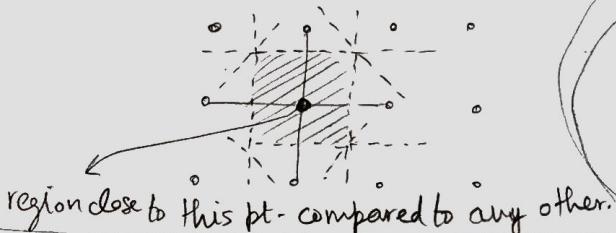
* The smallest such cell is called the primitive unit cell. (Defined to have 1 lattice site per unit)



\Rightarrow primitive unit cell has $\frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} = 1$ lattice per site.

IMPORTANT - All primitive unit cells have equal areas/volumes

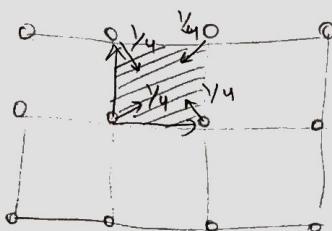
Wigner-Seitz cell: The space closest to one Bravais lattice pt. compared to any other.



A Wigner-Seitz cell is a primitive unit cell if we are dealing with a Bravais lattice, and not extra basis \vec{v} .

For lattices like Honeycomb, the W.S. cell isn't primitive. Try drawing the W.S. cell of B.L. underlying honeycomb.

Lecture - 10 (23/09)



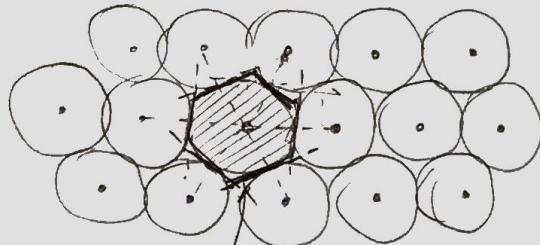
How many B.L. sites belong to a single unit cell?

Total no. of sites = $\frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} = 1$ total site

($\frac{1}{4}$ th contribution from each pt.)

NOTE: $V(\text{primitive unit cell}) = \frac{V_{\text{conv.}}}{\# \text{ of lattice sites}}$ (for primitive unit cells of pure B.L.)

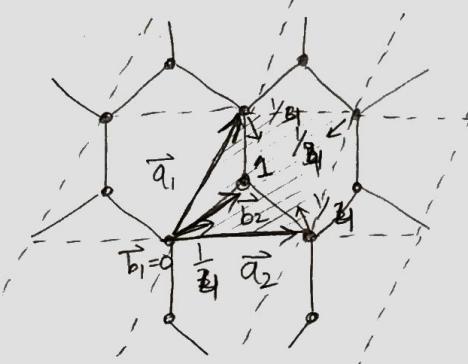
Let us now discuss the structure of sphere packing and its Wigner-Seitz unit cell.



Wigner-Seitz unit cell for a triangular lattice is the honey comb shape (hexagon).

Again, per unit cell, we have only 1 lattice site.

Let's now take the example of honey comb lattice.

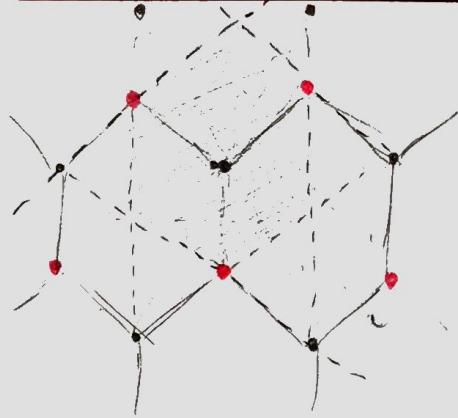


In the unit cell spanned by the primitive vectors \vec{a}_1, \vec{a}_2 & basis vectors \vec{b}_1, \vec{b}_2 , we see that the no. of lattice sites is
$$\# \text{ of lattice sites} = \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + 1 = 2.$$

★ NOTE:

For a crystal structure which can be described as a B.L. + a basis
then the # of sites in the unit cell spanned by the primitive lattice vectors
of the underlying B.L. will = n.

Note: A Bravais lattice always has the $\vec{b}_1=0$ vector to mark the origin point as a site as well.

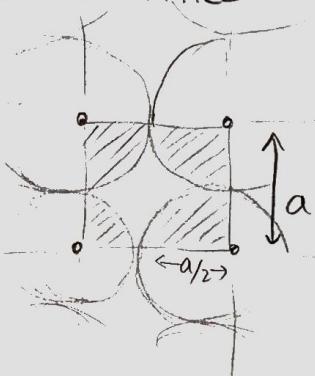


Wigner Seitz cell for the honeycomb lattice?

- points from back
- points from BL

- Packing fraction in 2D $f = \frac{\text{area occupied by circles in unit cell}}{\text{Total area available in unit cell}}$

① SQUARE LATTICE

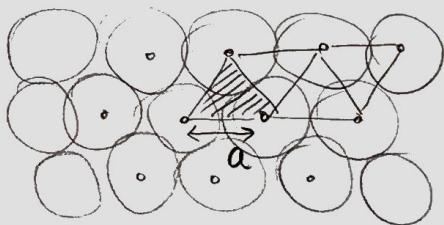


$$\text{Area of circles in unit cell} = \frac{\pi a^2}{4}$$

$$\text{Area of unit cell} = a^2$$

$$\Rightarrow f = \frac{\pi a^2}{4 a^2} = \frac{\pi}{4} \approx 0.785$$

② TRIANGULAR LATTICE



$$\text{Area of circles} = \frac{\pi}{2} \left(\frac{a}{2}\right)^2 = \frac{\pi a^2}{8}$$

$$\text{Area of unit cell} = \frac{\sqrt{3}}{4} a^2$$

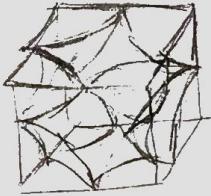
$$\Rightarrow f = \frac{\pi a^2 / 4}{2 \sqrt{3} a^2} = \frac{\pi}{2\sqrt{3}} \sim 0.906$$

HW find f for honeycomb lattice

B.L. unit cell: has 2 sites per cell $= \frac{2 \text{ A}_{\text{circle}}}{\text{A}_{\text{unit cell}}}$

- Packing in 3D

- SIMPLE CUBIC

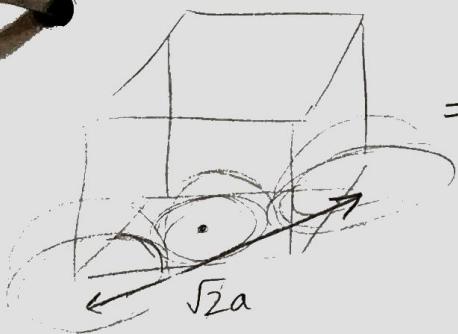


$$\text{Volume of spheres} = 8 \times \left[\frac{4}{3} \pi \left(\frac{a}{2} \right)^3 \cdot \frac{1}{8} \right] \\ = \frac{4}{3} \pi \frac{a^3}{8} = \frac{\pi a^3}{6}$$

$$\text{Volume of cube} = a^3$$

$$\Rightarrow f = \frac{\pi a^3}{6 a^3} = \frac{\pi}{6} \approx 0.52$$

- FACE CENTRED CUBIC



$$\sqrt{2}a = 4r$$

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

$$\Rightarrow V_{\text{spheres}} = \left[\frac{1}{8} \cdot \frac{4}{3} \pi \left(\frac{a}{2\sqrt{2}} \right)^3 \right] \times 8 + \left[\frac{1}{2} \cdot \frac{4}{3} \pi \left(\frac{a}{2\sqrt{2}} \right)^3 \right] \times 6$$

$$= 4V_0 = 4 \cdot \frac{4}{3} \pi \frac{a^3}{16\sqrt{2}} = \frac{\pi a^3}{2\sqrt{3}} =$$

$$V_{\text{cube}} = a^3$$

$$f = \frac{\pi a^3}{2\sqrt{3} a^3} = \frac{\pi}{2\sqrt{3}}$$

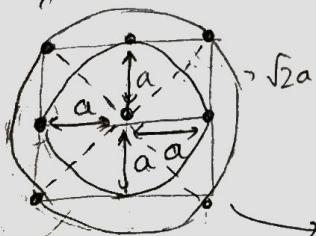
can also be thought
as coming from
of sites in a fcc
unit cell = 4

Lecture-11

(28/09)

Co-ordination number :- enumeration of the nearest no. of atoms close

to a given atom.

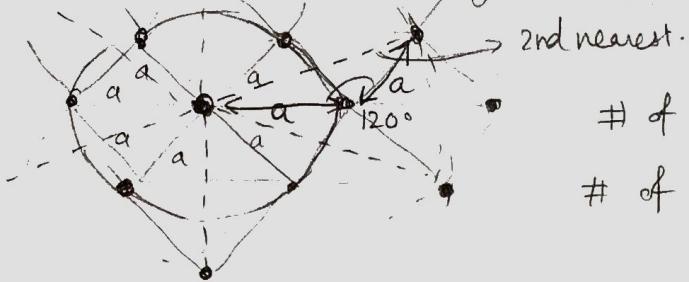


of 1st nearest neighbours at $a = 4$

of 2nd nearest neighbours at $\sqrt{2}a = 4$

square lattice.

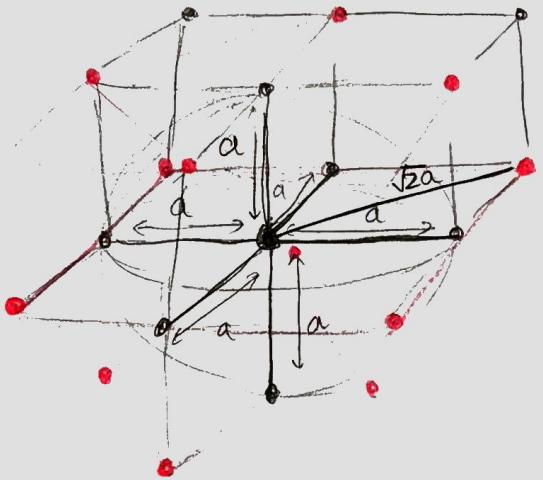
Let's now look at the triangular lattice



- # of first nearest at $a = 6$
- # of 2nd nearest at $\sqrt{3}a = 12$

Let's now move to 3D lattices. -

Simple cubic



Why is # of neighbours relevant?

Accounting for overlap of wavefn in lattice.

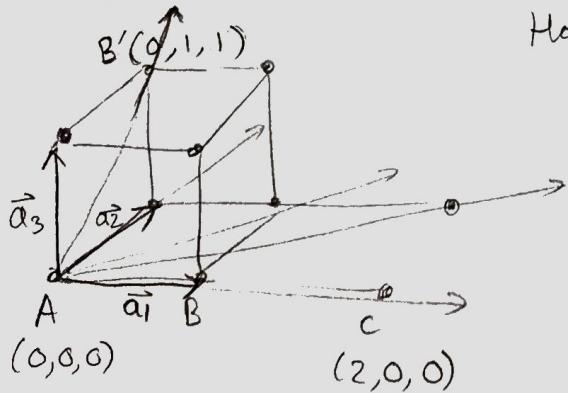
To choose to include overlap with nearby atoms or not.

- # of first nearest neighbours = 6 at a
- # of second nearest neighbours = 12 at $\sqrt{2}a$

HW - Find # of nearest neighbours (1st & 2nd) of bcc & fcc.

X X X

Directions in lattices.



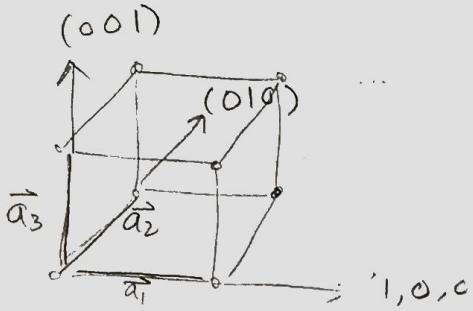
How do we describe these directions in lattices

$$\begin{aligned}\vec{R}_{C \rightarrow A} &= 2\vec{a}_1 + 0\vec{a}_2 + 0\vec{a}_3 \\ \Rightarrow \hat{\vec{R}}_{C \rightarrow A} &= \text{reduced form of } \vec{R} \text{ i.e. } \times \frac{1}{2} = [1, 0, 0]\end{aligned}$$

The components must $\in \mathbb{Z}$

we don't write this!

$$[2, 2] = [1, 1] \cancel{\equiv}$$



$[100]$, $[001]$ & $[010]$ are ill equivalent directions upto rotations by $\pi/2$ (due to symmetry of cubic lattice)

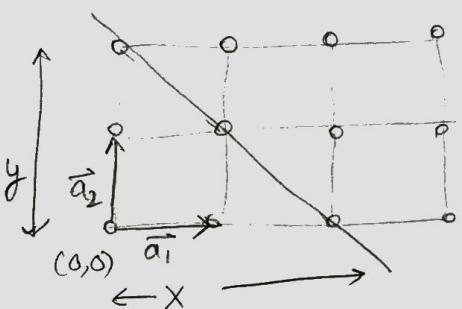
$$\langle 100 \rangle = [\pm 1, 0, 0], [0, \pm 1, 0], [0, 0, \pm 1]$$

Similarly

$$\langle 110 \rangle = [\pm 1, \pm 1, 0], [0, \pm 1, \pm 1], [\pm 1, 0, \pm 1]$$

So, $\langle \cdot \rangle$ define an equivalence class of directions. (due to symmetry of the lattice structure)

Lattice planes.



(1) look at the intercept of plane on primitive vectors. (x, y)

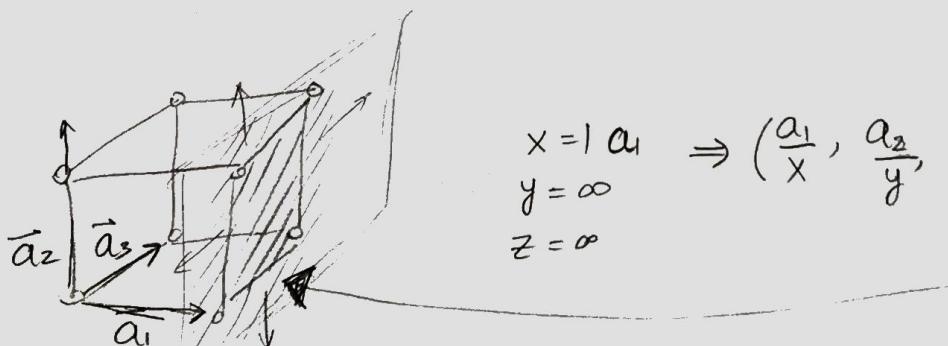
$$\rightarrow \left(\frac{x}{|\vec{a}_1|}, \frac{y}{|\vec{a}_2|} \right)$$

$$(2) \text{ Invert} \rightarrow \left(\frac{|\vec{a}_1|}{x}, \frac{|\vec{a}_2|}{y} \right)$$

$$(3) \text{ Reduce to smallest } \mathbb{Z} \Rightarrow (h, k)$$

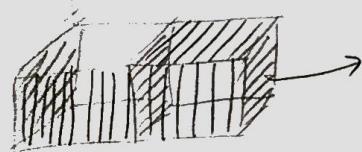
$$\text{In 3D} \rightarrow \left(\frac{x}{\vec{a}_1}, \frac{y}{\vec{a}_2}, \frac{z}{\vec{a}_3} \right) \rightarrow \left(\frac{\vec{a}_1}{x}, \frac{\vec{a}_2}{y}, \frac{\vec{a}_3}{z} \right) \rightarrow (\underline{h \ k \ l})$$

Miller indices.

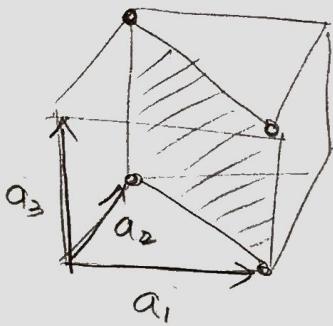


$$x = 1/a_1 \Rightarrow \left(\frac{a_1}{x}, \frac{a_2}{y}, \frac{a_3}{z} \right) \Rightarrow (\underline{1 \ 0 \ 0})$$

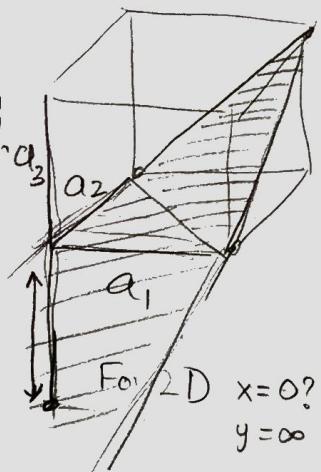
Miller indices
for this plane.



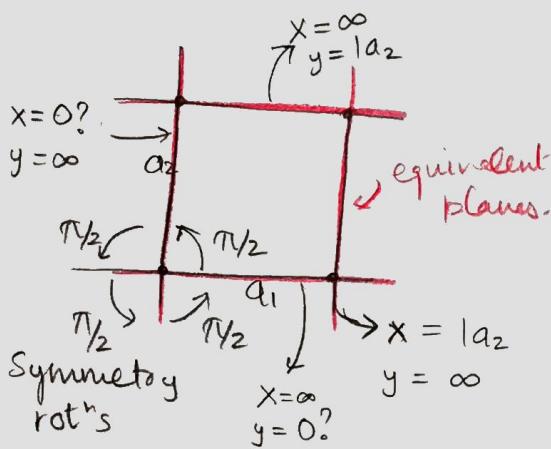
equivalent planes associated
via symmetry rot'n's $\Rightarrow \{100\} = (100)(001)(010)$



$$\begin{aligned}x &= 1a_1 \\y &= 1a_2 \\z &= \infty\end{aligned} \Rightarrow (1, 1, 0) \quad \text{Miller indices}$$



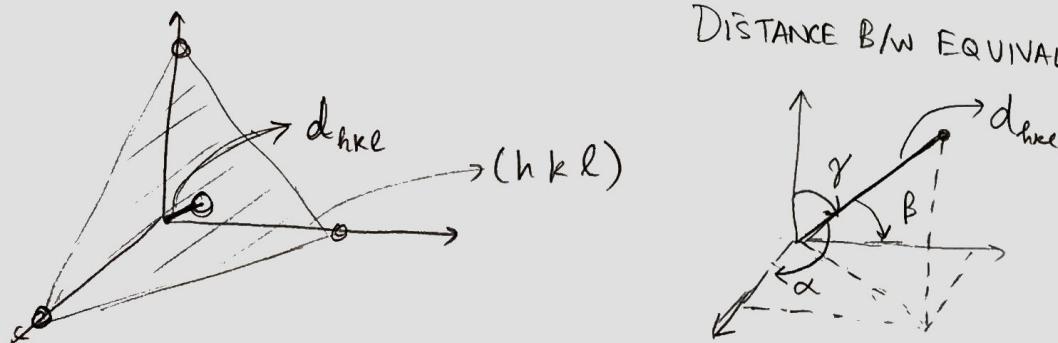
$$\begin{aligned}x &= -1a_1 \\y &= 1a_2 \\z &= 1a_3\end{aligned} \Rightarrow (1, 1, 1) \quad \text{Miller indices.}$$



Lecture - 12

(30/09)

DISTANCE B/W EQUIVALENT PLANES



$$d_{hkl} = x \cos \alpha = y \cos \beta = z \cos \gamma$$

Law of DCs.

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

(13)

$$\Rightarrow \frac{d_{hkl}^2}{x^2} + \frac{d_{hkl}^2}{y^2} + \frac{d_{hkl}^2}{z^2} = 1 \Rightarrow d_{hkl} = \frac{1}{\sqrt{\frac{1}{x^2} + \frac{1}{y^2} + \frac{1}{z^2}}}$$

$$(h k l) = \text{reduc} \left(\frac{|a_1|}{x}, \frac{|a_2|}{y}, \frac{|a_3|}{z} \right)$$

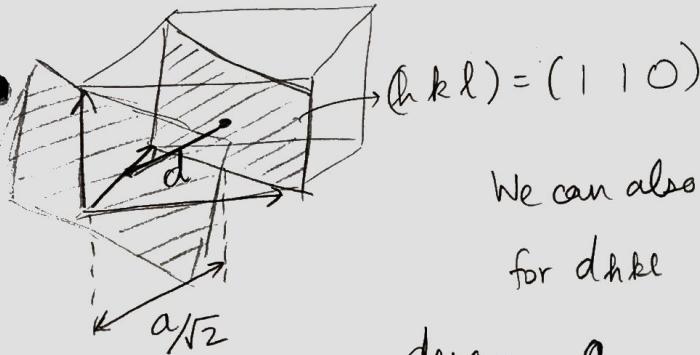
\Rightarrow we can write

$$h = n \frac{|a_1|}{x}, \quad k = n \frac{|a_2|}{y}, \quad l = n \frac{|a_3|}{z} \quad n \rightarrow \text{reduction integer.}$$

$$\Rightarrow x = \frac{n|a_1|}{h}, \quad y = \frac{n|a_2|}{k}, \quad z = \frac{n|a_3|}{l}$$

$$\Rightarrow d_{hkl} = \frac{n}{\sqrt{\frac{h^2}{|a_1|^2} + \frac{k^2}{|a_2|^2} + \frac{l^2}{|a_3|^2}}}$$

$$\text{For a cubic unit cell, } |a_1| = |a_2| = |a_3| = a \Rightarrow d_{hkl} = \frac{na}{\sqrt{h^2 + k^2 + l^2}}$$



We can also get $a/\sqrt{2}$ using the expression for d_{hkl}

$$d_{hkl} = \frac{a}{\sqrt{1+1+0}} = \frac{a}{\sqrt{2}}$$

Direct imaging techniques - STM (Scanning Tunneling microscope)
 TEM (Tunneling electron microscope)

Indirect methods: Local - X-ray photoemission spectroscopy

Bulk - Diffraction (X-ray, neutrons)

Lee-13
 (01/09/21)

For probing the length scale of atomic scale, $E = \frac{hc}{\lambda} \sim \text{keV}$ (X-rays)
 $\lambda < \text{\AA}$

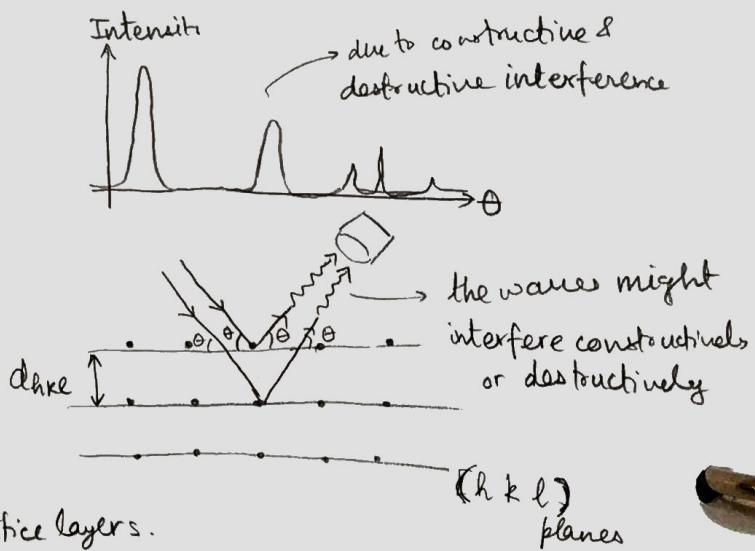
The spectroscopy of the KE of electrons that come out when we strike the material with X-ray photons gives us the information about energy spectrum of atoms in lattice.

X-ray diffraction.



$$\Delta d = 2d_{hkl} \sin\theta$$

↑
 path difference b/w waves
 reflected from the first & second lattice layers.



For constructive interference,

(we are assuming elastic reflection here.)

$$2d_{hkl} \sin\theta = n\lambda$$

Bragg's law

order of diffraction

Confusions:

- ① Miller indices of a lattice. Is it dependent on how we define the Bravais lattice?
- ② finding directions & miller indices.
- ③ Re-attempt quiz problems.

Lecture-14

(4/10/21)

Read:
Ashcroft, Mermin Ch-4, 6, 7

①

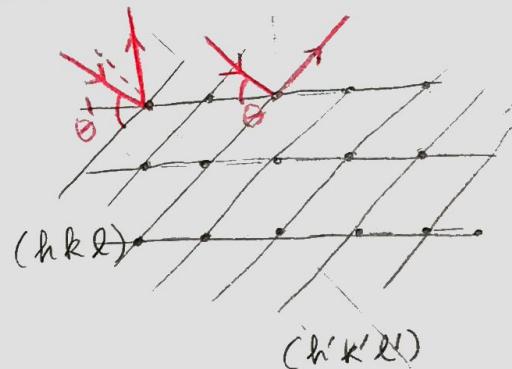
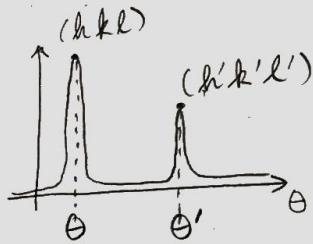
For first order scattering ($n=1$) $2d_{hkl} \sin\theta = \lambda$

$$\Rightarrow \frac{\lambda}{2d_{hkl}} \leq 1 \text{ for probing this scale.}$$

→ (scattering with the first plane)

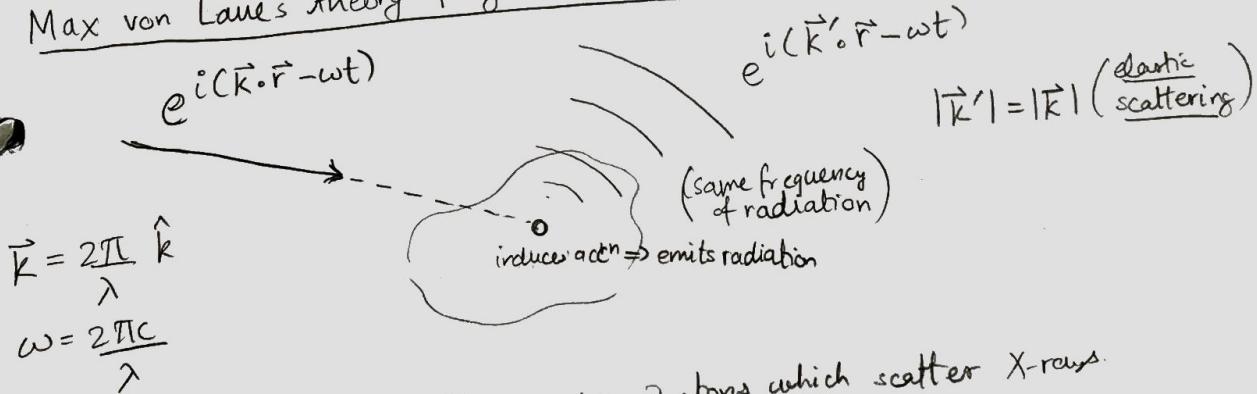
Given a $(h k l)$ plane, the first order scattering only happens constructively for a given Θ . \therefore Each peak can be associated to a $((h k l))$

plane-

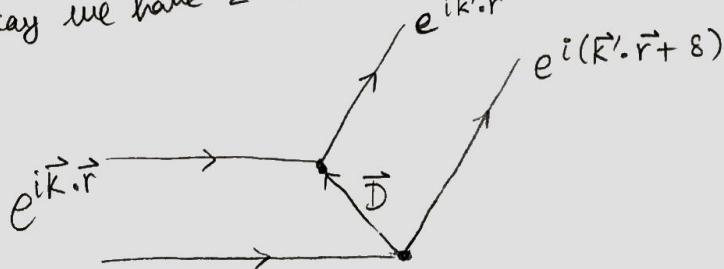


A better theory was given by Max von Laue

Max von Laue's theory of general scattering.



Let's say we have 2 scatterers i.e. 2 atoms which scatter X-rays.



δ = phase lag of scattered ray b/w 1 & 2.

(2)

Total field at the detector-

$$= \tilde{A} [e^{i\vec{k}' \cdot \vec{r}} + e^{i(\vec{k}' \cdot \vec{r} + \delta)}] = \tilde{A} e^{i\vec{k}' \cdot \vec{r}} (1 + e^{i\delta})$$

(assuming scatterers are identical)

$$\delta \equiv \text{phase lag} = 2\frac{\pi}{\lambda} (\text{path diff.})$$

$$\delta = 2\frac{\pi}{\lambda} [-\vec{D} \cdot \hat{k} + \vec{D} \cdot \hat{k}']$$

$$\frac{2\pi}{\lambda} \hat{k} = \vec{k} \quad \text{and} \quad \frac{2\pi}{\lambda} \hat{k}' = \vec{k}'$$

$$\Rightarrow \delta = (\vec{k}' - \vec{k}) \cdot \vec{D}$$

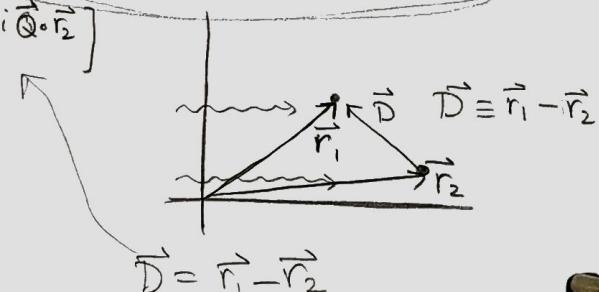
$$\Rightarrow E_{\text{det}} = \tilde{A} e^{i\vec{k}' \cdot \vec{r}} [1 + e^{i(\vec{k}' - \vec{k}) \cdot \vec{D}}]$$

$$= \tilde{A} e^{i\vec{k}' \cdot \vec{r}} [1 + e^{i\vec{Q} \cdot \vec{D}}]$$

$$= \underbrace{\tilde{A} e^{i\vec{Q} \cdot \vec{r}_2}}_A e^{i\vec{k}' \cdot \vec{r}} [e^{i\vec{Q} \cdot \vec{r}_1} + e^{i\vec{Q} \cdot \vec{r}_2}]$$

$$E_{\text{detector}} = A e^{i\vec{k}' \cdot \vec{r}} \sum_i e^{i\vec{Q} \cdot \vec{r}_i}$$

$$\vec{k}' - \vec{k} \equiv \vec{Q} = \text{scattering vector}$$



∴ Total field intensity at the detector-

$$I = |E|^2 = |\tilde{A}|^2 \left| \sum_i e^{i\vec{Q} \cdot \vec{r}_i} \right|^2$$

This is the fundamental formula. I can put in $\vec{r}_i = \vec{R}_i$ for pure B.L. or $\vec{r}_i = \vec{R}_i + \vec{b}_n$ for B.L. with a basis!

So, for a Bravais lattice crystal -

$$I_{\text{Bravais lattice}} \propto \left| \sum_{\vec{R}} e^{i\vec{Q} \cdot \vec{R}} \right|^2 \text{ where } \vec{R} \in \text{Bravais lattice vectors}$$

By changing the angle of detector, we change $\vec{Q} = \vec{k}' - \vec{k}$ since

\vec{k}' is essentially the direction of detector. The scatterers scatter in all the directions but in the analysis, we only consider one direction since that's what the detector

\vec{Q} is dependent upon Θ of detector.

We need to find \vec{Q} 's such that $e^{i\vec{Q} \cdot \vec{R}} = 1$ $\forall \vec{R} \in$ lattice for the intensity to be maximised. We introduce Reciprocal Lattices to handle this.

Reciprocal Lattice.

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

$$\begin{aligned} \vec{a}_i &\rightarrow \text{primitive } \vec{r} \\ n_i &\in \mathbb{Z} \end{aligned} \quad \left. \right\} \text{BoL.}$$

We can find a periodic wave vector $\vec{k} = \vec{G}$ which satisfies

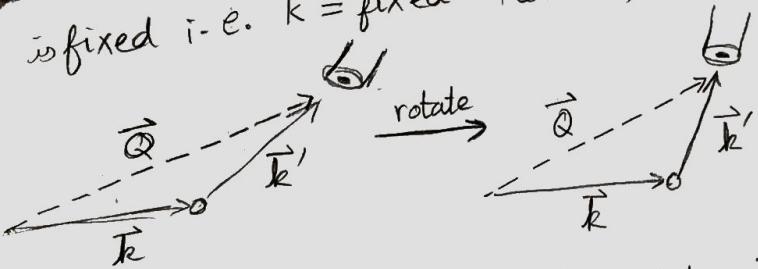
$$e^{i\vec{G} \cdot (\vec{r} + \vec{R})} = e^{i\vec{G} \cdot \vec{r}} \Rightarrow e^{i\vec{G} \cdot \vec{R}} = 1$$

i.e. it's periodic in the reciprocal lattice (with period \vec{R}).

$$\vec{G} \equiv \text{reciprocal lattice of } \vec{R}$$

(COSI 110)
Lec-15 For a general \vec{Q} , the plane wave doesn't have the periodicity of Bravais Lattice. Only special $\vec{Q} = \vec{G}$ satisfies the periodicity condition $e^{i\vec{G} \cdot \vec{R}} = 1 \Rightarrow \vec{G} \cdot \vec{R} = 2\pi m$

For a scattering experiment, ($\vec{Q} = \vec{k}' - \vec{k}$), the direction of incoming beam is fixed i.e. \vec{k} is fixed. However, \vec{k}' points in the direction of detector.



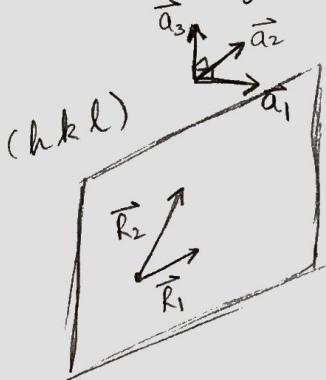
Hence, we only get sharp intensity at detector when \vec{k}' is s.t. $e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}} = e^{i\vec{Q} \cdot \vec{R}} \equiv e^{i\vec{G} \cdot \vec{R}} = 1$

We denote a general $\vec{k}' - \vec{k}$ by \vec{Q} , and the special vector which has $(\vec{k}' - \vec{k}) \cdot \vec{R} = \vec{Q} \cdot \vec{R} = 2\pi m$ is called $\vec{Q} = \vec{G}$ reciprocal lattice vector.

\vec{G} describes what's called a reciprocal lattice satisfying

$$e^{i\vec{G} \cdot \vec{R}} = 1 \Rightarrow \vec{G} \cdot \vec{R} = 2\pi m$$

\vec{G} is therefore normal to the Bravais lattice plane $\vec{R} \cdot$
 $\vec{a}_3 \vec{a}_2$ (h k l)



Say,

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

$$\vec{R_2} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3 \quad \text{are vectors in } (h k l) \text{ plane.}$$

\vec{R}_1 & \vec{R}_2 are two vectors in $(h k l)$ plane.

$$\begin{aligned}
 \vec{N} &= \vec{R}_1 \times \vec{R}_2 \quad N_i = \epsilon_{ijk} R_1^i R_2^j \\
 &= (n_2 m_3 - n_3 m_2) \vec{a}_2 \times \vec{a}_3 \\
 &\quad + (n_3 m_1 - n_1 m_3) \vec{a}_3 \times \vec{a}_1 \\
 &\quad + (n_1 m_2 - n_2 m_1) \vec{a}_1 \times \vec{a}_2 \\
 &= h \underbrace{\vec{a}_2 \times \vec{a}_3}_{\vec{b}_1} + k \underbrace{\vec{a}_3 \times \vec{a}_1}_{\vec{b}_2} + l \underbrace{\vec{a}_1 \times \vec{a}_2}_{\vec{b}_3}
 \end{aligned}$$

Normalization of \vec{b}_i 's:

We normalize the \vec{b}_i 's such that $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$. They are then constructed as follows -

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\overrightarrow{b}_2 = 2\pi \frac{\overrightarrow{a}_3 \times \overrightarrow{a}_1}{\overrightarrow{a}_1 \cdot (\overrightarrow{a}_2 \times \overrightarrow{a}_3)}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

where $(\vec{a}_1) \cdot (\vec{a}_2 \times \vec{a}_3) = \text{Vol. of}$
 $(\text{scalar triple product}) \quad \text{unit cell}$

Normalize by $\frac{2\pi}{V_{cell}}$

$$\boxed{V_{\text{reciprocal}} = \frac{(2\pi)^3}{V_{\text{direct}}}}$$

prove this.

Therefore the normal vector is now written as -

$$\vec{N} = h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3 \rightarrow \vec{N} \text{ is itself a Bravais lattice!}$$

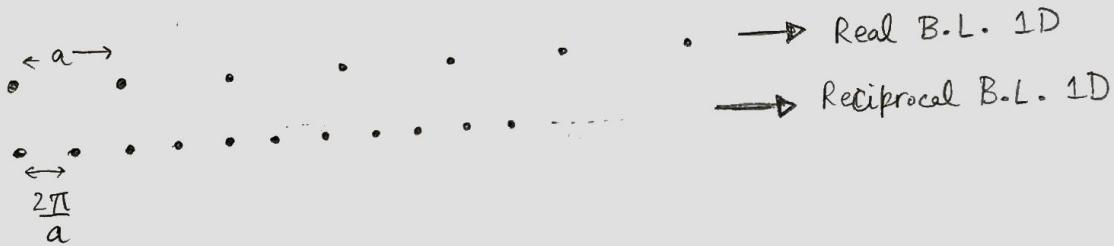
$$\Rightarrow \boxed{\vec{N} \cdot \vec{R} = 2\pi m} \quad (\text{using } \vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}) \quad m = (n_1 h + n_2 k + n_3 l)$$

\therefore We have arrived at the condition for the reciprocal lattice!

Thus, the reciprocal lattice vector $\vec{N} = \vec{G}_1$ is a B.L. in reciprocal space.

* For 1D, if $\vec{R} = n\vec{a}$, then the reciprocal lattice has to satisfy

$$\vec{G}_1 \cdot \vec{R} = 2\pi m \Rightarrow \vec{G}_1 = \frac{2\pi}{|\vec{a}|} m' \hat{a}$$



* For 2D square lattice

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 = n_1 \hat{i} + n_2 \hat{j}$$

Now, we can include a hypothetical third axis of arbitrary length, normal to the plane in which \vec{a}_1 and \vec{a}_2 reside.

$$\vec{a}_3 = a_3 \hat{k}$$

$$\Rightarrow \vec{b}_1 = \frac{2\pi (\vec{a}_2 \times \vec{a}_3)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_2 = \frac{2\pi (\vec{a}_3 \times \vec{a}_1)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

For a square lattice

$$\vec{a}_1 = a\hat{i}, \quad \vec{a}_2 = a\hat{j} \quad \vec{a}_3 = a\hat{k} \text{ (hypothetical)}$$

$$\vec{b}_1 = 2\pi \frac{a\hat{j} \times \hat{k}}{a^2 a_3} = \frac{2\pi}{a} \hat{i}$$

$$\vec{b}_2 = 2\pi \frac{a\hat{k} \times \hat{i}}{a^2 a_3} = \frac{2\pi}{a} \hat{j} \quad \Rightarrow \quad \vec{G} = \frac{2\pi}{a} (h\hat{i} + k\hat{j})$$

★ Another important point to note -

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

The reason we wrote the components as h, k, l & the Miller indices of the plane with same $(h k l)$ is because they are indeed the same. $(h k l)$ are the Miller indices of the plane \perp to \vec{G} .

Prove it!

Since, $d_{hkl} \equiv$ spacing b/w successive real space lattice planes.

$\Rightarrow \frac{2\pi}{d_{hkl}}$ \rightarrow shortest reciprocal lattice vector normal to plane (spacing) $(h k l)$

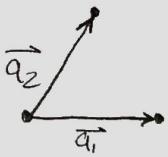
H.W. - Construct reciprocal lattice vectors for -

- (1) Triangular lattice (2D)
- (2) bcc lattice (3D)

Need to properly understand the relation b/w reciprocal lattice vector, $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ and the planes $(h k l)$.

Reciprocal lattice vectors

(1)



$$\vec{a}_2 = \begin{pmatrix} R(60^\circ) \end{pmatrix} \begin{pmatrix} \vec{a}_1 \end{pmatrix}$$

$$\vec{a}_2 = \begin{pmatrix} \cos 60^\circ & -\sin 60^\circ \\ +\sin 60^\circ & \cos 60^\circ \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} - \frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \\ +\frac{\sqrt{3}}{2} \end{pmatrix}$$

$$\vec{a}_2 = \frac{1}{2}\hat{i} + \frac{\sqrt{3}}{2}\hat{j} + 0\hat{k}$$

$$\vec{a}_1 = 1\hat{i} + 0\hat{j} + 0\hat{k}$$

$$\vec{a}_3 = 0\hat{i} + 0\hat{j} + 1\hat{k}$$

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_1 = 2\pi \frac{\left(\frac{\sqrt{3}}{2}\hat{i} - \frac{1}{2}\hat{j}\right)}{\frac{\sqrt{3}}{2}} = \frac{2\pi}{\sqrt{3}} (\sqrt{3}\hat{i} - \hat{j})$$

$$\vec{b}_2 = 2\pi \left(\frac{2\hat{j}}{\sqrt{3}} \right) = \frac{2\pi}{\sqrt{3}} (2\hat{j})$$

$$\vec{b}_1 = \frac{2\pi}{\sqrt{3}} [h(\sqrt{3}\hat{i} - \hat{j}) + k(2\hat{j})]$$

$$(\vec{a}_2 \times \vec{a}_3)_i = \epsilon_{ijk} (\vec{a}_2)^j (\vec{a}_3)^k$$

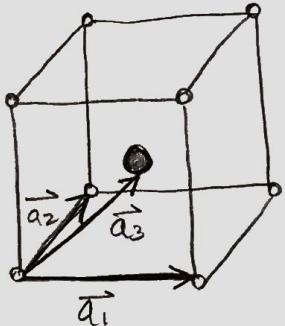
$$= \left(\frac{\sqrt{3}}{2}\right)\hat{i} + \left(-\frac{1}{2}\right)\hat{j} + \hat{k}(0)$$

$$= \frac{\sqrt{3}}{2}\hat{i} - \frac{1}{2}\hat{j}$$

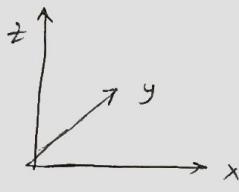
$$\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \frac{\sqrt{3}}{2}$$

$$\vec{a}_3 \times \vec{a}_1 = \hat{j}$$

(2) Reciprocal lattice vectors for bcc



$$\vec{a}_1 = \hat{i}a \quad \vec{a}_2 = \hat{j}a \quad \vec{a}_3 = \frac{a}{2}(\hat{i} + \hat{j} + \hat{k})$$



$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{a}_2 \times \vec{a}_3 = \frac{a^2}{2}(-\hat{k} + \hat{i})$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

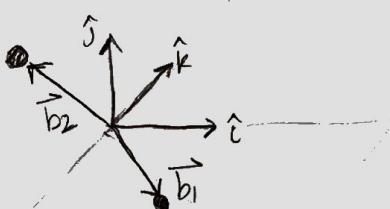
$$\vec{a}_3 \times \vec{a}_1 = \frac{a^2}{2}(-\hat{k} + \hat{j})$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{a}_1 \times \vec{a}_2 = \hat{k}a^2$$

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{i} - \hat{k}) \quad \vec{b}_2 = \frac{2\pi}{a}(\hat{j} - \hat{k}) \quad \vec{b}_3 = \frac{2\pi}{a}(2\hat{k})$$

$$\Rightarrow \vec{G} = \frac{2\pi}{a} [h(\hat{i} - \hat{k}) + k(\hat{j} - \hat{k}) + l(2\hat{k})]$$

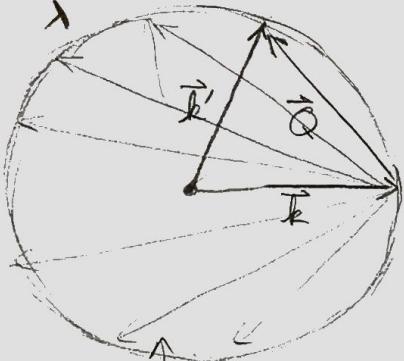


Lecture - 16

(7/10/21)

Ewald construction (or Ewald's sphere)

$$|\vec{k}'| = |\vec{k}| = 2\pi$$



$$\vec{Q} \equiv \vec{k}' - \vec{k}$$

As \vec{k}' moves around, it spans a circle (or a sphere).

Let's take the example of a square lattice (a, a) . The reciprocal lattice of this is a square lattice of side $\frac{2\pi}{a}$.

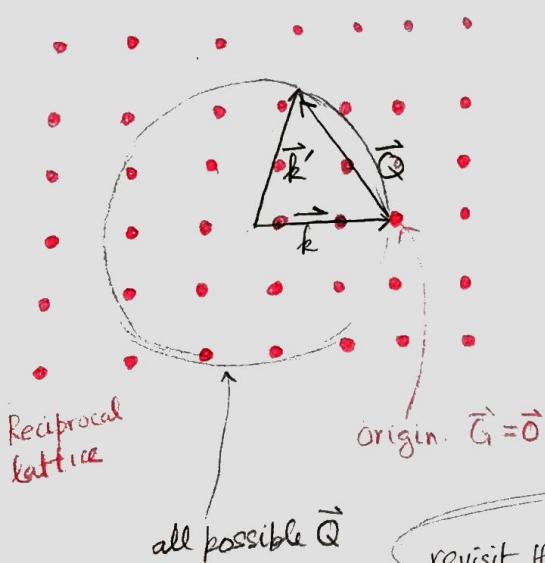
$$\vec{G} = \frac{2\pi}{a} (h\hat{i} + k\hat{j})$$

how do we know
the reciprocal

lattice vector if we

didn't know what $(h k l)$ are?

Or do we have to know the Miller indices $(h k l)$ beforehand?



The **reciprocal lattice points** are the values where the Bragg condition is satisfied, i.e. if \vec{Q} 's tip lies on the tip of a reciprocal lattice point,

then $\vec{Q} = \vec{G}$ (for the points that lie on Ewald's sphere)

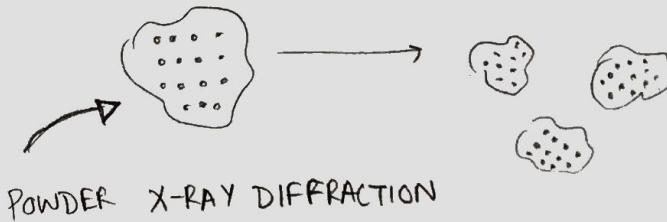
revisit the argument of \vec{Q} 's tip on point \Rightarrow Bragg condition is satisfied.

For a given lattice, the unit length of reciprocal lattice is fixed $\frac{2\pi}{a}$.

And for a given λ , $|\vec{k}| = \frac{2\pi}{\lambda}$ a.k.a. the radius of Ewald sphere is fixed.

λ can be varied continuously in synchrotron facilities. For fixed λ , you can spin the sample instead.

Another way is to powder the sample.



So we create a lot of crystals with all the possible orientations. This way we won't even have to rotate the sample.

Before moving, we remember the Wigner-Seitz cell. The Wigner-Seitz cell of a direct B.L. is the region of space closer to one B.L. point than any other.

Could be obtained by taking \perp bisectors b/w distance of any two neighbouring lattice sites. The region falling inside these \perp bisectors \equiv Wigner-Seitz cell.

(k -space)

The Wigner-Seitz cell of the reciprocal lattice is known as the 1st Brillouin zone.

- H.W. Show that the reciprocal lattice of the reciprocal lattice is indeed the direct lattice.

$$\begin{array}{l}
 \text{(a) bcc} \xrightarrow{\text{reciprocal}} \text{fcc } (4\pi/a) \\
 \text{(a) fcc} \xrightarrow{\text{reciprocal}} \text{bcc } (4\pi/a) \\
 \text{hexagonal (3D)} \xrightarrow{\text{reciprocal}} \text{hexagonal (3D)} \\
 \text{(a) square/cubic} \longrightarrow \text{square/cubic } (2\pi/a)
 \end{array}$$

VIBRATIONS IN LATTICES

(LATTICE DYNAMICS)

Since $V(r)$ has a minima at $r=r_0$, we can Taylor expand about this point.

$$V(r) = V(r_0) + \frac{dV}{dr} \Big|_{r_0} (r-r_0) + \frac{1}{2!} \frac{d^2V}{dr^2} \Big|_{r_0} (r-r_0)^2 + \dots \text{ (dis)}$$

V(r)

r

repulsive

attractive

equilibrium position.

$$\Rightarrow V(r) \approx V_{\text{offset}} + \frac{1}{2} \frac{d^2V}{dr^2} \Big|_{r_0} (r-r_0)^2$$

ignoring the offset since it's not relevant

$$V(r) \approx \underbrace{\frac{1}{2} \frac{d^2V}{dr^2}}_{\uparrow \text{spring constant.}} \Big|_{r=r_0} (r-r_0)^2 \longrightarrow \text{Harmonic pot.}$$

Since the energy of a particle in this potential is $E = \frac{p^2}{2m} + \frac{1}{2} kx^2$

$$\text{By Virial thm, } \left\langle q_i \frac{\partial H}{\partial q_k} \right\rangle = \delta_{ik} k_B T$$

$$\frac{\partial H}{\partial p} = \frac{p}{m}, \quad \frac{\partial H}{\partial x} = kx \Rightarrow \left\langle p \frac{\partial H}{\partial p} \right\rangle = \left\langle \frac{p^2}{m} \right\rangle = k_B T$$

$$\left\langle x \frac{\partial H}{\partial x} \right\rangle = \left\langle kx^2 \right\rangle = k_B T$$

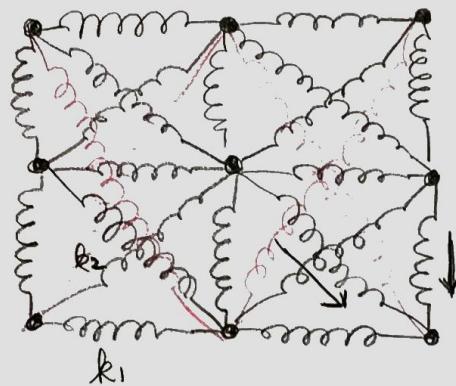
$$\Rightarrow \left\langle \frac{p^2}{2m} \right\rangle = \frac{k_B T}{2} \quad \left\langle \frac{kx^2}{2} \right\rangle = \frac{k_B T}{2}$$

$$\therefore \underline{\underline{\langle E \rangle}} = \langle K \rangle + \langle V \rangle = \frac{k_B T}{2} + \frac{k_B T}{2} = \underline{\underline{k_B T}}$$

\therefore The energy fluctuations at equilibrium $r=r_0$ is of the order $\sim k_B T$. So, the harmonic approximation is valid when $k_B T \ll \mid V_0 \mid$

$k_B T$ at room temperature $300\text{ K} \approx 25\text{ meV}$ ($1\text{ eV} \sim 10^4\text{ K}$)

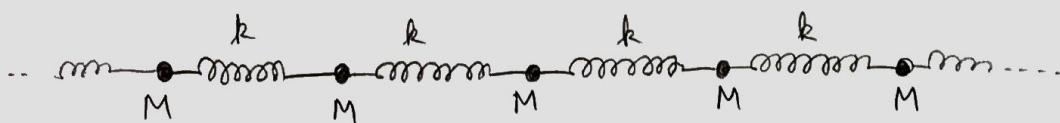
At room temperature, the lattice can be considered as a collection of balls & springs.



the spring constant
is actually different
in different directions.

\therefore the interaction of each & every spring mass is a complicated problem to handle. However, it is reasonable to assume that only the nearest neighbours have a considerable enough interaction.

So we'll start with a 1D monoatomic chain as the model of a solid.



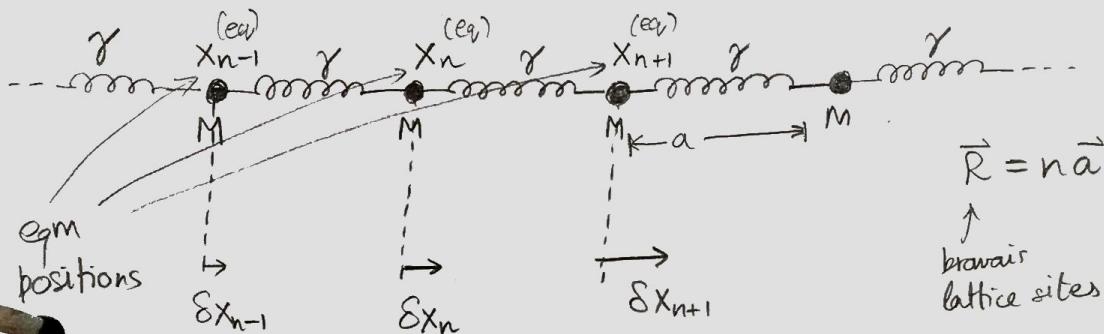
Lecture-17

(08/10/2021)

what is x_n in terms
of δx_n ?

Vibrations in lattices

We'll start with a 1D model (mono-atomic) of a chain of atoms (infinite chain)



$$V_{\text{tot}} = \sum_i V_{i,i+1} = \frac{1}{2} \gamma \sum_i (x_{i+1} - x_i - a)^2 = \frac{1}{2} \gamma \sum_i (\delta x_{i+1} - \delta x_i)^2$$

x_i 's \rightarrow current position of atom i

Force on n^{th} atom

$$F_n = -\frac{\partial V_{\text{tot}}}{\partial x_n} = -\gamma [-(x_{n+1} - x_n - a) + (x_n - x_{n-1} - a)]$$

$$= -\gamma [\delta x_n - \delta x_{n-1} - \delta x_{n+1} + \delta x_n]$$

$$M \ddot{x}_n = -\gamma [2\delta x_n - \delta x_{n+1} - \delta x_{n-1}] = -2\gamma \delta x_n + \gamma (\delta x_{n+1} + \delta x_{n-1})$$

$$\underline{M \ddot{x}_n = -2\gamma \delta x_n + \gamma (\delta x_{n+1} + \delta x_{n-1})}$$

So, we choose an ansatz of the form of a wave-

$$\delta x_n = A e^{i(k \frac{n}{a} - \omega t)} = A e^{i(kna - \omega t)} \leftarrow \text{plane waves at the sites of the lattice.}$$

$$\Rightarrow -\omega^2 M A e^{i(kna - \omega t)} = -2\gamma A e^{i(kna - \omega t)}$$

$$+ \gamma A e^{i(kna - \omega t)} (e^{ika} - e^{-ika})$$

$$-\omega^2 M = -2\gamma + \gamma(e^{ika} + e^{-ika})$$

$$\omega^2 M = 2\gamma(1 - \cos(ka)) = 4\gamma \sin^2\left(\frac{ka}{2}\right)$$

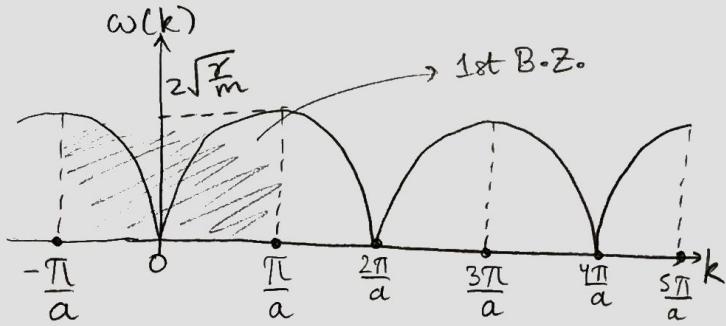
$$\Rightarrow \omega = 2\sqrt{\frac{\gamma}{M}} \left| \sin\left(\frac{ka}{2}\right) \right| \rightarrow \text{ansatz is a soln if } \omega \text{ is this value.}$$

We allow k to be both \pm .

DISPERSION
RELATION FOR 1D CHAIN.

The phase velocity of this wave would be $v_{\text{phase}} = \frac{\omega}{k}$

group velocity of this wave would be $v_{\text{group}} = \frac{\partial \omega}{\partial k}$.



Let's also check if the periodicity of a in real space translates to periodicity of $\frac{2\pi}{a}$ in k -space.

$$\delta x_n = A e^{i(kna - \omega t)}$$

$$\text{take } k \rightarrow k + \frac{2\pi n}{a} \Rightarrow \delta x_n(k) = \delta x_n\left(k + \frac{2\pi n}{a}\right)$$

\Rightarrow Periodicity of $\frac{2\pi}{a}$.

Reminder: 1st Brillouin zone \equiv WS cell of reciprocal lattice.

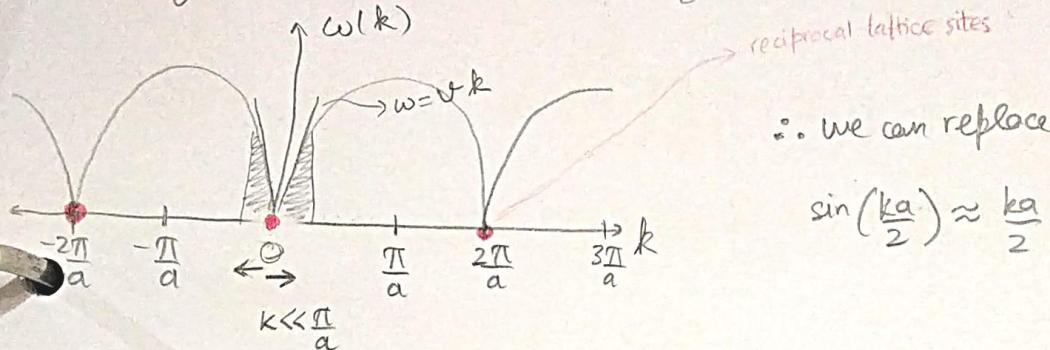
The real space lattice is $\vec{R} = n a \hat{i}$ \Rightarrow First Brillouin zone is
 \Rightarrow The reciprocal lattice is $\vec{G} = \frac{2\pi m}{a} \hat{i}$ $\left[-\frac{\pi}{a}, +\frac{\pi}{a} \right]$

Rewriting the dispersion relation

$$\omega(k) = 2 \sqrt{\frac{\chi}{M}} \left| \sin\left(\frac{ka}{2}\right) \right| \quad ; \quad k = \frac{2\pi}{\lambda}$$

For long wavelength modes, k is small $k \ll \frac{\pi}{a} \Rightarrow ka \ll \pi$

Therefore we move only in a small region of the 1st B.Z.



∴ we can replace

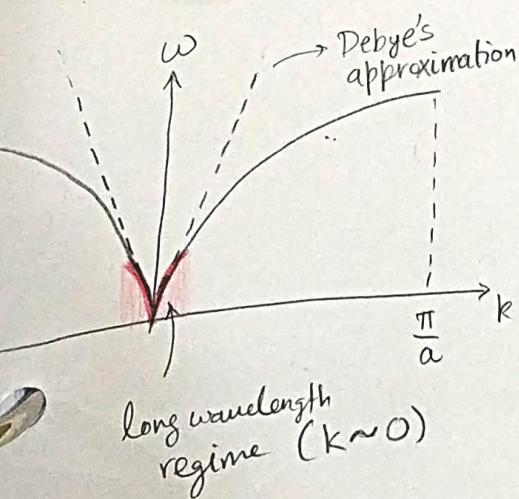
$$\sin\left(\frac{ka}{2}\right) \approx \frac{ka}{2}$$

$$\Rightarrow \text{For long wavelengths, } \omega(k) \approx 2 \sqrt{\frac{\chi}{M}} \frac{ka}{2} = \left(a \sqrt{\frac{\chi}{M}}\right) k = v_F k$$

∴ long wavelengths causes the discreteness & periodicity of the lattice to be invisible to the wave.

$$\underline{\omega(k) = v_F k} \quad (\text{linear dispersion}) \quad \text{for } \lambda \gg 1 \\ (\text{sound waves in solids})$$

$$v_F = v_g = v = \sqrt{\frac{\chi}{M}} a$$



At the edge of the Brillouin zone,

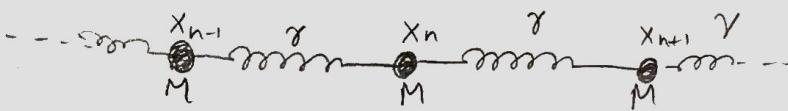
$$\omega(k) = 2 \sqrt{\frac{\chi}{M}} \left| \sin\left(\frac{\pi}{a} \cdot \frac{a}{2}\right) \right| = 1 \\ = 2 \sqrt{\frac{\chi}{M}}$$

$$\delta x_n (k = \pm \frac{\pi}{a}) = A e^{-i \omega t} e^{i n \pi}$$

This is what happens for the shortest λ , since the shortest wavelength mode has $\lambda = 2a$.

$$v_F = \left. \frac{\partial \omega}{\partial k} \right|_{k=\frac{\pi}{a}} = 0 \quad (k = \frac{\pi}{a})$$

Monatomic chain



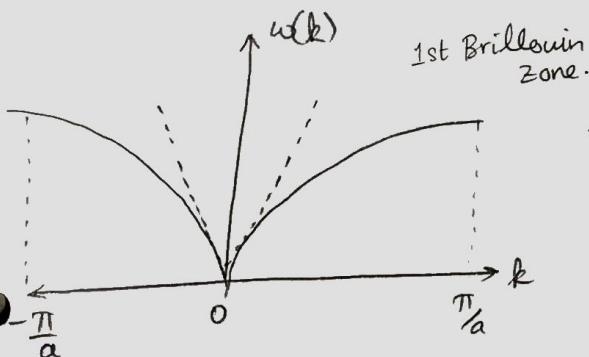
$$\delta x_n = A e^{i(kna - \omega t)} \quad \} \text{ normal mode}$$

Dispersion relation $\omega(k) = \sqrt{\frac{\gamma}{M}} \left| \sin\left(\frac{ka}{2}\right) \right|$

Also, δx_n is periodic by the reciprocal lattice vector

$$\delta x_n\left(k + \frac{2\pi}{a} b\right) = \delta x_n(k)$$

$$\omega\left(k + \frac{2\pi}{a} b\right) = \omega(k)$$



this is the analysis for an infinite chain, and ∴ any value of k is possible.

However, for a finite chain, the analysis is a tad bit different.

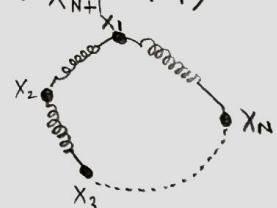
(1) the end atoms can be considered fixed.

(2) or we can use periodic boundary conditions. ($x_{N+1} = x_1$)

$$\Rightarrow \delta x_{i+N} = \delta x_i$$

$$\Rightarrow A e^{i(k(i+N)a - \omega t)} = A e^{i(kia - \omega t)}$$

$$\therefore e^{ikNa} = 1 \quad \text{or } k = \frac{2\pi b}{Na}$$



Thus, periodic BCs impose a quantization condition on k .

∴ k can now take N values b/w $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$ in the 1st Brillouin zone.

At 300K, the heat capacity of all the solids was almost the same $\approx 3R$

\uparrow
gas constant (8.314 J mol^{-1})

At temp. T, $\langle E \rangle = k_B T$ per dimⁿ $\Rightarrow \langle E \rangle = 3k_B T$ in 3D per atom

$$\therefore C \text{ (heat capacity)} = \frac{\partial \langle E \rangle}{\partial T} = \underline{3k_B} = \underline{3R \text{ mol}^{-1}}$$

Lecture-19

(12/10/2021)

Heat capacity of Solids:

For most solids, it was observed that $C = 3k_B$ per atom or $3R$ per mole.

at room temperature $\sim 300\text{K}$. This is known as Dulong-Petit law.

Boltzmann \rightarrow he modelled the solid by $3N$ harmonic oscillators.

$\Rightarrow \langle E \rangle = 3Nk_B T$ where N is the no. of particles

$$\therefore C = \frac{\partial \langle E \rangle}{\partial T} = 3k_B \text{ per atom/particle.}$$

Some exceptions to this law were materials like diamond which had $C \sim k_B$ per atom at room temp. And as technology improved, and experiments were done at low temperatures, C was found to be $\ll 3k_B$ and

$C \rightarrow 0$ as $T \rightarrow 0$.

Einstein in 1907 used Boltzmann's idea of 3N oscillators and added QM to the model. This was actually done 19 years before QM was even formalized.

A quantum mechanical oscillator has the energy eigenvalues quantised as follows-

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad \begin{aligned} n &= \text{excitation mode \#} \\ \omega &= \text{oscillator frequency.} \end{aligned}$$

If we take a collection of such oscillators in thermal eq^m (canonical system),

then

$$\langle E \rangle = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad \text{where } Z \text{ is the canonical partition function.}$$

$$\langle E \rangle = \hbar\omega [n_B(\beta\hbar\omega) + \frac{1}{2}] \text{ where } n_B(\beta\hbar\omega) = \frac{1}{e^{\beta\hbar\omega} - 1} \quad (\text{Bose factor.})$$

For N particles & 3 dim's,

$$\langle E \rangle = 3Nk\omega \left[n_B(\beta k\omega) + \frac{1}{2} \right]$$

$$\therefore C_E = \frac{1}{N} \frac{\partial \langle E \rangle}{\partial T} = 3k\omega \frac{(e^{\beta k\omega})}{(e^{\beta k\omega} - 1)^2} \cdot \left(\frac{k\omega k_B}{k_B^2 T^2} \right)$$

$$C_E = \frac{3k_B (\beta h\omega)^2 e^{\beta h\omega}}{(e^{\beta h\omega} - 1)^2}$$

← specific heat capacity
in Einstein's model.

(4)

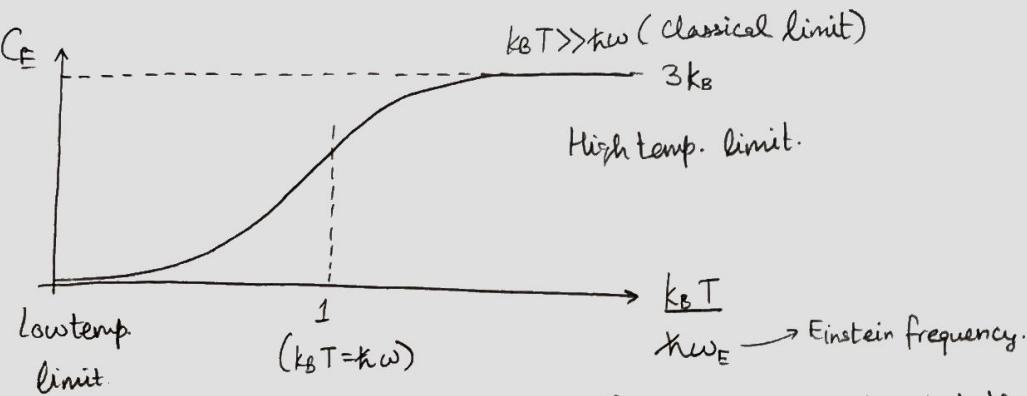
High temp. limit. $k_B T \gg \hbar\omega$ or $\beta\hbar\omega \ll 1$

$$C_E \approx \frac{3k_B (\beta\hbar\omega) (1 + \beta\hbar\omega)}{\cancel{(1 + \beta\hbar\omega)^2}} \approx 3k_B \rightarrow \text{Dulong - Petit law is recovered.}$$

Low temp. limit. $k_B T \ll \hbar\omega$ or $\beta\hbar\omega \gg 1$

$$C_E \approx \frac{3k_B e^{\beta\hbar\omega}}{e^{2\beta\hbar\omega}} \approx \frac{3k_B (\beta\hbar\omega)^2}{e^{\beta\hbar\omega}} = \frac{3(\hbar\omega)^2}{k_B^2 T^2} e^{-\hbar\omega/k_B T}$$

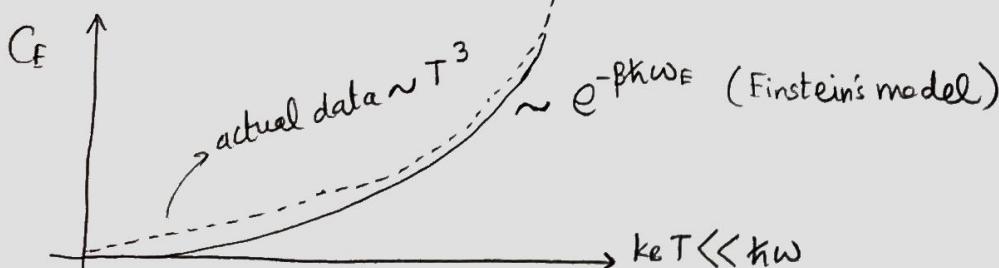
As $T \rightarrow 0$, the exponential decays faster $\Rightarrow C_E \sim 0$ as $T \rightarrow 0$



ω_E is a fit parameter since we don't know beforehand what the frequency of atoms is.

The reason why $k_B T \ll \hbar\omega$ gives $C_E \sim 0$ is because an excitation of oscillator requires energy of $\hbar\omega$. If the thermal energy $k_B T$ is less than $\hbar\omega$, then the SHOs would be stuck in their ground states.

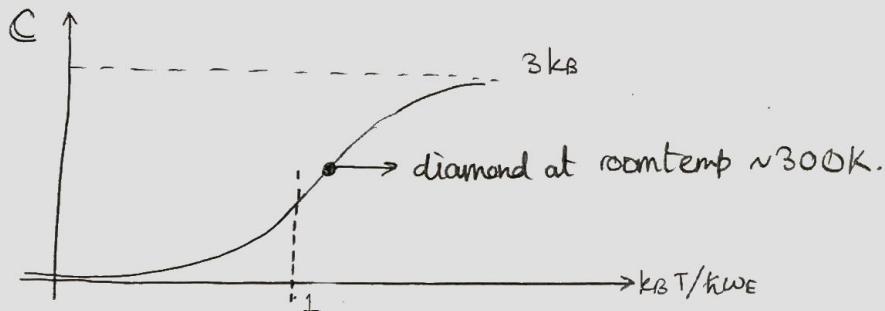
However, this is not a perfect model.



(5)

For a classical oscillator, $\omega_E \sim \sqrt{\frac{\gamma}{M}}$ $\gamma \rightarrow$ spring constant.

So, classically, we can say that M is very low & due to its hardness and the strong interactions $\Rightarrow \gamma$ is very high $\Rightarrow \omega_E$ is very high for diamond.

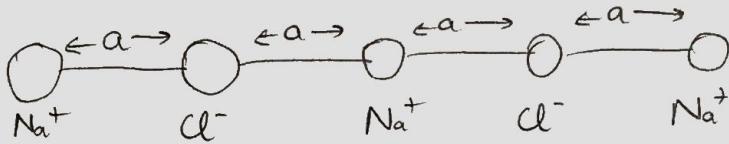


\therefore At room temp., diamond's $\hbar\omega_E$ is not much smaller compared to the $k_B T$. i.e. $k_B T > \hbar\omega_E$ but not by a lot,

so, $C \left(\frac{k_B T}{\hbar\omega_E} \right) \Big|_{T \sim 300K}$ for diamond $\sim 1 k_B$ per atom.

For revision-
 → read ch-4, 5, 6 of Ashcroft-Mermin. Can also have a look at Kittel.
 → Hook & Hall also has problems.
 → Try as many problems as you can.

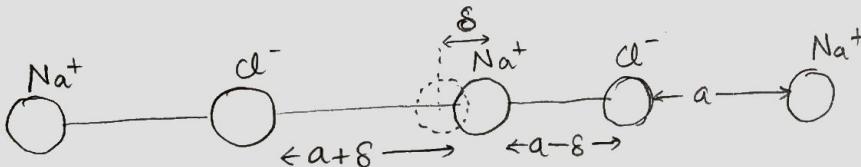
- ① Find the reciprocal lattice of triangular lattice (2D) & hexagonal lattice (3D).
- ② Prove that $\frac{2\pi}{d_{hkl}}$ is shortest reciprocal lattice vector \perp to $(h k l)$
- ③ Packing fraction of hcp and simple hexagonal.
- ④ Problem 2.8 Simon book., Problem 5.1 Ashcroft.
- ⑤ CSIR and GATE problems.

1.

$$U_{Na^+(a)} = 2 \left[-\frac{e^2}{4\pi\epsilon_0 a} + \frac{e^2}{4\pi\epsilon_0(2a)} + \frac{e^2}{4\pi\epsilon_0(3a)} + \dots \right]$$

$$= -\frac{2e^2}{4\pi\epsilon_0 a} \left[1 - \frac{1}{2} + \frac{1}{3} - \dots \right] = -\frac{2\ln 2 e^2}{4\pi\epsilon_0 a} = -\frac{M_a e^2}{4\pi\epsilon_0 a}$$

If one of the Na^+ atoms is displaced by δ



$$\text{So, } U_{Na^+(\delta)} = -\frac{e^2}{4\pi\epsilon_0(a+8)} - \frac{e^2}{4\pi\epsilon_0(a-\delta)} + \frac{e^2}{4\pi\epsilon_0(2a+8)} + \frac{e^2}{4\pi\epsilon_0(2a-\delta)}$$

$$= -\frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{a+8} + \frac{1}{a-\delta} - \left(\frac{1}{2a+8} + \frac{1}{2a-\delta} \right) + \frac{1}{3a+8} + \frac{1}{3a-\delta} + \dots \right]$$

$$\frac{1}{na+8} + \frac{1}{na-\delta} = \frac{(na-8) + (na+8)}{(na+8)(na-8)} = \frac{2na}{(na)^2 - 8^2}$$

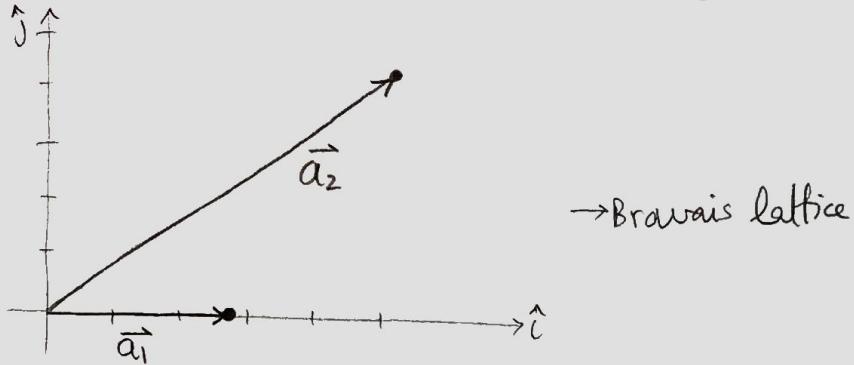
$$= \frac{2na}{1 - \frac{8^2}{(na)^2}} \cdot \frac{1}{(na)^2} = \frac{2na}{(na)^2} \left(1 - \frac{8^2}{(na)^2} \right)^{-1} \approx \frac{2}{na} \left(1 + \frac{8^2}{(na)^2} \right)$$

$$\Rightarrow U_{Na^+(\delta)} = \sum_{n=1}^{\infty} \left(\frac{2}{na} + \frac{8^2}{(na)^2} \right) (-1)^n$$

$$= -\frac{e^2}{4\pi\epsilon_0} \left(\left[1 - \frac{1}{2} + \frac{1}{3} - \dots \right] + 8^2 \left(1 - \frac{1}{4} + \frac{1}{9} - \frac{1}{16} + \dots \right) \right)$$

$$= -\frac{e^2}{4\pi\epsilon_0 a} 2\ln 2 + 8^2 \left(1 - \frac{1}{4} + \frac{1}{9} - \frac{1}{16} + \dots \right) \rightarrow \text{correction}$$

2. $\vec{a}_1 = 0.25\hat{i}$ and $\vec{a}_2 = 0.5\hat{i} + 0.4\hat{j}$.



$$\vec{a}_3 = \hat{k}$$

→ Bravais lattice

reciprocal lattice vectors can be found out as follows -

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|}$$

$$\vec{a}_2 \times \vec{a}_3 = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ 0.5 & 0.4 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|}$$

$$= \hat{i}(0.4) + \hat{j}(-0.5)$$

$$= 0.4\hat{i} - 0.5\hat{j}$$

$$\vec{b}_1 = 2\pi \frac{(0.4\hat{i} - 0.5\hat{j})}{0.1}$$

$$\vec{a}_3 \times \vec{a}_1 = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ 0 & 0 & 1 \\ 0.25 & 0 & 0 \end{vmatrix}$$

$$= \hat{i}(0) + \hat{j}(0.25) + \hat{k}(0)$$

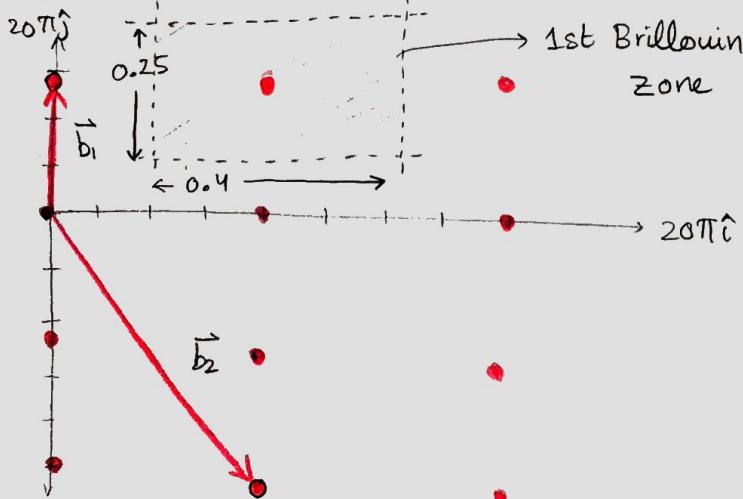
$$= 0.25\hat{j}$$

$$\vec{b}_2 = 2\pi \frac{(0.25\hat{j})}{0.1}$$

$$\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = 0.4 \times 0.25 = 0.1$$

$$\Rightarrow \boxed{\vec{b}_1 = 20\pi(0.4\hat{i} - 0.5\hat{j})}$$

$$\boxed{\vec{b}_2 = 20\pi(0.25\hat{j})}$$



(3)

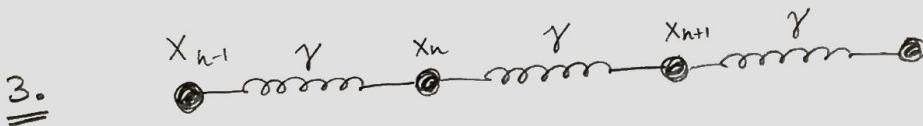
Distance b/w lattice planes of family (13)

$$d_{hk} = \frac{1}{\sqrt{\frac{1}{x^2} + \frac{1}{y^2}}} = \frac{1}{\sqrt{\frac{h^2}{|\vec{a}_1|^2} + \frac{k^2}{|\vec{a}_2|^2}}} \quad h=1 \quad k=3$$

$$|\vec{a}_1| = 0.25$$

$$|\vec{a}_2| = \sqrt{(0.5)^2 + (0.4)^2}$$

$$\Rightarrow d_{hk} = \frac{1}{\sqrt{\frac{1}{0.25} + \frac{9}{0.41}}} = \frac{1}{\sqrt{4 + 21.95}} = \frac{1}{5.09} \approx \underline{\underline{0.1963}}$$



$$V = \frac{1}{2} \gamma \sum_i (\delta x_{i+1} - \delta x_i)^2$$

$$F_n = -\frac{\partial V}{\partial x_n} - \beta \dot{x}_n \rightarrow \text{damping term}$$

$$M \ddot{\delta x}_n = -2\gamma \delta x_n + \gamma (\delta x_{n+1} + \delta x_{n-1}) - \beta \dot{\delta x}_n$$

Choose a trial solⁿ $\delta x^n = A e^{i(kna - wt + \alpha)}$

$$M \ddot{\delta x}_n = -\omega^2 M A e^{i(kna - wt + \alpha)} = -2\gamma A e^{i(kna - wt + \alpha)} \\ + \gamma (A e^{i(kna - wt + \alpha)} (e^{ika} - e^{-ika}))$$

$$-i\omega \beta A e^{i(kna - wt + \alpha)}$$

$$-\omega^2 M = -2\gamma + \gamma (e^{ika} + e^{-ika}) - i\omega \beta$$

$$\omega^2 M = 2\gamma(1 - \cos ka) + i\omega \beta$$

$$\omega^2 M - \omega(i\beta) - 4\gamma \sin^2\left(\frac{ka}{2}\right) = 0$$

$$\omega = i\beta \pm \frac{\sqrt{-\beta^2 + 4M\gamma \sin^2 \frac{ka}{2}}}{2M}$$

u. \vec{R} with a basis \vec{b}_1 and \vec{b}_2

$$\text{Total field at detector} = \tilde{A} [e^{i\vec{k} \cdot \vec{r}} + e^{i(\vec{k}' \cdot \vec{r}) + \delta}]$$

$$\delta = (\vec{R} - \vec{k}) \cdot \vec{D}$$

$$\Rightarrow E_{\text{det}} = \tilde{A} e^{i\vec{k} \cdot \vec{r}} [1 + e^{i(\vec{k}' - \vec{k}) \cdot \vec{D}}]$$

Now

$$\begin{aligned}\vec{d}_1 &= \vec{r}_1 + \vec{b}_1 \\ \vec{d}_2 &= \vec{r}_2 + \vec{b}_2 \\ \vec{D} &= (\vec{r}_1 - \vec{r}_2) + (\vec{b}_1 - \vec{b}_2)\end{aligned}$$

(5)

$$F_{\text{det}} = \tilde{A} e^{i \vec{k}' \cdot \vec{r}} \left[1 + e^{i \vec{Q} \cdot (\vec{r}_1 - \vec{r}_2)} e^{i(\vec{b}_1 - \vec{b}_2) \cdot \vec{Q}} \right]$$

$$= \tilde{A} e^{i \vec{k}' \cdot \vec{r}} e^{-i \vec{Q} \cdot \vec{r}_2} e^{-i \vec{Q} \cdot \vec{b}_2} \left(e^{i \vec{Q} \cdot \vec{b}_1} e^{i \vec{Q} \cdot \vec{r}_1} + e^{i \vec{Q} \cdot \vec{b}_2} e^{i \vec{Q} \cdot \vec{r}_2} \right)$$

generalise

$$= A \sum_i e^{i \vec{Q} \cdot \vec{r}_i} \sum_j e^{i \vec{Q} \cdot \vec{b}_j}$$

$$\Rightarrow \text{Intensity } I \propto \left| \sum_i e^{i \vec{Q} \cdot \vec{r}_i} \right|^2 \left| \frac{\sum_j e^{i \vec{Q} \cdot \vec{b}_j}}{|S|^2} \right|^2$$

$$S = \sum_i e^{i \vec{Q} \cdot \vec{b}_i} \quad \rightarrow \text{structure factor}$$

$$\text{For bcc, we can take } \vec{b}_1 = 0 \quad \vec{b}_2 = \frac{a}{2} (\hat{i} + \hat{j} + \hat{k})$$

$$S = e^{i \vec{Q} \cdot \vec{0}} + \exp \left[i \frac{a}{2} (\hat{i} + \hat{j} + \hat{k}) \cdot \vec{Q} \right]$$

A general reciprocal lattice vector & cubic lattice has the form

$$\vec{Q} = \frac{2\pi}{a} (h\hat{i} + k\hat{j} + l\hat{k})$$

$$\Rightarrow \vec{Q} \cdot \vec{b}_2 = \frac{i\pi (2\pi)}{2a} (h+k+l)$$

$$\text{So, } S_{\text{bcc}} = 1 + e^{i\pi(h+k+l)} = 1 + (-1)^{h+k+l}$$

$$= \begin{cases} 2 & \text{for } h+k+l = \text{even} \\ 0 & \text{for } h+k+l = \text{odd.} \end{cases}$$

So, S vanishes when $h+k+l = \text{odd}$ #

Lecture - 20

(25/10/2021)

Einstein's model of a solid - (N atoms in 3D)

$$\langle E_n \rangle = 3Nk\omega \left(n_B(\beta\hbar\omega) + \frac{1}{2} \right)$$

$$C_E = \frac{3k_B (\beta k_B\omega)^2 e^{\beta k_B\omega}}{(e^{\beta k_B\omega} - 1)^2} = \frac{1}{N} \frac{\partial \langle E_n \rangle}{\partial T}$$

However at low T, $C_{\text{exp}} \sim T^3$ whereas Einstein model says that

$$C_E \sim e^{-\beta k_B\omega}$$

Debye corrected the model in the following way -

Vibrations in solids should be looked at as sound waves, i.e. we take the dispersion relation $\omega(k) = v k$.

$$\langle E \rangle = 3 \sum_k k \omega(k) \left[n_B + \frac{1}{2} \right]$$

↑
3 polarizations of the sound waves

due to the dense sum of k , $\sum_k \rightarrow \frac{L}{2\pi} \int dk$

$\frac{2\pi}{L}$ is the separation b/w the allowed k -points.

Lecture - 21 (26/10/2021)

The Einstein model assumes $3N$ independent oscillators all with frequency ω_E

So, the energy of a single oscillator is $E_n = \hbar\omega_E \left(n + \frac{1}{2} \right)$

The thermal avg. of a single oscillator thus is equal to

$$\langle E_n \rangle = \hbar \omega_E \left(n_B (\beta \hbar \omega_E) + \frac{1}{2} \right)$$

(2)

So, total $E = \sum_{\text{all oscillators}} \langle E_n \rangle$

So, for N atoms in 3D, we can consider $3N$ independent oscillators

$$\Rightarrow E = \sum_{j=0}^{3N} \langle E_n \rangle = 3N \langle E_n \rangle \Rightarrow C_E = \frac{\langle E_n \rangle}{N \Delta T} = \frac{3k_B (\beta \hbar \omega_E)^2}{(e^{\beta \hbar \omega_E} - 1)^2}$$

The problem of inconsistency of C_E at low temps was solved by Debye.

Debye model.

Lattice vibrations are sound waves!

That meant

Energy of a specific mode given by $\omega(\vec{k})$ $\langle E_n \rangle = \hbar \omega(\vec{k}) \left[n_B (\beta \hbar \omega(\vec{k})) + \frac{1}{2} \right]$ where $\omega(\vec{k}) = v |\vec{k}|$

So, ω_E is no longer a const. parameter.

So, the total energy will be-

$$\text{Total energy} = \sum_{\text{sum over } \vec{k}} \hbar \omega(\vec{k}) \left[n_B (\beta \hbar \omega(\vec{k})) + \frac{1}{2} \right]$$

Every sound wave mode with a given \vec{k} will have 3 polarizations, so

the total energy is-

$$E_T = 3 \cdot \sum_{\vec{k}} \hbar \omega(\vec{k}) \left[n_B (\beta \hbar \omega(\vec{k})) + \frac{1}{2} \right]$$

↓
1 - longitudinal
2 - transverse
assuming the 3 polarizations have the same velocity

3 polarizations for solids.

1 polarization for liquids. (only longitudinal).

(3)

The sum over \vec{k} can be approximated as an integral.

In 1D, $\sum_{\vec{k}} = \# \text{ of } k\text{-points.}$

$$\text{So, } \left(\frac{2\pi}{L}\right) \cdot \sum_{\vec{k}} = \int dk = \text{length of the } k\text{-line.}$$

\uparrow
spacing b/w
 k points

$$\Rightarrow \sum_{\vec{k}} (\text{in 1D}) = \frac{L}{2\pi} \int dk.$$

$$\text{Similarly, in 3D, } \sum_{\vec{k}} = \left(\frac{L}{2\pi}\right)^3 \int d^3\vec{k}$$

$$\text{So, } E_{\text{total}} = \left(\frac{L}{2\pi}\right)^3 \cdot 3 \int d^3\vec{k} \ h \omega(\vec{k}) \left[n_B(\beta h \omega(\vec{k})) + \frac{1}{2} \right]$$

$$\omega(\vec{k}) = V |\vec{k}| \text{ in Debye's case}$$

Assuming isotropic velocity of sound in solids, $\int d^3\vec{k} = \int 4\pi k^2 dk$

$$E_{\text{total}} = \frac{L^3}{4\pi^2 \cdot 2\pi} \cdot 3 \cdot 4\pi \int_0^\infty h \omega(k) \left[n_B(\beta h \omega(k)) + \frac{1}{2} \right] k^2 dk$$

$$\text{Using } \omega = V k, \Rightarrow dk = \frac{d\omega}{V} \text{ and } k = \frac{\omega}{V}$$

$$E_{\text{tot}} = \frac{3 L^3}{2\pi^2} \int_0^\infty d\omega \frac{\omega^2}{V^3} h \omega \left[n_B(\beta h \omega) + \frac{1}{2} \right]$$

$$= \frac{3 L^3}{2\pi^2 V^3} \int_0^\infty d\omega \omega^2 h \omega \left[n_B(\beta h \omega) + \frac{1}{2} \right]$$

Now we define $\boxed{g(\omega) = \frac{3 L^3 \omega^2}{2\pi^2 V^3}}$ \rightarrow density of states in 3D

$g(\omega)d\omega = \# \text{ of modes b/w } \omega \text{ & } \omega + d\omega$

If we rewrite $g(\omega) = N \frac{3\omega^2}{2\pi^2 V^3} \left(\frac{N}{L^3} \right)$ no. of atoms per volume $\rightarrow \text{density} = n$

$$\Rightarrow g(\omega) = N \cdot \frac{3\omega^2}{2\pi^2 V^3 n} = N \frac{9\omega^2}{\omega_D^3}$$

where $\omega_D^3 = 6\pi^2 n V^3$ \rightarrow Debye frequency.

Now,

$$E_{\text{total}} = \frac{9Nk}{\omega_D^3} \int_0^\infty d\omega \omega^3 \left[n_B(\beta\hbar\omega) + \frac{1}{2} \right]$$

$$= \frac{9Nk}{\omega_D^3} \int_0^\infty d\omega \omega^3 \cdot \frac{1}{e^{\beta\hbar\omega} - 1} + (\text{Temperature independent terms})$$

$$\text{substituting } x = \beta\hbar\omega \Rightarrow \omega = \frac{x}{\beta\hbar}$$

$$E_{\text{tot}} = \frac{9Nk}{\omega_D^3} (\beta\hbar)^4 \underbrace{\int_0^\infty dx x^3 \cdot \frac{1}{e^x - 1}}_{g_4(z=1) = \zeta(4) = \frac{\pi^4}{15}} + (\text{Temp. indp.})$$

$$E_{\text{tot}} = \frac{9N k_B T^4}{(\hbar \omega_D)^3} \cdot \frac{\pi^4}{15} + (\text{zero-pt. energy at } T=0)$$

So, heat capacity in Debye model

$$C_E = \frac{1}{N} \frac{\partial \langle E \rangle_{\text{tot}}}{\partial T} \sim T^3$$

For a dispersion of the form $\omega \propto k^s \Rightarrow E \sim T^{3/s+1} \Rightarrow C_E \sim T^{3/s}$

In the Debye model, there were an ∞ no. of modes which went into 'E' (the integral from 0 to ∞). Also, Debye's model predicts that the dependence is T^3 all the way but it should saturate after a certain $\frac{k_B T}{\hbar \omega}$ ratio.

To fix this, Debye integrated upto a cutoff frequency. ω_{cutoff}

$$\int_0^{\omega_{\text{cutoff}}} d\omega g(\omega) \longrightarrow \text{should give the total no. of modes.}$$

As we knew from the vibration model of lattice, the # of modes = # of oscillators.

$$\therefore \int_0^{\omega_{\text{cutoff}}} d\omega g(\omega) = 3N$$

$$\frac{9N}{\omega_D^3} \int_0^{\omega_{\text{cutoff}}} \omega^2 d\omega = 3N \left(\frac{\omega_{\text{cutoff}}}{\omega_D} \right)^3 = 3N$$

$$\Rightarrow \boxed{\omega_{\text{cutoff}} = \omega_D}$$

\therefore The actual expression for E_{tot} is calculated as.

$$E_{\text{tot.}} = \frac{9Nk}{\omega_D^3} \int_0^{\omega_D} \frac{d\omega \omega^3}{e^{B\hbar\omega} - 1}$$

For low T such that $k_B T \ll \hbar \omega_D$, the \int_0^∞ assumption is good enough. For high T , i.e. $k_B T \gg \hbar \omega_D$, this gives the Duhong-Petit law.
 $(e^x - 1 \approx x \text{ for low } x)$

Another important remark is that the most general expression for E is

$$E = 3 \int d^3 \vec{k} \, \text{tr} \omega(\vec{k}) \left[n_B(\beta \hbar \omega(\vec{k})) + \frac{1}{2} \right]$$

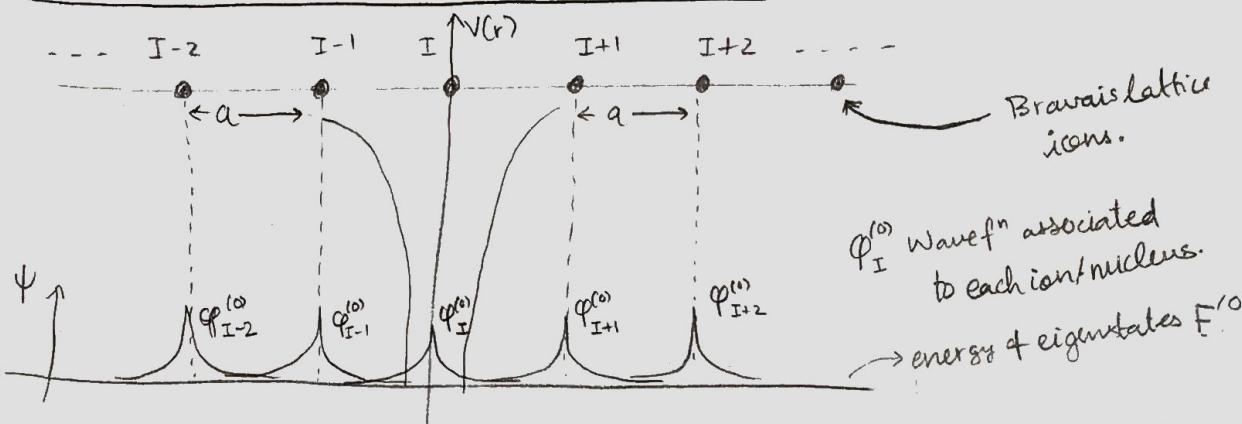
for the Einstein case, $\omega(\vec{k}) = \omega_E$.

For the Debye case, $\omega(\vec{k}) = V |\vec{k}|$

For the 1D chain case, $\omega(\vec{k}) = 2 \sqrt{\frac{\gamma}{M}} \left| \sin\left(\frac{ka}{2}\right) \right|$

} different dispersion relations

TIGHT-BINDING MODEL (FOR 1-D CHAIN)



$\phi_I^{(0)}$ Wavefn associated to each ion/nucleus.
→ energy & eigenstates $E^{(0)}$

$$R_I = aI \quad H_I^{(0)} = -\frac{k^2}{2m} \nabla^2 + V(r - R_I) \rightarrow \text{Hamiltonian of an } e^- \text{ associated to nucleus } I.$$

The $H_I^{(0)} \phi_I^{(0)} = E^{(0)} \phi_I^{(0)}$ is already solved # I.

The Hamiltonian of a single electron in the above periodic potential -

$$H = -\frac{k^2}{2m} \nabla^2 + \sum_I V_I \quad (\text{assuming no } e^-e^- \text{ repulsion}).$$

$$\hat{H}\psi = E\psi$$

$$\text{LCAO trial wavefn} \rightarrow \psi = \sum_J a_J \phi_J^{(0)}$$

Plugging into the eigenvalue eqn, we get -

$$\left[-\frac{k^2}{2m} \nabla^2 + \dots + V_{I-1} + V_I + V_{I+1} + \dots \right] \sum_I a_I \phi_I^{(0)} = E \sum_I a_I \phi_I^{(0)}$$

Now, just like in covalent bonding Hamiltonian, we can absorb $-\frac{k^2}{2m} \nabla^2$ with V_I to make the unperturbed Hamiltonian $H_I^{(0)}$

$$\text{LHS: } \left[-\frac{k^2}{2m} + V_I + \underbrace{\sum_{J \neq I} V_J}_{\Delta V_I} \right] (\dots + a_{I-1} \phi_{I-1} + a_I \phi_I + a_{I+1} \phi_{I+1} + \dots)$$

$$\Rightarrow = \left[H_I^{(0)} + \Delta V_I \right] [\dots a_{I-1} \varphi_{I-1}^{(0)} + \underbrace{a_I \varphi_I^{(0)}}_{\downarrow} + a_{I+1} \varphi_{I+1}^{(0)} + \dots]$$

$$= \dots + \underbrace{a_I E^{(0)} \varphi_I}_{\downarrow} + a_I \Delta V_I \varphi_I + \dots$$

The \dots terms are basically similar, with the operator on the left assumed to become $[H_J^{(0)} + \Delta V_J]$ for the J^{th} site

$$\text{So LHS} = \dots + \underbrace{a_{I-1} E^{(0)} \varphi_{I-1}}_{\downarrow} + a_{I-1} \Delta V_{I-1} \varphi_{I-1} + \underbrace{a_I E^{(0)} \varphi_I}_{\downarrow} + a_I \Delta V_I \varphi_I$$

$$+ \underbrace{a_{I+1} E^{(0)} \varphi_{I+1}}_{\downarrow} + a_{I+1} \Delta V_{I+1} \varphi_{I+1} + \dots \quad -(1)$$

Projecting the eqn (1) along $\langle \varphi_I |$ i.e. $\langle \varphi_I | \text{eqn 1} \rangle -$
 (where we assume negligible overlap $\langle \varphi_I | \varphi_J \rangle = \delta_{IJ}$)

$$\dots a_{I-1} \langle \varphi_I | \Delta V_{I-1} | \varphi_{I-1} \rangle + \underbrace{E a_I \varphi_I}_{\downarrow} + a_I \langle \varphi_I | \Delta V_I | \varphi_I \rangle + a_{I+1} \langle \varphi_I | \Delta V_{I+1} | \varphi_{I+1} \rangle$$

$$+ \dots$$

$$= E a_I$$

By symmetry considerations,

$$\langle \varphi_I | \Delta V_{I-1} | \varphi_{I-1} \rangle = \langle \varphi_I | \Delta V_{I+1} | \varphi_{I+1} \rangle \equiv t$$

$$\langle \varphi_I | \Delta V_I | \varphi_I \rangle \equiv \Delta E_0 \quad (\text{should be same } \forall I \text{ by periodicity})$$

The \dots terms in the above expression has terms like $\langle \varphi_I | \Delta V_J | \varphi_J \rangle$

where $J > I+1$ or $J < I-1$, so we neglect them ≈ 0 i.e.

$$\Rightarrow \boxed{a_{I-1} t + a_I (E^{(0)} + \Delta E_0) + a_{I+1} t = a_I E}$$

we only consider interaction with nearest neighbours

The matrix form of this eqn would look like -

$$\begin{pmatrix} 0 & t & E^{(0)} + \Delta E_0 & t & 0 & \dots & 0 \\ t & 0 & t & E^{(0)} + \Delta E_0 & t & 0 & \dots \\ 0 & t & 0 & t & E^{(0)} + \Delta E_0 & t & 0 \\ t & 0 & t & E^{(0)} + \Delta E_0 & t & 0 & \dots \end{pmatrix} \begin{pmatrix} a_{I-1} \\ a_I \\ a_{I+1} \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_{I-1} \\ a_I \\ a_{I+1} \\ \vdots \end{pmatrix}$$

$$(a_{I-1} + a_{I+1})t + a_I(E^{(0)} + \Delta E_0) = a_I E$$

Use the ansatz: $a_I = e^{iq^I}$

Plugging the ansatz into the above eqn, we get the form -

$$(e^{iq(I-1)} + e^{iq(I+1)})t + e^{iq^I}(E^{(0)} + \Delta E_0) = e^{iq^I} E$$

$$(e^{-iq} + e^{iq})t + E^{(0)} + \Delta E_0 = E$$

$$\Rightarrow E = E^{(0)} + \Delta E_0 + 2t \cos q \quad \text{for } a_I = e^{iq^I}$$

unique sol's only for q within a band of 2π .

The exact value of q does not matter! What matters is the value taken

by e^{iq^I} and $\cos q$, which is periodic by 2π .

$$\psi = \sum_J a_J \varphi_J^{(0)} \Rightarrow \psi_q = \sum_J e^{iq^J} \varphi_J^{(0)} \quad q \rightarrow \text{a quantum no. in some sense.}$$

$$E_q = E^{(0)} + \Delta E_0 + 2t \cos q.$$

$$q \equiv q + 2\pi N$$

$$\Delta E_0 = \langle \varphi_I | \Delta V_I | \varphi_I \rangle$$

$$t = \langle \varphi_I | \Delta V_{I-1} | \varphi_{I-1} \rangle$$

Sol's are periodic in $q \equiv q_j$ in the range $(-\pi, \pi]$

(4)
same wavefⁿ
but localised
around diff.
 R_J

Change variables to $q = ka$.

$$\rightarrow \varphi_j^{(0)}(r) = \varphi(r - R_J)$$

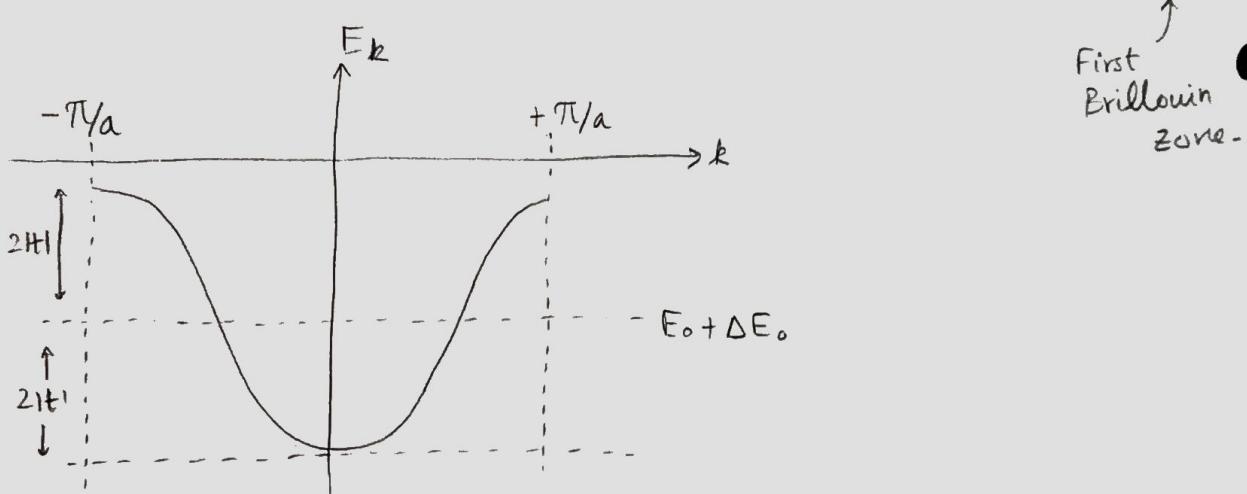
$$\Psi_k(r) = \sum_J e^{ikaJ} \varphi(r - R_J)$$



$$\left\{ \begin{array}{l} \Psi_k(r) = \sum_J e^{ikaJ} \varphi(r - R_J) \\ E_k = E_0 + \Delta E_0 + 2t \cos(ka) \end{array} \right.$$

R_J Bravais lattice
vectors
 $J \cdot a$

periodic in k -space with the period $\frac{2\pi}{a}$, so we take the range $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$



If we had an N -atom chain, we use the Bon von Karman

(periodic) boundary conditions, which says

$$1^{\text{atom}} = (N+1)^{\text{th atom}}$$

$$\psi_k(r + Na) = \psi_k(r)$$

$$\sum_J e^{ikaJ} \varphi(r + Na - R_J) = \psi_k(r)$$

$$\sum_J e^{ikaJ} \varphi(r - (J-N)a) = \psi_k(r)$$

$$\text{We do } J' = J - N \Rightarrow J = J' + N$$

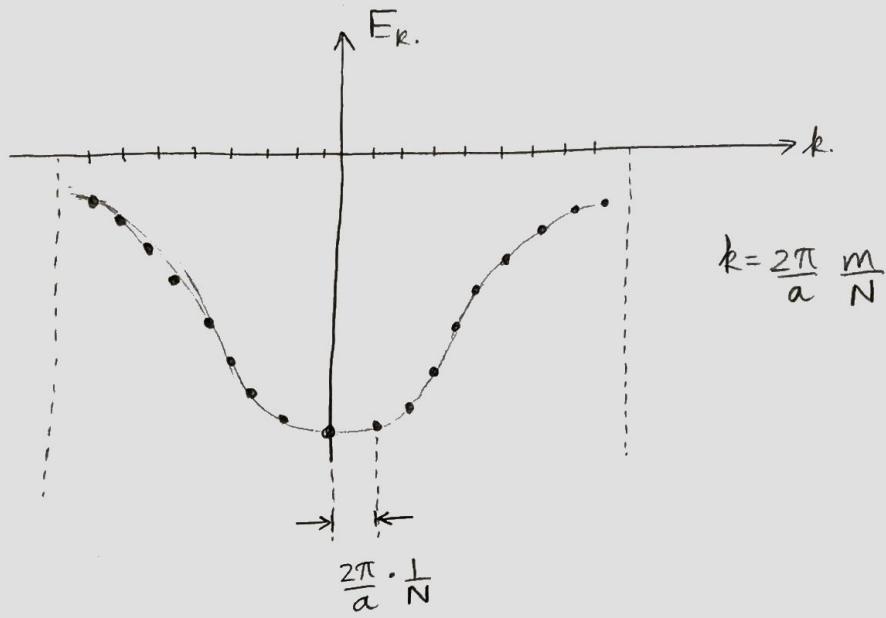
$$\sum_{J'} e^{ika(J'+N)} \cdot \varphi(r - J'a) = e^{ikNa} \sum_{J'} e^{ikaJ'} \cdot \varphi(r - J'a)$$

$$\Rightarrow \underline{e^{ikaN} = 1}$$

So, k is now quantized for periodic boundary conditions applied to N -atoms.

$$k = \frac{2\pi}{a} \frac{m}{N}$$

k can take only N different values in the B.Z. instead of ∞ .



Since we have N atoms, and we have N e^- s corresponding to this lattice \Rightarrow our Brillouin zone is only half filled since each site can occupy $2e^-$ s due to Pauli principle. So, we only have a half-filled bands. More about bands in the next lecture.

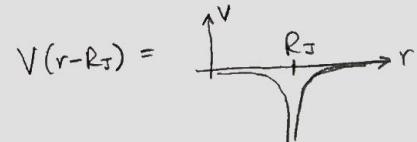
Lecture - 24

(01/11/2021)

Tight binding model review

$$H = \frac{\hbar^2}{2m} \nabla^2 + \sum_j V(r - R_j) \quad \text{where } V(r) = V_{\text{total}}$$

$$\Psi_k(r) = \sum_j e^{ikR_j} \psi(r - R_j)$$



$$E_k = E_0 + \Delta E_0 + 2t \cos ka$$

Solutions $\Psi_k(r)$ & energies E_k are periodic in k-space by period $\frac{2\pi}{a}$.

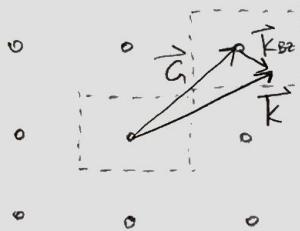
One of the most natural zones for the unique sol'n's is given by

$$-\frac{\pi}{a} < k \leq \frac{\pi}{a} \rightarrow \text{1st Brillouin zone.}$$

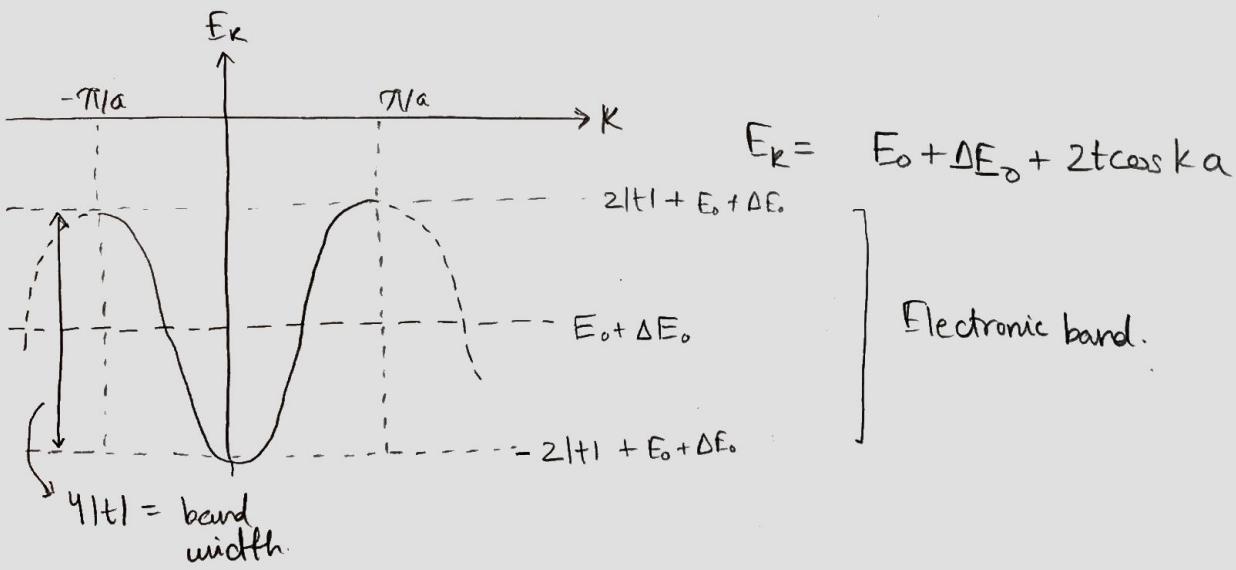
Any k outside the B.Z. can be written as

$$\vec{k} = \vec{G} + \vec{k}_{BZ}$$

\uparrow
reciprocal lattice vector.



(similarly, prove that
 $\Psi_k = \Psi_{k_{BZ}}$)



But how many k 's are in the band, considering $k \in B.Z.$ Since we had restricted our solid to a finite no. of atoms, i.e. we had an N atom chain, & if we apply Born von Karman b.c.s (or periodic bcs),

then k is quantized.-

$$k = \frac{2\pi}{a} \frac{m}{N} \quad -\frac{N}{2} < m \leq \frac{N}{2}$$

$$\therefore \boxed{\# \text{ of } k\text{-states within B.Z.} = N = \# \text{ of atoms in the lattice.}}$$

↑ very imp.
property!

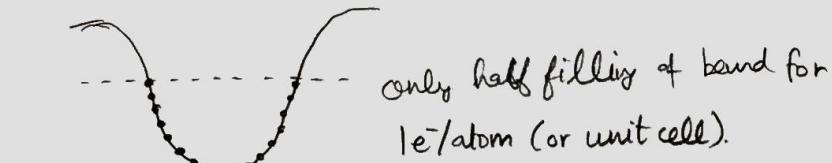
If the lattice were made of H-atoms, then we'd have one electron per atom, and N atoms \Rightarrow total no. of e^- in 1D chain = N

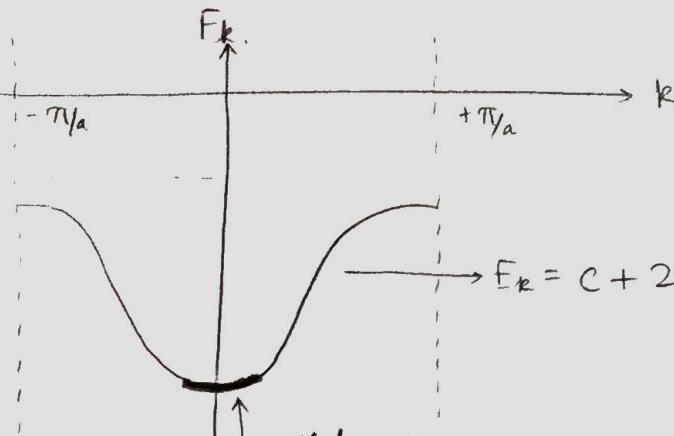
To fill the band with e^- s, we realize that each k -state can accommodate 2 electrons due to Pauli-principle (in the absence of an external \vec{B} field.)

Doing this, we realize that e^- s only fill half of the band, and the other half is unoccupied (for the case of 1 e^- / atom, here H).

This is because each k -state can be occupied by no more than 2 e^- s i.e. \uparrow and \downarrow . The band will be fully filled for He which has 2 e^- /unit cell.

$\boxed{\text{The maximum no. of electrons in a band can be 2 electrons per unit cell, (in the absence of spin-deg-breaking } \vec{B}/E \text{ field.)}}$





$$\text{small } k, E_k \approx c - 2|t| \left[1 - \frac{k^2 a^2}{2} \right]$$

$$t < 0$$

$$t = \langle \varphi_i | \underbrace{\Delta V_{I+1}}_{(-)} | \varphi_{i+1} \rangle$$

$$E_k = c' + |t| k^2 a^2 \rightarrow \text{similar to free particle energy.}$$

rest mass
For a free particle, $E_k = \sqrt{c^2 + \frac{\hbar^2 k^2}{2m}}$

so, in analogy to the free particle energy, we define an effective mass

m^* of \bar{e} 's with very small k in the band-

$$\frac{\hbar^2 k^2}{2m^*} = a^2 k^2 |t| \Rightarrow m^* = \frac{\hbar^2}{2a^2 |t|} \quad \begin{matrix} \text{Effective} \\ \text{mass} \\ \text{at bottom} \\ \text{of band!} \end{matrix}$$

$$m^* \propto (\text{band width})^{-1}$$

The above analysis was for the case when we had started filling the band and $k \ll \pi$.

At the top of the band however, $k \approx \frac{\pi}{a}$ or $ka \approx \pi$, then

$$\cos(ka - \pi) = f(\pi) + f'(\pi)ka + \frac{f''(\pi)k^2 a^2}{2} + \dots \Rightarrow -\cos ka = 1 - \frac{k^2 a^2}{2} + \dots$$

$$\Rightarrow E_k \approx c - 2|t| \left(-1 + \frac{k^2 a^2}{2} \right) = c' - |t| k^2 a^2 \Rightarrow \cos(ka) \approx -1 + \frac{k^2 a^2}{2}$$

$$\Rightarrow m^* = \frac{-\hbar^2}{2a^2 |t|}$$

Effective mass at the top of the band!

Electrons at the top of the bands are called holes.

Another property of the wavefn's in tight binding model.

$$\Psi_k(r) = \sum_I e^{ikR_I} \varphi(r - R_I)$$

If we go forward to $r \rightarrow r + R_J \rightarrow$ B.L. vector

$$\Psi_k(r + R_J) = \sum_I e^{ikR_I} \varphi(r + R_J - R_I) = \sum_I e^{ikR_I} \varphi(r - (R_I - R_J))$$

$$\text{Define } I' \equiv I - J \Rightarrow I = I' + J$$

$$\Rightarrow \Psi_k(r + R_J) = \sum_{I'} e^{ikR_J} e^{ikR_{I'}} \varphi(r - R_{I'}) = e^{ikR_J} \underbrace{\sum_{I'} e^{ikR_{I'}} \varphi(r - R_{I'})}_{\Psi_k(r)}$$

$$\Rightarrow \Psi_k(r + R_J) = e^{ikR_J} \Psi_k(r)$$

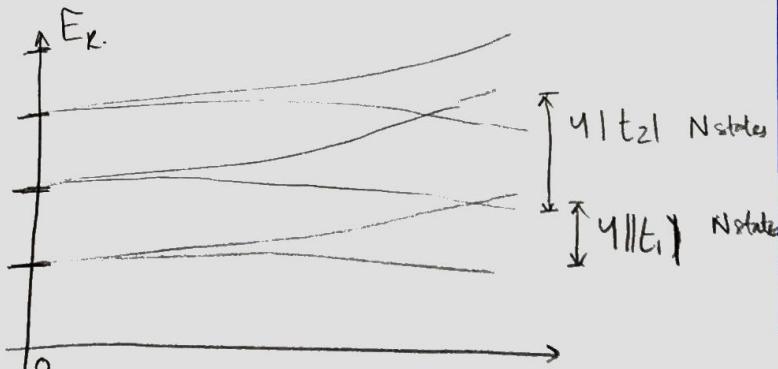
$$\Leftrightarrow \boxed{\Psi_k(r) = e^{ikr} u_k(r)} \quad \text{where } u_k(r + R_J) = u_k(r)$$

$$\begin{aligned} \Psi_k(r + R_J) &= e^{ikR_J} e^{ikr} u_k(r + R_J) \\ &= e^{ikR_J} e^{ikr} u_k \\ &= e^{ikR_J} \Psi_k(r) \end{aligned}$$

\therefore The wavefn of an electron moving in a periodic potⁿ can be written in the above form. This is called BLOCH'S THEOREM.

Lecture - 25.
(02-11-2021)

GENERIC PERIODIC POTENTIALS



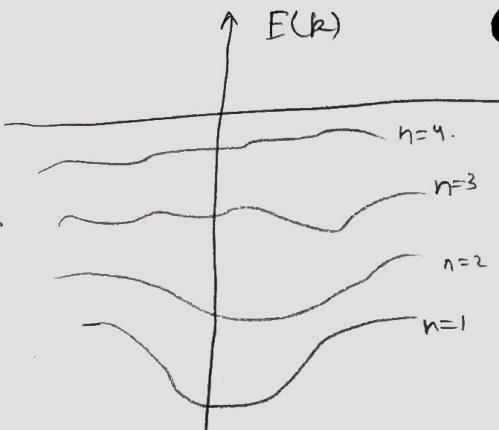
N - atoms with
 j - orbitals.
(doubly degenerate).

j bands with N states
each (doubly degenerate)

Apart from labelling the states with just k , we also need to specify the band index n as well.

$\psi_k^{(n)}(\vec{r})$ and $E_k^{(n)}(\vec{r})$

band
structure
diagram



Periodic potentials -

$$\text{If } H \equiv -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}); \quad V(\vec{r} + \vec{R}) = V(\vec{r})$$

Then the sol's of this H have the following form - $H \psi(\vec{r}) = E \psi(\vec{r})$

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

↑
periodic in \vec{R}

BLOCH's THM.
↓ plane wave.

where ψ and energies can be characterized by a quantum no. \vec{k} which is itself periodic in reciprocal space, where $\vec{k} \in \text{1st B.Z.}$

Some properties of \vec{k}

Is \vec{k} a momentum? Operate with \hat{p}

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial \vec{r}} = -i\hbar \vec{\nabla}$$

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

$$-i\hbar e^{i\vec{k} \cdot \vec{r}} \vec{\nabla} u_{\vec{k}}(\vec{r})$$

$\Rightarrow \psi_{\vec{k}}(\vec{r})$ is not a momentum eigenstate, nor is \vec{k} a momentum eigenvalue.

For a general dispersion $\omega(\vec{k})$

$$v = \frac{\partial \omega}{\partial k} = \frac{1}{\hbar} \frac{\partial \hbar \omega}{\partial k} = \frac{1}{\hbar} \frac{\partial E}{\partial k} \rightarrow \text{in 1D}$$

In 3D, the group velocity of an e^- in a Bloch wave will be

$$\boxed{\vec{v} = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} E(\vec{k})}$$

If there is an external force F on an electron, then change in its energy will be

$$\delta E = F \delta x = F v \delta t$$

$$\text{In 1D, } \delta E = \frac{F}{\hbar} \frac{\partial E}{\partial k} \delta t$$

$$\text{But } \delta E = \left(\frac{\partial E}{\partial k} \right) \delta k$$

$$\Rightarrow \boxed{F = \left(\frac{1}{\hbar} \right)^{-1} \lim_{\delta t \rightarrow 0} \frac{\delta k}{\delta t} = \hbar \frac{dk}{dt} \quad \text{in 1D}}$$

$$\text{In 3D, } \delta E = \frac{F}{\hbar} \vec{\nabla}_{\vec{k}} E(\vec{k}) \delta t$$

$$\text{but } \delta E = \vec{\nabla}_{\vec{k}} E(\vec{k}) \cdot \delta \vec{k}$$

$$\Rightarrow \boxed{\vec{F} = \left(\frac{1}{\hbar} \right)^{-1} \frac{d \vec{k}}{dt} = \hbar \frac{d \vec{k}}{dt} \quad \text{in 3D}}$$

In 1D,

$$\frac{dv}{dt} = \frac{d}{dt} \left(\frac{1}{\hbar} \frac{dE}{dk} \right) = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt}$$

$$= \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \cdot F \Rightarrow F = \frac{k^2}{\hbar^2} \frac{dv}{dt} = \left(\frac{k^2}{d^2 E / dk^2} \right) \frac{dv}{dt} = m^* \frac{dv}{dt}$$

$$\Rightarrow \boxed{m^* = \frac{\hbar^2}{d^2 E / dk^2}} \rightarrow \text{Effective mass at any } \vec{k}.$$

$\hbar \vec{k} \rightarrow \text{crystal momentum}$

Lecture - 26

(08-11-21)

If $V(\vec{r})$ has the periodicity of the B.L. i.e. $V(\vec{r} + \vec{R}) = V(\vec{r})$, then the wavefn can be labelled as -

$$\psi^k(\vec{r}) = u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \quad \vec{k} \in B.Z. \quad \text{Bloch's thm.}$$

If we plug this soln into the eigenvalue eqn $H\psi = E\psi$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}} = E(\vec{k}) u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$$

$$-\frac{\hbar^2}{2m} (u_k \nabla^2 e^{i\vec{k} \cdot \vec{r}} + e^{i\vec{k} \cdot \vec{r}} \nabla^2 u_k(\vec{r}) + 2 \vec{\nabla} u_k \cdot \vec{\nabla} e^{i\vec{k} \cdot \vec{r}})$$

On simplifying -

$$\left[\frac{\hbar^2}{2m} \left(\frac{1}{i} \vec{\nabla} + \vec{k} \right)^2 + V(\vec{r}) \right] u_k(\vec{r}) = E(\vec{k}) u_k(\vec{r})$$

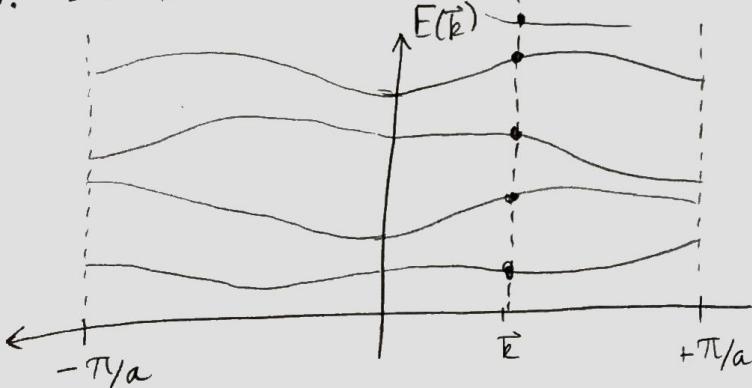
$$\left[-\frac{\hbar^2}{2m} (\nabla^2 + 2i\vec{k} \cdot \vec{\nabla} - |\vec{k}|^2) + V(\vec{r}) \right] u_k(\vec{r}) = E(\vec{k}) u_k(\vec{r})$$

$$\Rightarrow \tilde{H}_k u_k = E(\vec{k}) u_k$$

new eigenvalue eqn.

\tilde{H}_k is NOT the Hamiltonian.

H.W. - show that $E(\vec{k}) = E(-\vec{k}) \rightarrow$ (inversion symmetry of energy spectrum)



The curves
are continuous!
and have inversion
symmetry + periodicity

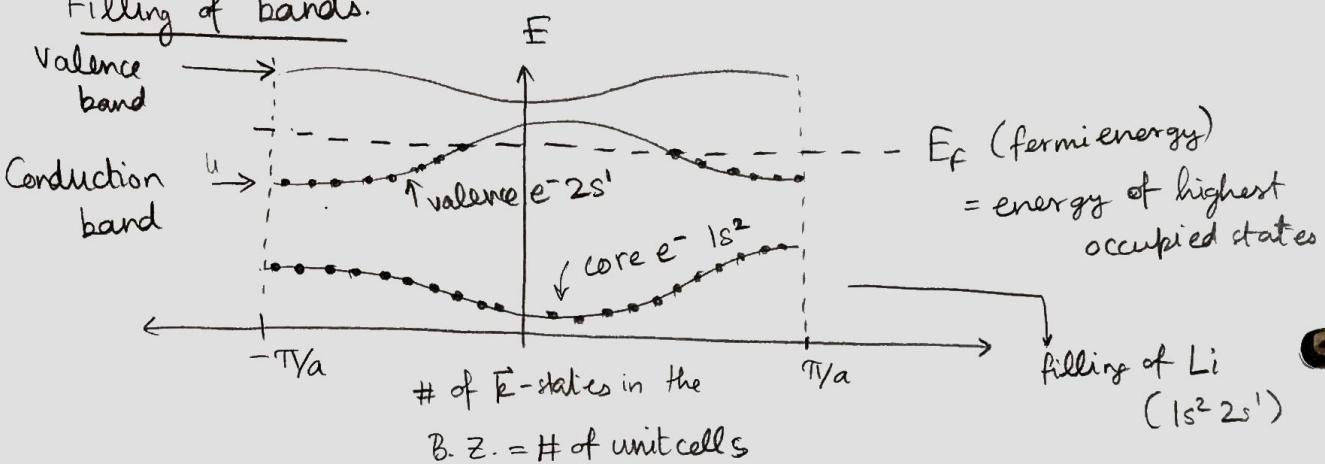
$$\therefore \left. \frac{dE}{dk} \right|_{k=\pm \frac{\pi}{a}} = 0$$

As a consequence of periodicity in \vec{k} space, continuous nature of $E(\vec{k})$ and inversion symmetry in \vec{k} -space [$E(\vec{k}) = E(-\vec{k})$]

$$\Rightarrow \boxed{\nabla_{\vec{k}} E(\vec{k}) = 0}$$

at B.Z. boundaries and the zone centre.

Filling of bands.



So, we get a partially filled band for the case of Lithium.

For Mg ($1s^2 2s^2 2p^6 3s^2$), $1s^2 2s^2 2p^6$ acts as core states and $3s^2$ completely fills the highest band.

For partially occupied bands, we have zero energy excitations available since we have higher energy levels just in the zero limit vicinity, so even a small push can cause the electrons to occupy a higher energy level. These are (like E field) metals. (like Li)

For a completely filled highest band however, only finite energy excitations are available, so a significant amount of energy is needed to excite the electrons. These are insulators.

(3)

So, we'd expect something like

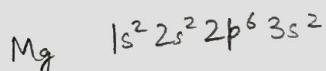
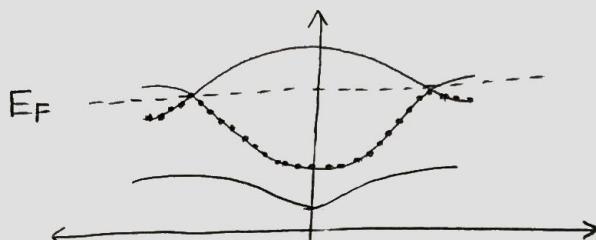
of electrons / per unit cell odd $\xleftarrow{?}$ Metal ?

of electrons / per unit cell even $\xleftarrow{?}$ Insulator ?

However, this correspondence is NOT true in general.

If we find that a material is an insulator, that definitely implies
Insulator \Rightarrow even no. of e⁻s / each unit cell.

However, Mg despite having even no. of e⁻s / unit cell isn't really
an insulator.

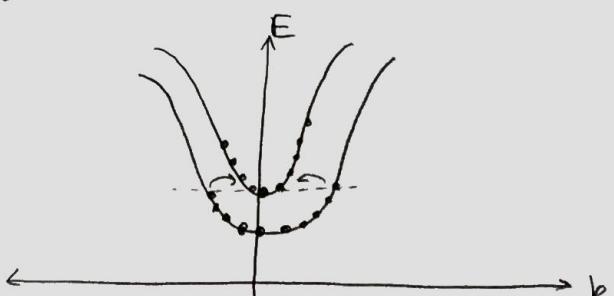


The possibility of crossing of bands, like in Mg despite having an even no. of e⁻s / unit cell, allows for zero energy excitations, & hence

Mg is a metal!

Another example of a band structure which is a metal despite having even no. of e⁻ / unit cell

Band 2 isn't strictly higher than Band 1 for all values of k. So, zero energy excitations are available!



(4)
Therefore, the correct correspondance is -

of e⁻s / unit cell is odd \implies Metals

of e⁻s / unit cell is even \Leftarrow Insulators

Proof for $E(\vec{k}) = E(-\vec{k})$

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$$

$$H \Psi_k(\vec{r}) = E(k) \Psi_k(\vec{r}) ; \quad \Psi_k(\vec{r}) = u_k e^{i\vec{k}\cdot\vec{r}}$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] u_k e^{i\vec{k}\cdot\vec{r}} = E(k) u_k e^{i\vec{k}\cdot\vec{r}}$$

$$\cancel{\left[-\frac{\hbar^2}{2m} \nabla^2 + 2i\vec{k}\vec{\nabla} - |\vec{k}|^2 \right]} u_k e^{i\vec{k}\cdot\vec{r}} = E(k) u_k e^{i\vec{k}\cdot\vec{r}}$$

$$-\frac{\hbar^2}{2m} \left[\nabla^2 + 2i\vec{k}\vec{\nabla} - |\vec{k}|^2 \right] u_k = E(k) u_k$$

$$H_k u_k = E_k u_k$$

①

so $u_k, E(k)$ are solns. of the eigenvalue Eqn.
2nd order diff.

$$\text{Take } \vec{k} \rightarrow -\vec{k}$$

$$H_{-\vec{k}} = -\frac{\hbar^2}{2m} \left[\nabla^2 - 2i\vec{k}\vec{\nabla} - |\vec{k}|^2 \right]$$

only change

$$= H_{\vec{k}}^* \quad (\text{conjugate of } H_k)$$

Lets take conjugate of Eqn. ①.

$$H_{\vec{k}}^* u_{\vec{k}}^* = E(\vec{k}) u_{\vec{k}}^*$$

$E(\vec{k})$ is a real #.

$$\text{But } H_{\vec{k}}^* = H_{-\vec{k}}$$

$$\therefore H_{-\vec{k}} u_{\vec{k}}^* = E(\vec{k}) u_{\vec{k}}^*$$

i.e. $u_{\vec{k}}^*$ is an eigenfunction of $H_{-\vec{k}}$ with same Eigenvalue / energy $E(\vec{k})$.

\therefore Taking $\vec{k} \rightarrow -\vec{k}$; wave function changes to its complex conjugate & $E(-\vec{k}) = E(\vec{k})$.

Lecture - 27

(09/11/2021)

Free electron model.

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \quad \text{where } V(\vec{r} + \vec{R}) = V(\vec{r})$$

$\forall \vec{r} \in B_o L.$

If the electrons experience nearly 0 potential in their vicinity, we can take $V(\vec{r}) = 0$

H - 1s ¹	{ These valence e ⁻ s experience an inert core in their lower shells.
Li - 2s ¹	
Na - 3s ¹	
K - 4s ¹	
Rb - 5s ¹	

The valence electrons screen the positive charge from the positive ions, resulting in a net 0 potential for other electrons.

- (1) outermost e⁻s are weakly bound & hence easily polarizable.
 (2) electrons screen the ionic potⁿ very efficiently.

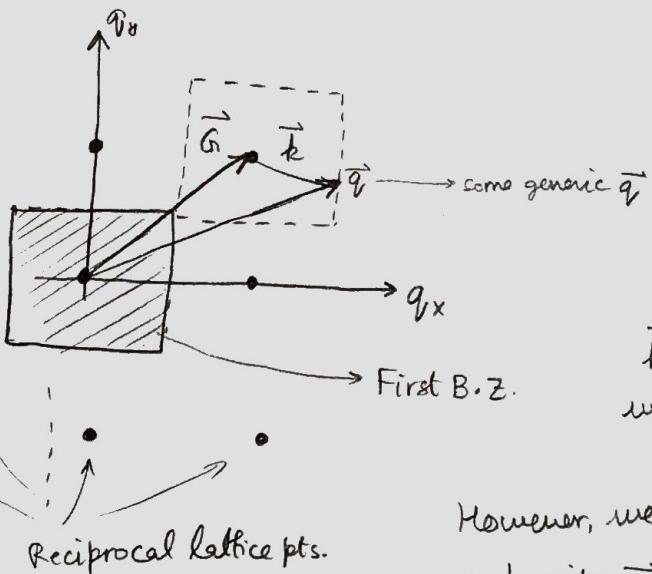
So, H is just $H = -\frac{\nabla^2 \hbar^2}{2m}$ and $\psi = e^{i\vec{q} \cdot \vec{r}}$. \vec{q} can be any wave vector.

However, the potⁿ here is still periodic since $V(\vec{r}) = 0$. In fact, it is continuously periodic for any $\vec{r} = \vec{L}$.

So, Bloch solⁿs $\psi_k(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$ where $\vec{k} \in B_o Z$.

are still valid wavefunctions.

Now we want to write ψ (plane wave) in the Bloch form.



\vec{k} must lie in the first B.Z.
whereas \vec{q} can lie anywhere.

However, we can move to a nearby B.Z.
and write \vec{q} as a sum of reciprocal lattice
vector \vec{G} and \vec{k} .

$$\Rightarrow \vec{q} = \vec{G} + \vec{k}$$

Plugging this into the plane wave soln -

$$\psi = e^{i\vec{q}\cdot\vec{r}} = e^{i(\vec{G} + \vec{k})\cdot\vec{r}} = \underbrace{e^{i\vec{G}\cdot\vec{r}}}_{\text{periodic in Bravais lattice}} e^{i\vec{k}\cdot\vec{r}}$$

$$e^{i\vec{G}\cdot(\vec{r} + \vec{R})} = e^{i\vec{G}\cdot\vec{R}} e^{i\vec{G}\cdot\vec{r}} \\ = e^{i\vec{G}\cdot\vec{r}}.$$

So, here $U(\vec{r}) = e^{i\vec{G}\cdot\vec{r}}$ (periodic fn in \vec{R})

$$\Rightarrow \boxed{\psi_k = e^{i\vec{G}\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}}} \rightarrow \text{plane wave soln in Bloch form.}$$

$U_k(\vec{r})$

$$\text{For 1-D, } \vec{G} = \frac{2\pi}{a} n \hat{i} \quad n \in \mathbb{Z}$$

So, if we fix the \vec{k} , we can still vary \vec{G} and we'll get an ∞
number of energies & wavefn's. For each \vec{k} , we'll get a different
set of infinite solutions.

Disclaimer: n is NOT the band index here.

Energies of the free particle.

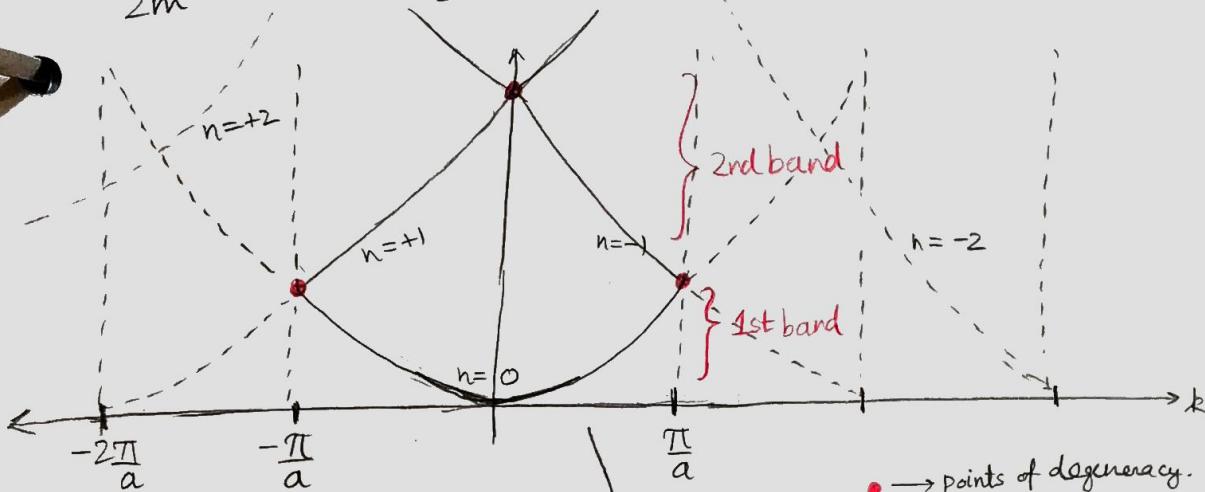
$$E = \frac{\hbar^2 |\vec{q}|^2}{2m} \Rightarrow E = \frac{\hbar^2}{2m} |\vec{G} + \vec{k}|^2$$

Let us now construct the band structure of free electron model -

In 1-D, $\psi(\vec{r}) = e^{iGr} e^{ikr}$ with $k \in B.Z.$ i.e. $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$

$$G = \frac{2\pi}{a} n$$

$$E = \frac{\hbar^2}{2m} (G+k)^2 = \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} n + k \right)^2$$



$$n=0 \Rightarrow E = \frac{\hbar^2 k^2}{2m}$$

$$n=1 \Rightarrow E = \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} + k \right)^2$$

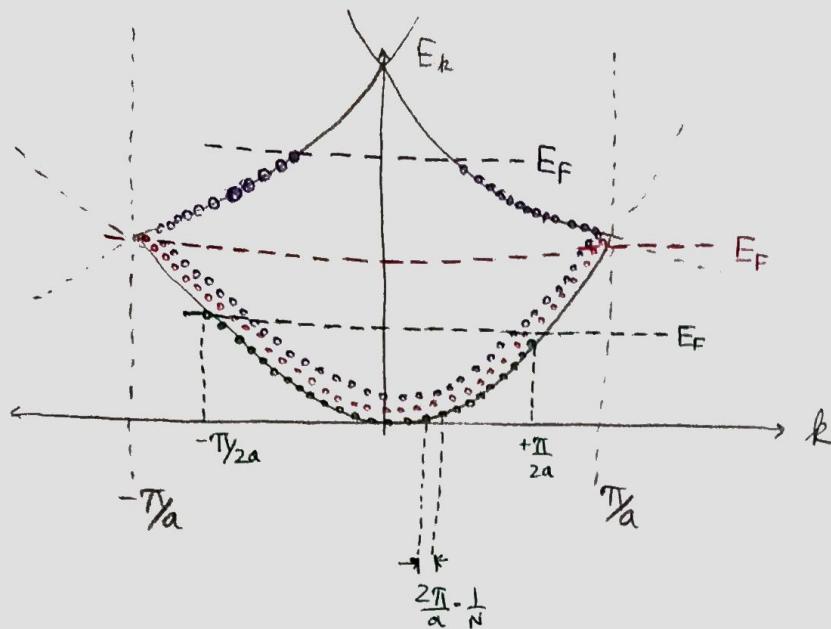
$$n=-1 \Rightarrow E = \frac{\hbar^2}{2m} \left(k - \frac{2\pi}{a} \right)^2$$

→ points of degeneracy.

Degeneracies at band edges & band centres.

► NO GAPS IN THIS
BAND STRUCTURE!

WE WILL ALWAYS HAVE
INFINITESIMALLY SMALL THERMAL
EXCITATIONS POSSIBLE!



$1e^-/\text{unit cell}$
 $2e^-/\text{unit cell}$
 $3e^-/\text{unit cell}$
 ↑
 these are the total no. of e^- ,
 not just valence e^- .

So, no matter the # of e^- s/unit cell, \exists infinitesimally close excitations always, and hence free electron model always models metals. Whatever the filling, we'll end up with a metal. Just the E_F keeps changing.

for $1e^-/\text{unit cell}$

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

$$\Rightarrow E_F = \frac{\hbar^2 \pi^2 n^2}{8m}$$

For $2e^-/\text{unit cell}$

$$E_F = \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2 \quad \text{and} \quad n = \frac{2}{a} \text{ now}$$

$$\Rightarrow E_F = \frac{\hbar^2 \pi^2}{8m} n^2$$

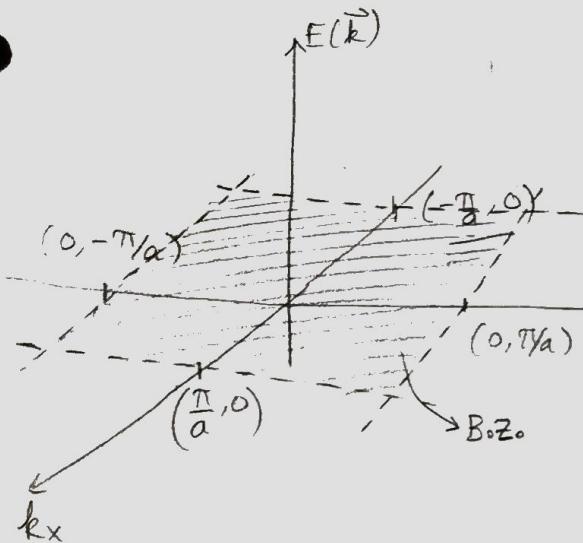
density of e^- s in the solid $\equiv n$

$$\text{for } 1e^- \text{ per unit cell, } n = \frac{1}{a}$$

($1e^-$ per unit cell of size a)

So,
$$E_F = \frac{\hbar^2 \pi^2}{8m} n^2$$
 is a general expression for a 1D lattice!

If we do this for $d=2$ dimensions-

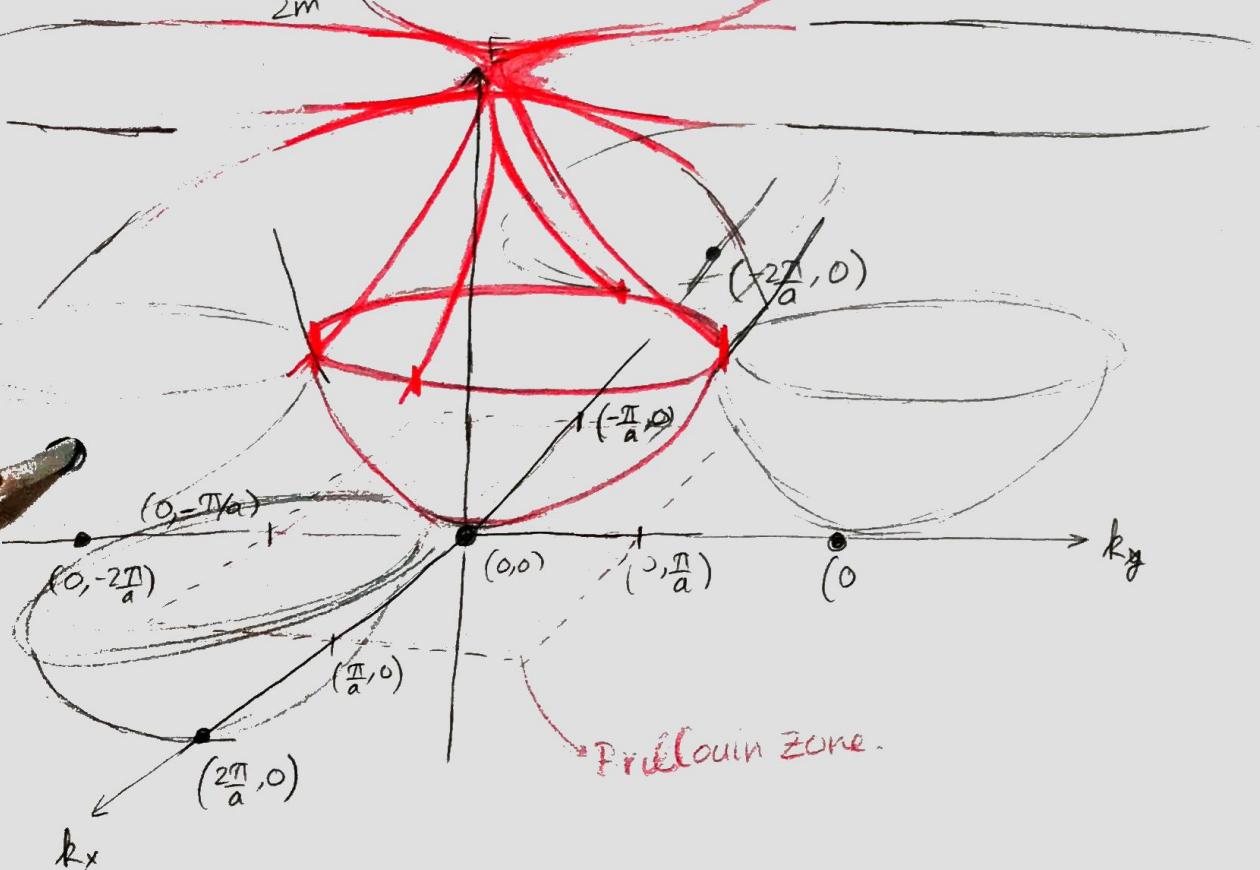


$$E(\vec{k}) = \frac{\hbar^2}{2m} |\vec{G} + \vec{k}|^2$$

reciprocal
lattice
vectors.

$$\vec{G} = \frac{2\pi}{a} (n_1, n_2)$$

So, $E = \frac{\hbar^2}{2m} \sqrt{|\vec{G} + \vec{k}|^2}$ are a set of parabolas centred at $-\vec{G}$.



Precouin zone.

Lecture - 28
 (14-11-2021)

Free electron model (recap)

$$\hat{H}\psi = E\psi \quad \text{with} \quad \hat{H} = -\frac{\hbar^2}{2m} \nabla^2$$

The solns are the free particle waves $\psi = \frac{1}{\sqrt{V}} e^{i\vec{q} \cdot \vec{r}}$

In the Bloch form, this soln can be written by putting $\vec{q} = \vec{G} + \vec{k}$

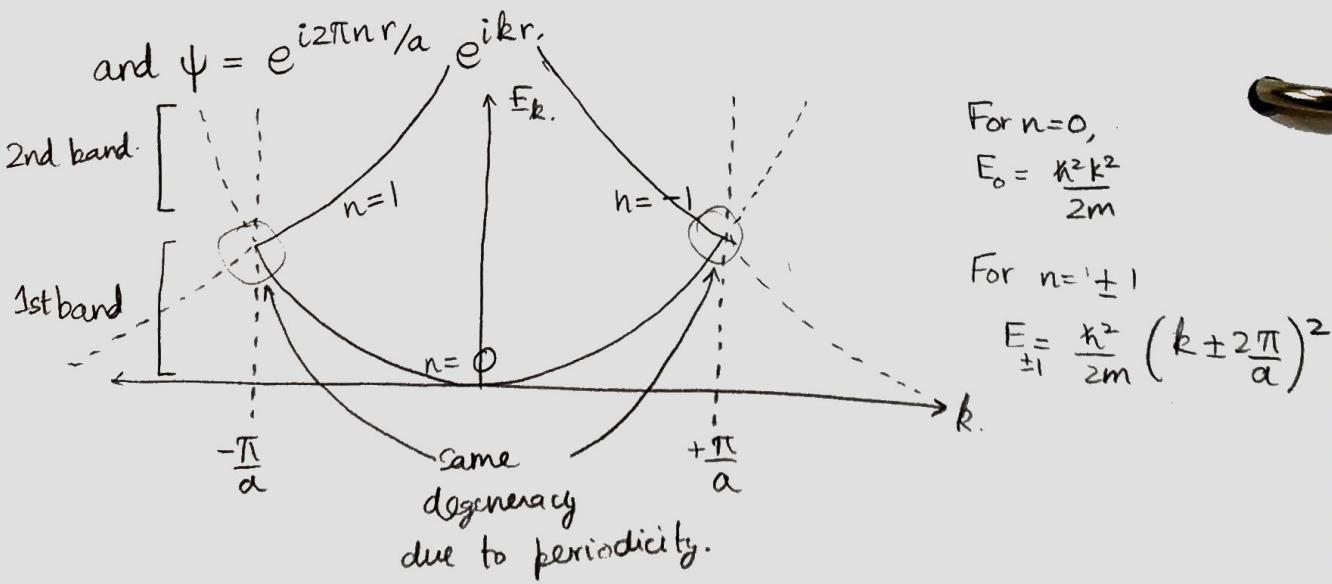
where \vec{G} is a reciprocal lattice vector & $\vec{k} \in B.Z.$

$$\Rightarrow \psi = \underbrace{\frac{1}{\sqrt{V}} e^{i\vec{G} \cdot \vec{r}}}_{\downarrow} e^{i\vec{k} \cdot \vec{r}} = u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$$

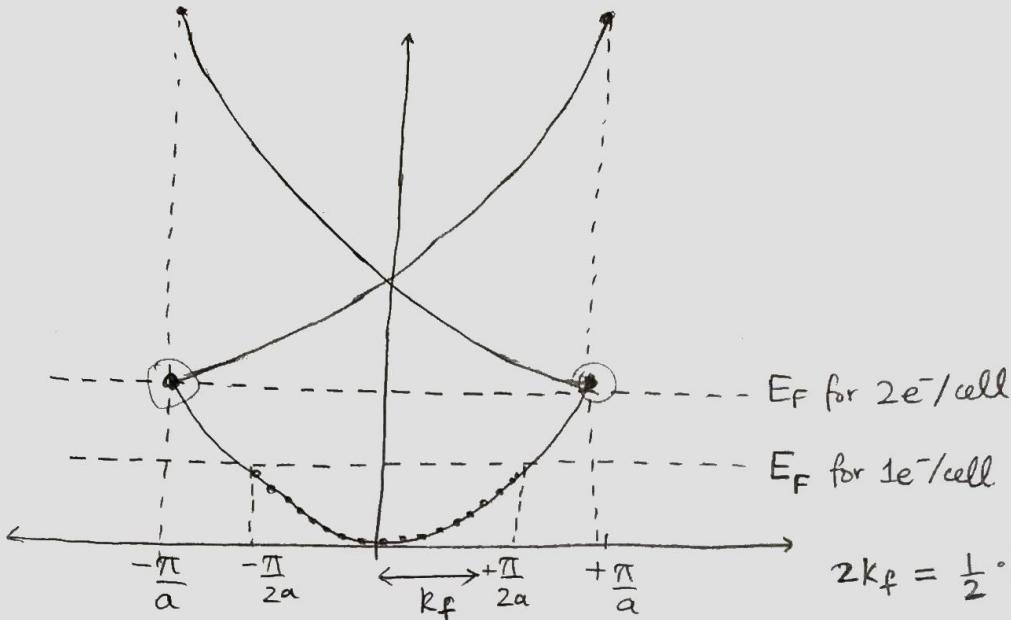
$u_k(\vec{r}) \rightarrow \text{periodic in } \vec{R}.$

Energy of the free particles - $E = \frac{\hbar^2 |\vec{q}|^2}{2m} = \frac{\hbar^2 |\vec{G} + \vec{k}|^2}{2m}$

In 1D, $G = \frac{2\pi}{a} n \Rightarrow E = \frac{\hbar^2}{2m} \left(\frac{2\pi n}{a} + k \right)^2 \quad k \in \left(-\frac{\pi}{a}, \frac{\pi}{a} \right]$



(7)



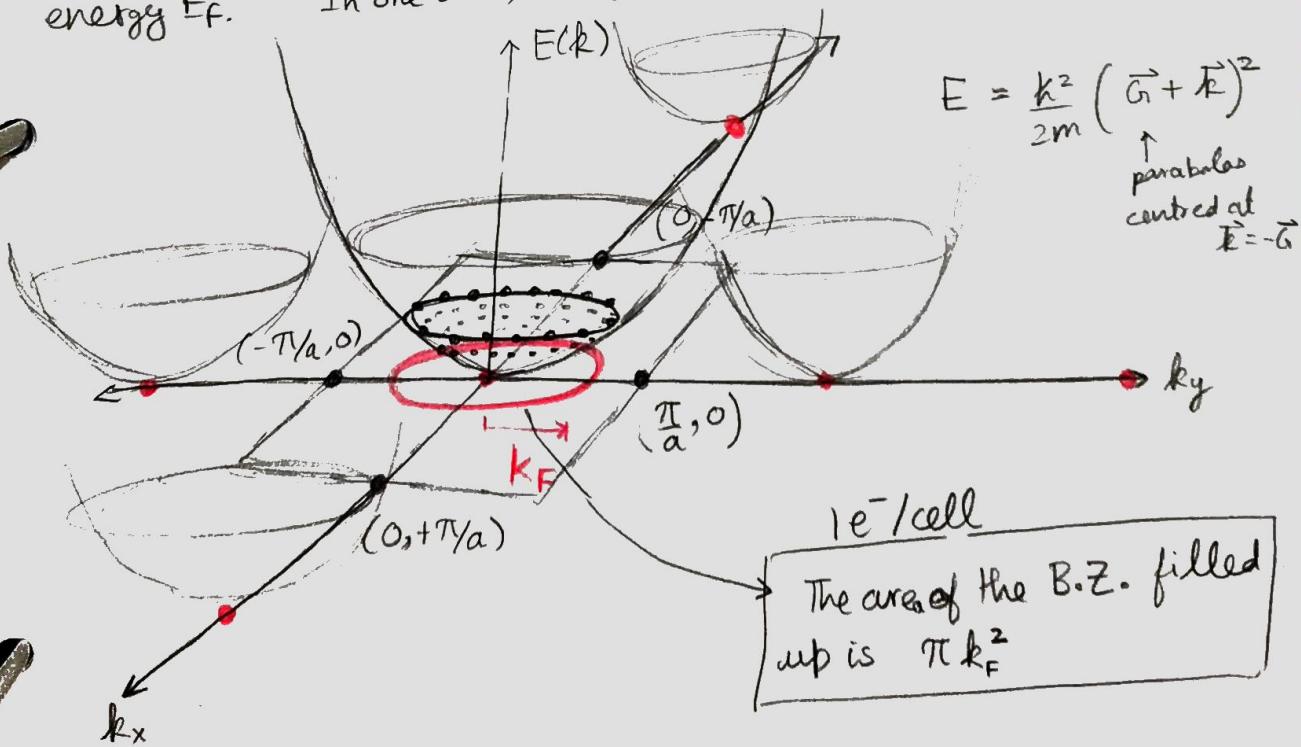
$$2k_F = \frac{1}{2} \cdot \left(\frac{2\pi}{a}\right)$$

$$E_F (\text{for } 1e^-/\text{cell}) = \frac{\hbar^2}{2m} \left(\frac{\pi}{2a}\right)^2$$

Define $n = \text{no. density of } e^- \text{ in B.Z.}$
 $\Rightarrow \text{here } n = \frac{1}{a}$

$$\Rightarrow E_F = \frac{\hbar^2 \pi^2 n^2}{8m} \quad \text{and} \quad k_F = \frac{\pi}{2a} \quad \text{for 1D and } 1e^-/\text{cell}$$

Fermisurface \equiv a surface in k -space made up by all states at energy E_F . In one dimⁿ, it is just two points.



1e^-/cell

The area of the B.Z. filled up is πk_F^2

For $1e^-/\text{cell}$, area filled $\doteq \frac{1}{2}$ (area of B.Z.)

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

this 1 comes from $1e^-/\text{cell}$.
and 2 in denominator from deg. due to spin.

$$\Rightarrow k_F = \sqrt{\frac{2\pi}{a^2}}$$

for $1e^-$ per cell. and 2D

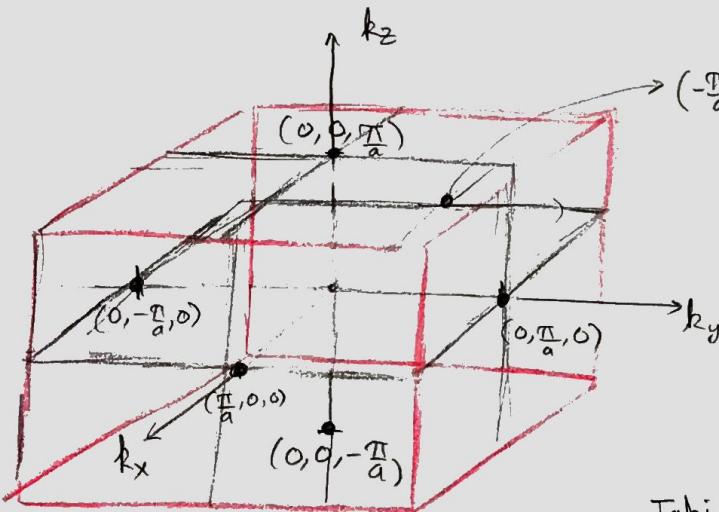
Using this, we can also find out $E_F = \frac{k^2}{2m}$ $k_F^2 = \frac{k^2}{2m} \cdot \frac{4\pi}{a^2} = \frac{k^2 \pi}{ma^2}$

In 2-D, $n = \frac{1}{a^2}$ (for $1e^-/\text{cell}$)

\nwarrow area of a unit cell
of B.L.

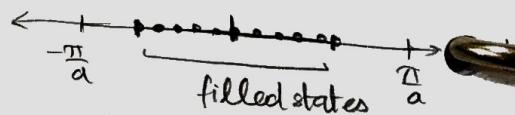
$$\therefore E_F = \frac{k^2 \pi}{m} n \quad \text{for 2D.}$$

Find E_F as a fn of n for

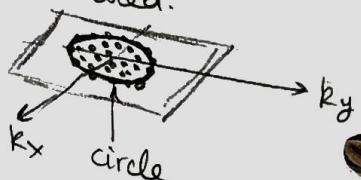


For $1e^-$

In 1D, the filling took place over a line.


filled states
since the filling should happen symmetrically in all directions,
we get a line centred at 0.

Taking this to 2D, filling should happen symmetrically in k_x & k_y directions, so we get a circular area.



Carrying this principle to 3D, our Fermisurface should be a sphere.

(9)

So, for $1 e^-/\text{cell}$ ($n = \frac{1}{a^3}$), in 3D, we should have -

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

$$\Rightarrow k_F^3 = \frac{3\pi^2}{a^3} \quad \text{or} \quad k_F = \left(\frac{3\pi^2}{a^3} \right)^{1/3} \quad \text{for 3D and } 1e^-/\text{cell}$$

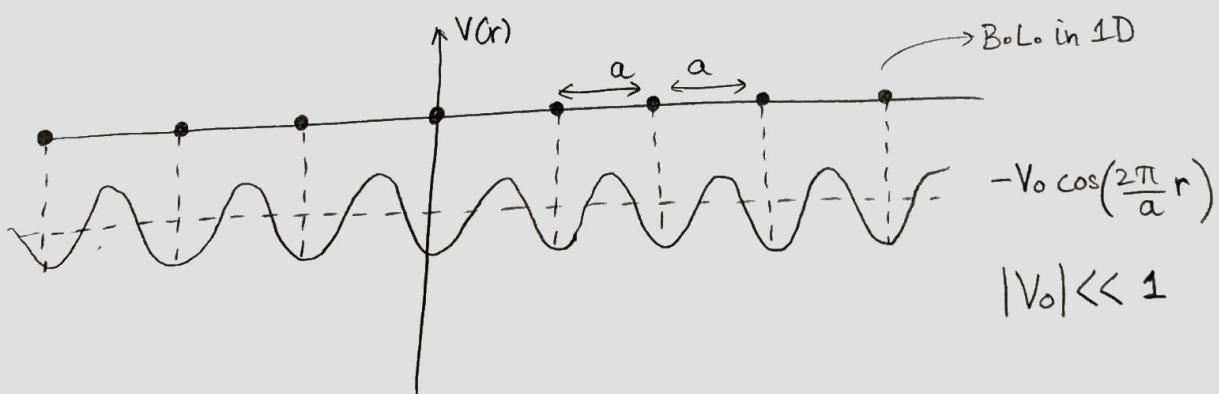
$$\text{So, } E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(3\pi^2 \right)^{2/3} \cdot \frac{1}{a^2} \quad \text{but } n^{2/3} = \frac{1}{a^2}$$

$$\Rightarrow E_F = \frac{\hbar^2 (3\pi^2)^{2/3}}{2m} n^{2/3} \quad \text{for 3D}$$

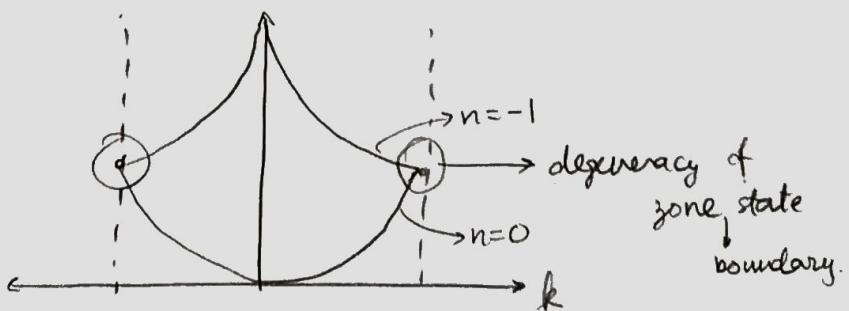
NEARLY-FREE ELECTRON MODEL.

$$\therefore \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \quad \text{where } |V(\vec{r})| \ll |\text{K.E.}|$$

↑
weak.



We have degeneracy of states at zone boundaries in free e^- model.



So, we can use time-ind. perturbation theory here on top of the

vanilla free e-model, and add a $\hat{H}' = -V_0 \cos\left(\frac{2\pi}{a} r\right)$ perturbation

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'$$

(1) For non-degenerate case -

$$E^{(1)} = \langle \psi_k | \hat{H}' | \psi_k \rangle \rightarrow \text{first order correction.}$$

(2) For the degenerate case -

We form the $H'_{ij} = \langle \psi_k^i | V | \psi_k^j \rangle$ matrix, whose eigenvalues give us the correction to first order. ($\psi_k^{(0)}, \psi_k^{(1)}$ are deg-eigenf's)

Normalization of Bloch wave:

$$\tilde{\psi}_k = u_k e^{i\vec{k} \cdot \vec{r}}$$

We do box normalization within a unit cell -

$$\int_{\text{unitcell}} |\tilde{\psi}_k|^2 d^3r = 1 \Rightarrow \psi_k = \frac{\tilde{\psi}_k}{\sqrt{V}} \Rightarrow \text{for 1D} \Rightarrow \psi_k = \frac{u_k e^{i\vec{k} \cdot \vec{r}}}{\sqrt{a}}$$

$$\text{So, } \psi_k = \frac{e^{i\vec{G} \cdot \vec{r}} e^{i\vec{k} \cdot \vec{r}}}{\sqrt{a}} = \frac{e^{i2\pi n r/a} e^{i k r}}{\sqrt{a}}$$

- For $n=0$, (non-deg. case)

$$E^{(1)} = \int_0^a dr \frac{e^{-ikr}}{\sqrt{a}} \cdot \left(-V_0 \cos\left(\frac{2\pi}{a} r\right) \right) \cdot \frac{e^{ikr}}{\sqrt{a}}$$

$$= -\frac{V_0}{a} \int_0^a \cos\left(\frac{2\pi}{a} r\right) dr = \underline{\underline{0}}$$

This actually generalizes to arbitrary n . The first order corrections for non-deg. states = 0 $\forall n$.

11

• For the degenerate case where the $n=0 \leftrightarrow n=1$ boundaries meet, ($k = \pi/a$)

$$\psi_k^0 = \frac{1}{\sqrt{a}} e^{ikr} = \frac{e^{i\pi r/a}}{\sqrt{a}}$$

$$\psi_k^{-1} = \frac{1}{\sqrt{a}} e^{iGr} e^{ika} = \frac{e^{-i2\pi/a r}}{\sqrt{a}} e^{i\pi r/a} = \frac{e^{-i\pi r/a}}{\sqrt{a}}$$

Now both $\langle \psi^0 | H' | \psi^0 \rangle = \langle \psi^{-1} | H' | \psi^{-1} \rangle = -\frac{V_0}{a} \int_0^a dr e^{\mp i\frac{\pi r}{a}} \cos\left(\frac{2\pi}{a}r\right) e^{\pm i\frac{\pi r}{a}}$

$= 0$

$$\text{So, } H'_{00} = H'_{-1,-1} = 0$$

$$\begin{aligned} H'_{0,-1} &= \int_0^a dr \frac{e^{-i\pi r/a}}{\sqrt{a}} \cdot \left(-V_0 \cos\left(\frac{2\pi}{a}r\right)\right) \frac{e^{-i\pi r/a}}{\sqrt{a}} \\ &= -\frac{V_0}{a} \int_0^a dr \cos\left(\frac{2\pi}{a}r\right) e^{-2i\pi r/a} \\ &= -\frac{V_0}{a} \int_0^a dr \left(\frac{e^{i2\pi r/a} + e^{-i2\pi r/a}}{2} \right) e^{-i2\pi r/a} \\ &= -\frac{V_0}{2a} \int_0^a dr \left(1 + e^{-i4\pi r/a} \right) \end{aligned}$$

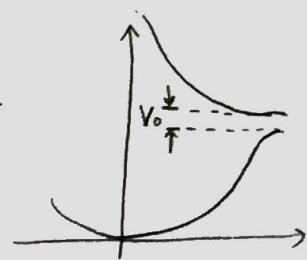
(again by the same logic)

$$\therefore H'_{0,-1} = -\frac{V_0}{2} = H'_{-1,0}$$

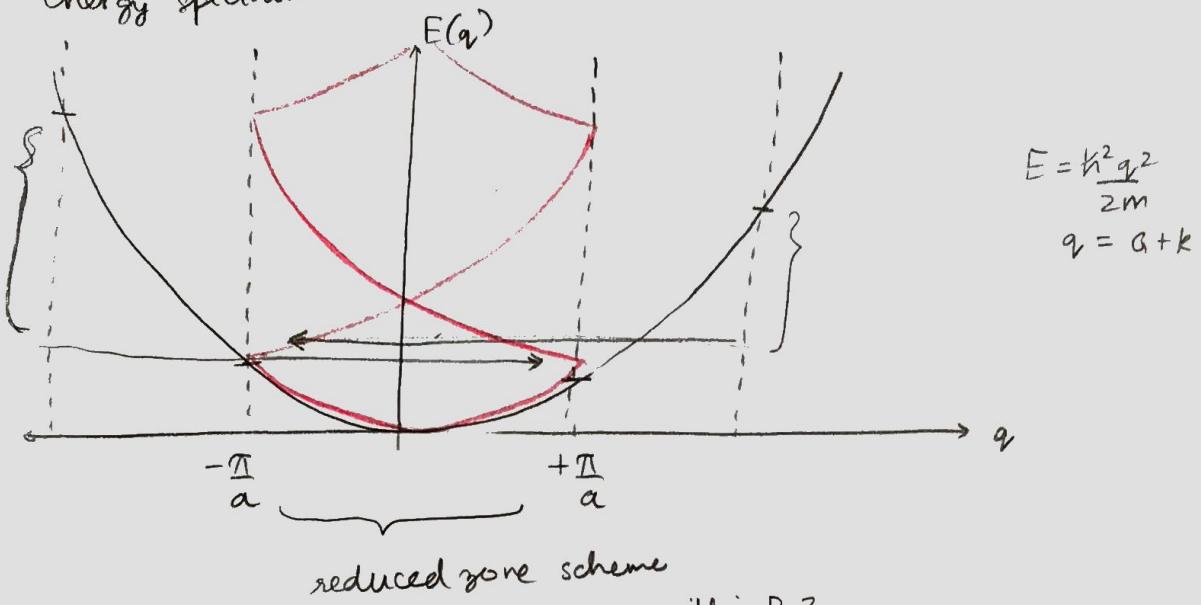
$$\Rightarrow H' = \begin{pmatrix} 0 & -V_0/2 \\ -V_0/2 & 0 \end{pmatrix} = -\frac{V_0}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

The eigenvalues of σ_x are $\pm 1 \Rightarrow E_{n=0}^{(1)} = -V_0/2$
 $E_{-1}^{(1)} = +V_0/2$

We have a gap!



An equivalent way of interpreting the free electron model energy spectrum -



reduced zone scheme

"unwrap up the energy spectrum within B.Z."

Quasi-free electron model (Nearly-free e⁻-model).

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \\ \rightarrow -V_0 \cos\left(\frac{2\pi}{a} r\right) \equiv H'$$

- For states which are non-deg.-

$$\Delta E^{(1)} = \langle \psi_k | H' | \psi_k \rangle \equiv 0 \quad \text{for non-boundaries}$$

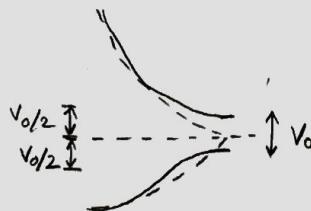
- For states which are degenerate (zone boundaries & zone centre) -

$$\Delta E_{i,j}^{(1)} \text{ are the eigenvalues of } \begin{pmatrix} H'_{0,0} & H'_{0,-1} \\ H'_{-1,0} & H'_{-1,-1} \end{pmatrix}$$

where ψ_0 and ψ_{-1} are the degenerate states at $n=0$ & $n=-1$ with $k = \pm \pi/a$.

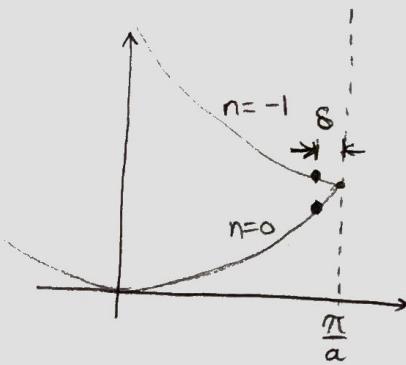
$$\Rightarrow \Delta E_0^{(1)} = -V_0/2$$

$$\Delta E_{-1}^{(1)} = +V_0/2$$



A bandgap of size V_0 !!!

But we've only shown the gap exists at the boundary, not for the points δ away in k -space.



$$\begin{aligned}\Psi_0 &= e^{ior} \frac{e^{ikr}}{\sqrt{a}} \Big|_{k=\frac{\pi}{a}-\delta} = \frac{e^{i\frac{\pi r}{a}} e^{-i\delta r}/\sqrt{a}}{} \\ \Psi_{-1} &= e^{-i\frac{2\pi r}{a}} \frac{e^{ikr}}{\sqrt{a}} \Big|_{k=\frac{\pi}{a}-\delta} = \frac{e^{-i\frac{2\pi r}{a}} e^{i\frac{\pi r}{a}} e^{-i\delta r}/\sqrt{a}}{} \\ &= e^{-i\frac{\pi r}{a}} e^{-i\delta r}/\sqrt{a}\end{aligned}$$

Using these states for Deg. TIPT ($i, j \in \{0, -1\}$), the eigenvalues of $H'_{ij} = \langle \psi_i | H' | \psi_j \rangle$ are the corrections to first order.

Again $\langle \psi_0 | H' | \psi_0 \rangle = - \int_0^a dr V_0 \cos\left(\frac{2\pi r}{a}\right) \cdot (\text{phase}) \cdot (\text{phase}^{-1}) = 0$

Similarly $\langle \psi_1 | H' | \psi_1 \rangle = 0$

$$\begin{aligned}\text{But } \langle \psi_0 | H' | \psi_{-1} \rangle &= \int_0^a dr (-V_0) \cos\left(\frac{2\pi r}{a}\right) \frac{e^{i\delta r}}{\sqrt{a}} e^{-i\frac{\pi r}{a}} \frac{e^{-i\delta r}}{\sqrt{a}} e^{i\frac{\pi r}{a}} \\ &= -\frac{V_0}{a} \int_0^a dr \left(e^{i\frac{2\pi r}{a}} + e^{-i\frac{2\pi r}{a}} \right) \cdot e^{-2i\frac{\pi r}{a}} \\ &= -\frac{V_0}{2a} \int_0^a dr (1 + e^{-i4\pi r/a})\end{aligned}$$

(the 8's shouldn't have cancelled)

Tight Binding

Quasi-free e^-

- band width $\propto |t|$
(narrow bands)
- large gaps. $\sim eV$

- parabolic structure with large bandwidth.

- small gaps $\sim V_0$ (small potn)

Qualitatively similar structure

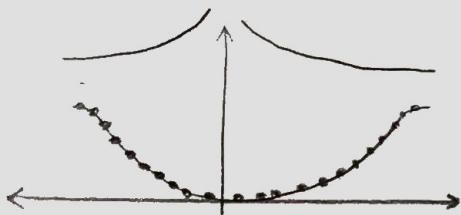
1 For $1 e^-/\text{cell}$ materials, the band filling is partial & is modelled well by quasi-free e^- model. (like Li, Na)

2 Good for modelling fully filled bands. (like inert gases)

A cleaner picture.

TIGHT BINDING

- very large band gaps \sim eV.
- small band width $\propto |t|$

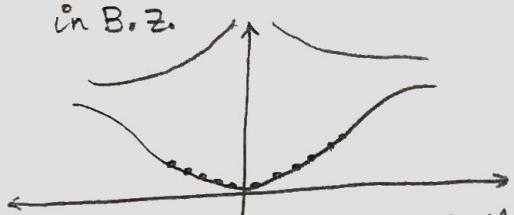


Good for modelling inert gases. (Ar, Kr)

end of P.T.

QUASI-FREE e^- model

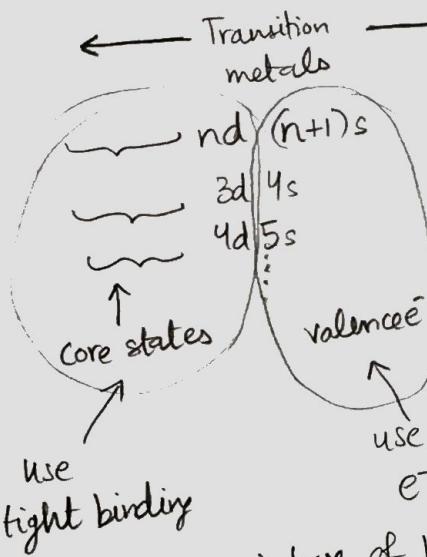
- small bandgap $\sim V_0$
- large band width. Full parabola in B.Z.



Good for modelling $1e^-/\text{cell}$ materials (Li, Na)

(away from perturbation)

start of P.T.



So, we use a mixture of both models to model materials like transition metals.

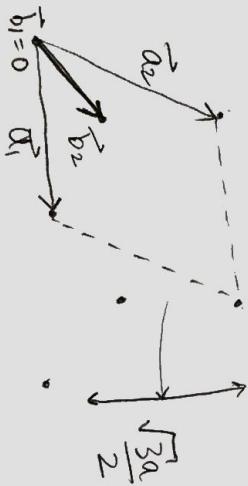
Qualitative structure remains same. Details may differ.

(1)

Practice problems from question papers.

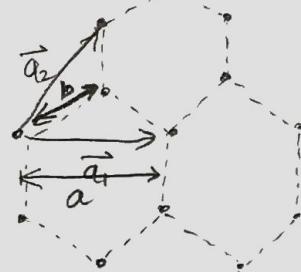
3. (2011)

(CSIR)



$$A = \frac{\sqrt{3}}{2} a^2$$

but a here isn't the
lattice spacing



7. (2012)

$$E \sim \int_0^\infty dk 4\pi k^2 \frac{\omega(k)}{e^{\beta \hbar \omega} - 1}$$

$$\text{so if } \omega \sim k^s \Rightarrow k \sim \omega^{1/s} \quad dk = \frac{1}{s} \omega^{1/s-1} d\omega$$

$$E \sim \int_0^\infty d\omega \omega^{1/s-1} \omega^{2/s} \cdot \frac{\omega}{e^{\beta \hbar \omega} - 1} \sim \int_0^\infty d\omega \frac{\omega^{3/s}}{e^{\beta \hbar \omega} - 1}$$

$$\text{Put } x = \beta \hbar \omega \Rightarrow d\omega = \frac{dx}{\beta \hbar} \quad \text{and } \omega = \frac{x}{\beta \hbar}$$

$$E \sim \int_0^\infty dx \frac{x^{3/s}}{e^x - 1} \cdot \left(\frac{1}{\beta \hbar}\right)^{\frac{3}{s}+1} \Rightarrow E \sim T^{\frac{3}{s}+1}$$

$C_E \sim \frac{\partial E}{\partial T} \sim T^{3/s}$

for $\omega \sim k^s$

12. (2012)

$$\epsilon_k = \beta (\cos k_x a + \cos k_y a + \cos k_z a)$$

$$m^*|_{\text{boundary}} = \frac{\hbar^2}{\nabla^2 E}|_{\text{boundary}}$$

$$\nabla_k^2 E = \left(\frac{\partial^2}{\partial k_x^2} + \frac{\partial^2}{\partial k_y^2} + \frac{\partial^2}{\partial k_z^2} \right) \epsilon_k = -\beta a^2 (\cos k_x a + \cos k_y a + \cos k_z a)$$

At the boundary of first B.Z. $k_x = \pm \frac{\pi}{a} = k_y = k_z$

$$\nabla_k^2 E|_{\text{bound.}} = -\beta a^2 (-1 - 1 - 1) = 3\beta a^2 \Rightarrow m^* = \frac{\hbar^2}{3\beta a^2}$$

13. (2012) Vol. of unit cell = a^3

monovalent $\Rightarrow 1e^-/\text{unit cell}$ (other are core e^- s.)

When we do the filling of electrons with a metal which has an fcc structure, then do we take the unit cell to have 4 atoms or 1 atom?

because this will affect the no. density $= \frac{N}{V}$ for the unit cell.

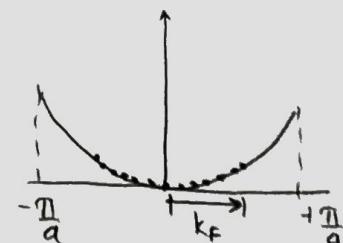
16. (2012)

$$\epsilon_k = 2\epsilon_0 \left[\sin^2 \frac{ka}{2} - \frac{1}{6} \sin^2 ka \right]$$

no. of e^- s per atom in conduction band = $\frac{1}{3}$

$$2k_F = \frac{1}{3} \cdot \frac{1}{2} \left(\frac{2\pi}{a} \right) \quad \begin{matrix} \uparrow & \uparrow \\ \text{spin deg.} & \end{matrix} \quad \Rightarrow k_F = \frac{\pi}{6a}$$

due to
no. density



However, this gives the wrong result for $E_F \approx \epsilon_0/25$

The correct answer $E_F = \epsilon_0/4$ demands $k_F = \frac{\pi}{3a}$ How?

17. (2012)

(3)

 $g(\omega) d\omega = \text{no. of modes b/w } \omega \text{ & } \omega + d\omega$

$$\int g(\omega) d\omega = \left(\frac{L}{2\pi} \right)^2 d^2 \vec{k} = \left(\frac{L}{2\pi} \right)^2 dk_x dk_y = \frac{L^2}{(2\pi)^2} \int_0^{2\pi} \int_0^{2\pi} dk dk$$

$$g(\omega) d\omega = 2\pi k dk \left(\frac{L}{2\pi} \right)^2$$

$$\text{For } \varepsilon \sim k \quad dk = d\varepsilon$$

$$g(\omega) d\omega = 2\pi \varepsilon d\varepsilon$$

19. (2013) $E = E_0 - \beta (\cos k_x a + \cos k_y a + \cos k_z a)$

$$\nabla_{\vec{k}}^2 E = \left(\partial_{k_x}^2 + \partial_{k_y}^2 + \partial_{k_z}^2 \right) (E_0 - \beta (\cos k_x a + \cos k_y a + \cos k_z a)) \\ = +\beta a^2 (\cos k_x a + \cos k_y a + \cos k_z a)$$

so, near the bottom of the band $\nabla_{\vec{k}}^2 E \Big|_{k_i=0} = 3\beta a^2 ??$

But the correct ans. says near the bottom,

you first Taylor expand-

$$\cos k_x a = 1 - \frac{(k_x a)^2}{2} \Rightarrow E = E_0 - \beta \left(3 - \frac{|\vec{k}|^2}{2} a^2 \right)$$

So, $\partial_{\vec{k}}^2 E = \beta a^2 ??$

What the hell???

20. (2014) $\varepsilon = -4\varepsilon_0 \left(\cos \frac{k_x a}{2} \cos \frac{k_y a}{2} + \cos \frac{k_y a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_z a}{2} \cos \frac{k_x a}{2} \right)$

$$v = \frac{1}{h} \left(\frac{\partial}{\partial k_x}, \frac{\partial}{\partial k_y}, \frac{\partial}{\partial k_z} \right) \varepsilon_k = +\frac{2\varepsilon_0 a}{h} \left(\sin \frac{k_x a}{2} \left(\cos \frac{k_y a}{2} + \cos \frac{k_z a}{2} \right), \sin k_y \dots, \sin k_z \dots \right)$$

at $(\frac{\pi}{a}, 0, 0) = \vec{k} \Rightarrow v = \frac{2\varepsilon_0 a}{h} (1 (1+1)) = \frac{4\varepsilon_0 a}{h} \hat{k}_x$

$$m_{ij}^* = \frac{\hbar^2}{\left(\frac{\partial^2 E}{\partial k_i \partial k_j}\right)} \rightarrow \text{effective mass tensor.}$$

36. (2015)

For Bloch's th^m, $\psi = u_k(r) e^{ikr}$ $u_k(r+a) = u_k(r)$

$$\cos\left(\frac{\pi}{2a}(x+a)\right) = \cos\left(\frac{\pi x}{2a} + \frac{\pi}{2}\right) \times \cos\left(\frac{2\pi x}{a} + a\right) = \cos\left(\frac{2\pi x}{a} + 2\pi\right) = \cos\left(\frac{2\pi x}{a}\right) \checkmark$$

$$\omega = ck.$$

$$\int_0^{\omega_0} g(\omega) d\omega = \# \text{ of modes} = \# \text{ of oscillators} = N = na$$

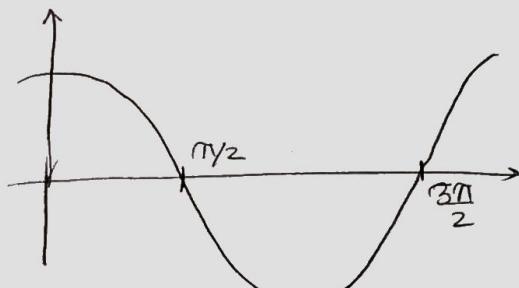
$$g(\omega) d\omega = \frac{a}{2\pi} dk = \frac{a}{2\pi} \cdot \frac{d\omega}{c}$$

$$\text{So, } \frac{a}{2\pi c} \int_0^{\omega_0} d\omega = \omega_0 \frac{dk}{2\pi c} = n\delta \Rightarrow \omega_0 = 2\pi n c$$

39. (2015)

$$\epsilon(k) = A - B \cos(2ka)$$

$$\frac{\partial \epsilon}{\partial k} = +2aB \sin(2ka) \quad \frac{\partial^2 \epsilon}{\partial k^2} = 4a^2 B \cos(2ka)$$



$$2ka \in \left(\frac{\pi}{2}, \frac{3\pi}{2}\right)$$

$$k \in \left(\frac{\pi}{4a}, \frac{3\pi}{4a}\right)$$

$$45. (2017) \quad E = \hbar v |\vec{k}| \quad (2-D)$$

$$|\vec{k}_F| = ?^2 \quad \text{for 2D} \quad \boxed{\pi^2 k_F^2 = \frac{N}{2} \left(\frac{2\pi}{a}\right)^2} = \frac{1}{2} \frac{4\pi^2 N}{a^2} \quad k_F^2 = \frac{2\pi^2 N}{a^2}$$

$$\epsilon_F = \hbar v \sqrt{\frac{2\pi N}{a^2}} = \hbar v \sqrt{2\pi n}$$

$$\boxed{n = \frac{\epsilon_F^2}{2\pi k_F^2 v^2}}$$

7. (2010)

(GATE)

5

$$\pi k_F^2 = \frac{N}{2} \cdot \left(\frac{2\pi}{a}\right)^2 \Rightarrow k_F = \sqrt{2\pi n}$$

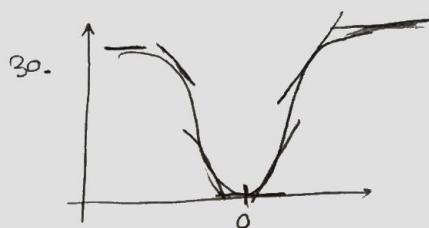
$$E_F = \frac{k^2}{2m} |k_F|^2 = \frac{k^2}{2m} \cdot 2\pi n \quad n = \frac{m E_F}{\pi k^2}$$

21. (2012)

$$V = \frac{\partial \omega}{\partial k_x} = \frac{\partial}{\partial k} \left(A \left| \sin \frac{ka}{2} \right| \right) \Big|_{k=\pi/a} = \frac{\partial}{\partial k} \left(A \sin \frac{ka}{2} \right) \Big|_{k=\frac{\pi}{a}} = \frac{aA}{2} \cos \frac{ka}{2} \Big|_{k=\frac{\pi}{a}}$$

$$= 0$$

26. ? (2013) ???



$$\begin{aligned} & \frac{3\sqrt{3}}{2} a^2 \\ & \rightarrow \frac{3\sqrt{3}}{2} \cdot \left(\frac{2\pi}{a}\right)^2 \\ & = \frac{3\sqrt{3}}{2} \cdot \frac{4\pi^2}{a^2} \end{aligned}$$

(CSIR-NET)

13. (2012) I had a question if I should choose the unit cell of fcc which has 4 atoms or 1 atom to construct the band structure from and calculate E_F . ANSWER: It doesn't matter!

If I choose the unit cell which has 1 atom /unit cell, then I'll have to construct a weird looking unit cell, with some weird volume. Alternatively, I can choose the unit cell with 4 atoms per unit cell which has $V=a^3$. Anyways, we'll have $n = \frac{4}{a^3}$

$$\text{so, } E_F = \frac{k^2 k_F^2}{2m}$$

$$k_F = \left(\frac{12\pi^2}{a^3} \right)^{1/3}$$

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

$$k_F^3 = \frac{3\pi^2 \cdot 4}{a^3}$$

(and the associated B.Z.
size will be a simple
 $\frac{(2\pi)^3}{V} = \left(\frac{2\pi}{a} \right)^3$)

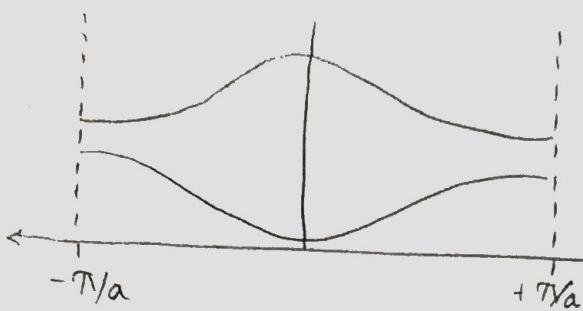
4 comes from $4e^-/\text{cell}$
2 comes from spin deg.

(1)

Lecture - 31

(16-11-2021)

BAND STRUCTURES IN NEARLY FREE e^- MODEL.

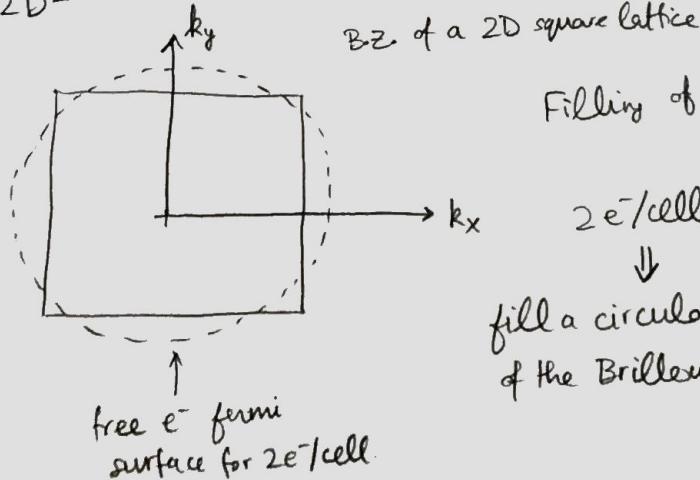


$1e^-/\text{cell} \Rightarrow$ half filling of first band
(negligible energy thermal excitations possible)

$2e^-/\text{cell} \Rightarrow$ fully filled first band
(gap E_{gap} exists b/w the occupied & next higher energy levels.)

Unexpectedly though, Ca, Mg and other elements with $2e^-/\text{cell}$ are still metals, whereas the band structure theory predicts something completely different. This is because we simplified the materials as 1D-structures.

In 2D-



Filling of bands → in circular symmetry

$2e^-/\text{cell}$ in 2D

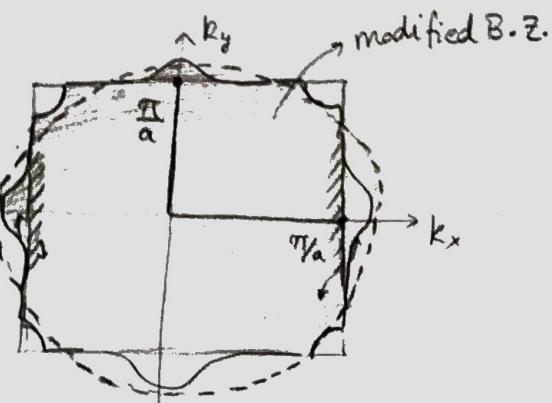


fill a circular zone equal to the area of the Brillouin zone.

So in the case of band structure of nearly free e^- model -

extended zone

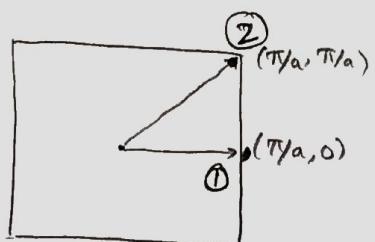
in 2D



$$E_{\text{zone boundary}} = E_{\text{free}} - \frac{V_0}{2}$$

(2)

The real reason why we have such a significant change in the B.Z. structure & filling is because unlike 1D, we do actually have room for more states to fill in the band in 2D. It's just that the states inside the B.Z. might have a higher energy than the states outside the B.Z., and that filling is more energetically preferred.



Energies at different zone boundaries is different.

$$E(\pi/a, \pi/a) > E(\pi/a, 0)$$

$$\frac{\hbar^2}{2m} \left(\frac{2\pi^2}{a^2} \right) > \frac{\hbar^2}{2m} \left(\frac{\pi^2}{a^2} \right)$$

Introducing perturbation \Rightarrow states inside B.Z. go down in energy.
states outside B.Z. go up in energy.

The states outside B.Z. are filled only because their energies happen to be lower than the states available inside, not because they are completely filled. (unlike the case ~~in 1D~~ in 1D where filling of band was the only reason to start filling another band).

Inside the B.Z., the energy of the highest available state (after introducing perturbation)

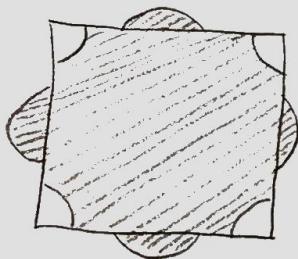
$$E_{\text{highest, BZ}} = E(\pi/a, \pi/a) = \left(2 \frac{\pi^2}{a^2} \right) \frac{\hbar^2}{2m} - \frac{V_0}{2} = E_2$$

whereas the lowest energy state just outside B.Z. is -

$$E_{\text{lowest, outside}} = \frac{\hbar^2}{2m} \left(\frac{\pi^2}{a^2} \right) + \frac{V_0}{2} = E_1$$

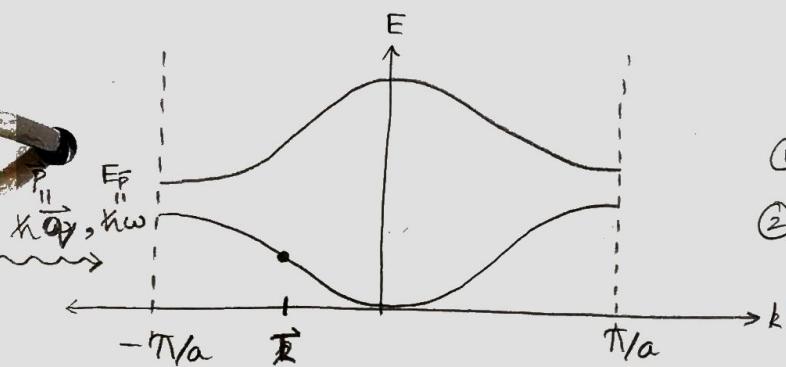
$E_1 < E_2$
 \Rightarrow fill states near E_1
 (outside B.Z.)

→ new Fermisurface.



$\therefore 2e^-/\text{cell}$ in 2D filling leaves some pockets of gaps in the Brillouin zone which allows for negligible thermal energy excitations & models a metal!

Optical Properties of solids.



If a photon interacts with the electrons, it must respect -

- ① Conservation of energy.
- ② conservation of momentum.

$$\vec{k} = \underbrace{\vec{k}}_{\substack{\uparrow \\ \text{Crystal mom}}} + \underbrace{\vec{G}}_{\substack{\uparrow \\ \text{actual momentum of } e^-}}$$

$$\text{so, } h(\vec{k} + \vec{G}) + h\vec{q} = h(\vec{k} + \vec{q}) + h\vec{G}$$

$\vec{k} \rightarrow \vec{k} + \vec{q}$

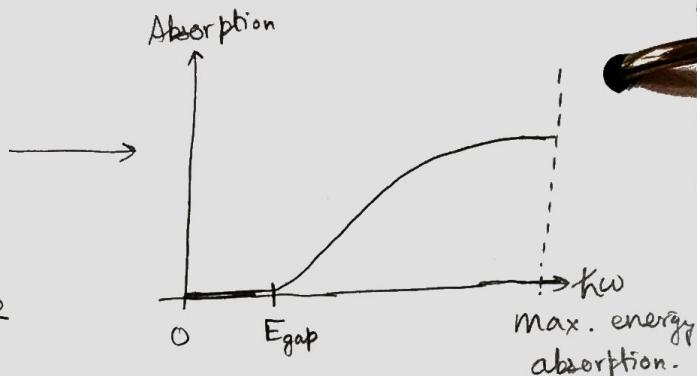
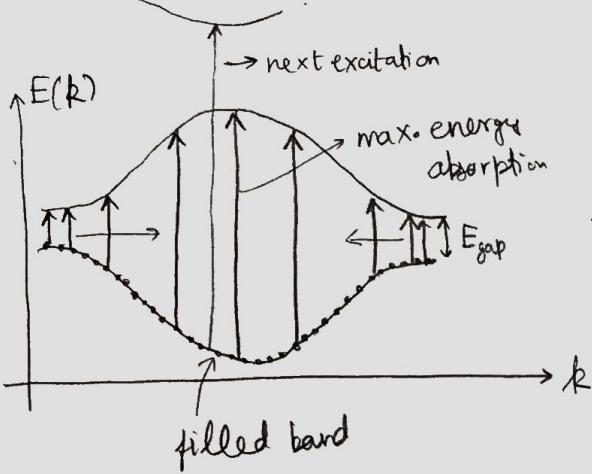
↑ just a reciprocal lattice \vec{v} .

(worrying only about \vec{k} in the B.Z.)

$$\text{wave no. of visible light} - q = \frac{2\pi}{\lambda} = \frac{2\pi}{5000\text{\AA}}$$

$$\text{size of B.Z.} = \frac{2\pi}{a} = \frac{2\pi}{5\text{\AA}}$$

\Rightarrow the change in momentum that a visible photon can cause is tiny AF, compared to the size of B.Z.



$$1.5 \text{ eV} < h\omega_{\text{visible}} < 3.2 \text{ eV}$$

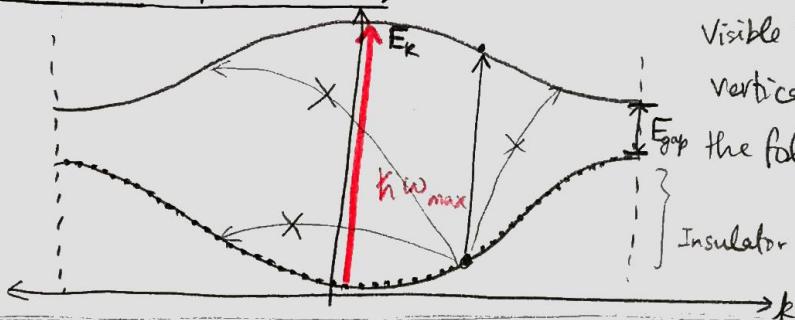
red ————— violet

If $E_{\text{gap}} > 3.2 \text{ eV}$ (Violet), then none of the visible photons are absorbed by the material, as discussed before ($h\omega_{\text{visible}}$ is tiny a.f. that it can at max cause transitions within the same band.) Materials where \nexists any absorption are transparent!

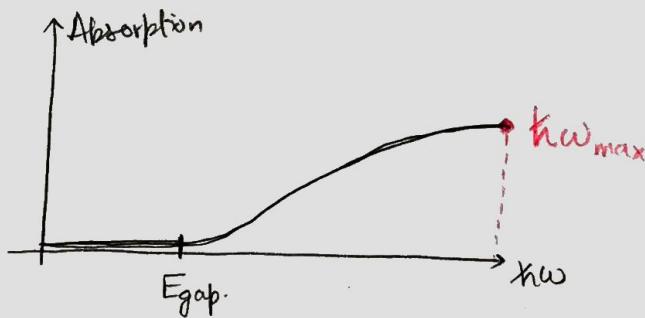
Materials with $E_{\text{gap}} < 1.5 \text{ eV}$ are opaque!

Lecture - 32

(18-11-2021)

Optical properties (of insulators)

Why are the vertical transitions allowed in the first place? They change the momentum by the reciprocal lattice vector \vec{G} and have a large enough energy gap already?



$$1.5\text{eV} < \text{Visible light} < 3.2\text{eV}$$

① If $E_{gap} > 3.2\text{ eV}$ (highest energy on visible spectrum), then no absorption for visible photons!

\Rightarrow transparent material!

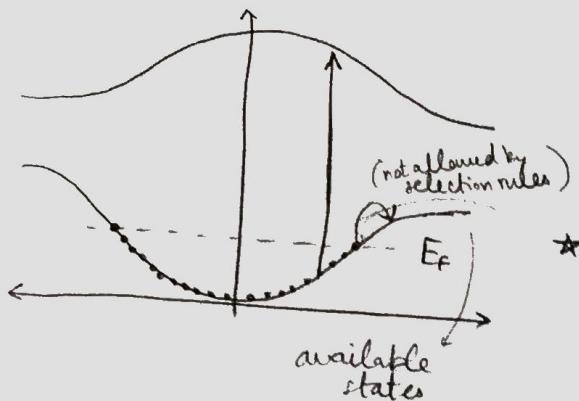
② If $E_{gap} < 1.5\text{eV}$ i.e. the whole of visible spectrum is absorbed by the material, then the material looks opaque!

To block a particular frequency of radiation, one can use a material which has that particular E_{gap} . Any frequency higher than E_{gap}/h will also be absorbed.

So, $E_{gap} \doteq \text{Energy of radiation you want to block.}$

Optical properties of metals. (partially filled bands)

(2)

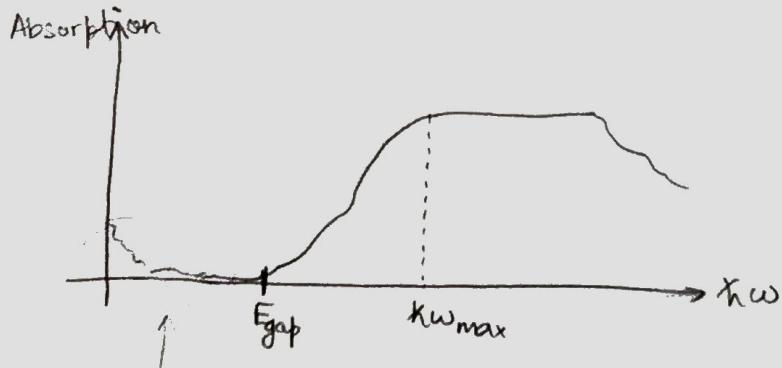


However, despite having nearby available, we must remember the selection rule for optical transition

- * The \vec{k} of the e^- can't be changed much by the visible photons.

so, we'll still only have vertical transitions for metals as well!

However, small energy & finite $\Delta\vec{k}$ transitions, despite being not allowed by selection rules still happen in metals due to scattering off photons with phonons, or impurities. Therefore, we even get non-zero absorption even below E_{gap} .



non-zero absorption
due to inelastic scattering \Rightarrow absorbs most of the visible spectrum.

Therefore, most metals appear opaque.

Even though scattering does exist in insulators as well, but the lack of closely energy levels prevents the absorption at low frequencies.

Electrical transport properties. (dynamics of e⁻s).

$$E(k) = \langle \psi_k | \hat{H} | \psi_k \rangle \xrightarrow{\text{Hamiltonian}} = \langle u_k | \hat{H}_k | u_k \rangle$$

↑ new effective Hamiltonian

$$\hat{H}_k = -\frac{\hbar^2}{2m} \left[\nabla_r^2 + 2i\vec{k} \cdot \vec{\nabla}_r - |\vec{k}|^2 \right] + V(\vec{r})$$

We are interested in finding out how the energy $E(\vec{k})$ of an electron changes with \vec{k} in the band structure.

$$\begin{aligned} \nabla_{\vec{k}} E(k) &= \nabla_{\vec{k}} \langle u_k | \hat{H}_k | u_k \rangle = \underbrace{\langle \nabla_{\vec{k}} u_k | \hat{H}_k | u_k \rangle}_{\langle u_k | E(\vec{k}) \rangle} + \langle u_k | \nabla_{\vec{k}} \hat{H}_k | u_k \rangle \\ &\quad + \underbrace{\langle u_k | \hat{H}_k | \nabla_{\vec{k}} u_k \rangle}_{\langle u_k | E(\vec{k}) \rangle} \\ &= \langle \nabla_{\vec{k}} u_k | E(\vec{k}) | u_k \rangle + \langle u_k | E(\vec{k}) | \nabla_{\vec{k}} u_k \rangle + \langle u_k | \nabla_{\vec{k}} \hat{H}_k | u_k \rangle \\ &= E(\vec{k}) [\langle \nabla_{\vec{k}} u_k | u_k \rangle + \langle u_k | \nabla_{\vec{k}} u_k \rangle] + \langle u_k | \nabla_{\vec{k}} \hat{H}_k | u_k \rangle \\ &= E(\vec{k}) \nabla_{\vec{k}} (\underbrace{\langle u_k | u_k \rangle}_{\nabla_{\vec{k}} \left(\frac{1}{V} \right) = 0}) + \langle u_k | \nabla_{\vec{k}} \hat{H}_k | u_k \rangle \\ &= \langle u_k | \nabla_{\vec{k}} \hat{H}_k | u_k \rangle \end{aligned}$$

$$\begin{aligned} \text{Now } \nabla_{\vec{k}} \hat{H}_k &= -\frac{\hbar^2}{2m} \nabla_{\vec{k}} \left(\nabla_r^2 + 2i\vec{k} \cdot \vec{\nabla}_r - |\vec{k}|^2 \right) + \vec{\nabla}_{\vec{k}} V(\vec{r}) \\ &= -\frac{\hbar^2}{2m} (2i\vec{\nabla}_r - 2\vec{k}) = \frac{\hbar}{m} (-i\hbar \vec{\nabla}_r + \hbar \vec{k}) \\ &= \frac{\hbar}{m} [\hat{p} + \hbar \vec{k}] \end{aligned}$$

$$\text{So, } \boxed{\vec{\nabla}_k E(\vec{k}) = \langle u_k | \frac{1}{m} (\hat{P} + \hbar \vec{k}) | u_k \rangle}$$

Now,

$$\begin{aligned}\vec{\hat{P}}_k &= \langle \psi_k | \hat{P} | \psi_k \rangle = \langle \psi_k | -i\hbar \vec{\nabla}_r | u_k e^{i\vec{k} \cdot \vec{r}} \rangle \\ &= -i\hbar \langle \psi_k | (\vec{\nabla}_r u_k) e^{i\vec{k} \cdot \vec{r}} + u_k \vec{\nabla}_r e^{i\vec{k} \cdot \vec{r}} \rangle \\ &= \langle \psi_k | -i\hbar e^{i\vec{k} \cdot \vec{r}} \vec{\nabla}_r u_k + \hbar \vec{k} u_k e^{i\vec{k} \cdot \vec{r}} \rangle \\ &= \langle u_k | -i\hbar \vec{\nabla}_r + \hbar \vec{k} | u_k \rangle = \langle u_k | \hat{P} + \hbar \vec{k} | u_k \rangle\end{aligned}$$

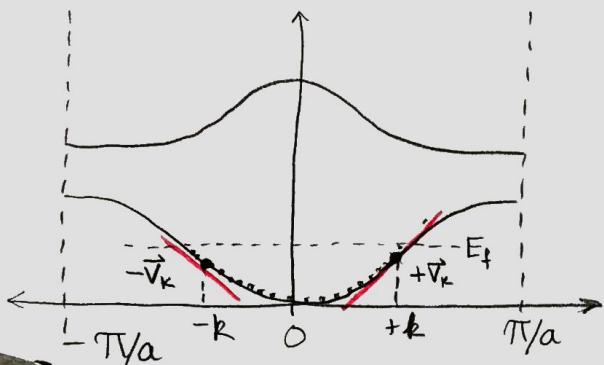
$$\text{So, } \boxed{\langle \hat{P} \rangle_{\psi_k} = \langle \hat{P} + \hbar \vec{k} \rangle_{u_k}}$$

$$\therefore \vec{\nabla}_k E(\vec{k}) = \frac{\hbar}{m} \langle \hat{P} \rangle_{\psi_k} \Rightarrow \boxed{\frac{1}{\hbar} \vec{\nabla}_k E(\vec{k}) = \frac{\langle \hat{P} \rangle_{\psi_k}}{m} = \vec{v}_k}$$

group velocity
of Bloch wave
 ψ_k .

Lecture - 33.

(22-11-21)

Dynamics of electrons (semi-classical treatment)

$$\vec{v}_k = \frac{1}{\hbar} \vec{\nabla}_k E_k$$

$$\begin{aligned}\vec{v}_{-\vec{k}} &= \frac{1}{\hbar} \left(-\frac{\partial}{\partial k_x}, -\frac{\partial}{\partial k_y}, -\frac{\partial}{\partial k_z} \right) E(-\vec{k}) \\ &= \frac{1}{\hbar} (-\vec{\nabla}_k) E(\vec{k}) \\ &= -\frac{1}{\hbar} \vec{\nabla}_k E_k = -\vec{v}_k\end{aligned}$$

$$\Rightarrow \vec{v}_{-\vec{k}} = -\vec{v}_k$$

$$\boxed{\vec{f} = \hbar \frac{d\vec{k}}{dt}} \rightarrow \text{change in } \vec{k} \text{ due to a real force } \vec{F}$$

$$\vec{j} \sim \sum_k -e \vec{v}_k = 0 \text{ in the ground state}$$

because for every e^- moving with a \vec{v}_k , \exists an e^- moving with $-\vec{v}_k$.
 So, in eq^m, the current ~ 0 . So, at eq^m, \nexists any difference of conductivity b/w fully & partially filled bands, because even completely filled bands don't have any current.

If we turn on an electric field \vec{E} , $\vec{f}_{ext} = -e \vec{E} \doteq \hbar \frac{d\vec{k}}{dt}$

~~energy~~ $\frac{d\vec{E}}{dt} = \vec{F} \cdot \vec{v} = -e \vec{E} \cdot \vec{\nabla}_k E(\vec{k})$

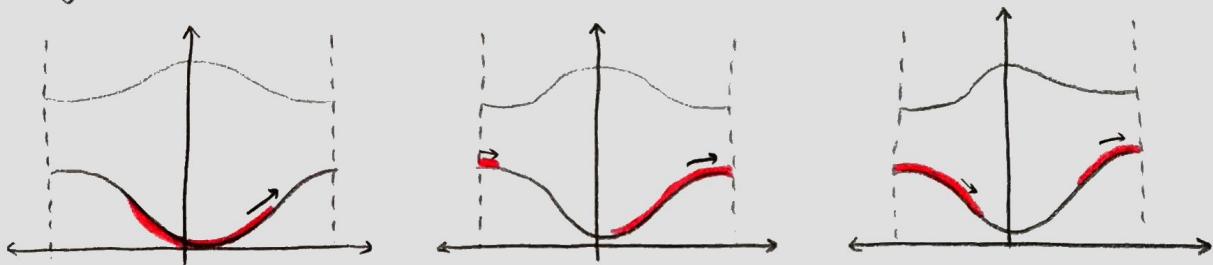
In 1D,

$$\frac{dE}{dt} = \frac{dE}{dk} \frac{dk}{dt} = \hbar v \frac{dk}{dt}$$

$$\text{So, } \hbar \cancel{\frac{dk}{dt}} = -e \vec{E} \cancel{\frac{dE}{dk}} \Rightarrow \boxed{\hbar \frac{dk}{dt} = -e \vec{E}}$$

so, application of \vec{E} results in a change of quantum no. k with time.

$\frac{dk}{dt}$ is independent of k , so every e^- with some k experiences the same changes.



so, the e^- filling structures rigidly keeps sliding across the band structure.

$$\hbar \frac{dk}{dt} = -e \vec{E} \Rightarrow \Delta t = \frac{\hbar \Delta k}{e \vec{E}} \text{ in 1D.}$$

so, the time it takes to cycle back to the $t=0$ state is given by -

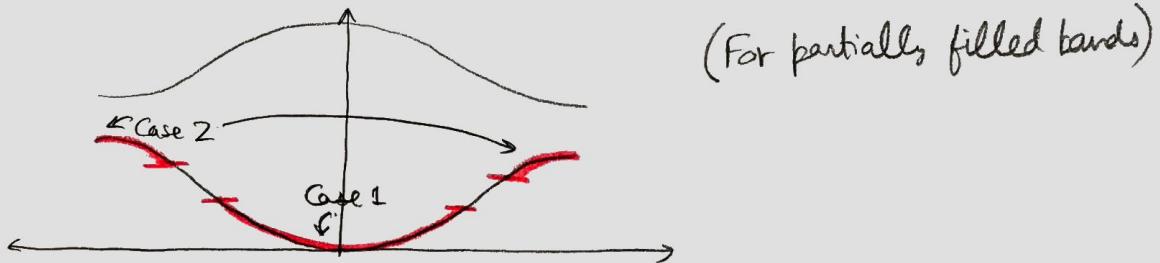
$$\Delta t = \frac{\hbar}{e \vec{E}} \left(\frac{2\pi}{a} \right) = \frac{\hbar}{e E a} \Rightarrow \text{as } E \uparrow, \text{ the time period } \Delta t \downarrow.$$

The application of \vec{E} also disturbs the balance of equal no. of e^- s with $+v_k$ & $-v_k$ velocities because as the filling of the band structure shifts, the balance breaks! \Rightarrow partial filling leads to net current!
(metals)

(3)

However, completely filled bands, the band structure essentially looks rigid because there are always as many e^- 's moving with $+\vec{v}_k$ as there are moving with $-\vec{v}_k$.

\therefore Fully filled bands (insulators) don't generate any current since the balance b/w $+\vec{k}$ states is intact!



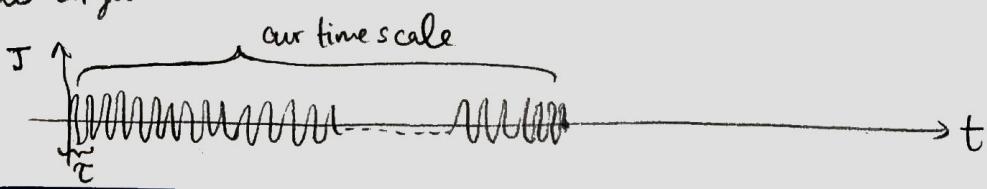
Over a time period $T = \Delta t = \frac{h}{ae\epsilon}$, the avg. current is actually 0.

If starts from zero, starts becoming positive band is max. positive when all the $+\vec{k}$ states are occupied, slowly starts decreasing as the structure comes out from the other side, again becomes 0, becomes negative, approaches a minima, increases, becomes 0, & completes a cycle.

But, avg. current is 0 over a time scale of $T \sim \frac{h}{ae\epsilon}$.

$\epsilon \sim 1 \text{ V/mm} \Rightarrow T \sim 10^{-10} \text{ s}$ and our time scales are much larger.

So, we actually won't see a current even if we have a partially filled band acc. to this argument.



Methods for probing the band structure-

- ARPEES = Angle Resolved Photo Emission Spectroscopy (~ 20 MeV)
- Quantum oscillations in magnetoresistance / magnetization.
- Density functional theory (DFT) calculations.

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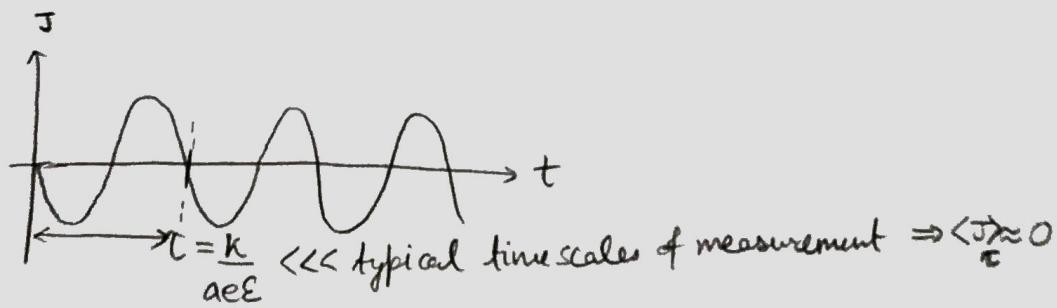
(23-11-21)

Last time we left at the surprising prediction that even partially filled bands give 0 average current!

In absence of \vec{E} , $J = \sum_k (-e) v_k = 0$ for both partially & fully filled bands

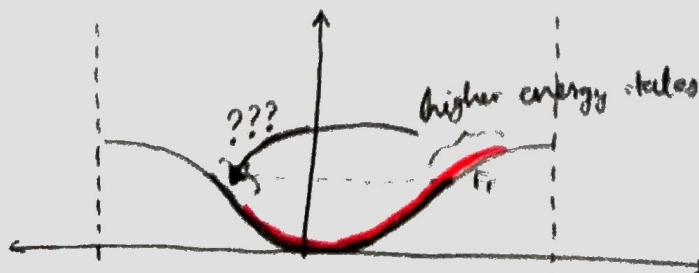
On application of \vec{E} , $\frac{dk}{dt} = -\frac{e\vec{E}}{\hbar} \Rightarrow$ the e^- s move rigidly through

the band structure in k -space. The time period of each k -state to return in the $t=0$ state is $T = \frac{2\pi\hbar}{ae\epsilon} = \frac{\hbar}{ae\epsilon} \approx 10^{-10}$ s for $E \sim 1$ V/mm



So, we're certainly missing something here.

Now, application of \vec{E} sets off the balance of filling, and we end up with some e^- s which have a higher E than the eqm configuration



So, nature, as usual tries to minimize the energy of the system, and tries to find a way to put the higher energy states into the leftover gap created.

And indeed, \exists mechanisms which try to bring back e^- s to eg^m configuration. One of the primary ones is inelastic scattering.

- (1) Scattering with impurities in lattice.
- (2) $e^- - e^-$ interactions.
- (3) scattering by phonons (lattice vibrations.)

These mechanisms can lead to the e^- that is being driven out of eg^m by \vec{E} to be pushed back into eg^m by taking e^- s from higher energies & scattering them to states with lower energies.

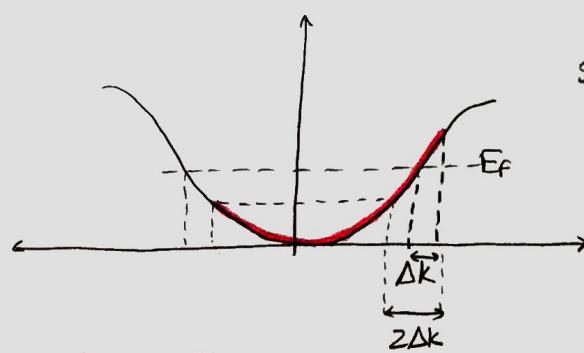
Average scattering time = T_s



So, we have a dynamic eg^m b/w

\vec{E} pushing the electrons upwards v/s

Scattering pushing e^- s back into lower E states.



Some Δk due to dynamic eg^m always exists!

$$\Delta k = -\frac{eE}{\hbar} T_s$$

3

Therefore, from $-(k_F - \Delta k)$ to $+(k_F - \Delta k)$, the current contribution is zero because of equal no. of $\pm v_k$ states.

However, the only contribution remains from the $k_F - \Delta k$ to $k_F + \Delta k$ region.

$$J = \sum_k (-e v_k) \sim \underbrace{2\Delta k}_{\# \text{ of } k\text{-states}} (-e v_k)$$

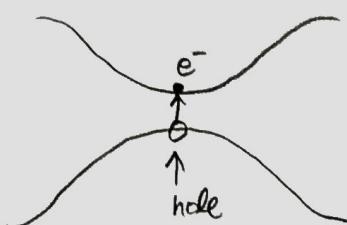
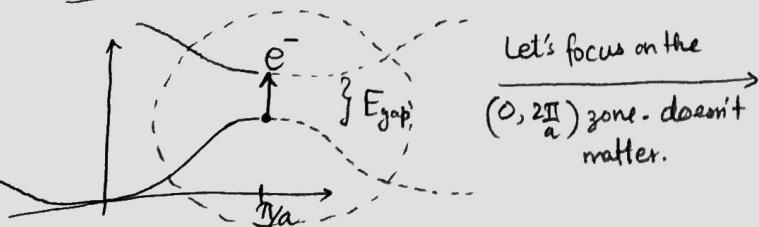
and we approximate $v_k \approx v_F \Rightarrow J \approx -2\Delta k \cdot e \cdot v_F$

$$\Rightarrow J = \frac{2e^2 T_s v_F E}{h} \quad \text{i.e. } J = \sigma E \quad \begin{matrix} \uparrow \\ \text{conductivity} \end{matrix} !!! \quad (\text{Ohm's law!})$$

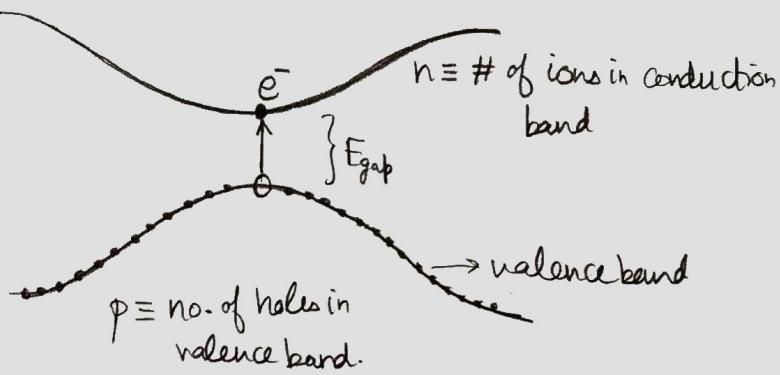
Emphasizing again, if we have a perfect lattice with no imperfections, no lattice vibrations, then we would have no currents. Only because of imperfections & scattering is it able to carry any current, otherwise the material is just an insulator.

SEMI-CONDUCTORS

Electrons & holes:



hole = absence of electron (vacant position.)



$n = p$ for conventional semiconductors since the no. of e^- s in the conduction band is equal to the no. of vacancies it left behind in valence band.

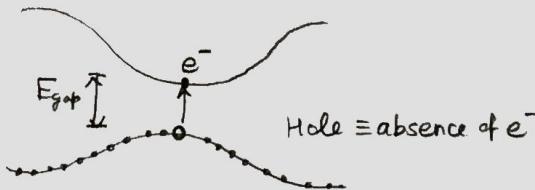
This is true for pure/intrinsic semiconductors.

One can change this situation by doping.

Doping \equiv introducing foreign elements in the material which bring a diff. # of e^- s compared to the parent element.

Lecture - 35

(25-11-2021)

Electrons & Holes:Room temp. $\sim 25 \text{ meV}$  $E_{\text{gap}} < 3 \text{ eV} \sim$ material is semiconductor.

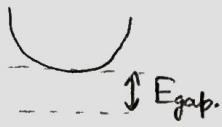
$$E_{\text{gap}}(\text{Si}) \sim 1.1 \text{ eV}$$

$$E_{\text{gap}}(\text{Ge}) \sim 0.7 \text{ eV}$$

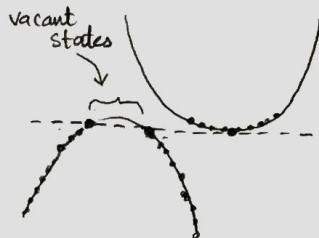
$$E_{\text{gap}}(\text{SiC}) \sim 2 \text{ eV}$$

$$E_{\text{gap}}(\text{GaAs}) \sim 1.4 \text{ eV}$$

We can also have situations like -

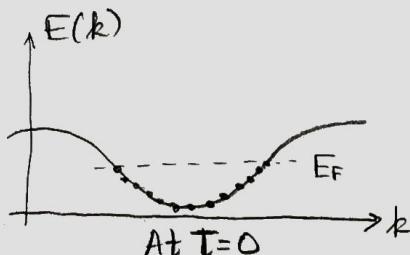


OR



Maxima & minima of valence &
conduction band on same \vec{k} = DIRECT GAP

Maxima & minima occur at
different \vec{k} = INDIRECT GAP

Dependence of band filling on temperature.

Occupation distribution for e^- s is determined by FD statistics -

$$f_{\text{FD}} = \frac{1}{e^{(E-\mu)/\beta} + 1}$$

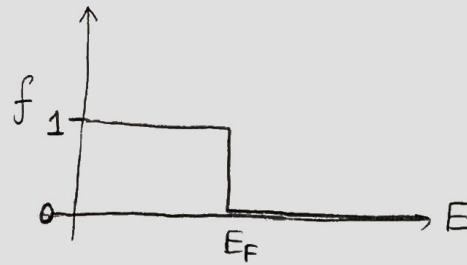
$$\mu = \text{chemical pot}^n = E_F$$

At $T=0$, $\beta \rightarrow \infty$, and $E-\mu = E-E_F \Rightarrow e^{\beta(E-E_F)} = \begin{cases} 0 & E \leq E_F \\ \infty & E > E_F \end{cases}$

$$\Rightarrow f_{FD} = \begin{cases} 1 & E \leq E_F \\ 0 & E > E_F \end{cases}$$

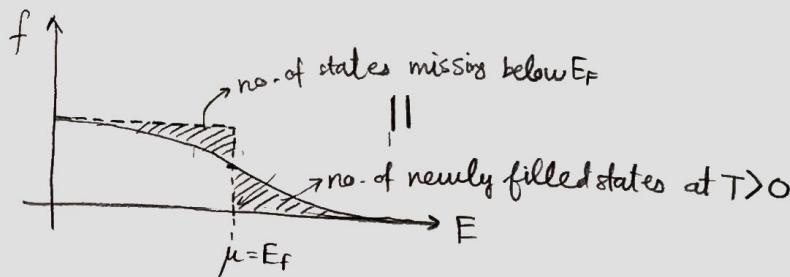
at $T=0$

i.e. 1 e^- per site.



At $T \neq 0$, only e^-s at E_F have the luxury of moving to higher unoccupied states.

So, the distribution of filling changes around E_F .



We need density of states $g(E)$ s.t. $g(E)dE = \# \text{ of states in the interval } E \text{ to } E+dE$.

In free e^- model, in 3D

$$E_F = (3\pi^2 n)^{2/3} \cdot \frac{k^2}{2m} \quad , \quad k_F = (3\pi^2 n)^{1/3}$$

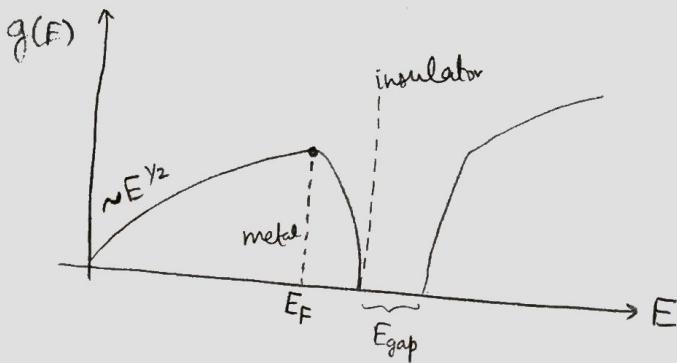
$$E = \frac{k^2}{2m_e} \left(3\pi^2 \frac{N}{V} \right)^{2/3} \quad N = \# \text{ of states filled} \quad (\text{works for any general filling})$$

$$g(E)dE \doteq \frac{dN}{dE} \cdot dE$$

$$\Rightarrow N = \frac{V}{3\pi^2} \left(\frac{2m_e E}{k^2} \right)^{3/2} \Rightarrow \frac{dN}{dE} = \frac{V}{3\pi^2} E^{1/2} \left(\frac{2m_e}{k^2} \right)^{3/2}$$

$$\text{So, } g(E) = \frac{V}{2\pi^2} \left(\frac{2m_e}{k^2} \right)^{3/2} E^{1/2}$$

(3)



∴ A metal is something where E_F lies at a finite value of $g(E)$.

If E_F lies at the boundary s.t. $g(E) \approx 0$, then the material is an insulator.

By defn $N = \int_0^\infty dE g(E)$ at $T=0$

$$\text{At finite } T \quad (T \neq 0), \quad N = \int_0^\infty g(E) f_{FD} dE$$

Normalization condition (gives μ)

Number of states filled above E_F

$$n = \int_{E_F}^\infty dE g(E) f_{FD}$$

Number of empty states below E_F
(not occupied)

$$p = \int_{-\infty}^{E_F} dE g(E) [1 - f_{FD}]$$

At finite temps, FD curve has a tail $\sim 4k_B T$.

Heat capacity

$$\text{Energy} = \underbrace{\# \text{ of } e^-}_{g(E) \Delta E} \times \underbrace{\text{avg. energy per } e^-}_{\frac{3}{2} k_B T}$$

$$= g(E_F) \cdot 4k_B T \cdot \frac{3}{2} k_B T$$

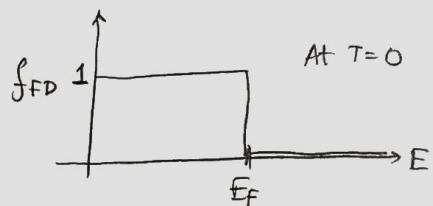
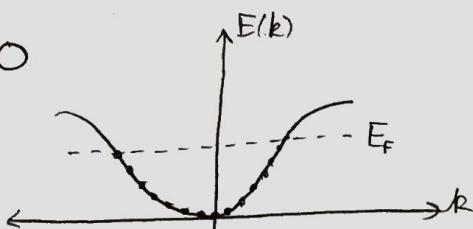
$$= 6k_B^2 T^2 g(E_F)$$

$$\Rightarrow C = \frac{\partial E}{\partial T} = 12k_B^2 g(E_F) T \equiv \gamma T \quad \gamma \sim 0.1 \text{ mJ K}^{-1}$$

Lecture -36
(26-11-2021)

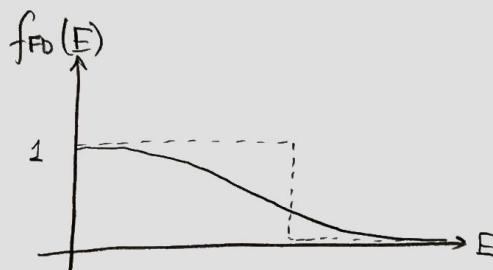
Metal at finite T.

At $T=0$



$$f_{FD}|_{T=0} = \Theta(E_F - E)$$

At $T \neq 0$



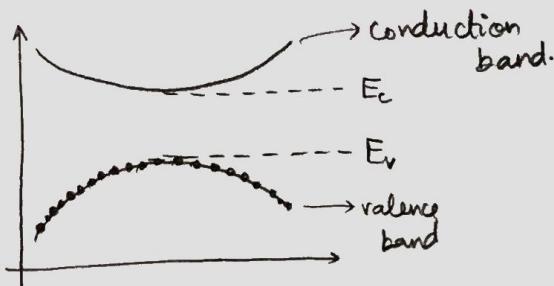
For 3D materials (free e⁻ model)

$$E_F = (3\pi^2 n)^{2/3} \frac{\hbar^2}{2m_e} \quad \text{and } n \sim 10^{28} \text{ e}^-/\text{m}^3 \Rightarrow E_F \sim 2-5 \text{ eV}$$

whereas $k_B T \sim 25 \text{ meV}$ around. So the tail $\sim k_B T$, is much smaller compared to E_F . However, that tail implies that \exists a finite probability that e⁻s occupy an energy level $> E_F$ and a finite probability that energy levels $< E_F$ are unoccupied.

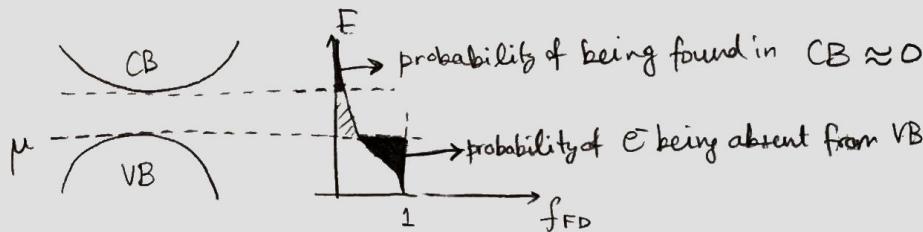
$$f_{FD}(E) = \frac{1}{e^{(E-\mu)\beta} + 1} \quad \text{for a metal, } \mu \approx E_F.$$

Semiconductors at finite T



$$E_{\text{gap}} \equiv E_c - E_v$$

If we put the chemical potential μ for semiconductors at E_v ,



So, probability of e⁻ states being unoccupied in VB $\neq 0$ whereas probability of e⁻s occupying states in CB ≈ 0 . } \Rightarrow can't put μ at E_v because then where the heck did the e⁻s go?

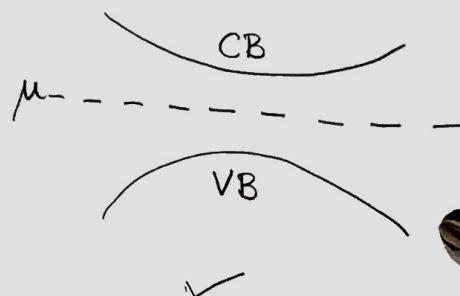
Probability of occupation of states below μ

$$\int_{-\infty}^{E_v} dE g_V(E) f_{\text{FD}} = N_{VB} < N_{\text{solid}}$$

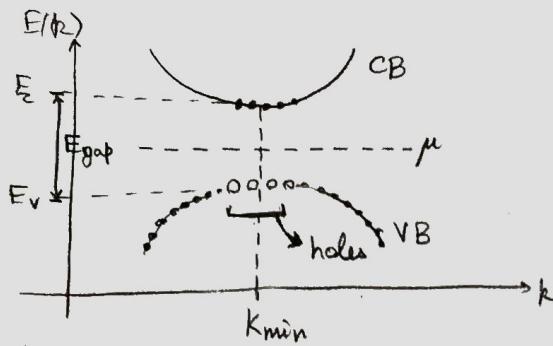
However $N_{CB} \approx 0$ since $f_{\text{FD}}(E_c) \approx 0$. So where did the $N_{\text{solid}} - N_{VB}$ electrons go?

Similarly, μ can't be put at E_c , because then we'll find more e⁻s in CB than went out of VB. So, μ should be somewhere in b/w.

$$\underline{E_v < \mu < E_c}$$



(3)

 $T \neq 0$

The motion of electrons and following the creation of empty e^- sites is much more complicated to interpret compared to simply calling the vacancy created as a hole and consider it as a fictitious (quasi-) particle, which now is interpreted to have a +ve charge.

+ve at bottom & C.B.

$$\text{Near the C.B. minima, } E \approx E_c + \underbrace{\frac{1}{2} \frac{d^2 E}{dk^2}}_{+ve at bottom} \cdot (k - k_{\min})^2$$

$$\approx E_c + \frac{\hbar^2}{2m_e^*} (k - k_{\min})^2$$

where

$$m_e^* = \frac{\hbar^2}{d^2 E / dk^2} > 0$$

(effective mass)

Eqⁿ of motion of the e^-

$$m_e^* \frac{dv}{dt} = -eE - \frac{m_e^* v}{\tau}$$

force due to E-field drag term

Near the V.B. maximum,

$$E = E_v + \underbrace{\frac{1}{2} \frac{d^2 E}{dk^2}}_{-ve at top of V.B.} \cdot (k - k_{\max})^2$$

But since $\frac{\partial^2 E}{\partial k^2} < 0 \Rightarrow m_e^* = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}} < 0 \Rightarrow$ we define
 $m_e^* = -m_{\text{hole}}^*$

s.t. $m_{\text{hole}}^* > 0$

So now, the equation of motion for e^- at top of V.B.

$$m_e^* \frac{dv}{dt} = -eE - m_e^* \frac{v}{T} \xrightarrow{\text{for holes}} m_h^* \frac{dv}{dt} = eE - m_h^* \frac{v}{T}$$

So the eqn of motion of hole looks identical to the eqn of motion of e^- with $m_e^* \rightarrow m_h^*$ and $e \rightarrow -e$

How do we observe the sign of the charge carriers?

Hall effect!

$$R_H = \frac{1}{nq}$$

↑
hall
constant

n = density of charge carriers
 q = charge

$$R_H(e^-) = -\frac{1}{ne} \leftarrow \text{electrons}$$

$$R_H(\text{holes}) = +\frac{1}{ne} \leftarrow \text{holes.}$$

Hall effect coefficient is positive for p -doped semiconductors.

∴ Holes are more than a mere math trick.

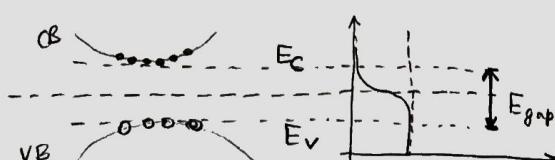
At $T \neq 0$

$$n = \frac{N_c}{V} = \frac{1}{V} \int_{E_c}^{\infty} dE g_c(E) f_{FD}$$

↑
number density
of e^- s in CB

$$p = \frac{N_p}{V} = \frac{1}{V} \int_{-\infty}^{E_v} dE g_v(E) \underbrace{[1 - f_{FD}]}_{\text{absence of electrons.}}$$

↑
number density
of holes in VB



Assuming that we have a free electron system (since $k_B T \ll E_{\text{gap}}$), we can calculate n & p integrals.

The $f_{FD}(E)$ close to C.B. minimum is given by -

$$f_{FD}(E) = \frac{1}{e^{(E-\mu)/k_B T}} \underset{k_B T \ll E_c - \mu}{\lim} \approx e^{-(E-\mu)/k_B T} \approx e^{-\beta(E-\mu)}$$

Similarly, the probability distribution for V.B. holes is -

$$1 - f_{FD} = \left| \frac{e^{(E-\mu)/k_B T}}{e^{(E-\mu)/k_B T} + 1} \right| \quad \begin{matrix} \\ E = E_V \Rightarrow E - \mu = E_V - \mu < 0 \end{matrix}$$

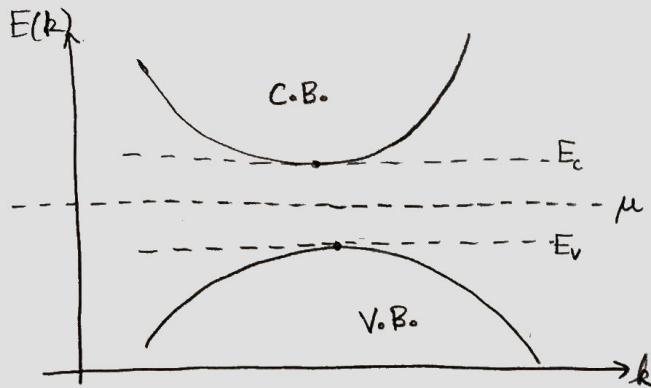
$$\Rightarrow e^{(E-\mu)/k_B T} + 1 \approx 1 \Rightarrow (1 - f_{FD}) \Big|_{\text{top of V.B.}} \approx e^{(E-\mu)/k_B T} = e^{-(\mu-E) \cdot \beta}$$

$$\text{So, } f_{FD}(E) \Big|_{\substack{\text{for es at bottom} \\ \text{of C.B.}}} \approx e^{-\beta(E-\mu)} \quad \& \quad (1 - f_{FD}(E)) \Big|_{\substack{\text{for holes at top} \\ \text{of V.B.}}} \approx e^{-\beta(\mu-E)}$$

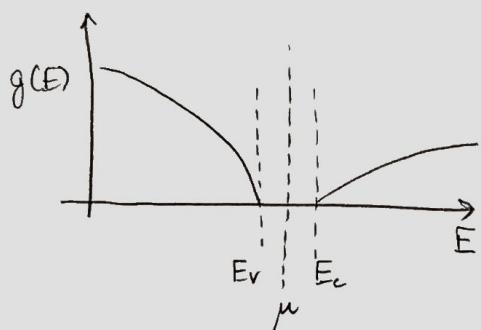
Using these approximations, & treating g_c & g_v as free electron density of states, one can calculate the n and p integrals.

Lecture - 37

(29-11-2021)

Semiconductor Physics (contd.)

$g_v > g_c$ why?



$$n = \frac{1}{\sqrt{V}} \int_{E_c}^{\infty} dE g_c(E) f_{FD}$$

↑
density of
e⁻s in C.B.

$$p = \frac{1}{\sqrt{V}} \int_{-\infty}^{E_v} dE g_v(E) (1 - f_{FD})$$

↑
density of holes
in V.B.

$$g_c(E) = \frac{V}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2}$$

$$g_v(E) = \frac{V}{(2\pi)^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} (E_v - E)^{1/2}$$

Assuming $E_{gap} \gg k_B T \Rightarrow (E_c - \mu) \gg k_B T$, then -

$$f_{FD} = \frac{1}{e^{(E-\mu)\beta} + 1} \approx e^{-(E-\mu)\beta} \quad \text{for C.B.} \quad (E_c - \mu)\beta \gg 1$$

$$1 - f_{FD} = \frac{e^{(E-\mu)\beta}}{e^{(E-\mu)\beta} + 1} \approx e^{+(E-\mu)\beta} \quad \text{for V.B.} \quad (\mu - E_v)\beta \gg 1$$

(7)

$$n = \frac{1}{N} \int dE \cdot \frac{1}{2\pi^2} \left(\frac{2me^*}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2} e^{-\beta(E-\mu)}$$

$$= \frac{1}{2\pi^2} \left(\frac{2me^*}{\hbar^2} \right)^{3/2} e^{\beta\mu} \int_{E_c}^{\infty} dE (E - E_c) e^{-\beta E}$$

$$= \frac{1}{2\pi^2} \left(\frac{2me^*}{\hbar^2} \right)^{3/2} e^{-\beta(E_c-\mu)} \int_{E_c}^{\infty} dE (E - E_c) e^{-\beta(E-E_c)}$$

Now define $\beta(E - E_c) \equiv x \Rightarrow \frac{dx}{\beta} = dE$

$$= \frac{1}{2\pi^2} \left(\frac{2me^* k_B T}{\hbar^2} \right)^{3/2} e^{-\beta(E_c-\mu)} \int_0^{\infty} dx x^{1/2} e^{-x}$$

$\underbrace{\qquad\qquad\qquad}_{\sqrt{\pi}/2}$

$$= 2 \underbrace{\left(\frac{2\pi m e^* k_B T}{\hbar^2} \right)^{3/2}}_{N_c} e^{-\beta(E_c-\mu)}$$

N_c
(effective # of electrons in the
conduction band.)

$$\text{So, } n = N_c(T) e^{-\beta(E_c-\mu)}$$

$$N_v(T) = N_c(T) \Big|_{m_e^* \rightarrow m_h^*}$$

$$\text{Similarly, } p = N_v(T) e^{-\beta(\mu-E_v)}$$

Now, let's do the following multiplication-

$$np = N_c N_v e^{-E_{gap}\beta}$$

$$\text{For intrinsic semiconductors, } n_i = p_i \Rightarrow n_i = p_i = \sqrt{N_c N_v} e^{-\beta E_{gap}/2}$$

\therefore the value of n_i (or p_i) then only depends upon E_{gap} , M_h^* , M_e^* .

- E_{gap} can be found using optical properties of materials
- To find m_e^* , m_h^* , we usually use cyclotron resonance methods

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

↑
cyclotron frequency.

————— n=3

————— n=2

————— n=1

Energy levels of cyclotron are quantized

$$E_n = \hbar \omega_c \left(n + \frac{1}{2} \right)$$

One varies ω_c , and as soon as $\omega = \omega_c$, we'll get a transition for the charged particle to a higher energy state & there will be a large absorption.

Once we know ω_c , we'll know what m^* is.

For Si, $m_e^* \approx 0.5$, and $m_h^* \approx 0.2$

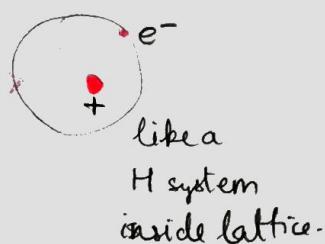
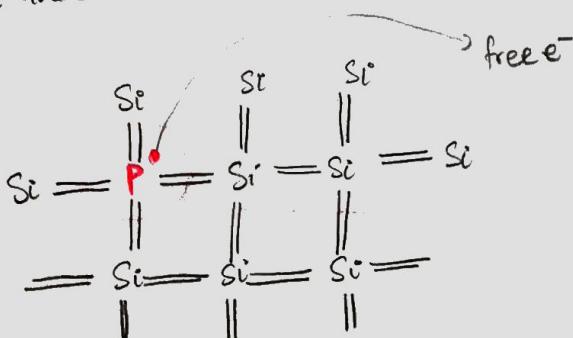
For GaAs, $m_e^* \approx 0.06$ and $m_h^* \approx 0.5$

At room temperature, $n \approx 10^{16} e^-/m^3$

but we only have $1e^-/10^{12} \text{ Si atoms}$. → not very useful.

So, we dope the semiconductors to enhance number density of e^- & holes.

Doping:-

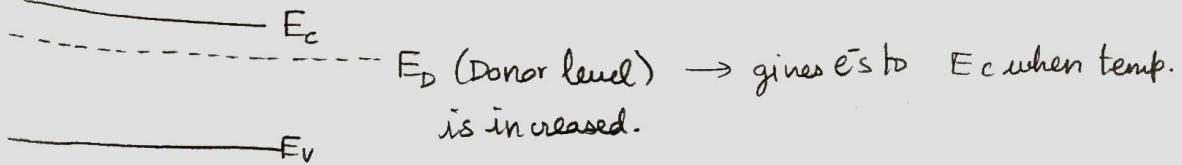


However, despite looking like a H-atom, \exists quite a few changes.

$$E_n = -\frac{m_e^* e^4}{32 \pi^2 \epsilon_0^2 \epsilon_r k^2} \cdot \frac{1}{n^2}$$

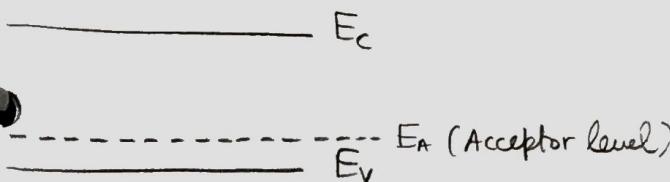
(9)

For Si, $m_e^* \sim 0.4$ & $E_F \sim 15 \Rightarrow E_{\text{binding}}(\text{Si}) \sim 40 \text{ meV}$



As soon as $E(T) \sim E_{\text{binding}}$, the E_D level gives e^- s to E_C .

If instead we would have doped with Boron (p -type), then we get an acceptor state



The current when both e^- s & holes are present-

$$\text{Electrons} \quad m_e^* \frac{dV_e}{dt} = -eE + -\frac{m_e^* V_e}{T_e} \Rightarrow m_e^* \left(\frac{dV_e}{dt} + \frac{V_e}{T_e} \right) = -eE$$

$$\text{Holes} \quad m_h^* \left(\frac{dV_h}{dt} + \frac{V_h}{T_h} \right) = eE$$

Steady state solⁿ: both e^- s & holes acquire a drift speed ($\Rightarrow \frac{dv}{dt} = 0$)

$$\text{so, in steady state} \quad V_e = -\frac{e T_e}{m_e^*} E$$

$$V_h = \frac{e T_h}{m_h^*} E$$

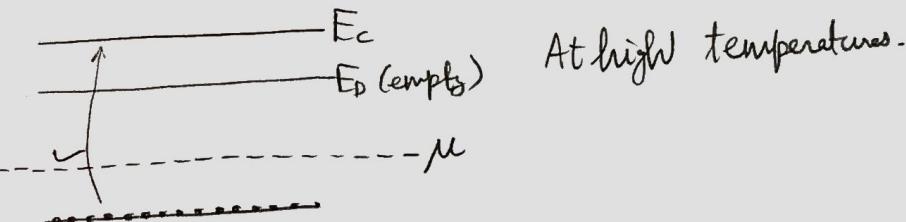
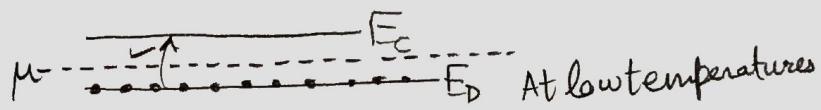
Total current $J = n(-eV_e) + p(eV_h)$

$$= \left(\frac{n e^2 T_e}{m_e^*} + \frac{p e^2 T_h}{m_h^*} \right) E \equiv \sigma E$$

$n p = \text{constant}$ at fixed T

So, only one of the carriers form a majority & the other goes down in number.

Placement of μ



Lecture-38

(30-11-21)

Magnetic properties can't be understood in the band structure formalism.

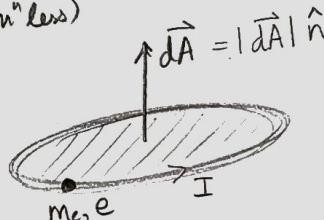
In free space, $\vec{B} = \mu_0 \vec{H}$ (rescaled versions of each other.)

The response of a medium to a magnetic field is generating magnetization
 $M \propto H$ (weakly magnetic materials).

$$\text{magnetization} \equiv \frac{\text{total magnetic moment}}{\text{volume}}$$

$$M = \chi H \quad \text{susceptibility (dim"less)}$$

$$\underline{\text{Magnetic moment}} \quad \vec{\mu} = I \vec{dA}$$



In general, every $\vec{\mu}$ is associated to a charged particle going around an axis, which also means

\exists a mass going around an axis \Rightarrow this must be related to \vec{L} .

$$\vec{\mu} = \gamma \vec{L}$$

↑ gyro magnetic ratio.

$$\text{For an electron, } I = -\frac{e}{T} = -\frac{e}{\left(\frac{2\pi r}{v}\right)} = -\frac{ev}{2\pi r} \Rightarrow \mu = -\frac{ev}{2\pi r} \cdot 2\pi r^2 = -\frac{evr}{2}$$

$$\mu = -\frac{evr}{2} \cdot \frac{m_e}{m_e} = -\frac{e}{2m_e} \cdot l \Rightarrow \boxed{\vec{\mu} = -\frac{e}{2m_e} \vec{L}}$$

$\gamma = -\frac{e}{2m_e}$ gyro magnetic ratio of electron.

This was a classical treatment.

Q mechanically, an e^- in atom has $|\vec{L}| = \hbar m_e$

$$\Rightarrow \mu_L = -\underbrace{\frac{e\hbar}{2m_e} m_e}_{\text{Bohr magneton } \mu_B} = \mu_B m_e$$

$$\mu_B \equiv \frac{e\hbar}{2m_e}$$

Bohr magneton μ_B

Energy of a magnetic moment $E = -\vec{\mu} \cdot \vec{B}$ orbital moment.

The electron however has an intrinsic spin as well. $S = \frac{1}{2} \Rightarrow m_s = \pm \frac{1}{2}$

$$\mu_s = g \mu_B m_s \Rightarrow \mu_s \approx \pm \mu_B$$

↑
electron's g-factor ≈ 2.002

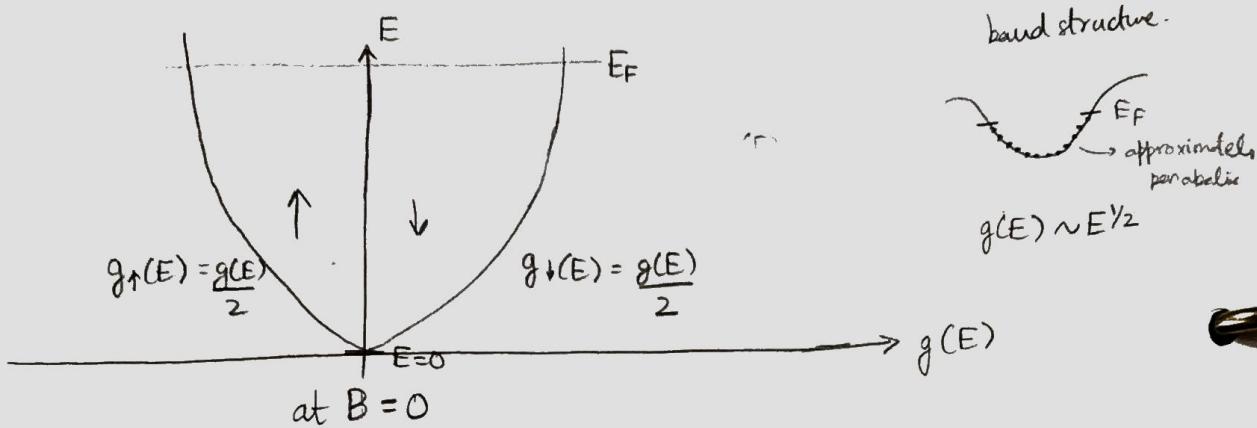
Pauli Paramagnetism (weak magnetism of free e^- gas from Band structures.)

$$M = \chi H$$

$\chi > 0 \rightarrow$ paramagnets (free spins, free e^- gas, localized).

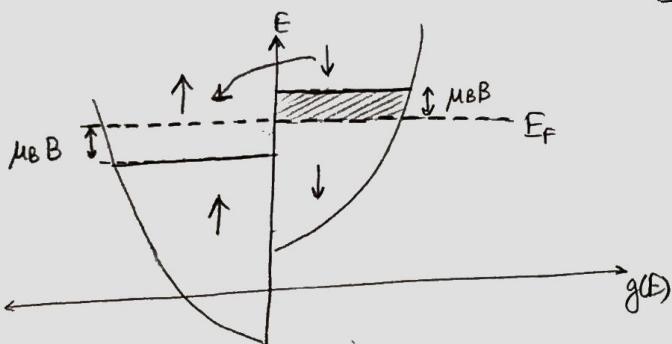
$\chi < 0 \rightarrow$ diamagnets (water, plastic).

Paramagnetism of quasi-free electrons.



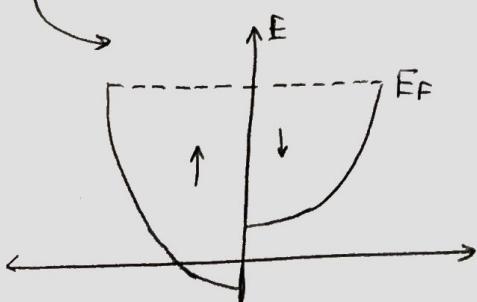
On turning on a field

$$E = -\vec{\mu} \cdot \vec{B} \quad \begin{cases} \downarrow \\ \uparrow \end{cases} = \mp \mu_B B.$$



↓ spin band higher than E_F
decays down to available states in the ↑
spin band lower than E_F

eventually becomes



Balance b/w ↑ & ↓ no. of electrons is destroyed.
Now we have more ↑ electrons than ↓ electrons.

So, change in the no. of ↑ & ↓ e^- s is $\Delta n = n_{\uparrow} - n_{\downarrow} = \frac{1}{2} g(E_F) \Delta E$

$$= \frac{1}{2} g(E_F) 2 \mu_B B.$$

$$= g(E_F) \mu_B B$$

Net magnetization

(3)

$$M = \mu_B \cdot \Delta n = \mu_B^2 g(E_F) B$$

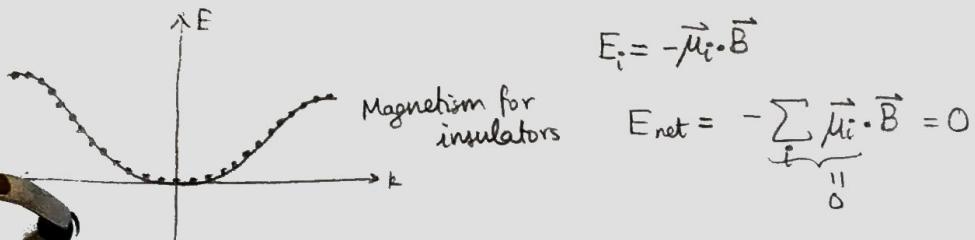
$$\Rightarrow M = \mu_B^2 g(E_F) \cdot (\mu_0 H) = \mu_0 \mu_B^2 g(E_F) H$$

and $\chi_p \equiv \frac{M}{H} = \mu_0 \mu_B^2 g(E_F)$

$$\frac{\chi_{\text{exit}}}{\chi_p} \approx 2 \text{ (Na)}$$

$$1.3 \text{ (Li)}$$

Mott Insulators (magnetism in insulators.)

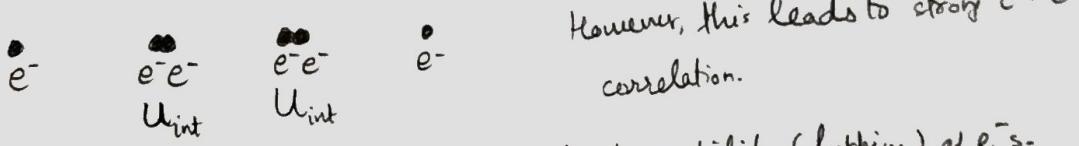


However, not all insulators have completely filled bands. $(\text{NiO}, \text{Fe}_3\text{O}_4, \text{CuO}$
have partially filled bands)

Let's take a material with $1e^-/\text{atom}$.



Since hopping is allowed, some e^- s might have double occupancy on some sites.



So, there surely exists a lowering of energy due to mobility (hopping) of e^- s.

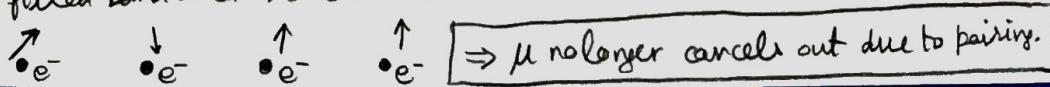
However, \exists an energy cost $= nU$

\hookrightarrow no. of doubly occupied sites.

Hopping energy t Repulsion energy U \rightarrow if $t \ll U$, then the e^- s won't hop & occupy the same state (with opposite spin.)

Despite being $1e^-/\text{atom}$ system, the material has immobile e^- s & is an insulator.

So, even a partially filled band is an insulator. This is known as a Mott insulator.



Lecture - 39

(02/12/21)

Magnetism of isolated atoms or ions.

$$\text{Hamiltonian} \quad H_0 = \sum_i \left(\frac{\vec{p}_i^2}{2m_e} + V(\vec{r}_i) \right) \quad \text{Hamiltonian for zero field.}$$

Introducing a magnetic field gives-

$$H = \sum_i \left(\frac{(\vec{p}_i + e\vec{A}(\vec{r}_i))^2}{2m_e} + V(\vec{r}_i) + g\mu_B \vec{S}_i \cdot \vec{B} \right) \quad S_i = \pm \frac{1}{2}$$

$$\nabla \times \vec{A} = \vec{B} \quad \text{We choose the London gauge. } \vec{A}(\vec{r}_i) = \frac{\vec{B} \times \vec{r}_i}{2}$$

$$H = \sum_i \left(\frac{\vec{p}_i^2}{2m_e} + V(\vec{r}_i) \right) + \frac{e^2}{2m_e} \sum_i \vec{A}(\vec{r}_i)^2 + \frac{e}{2m_e} (\vec{p}_i \cdot \vec{A} + \vec{A} \cdot \vec{p}_i) + g\mu_B \sum_i \vec{S}_i \cdot \vec{B}$$

$$\text{In the London gauge, } \vec{A} = \frac{\vec{B} \times \vec{r}}{2} \Rightarrow A_x = ar_y + br_z$$

and $[A_x, p_x] = [ar_y + br_z, p_x] = 0$ since both r_y & r_z commute with p_x .

$$\text{So, } \vec{p}_i \cdot \vec{A} + \vec{A} \cdot \vec{p}_i = 2\vec{A} \cdot \vec{p}_i$$

$$\Rightarrow H = H_0 + \left(\frac{e^2}{2m_e} \sum_i \left(\frac{(\vec{B} \times \vec{r}_i)^2}{4} + \frac{e}{2m_e} 2\vec{A} \cdot \vec{p}_i \right) + g\mu_B \sum_i \vec{S}_i \cdot \vec{B} \right)$$

$$= H_0 + \left[\sum_i \frac{e^2}{8m_e} (\vec{B} \times \vec{r}_i)^2 + \frac{e}{2m_e} (\vec{B} \times \vec{r}_i) \cdot \vec{k}_i \right] + g\mu_B \sum_i \vec{S}_i \cdot \vec{B}$$

$$H = H_0 + \sum_i \left(\frac{e^2}{8m_e} (\vec{B} \times \vec{r}_i)^2 + \frac{e}{2m_e} (\vec{r}_i \times \vec{p}_i) \cdot \vec{B} \right) + g\mu_B \sum_i \vec{S}_i \cdot \vec{B}$$

$\frac{e}{2m_e} \sum_i \vec{k}_i \vec{r}_i = \frac{e}{2m_e} \vec{L} \propto \mu_B \vec{L}$

$$H = H_0 + \frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r}_i)^2 + \mu_B (\vec{L} + g\vec{S}) \cdot \vec{B}$$

↓ ↑

Diamagnetic contrib. paramagnetic contrib. ($\chi > 0$)

Earth's magnetic field ≈ 0.5 Gauss $= 5 \times 10^{-5}$ T

Diamagnetic term.

$$\Delta E_d = \frac{e^2}{8me} \sum_i (\vec{B} \times \vec{r}_i)^2 \quad \text{let } \vec{B} = B\hat{z}$$

$$\Rightarrow \Delta E_d = \frac{e^2 B^2}{8me} \sum_i (x_i^2 + y_i^2)$$

$$\text{For symmetric shells, } x_i^2 = y_i^2 = z_i^2 = \frac{1}{3} r_i^2$$

$$\Rightarrow \Delta E_d = \frac{e^2 B^2}{8me} \sum_i \frac{2}{3} r_i^2 = \frac{e^2 B^2}{12me} \sum_i r_i^2 \quad (\text{sum over different orbitals})$$

$$\text{An average radius is defined as } r^2 \equiv \frac{1}{Z_i} \sum_i r_i^2$$

$$\Rightarrow \Delta E_d = \frac{Z_i e^2 B^2 r^2}{12me}$$

$$\text{Now, } M = -\frac{\partial F}{\partial B} \text{ for magnetic systems. } F = E - TS = E \text{ at } T=0$$

$$M \Big|_{T=0} = -\frac{\partial(\Delta E_d)}{\partial B} = -\frac{Z_i e^2 r^2}{6me} B = -\frac{Z_i \mu_0 e^2 r^2}{6me} H$$

$$\therefore \boxed{\chi = \frac{M}{H} = -\frac{Z_i \mu_0 e^2 r^2}{6me}} \quad \begin{matrix} \text{Diamagnetic contribution} \\ x < 0 \end{matrix}$$

$$\approx 10^{-5} \left(\frac{r}{a_0} \right)^2 \text{ (very small)}$$

Graphene has a high avg.-effective radius r , and so despite being a metal, graphene is diamagnetic.

Paramagnetic term.

$$\Delta E = \mu_B (\vec{L} + g \vec{S}) \cdot \vec{B}$$

Hund's rule

(1) Maximise \vec{S}

(2) Maximise \vec{L} .

(3) $\vec{J} = |\vec{L} \pm \vec{S}|$

+ more than half filled
- less than half filled

Example of Hund's rule.

$$Pr = []^4 f^3$$

$$\begin{array}{ccccccc} l=3 & & & & & & \\ L=-3 & -2 & -1 & 0 & 1 & 2 & 3 \end{array}$$

$$\begin{array}{ccccccc} -3 & -2 & -1 & 0 & 1 & 2 & 3 \\ \downarrow & & & & \downarrow & & \downarrow \end{array}$$

First rule: maximise $S \Rightarrow S = \frac{3}{2}$

Second rule: maximise $L \Rightarrow$ fill $l_f = 1, 2, 3$

Third rule: half filled $\Rightarrow \vec{J} = \vec{L} - \vec{S}$ (\vec{I} should point opposite to \vec{S})

$$J = (1+2+3) - \frac{3}{2} = 6 - \frac{3}{2} = \frac{9}{2}$$

Now, we want $(\vec{I} + g\vec{S})$, some evaluate it as follows-

$$\Delta E = \mu_B (\vec{I} + g\vec{S}) \cdot \vec{B} = \mu_B g_J \vec{J} \cdot \vec{B}$$

$$g_J = \text{Lande}' g\text{-factor}$$

$$= \frac{3}{2} + \frac{s(s+1) - l(l+1)}{2J(J+1)}$$

$$\text{Say } \vec{B} = B\hat{z}$$

$$\Rightarrow \Delta E = \mu_B g_J J_z \cdot B$$

$$J_z = -J, -J+1, \dots, J-1, J$$

$\uparrow (2J+1) \text{ values}$

$$Z = \sum_{J_z} e^{-\mu_B g_J B J_z \beta} \longrightarrow F = -k_B T \ln Z$$

$$\Rightarrow M = -\frac{N}{V} \frac{\partial F}{\partial B}$$

$$\text{Taking } J = \frac{1}{2} \Rightarrow J_z = \pm \frac{1}{2} \quad (g_J = 2 \text{ for a free } e^-)$$

$$Z = e^{-\mu_B B \beta} + e^{+\mu_B B \beta}$$

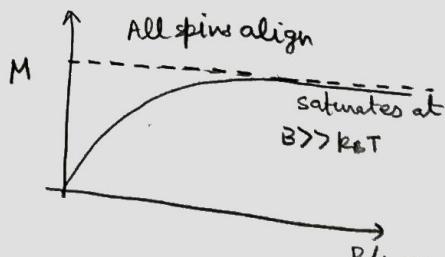
$$\Rightarrow M = -\frac{N}{V} k_B T \frac{\partial Z / \partial B}{Z} = -\frac{N}{V} \left[-\mu_B \beta e^{-\mu_B B \beta} + \mu_B \beta e^{+\mu_B B \beta} \right] \cdot k_B T$$

$$M = \frac{N}{V} \mu_B \tanh \left(\frac{\mu_B B}{k_B T} \right)$$

If $B \ll k_B T$

$$M \approx \frac{N}{V} \frac{\mu_B^2}{k_B T} B = \frac{N}{V} \frac{\mu_0 \mu_B^2}{k_B T} H$$

$$\Rightarrow \chi = \frac{M}{H} = \frac{N}{V} \frac{\mu_0 \mu_B^2}{k_B T}$$



Molar susceptibility: $\chi_A = \frac{N_A}{(N/V)}$

$$\Rightarrow \chi_{\text{molar}} = N_A \frac{\mu_0 M_B^2}{k_B T} \sim \frac{C}{T} \quad (\text{Curie law}). \quad \text{At } B \ll k_B T \\ \text{small field & large tempe.}$$

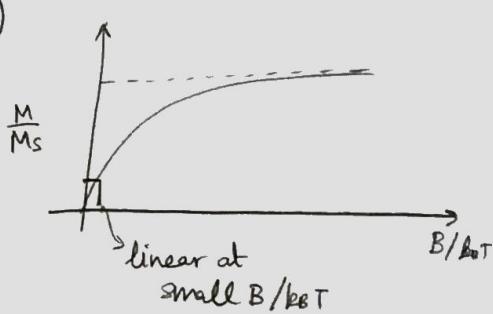
For a general J ,

$$Z = \sum_{J_z=-J}^{+J} e^{-g_J \mu_B B J_z / k_B T}$$

$$M = -\frac{\partial F}{V \partial B} \rightarrow \chi = \frac{M}{H} = \frac{N}{V} \mu_B J B_J \left(\mu_B g_J J B / k_B T \right) \\ \uparrow \text{do this} \quad \uparrow \text{Brillouin function}$$

$$B_J(x) \equiv \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$$

$$\coth(x) \approx \frac{1}{x} + \frac{x}{3} + O(x^3)$$



At small B & high T

$$\boxed{\chi = \frac{C}{T} = \frac{n \mu_0 M_B^2 g_J^2 J(J+1)}{3k_B T} = n \frac{\mu_0 M_{\text{eff}}^2}{3k_B T}}$$

$$M_{\text{eff}}^2 = \mu_B^2 g_J^2 J(J+1)$$

For rare earth elements (4f filling)

Ce, Pr, Nd, ... $\chi_{\text{free spin}}$ works quite well and gives very similar dependence as was worked out theoretically.

For transition metals however (3d filling) Cr, V, Mn, Fe, Co, ...

M_{eff} found from experiments is where $L=0$ & $J=s$

The orbital degree of freedom is "quenched" in d-orbital structure. The extended structure of d-orbitals is the reason for quenching.

Lecture - 40

(03/12/21)

In all the cases we've dealt with before, $B=0 \Rightarrow M=0$. No spontaneous magnetization.

In ferromagnets, all the spins (or more accurately, magnetic moment) point in the same direction.

$$H = g\mu_B \sum_i \vec{S}_i \cdot \vec{B} - \frac{1}{2} \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

$\underbrace{\phantom{g\mu_B \sum_i \vec{S}_i \cdot \vec{B}}}_{\text{Zeeman term}}$ $\underbrace{\phantom{- \frac{1}{2} \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j}}_{\text{exchange interaction.}}$



$J_{ij} > 0$ is the interaction b/w "spins" on sites i & j . $J_{ij} = J_{ji} > 0$

For $J_{ij} > 0 \Rightarrow$ alignment of spins because we want H to minimize (ferromagnet) $M \neq 0$

For $J_{ij} < 0 \Rightarrow$ anti-alignment of spins because H has to minimize. (anti-ferromagnet) $M=0$

However, if we have something like a 2-atom basis and have $J_{ij} < 0$, the M can still be $\neq 0$ due to difference in magnetic moments which don't exactly cancel out. These are called Ferrimagnets.



$$H = g\mu_B \sum_i \vec{S}_i \cdot \vec{B} - \frac{1}{2} \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

Assume:

- J_{ij} act only b/w nearest neighbours.
- Use mean field theory.

Mean Field Theory \rightarrow replace operators by their expectation values.

$$H = \sum_i g\mu_B \vec{S}_i \cdot \vec{B} - \frac{1}{2} \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j$$

\nearrow nearest neighbours.

Define an effective field seen by site i as -

$$g\mu_B \vec{B}_{\text{eff.}} \equiv g\mu_B \vec{B} - \frac{1}{2} \sum_j \vec{S}_j$$

Energy of the i^{th} spin-

$$\mathcal{H}_i = g\mu_B \vec{S}_i \cdot \vec{B}_{\text{eff}}$$

Same as the Hamiltonian for paramagnetic term with
 $\vec{B} \rightarrow \vec{B}_{\text{eff}}$

However, \vec{B}_{eff} is not a number. So we put $\vec{B}_{\text{eff}} \rightarrow \langle \vec{B}_{\text{eff}} \rangle$

$$g\mu_B \langle \vec{B}_{\text{eff}} \rangle = g\mu_B \vec{B} - \frac{1}{2} J \sum_j \underbrace{\langle \vec{S}_j \rangle}_{\text{doesn't depend on site } i} \quad \langle \vec{S}_j \rangle \equiv \langle \vec{S} \rangle$$

$$\Rightarrow \mathcal{H}_i = g\mu_B \vec{S}_i \cdot \langle \vec{B}_{\text{eff}} \rangle \\ = g\mu_B \vec{S}_i \cdot \left(g\mu_B \vec{B} - \frac{1}{2} J Z \langle \vec{S} \rangle \right)$$

$Z \equiv \text{no. of nearest neighbours to the site.}$

Now, take $\vec{B} = B \hat{z}$ & $S = \frac{1}{2}$ ($S_z = \pm \frac{1}{2}$)

$$Z = e^{-g\mu_B \langle \vec{B}_{\text{eff}} \rangle \beta/2} + e^{+g\mu_B \langle \vec{B}_{\text{eff}} \rangle \beta/2}$$

Now, let's calculate $\langle \vec{S}_i \rangle$

$$\langle S \rangle \equiv \langle \vec{S}_i \rangle = \sum_i S_i p(S_i) = \sum_i S_i \cdot \frac{e^{-g\mu_B \langle \vec{B}_{\text{eff}} \rangle S_i \beta}}{Z}$$

$$\langle S \rangle = -\frac{1}{2} \tanh \left(\frac{g\mu_B \langle \vec{B}_{\text{eff}} \rangle}{2k_B T} \right) = -\frac{1}{2} \tanh \left(\frac{g\mu_B B}{2k_B T} - \frac{J Z \langle S \rangle}{2k_B T} \right)$$

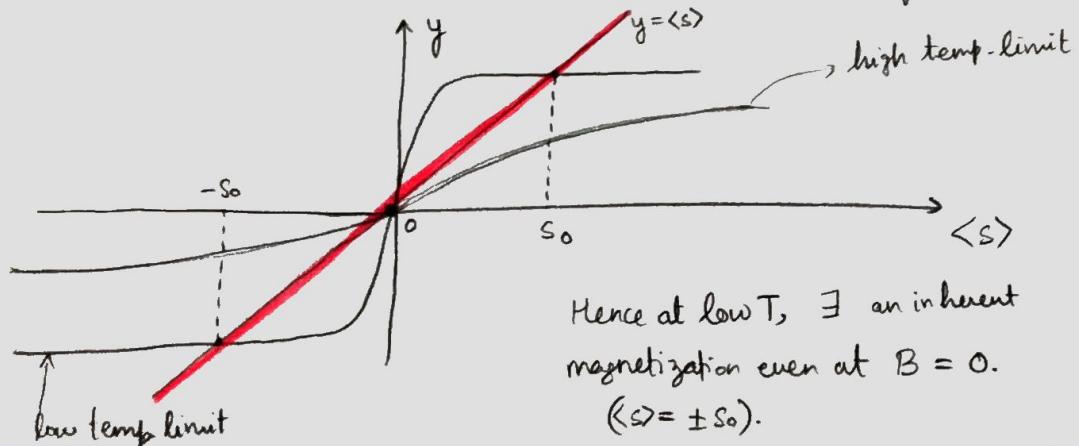
$$M = -g\mu_B \langle S \rangle \frac{N}{V} \quad (M \propto \langle S \rangle)$$

↑
transcendental eqn.

Put $B=0$ & plot RHS & LHS

$$\langle S \rangle = \frac{1}{2} \tanh \left(\frac{J Z \langle S \rangle}{4k_B T} \right)$$

$\langle S \rangle = \text{RHS}$



Hence at low T , \exists an inherent magnetization even at $B=0$.
 $(\langle S \rangle = \pm S_0)$.

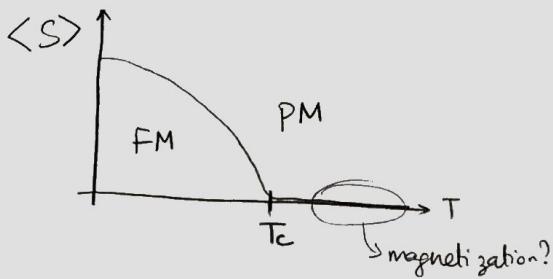
So, at high temp. \rightarrow paramagnet
at low temp. \rightarrow ferromagnet

This net magnetization occurs as the slope of $\tanh = \text{slope of linear fm}$

So, the critical temperature is calculated as follows-

$$\text{At low temps, } \tanh\left(\frac{JZ\langle S \rangle}{4k_B T}\right) \approx \left(\frac{J\langle S \rangle}{4k_B T}\right) \rightarrow \text{slope}$$

$$\Rightarrow \text{we get magnetization at } \frac{JZ}{4k_B T_c} = 1 \quad \text{or} \quad T_c = \frac{JZ}{4k_B}$$



None in absence of field. If we have a small field B, then-

$$\langle S \rangle \approx \frac{g_{MB}B}{2k_B T} - \frac{JZ\langle S \rangle}{2k_B T}$$

$$\langle S \rangle \left(1 + \frac{JZ}{2k_B T}\right) = \frac{g_{MB}B}{2k_B T}$$

$$\text{This will eventually give} - \chi = \frac{M}{H} = \chi_{\text{Curie}} \cdot \frac{1}{1 - T_c/T}$$