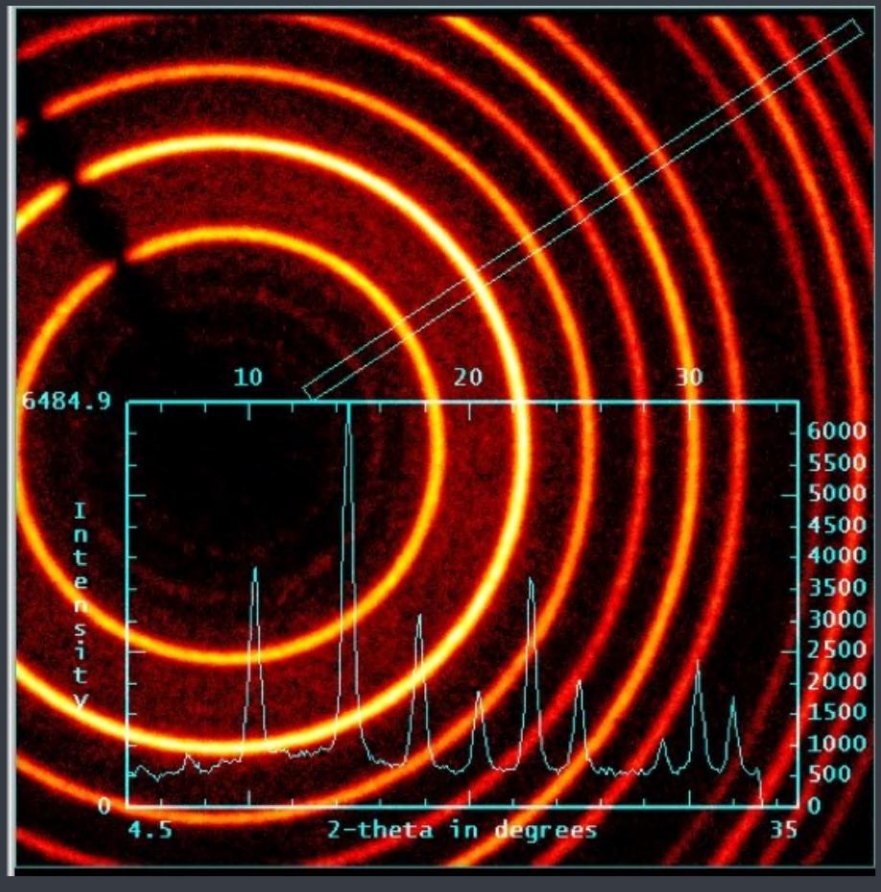
CONDENSED MATTER PHYSICS



Prof. Marco Grilli

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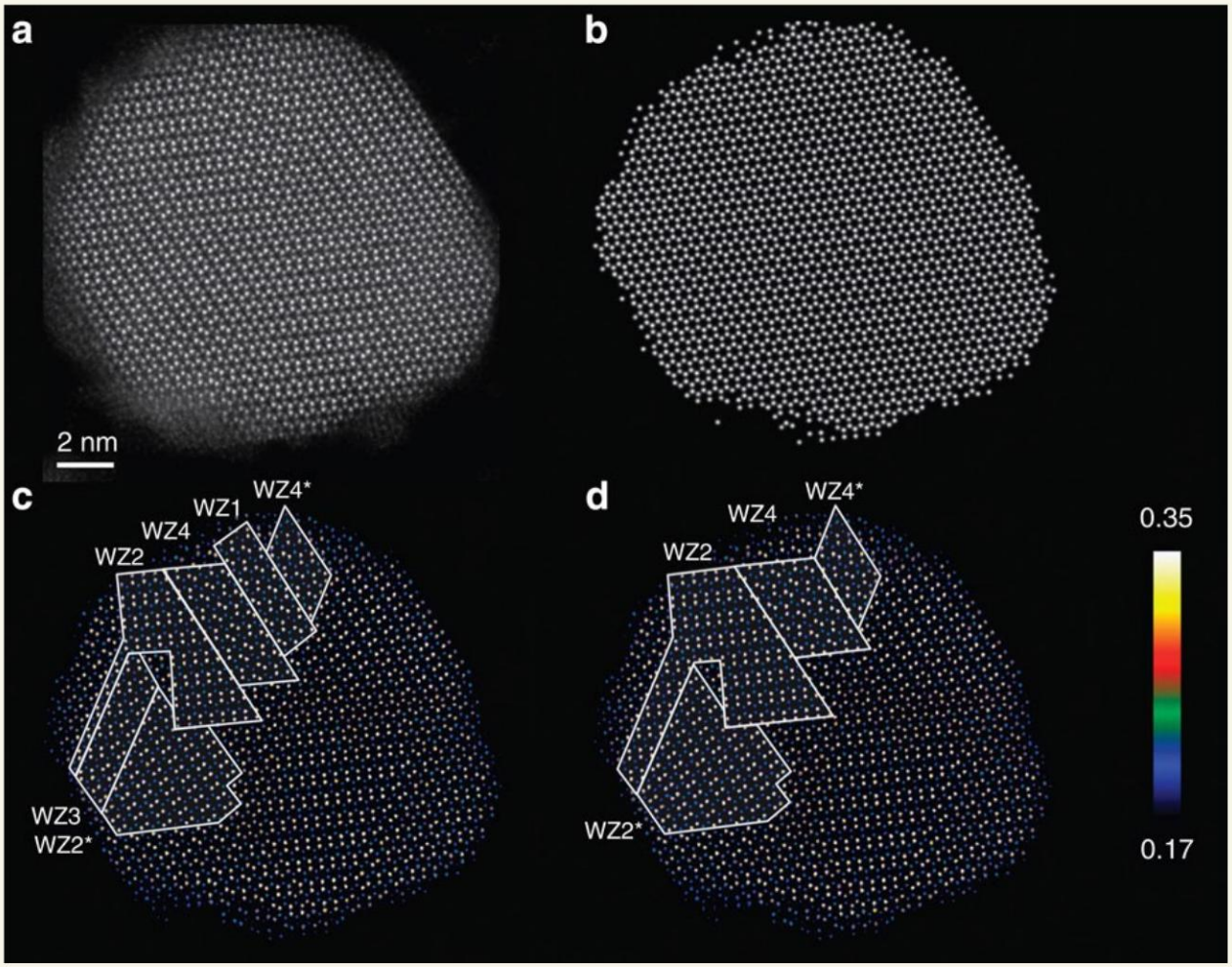
Disclaimer:
The following notes have not been fully reviewed, they could contain inaccuracies in physical arguments and may be present grammatical/ syntax english errors.
The author takes full responsibility for everything wrong that's written in this work and by no means the professor should be held accountable.

If you find any inaccuracies/typos you can send me an email to the address: angeloserrecchia.phys@gmail.com

Enjoy the reading and enjoy physics!

Angelo Serrecchia

Cap. 1
BRAVAIS LATTICES



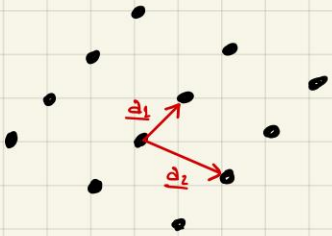
Ricevimento
Stanza 147 VEF , Mon. 14-15

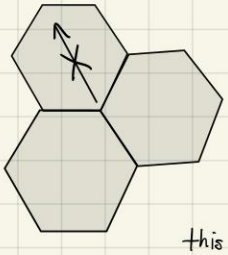
CLASSROOM CODE: CCNYN6Z

2 midterm tests : { 1st : diffraction & tight-binding ; 2nd : phonons }

BOOK: Ashcroft - Mermin

LATTICES: regular array of objects
CRYSTAL: regular array of atoms



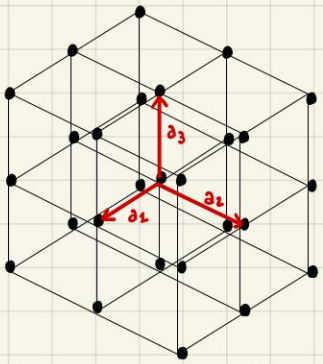


this is not a Bravais lattice

BRAVAIS LATTICE:

1) Whereever we sit we see always the same landscape
2) We can reach all the point of the lattice via:

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

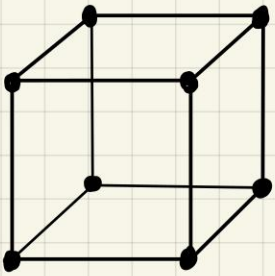


- n_1, n_2, n_3 are integers
- $\underline{a}_1, \underline{a}_2, \underline{a}_3$ live in different planes.

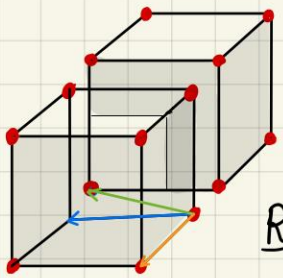
$\underline{a}_1, \underline{a}_2, \underline{a}_3$ are called **primitive vectors** of the Bravais lattice. The set of these vectors is not unique : there are ∞ nonequivalent choises.

EXAMPLES OF BRAVAIS LATTICES

Simple cubic :



Body centered cubic

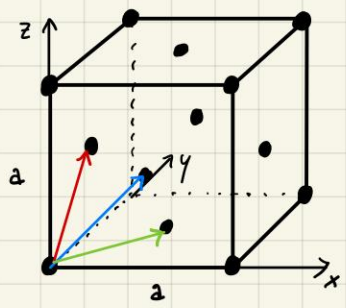


$$\begin{cases} \underline{a}_1 = a\hat{x} \\ \underline{a}_2 = a\hat{y} \\ \underline{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z}) \end{cases}$$

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

not in the same plane and integer numbers

Face centered cubic:



$$\begin{cases} \underline{a}_1 = \frac{a}{2}(\hat{y}+\hat{z}) \\ \underline{a}_2 = \frac{a}{2}(\hat{x}+\hat{z}) \\ \underline{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}) \end{cases}$$

set of 3 primitive vectors

↓

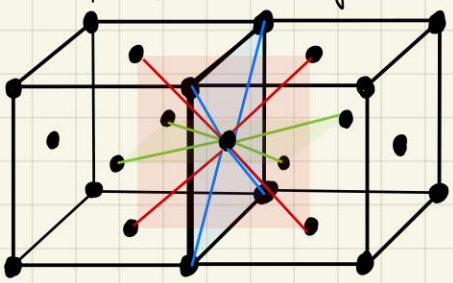
Any point can be reached by:

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

Number of nearest neighbours : (coordination number)

- body centered cubic : 8
- face centered cubic : 12
- simple cubic : 6

Example of # nearest neigbours in a FCC.



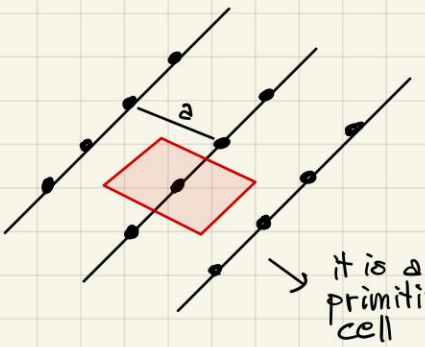
nn = 12

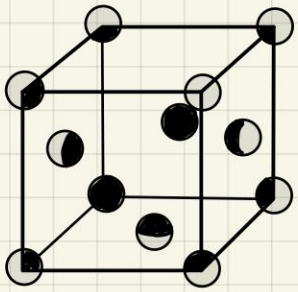
UNIT CELL : basic structure that we can replicate to fill all the bravais lattice

Example : for a simple cubic is the cube.

PRIMITIVE / ELEMENTARY UNIT CELL : a cell that contains 1 atom (it isn't unique)

Examples:

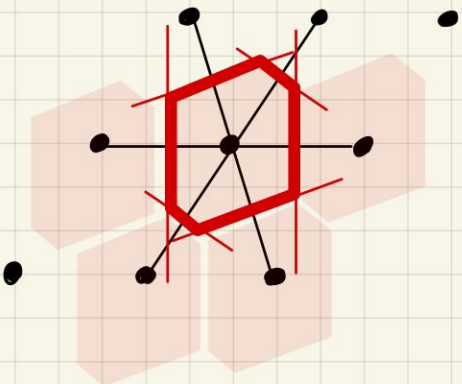




$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

→ it is not a primitive cell

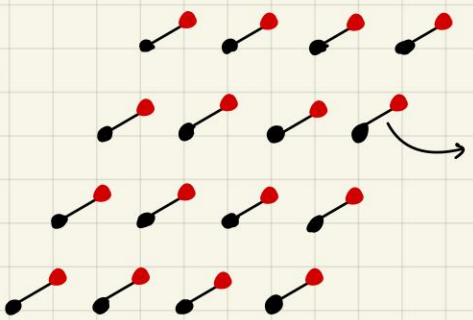
WIGNER-SEITZ PRIMITIVE CELL : this cell has the symmetry of the BL



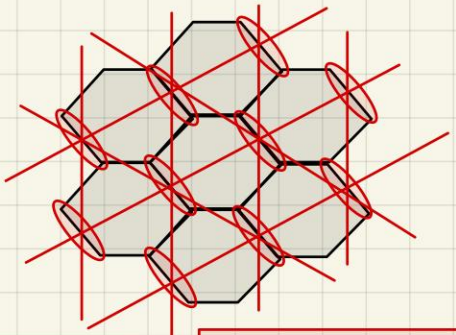
← W-S prescription to build a W-S cell.

BASIS :

Let's consider a B.L with 2 atoms : (biatomic lattice)



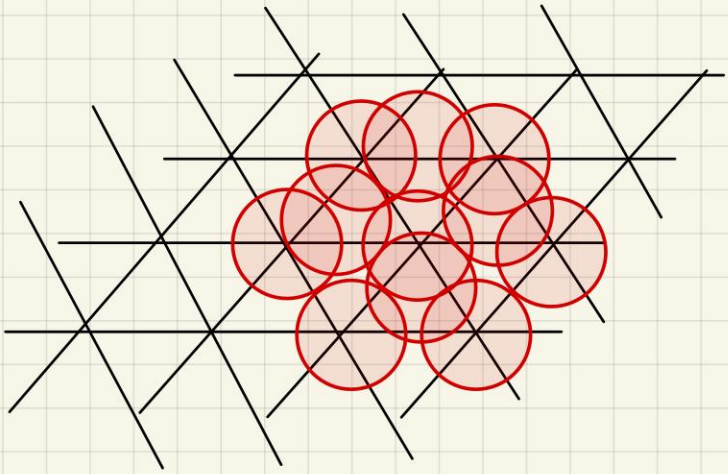
the honeycomb lattice is not a B.L.

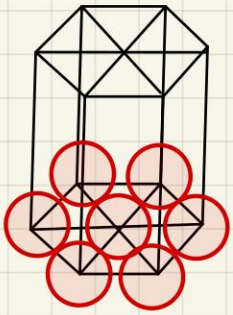


the triangular lattice is a BL →

the honeycomb lattice with a 2-points basis is a BL !

Honeycomb closed path lattice

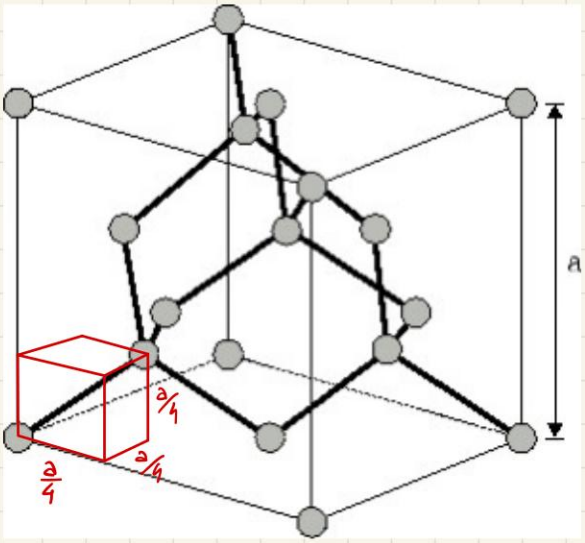




Diamond structure

FCC + basis

$$\underline{a} = \frac{a}{4}(\hat{x} + \hat{y} + \hat{z})$$

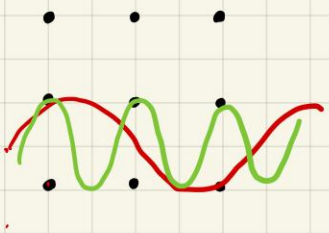


RECIPROCAL LATTICE:

Consider a set of points $\underline{R}$ constituting a B.L. Let's take a plane wave: $e^{i\underline{K}\cdot\underline{r}}$ ($\underline{K}$: plane vector).

For a generic $\underline{K}$ such plane wave will not have the periodicity of the BL:

$$\longrightarrow e^{i\underline{K}\cdot(\underline{r}+\underline{R})} \neq e^{i\underline{K}\cdot\underline{r}} \quad \text{(in general)}$$



Suppose now, we found a $\underline{K}$ such that:

$$e^{i\underline{K}(\underline{r}+\underline{R})} = e^{i\underline{K}\cdot\underline{r}} \quad \text{for all } R \in BL$$

How many $\underline{K}$ vectors enjoy this property? ∞.

The set of all wave vectors $\underline{K}$ that satisfy this condition is know as RECIPROCAL LATTICE.

$$e^{i\underline{K}\cdot(\underline{r}+\underline{R})} = e^{i\underline{K}\cdot\underline{r}} \longrightarrow \boxed{e^{i\underline{K}\cdot\underline{R}} = 1}$$

THE RECIPROCAL LATTICE IS A BRAVAIS LATTICE

Let $\underline{a}_1, \underline{a}_2, \underline{a}_3$ be a set of primitive vectors for the direct lattice.

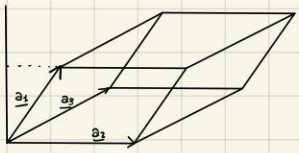
$$\longrightarrow \underline{R} = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3$$

Then the reciprocal lattice can be generated by:

$$\begin{cases} \underline{b}_1 = 2\pi \dfrac{\underline{a}_2 \times \underline{a}_3}{V} \\ \underline{b}_2 = 2\pi \dfrac{\underline{a}_3 \times \underline{a}_1}{V} \\ \underline{b}_3 = 2\pi \dfrac{\underline{a}_1 \times \underline{a}_2}{V} \end{cases}$$

- $\underline{a}_i \cdot \underline{b}_j = 2\pi\,\delta_{ij}$

$V = |\underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)|$ is the volume of the primitive cell:



→ So we can construct the reciprocal lattice via:

$$\underline{K} = k_1\underline{b}_1 + k_2\underline{b}_2 + k_3\underline{b}_3$$

$$\underline{K}\cdot\underline{R} = 2\pi(k_1n_1 + k_2n_2 + k_3n_3) \longrightarrow e^{i\underline{K}\cdot\underline{R}} = 1 \leftrightarrow \underline{K}\cdot\underline{R} = 2\pi\cdot n$$

$\longrightarrow k_1n_1 + k_2n_2 + k_3n_3 = n$ (integer) $\longrightarrow k_1, k_2, k_3$ are integers

$\longrightarrow$ the reciprocal lattice is a Bravais Lattice with $\underline{b}_i$ as primitive vectors.

Examples:

- The reciprocal lattice of a simple cubic is a simple cubic.
- The reciprocal lattice of a BCC is a FCC.
- The reciprocal lattice of a FCC is a BCC.

THE RECIPROCAL OF THE RECIPROCAL LATTICE

The reciprocal of the reciprocal lattice is the set of all vectors G satisfying:

$$e^{i\,\underline{G}\cdot\underline{K}} = 1 \qquad \forall\, \underline{K} \text{ in the reciprocal lattice}$$

Since any direct lattice vectors has this property $e^{i\,\underline{K}\cdot\underline{R}} = 1$

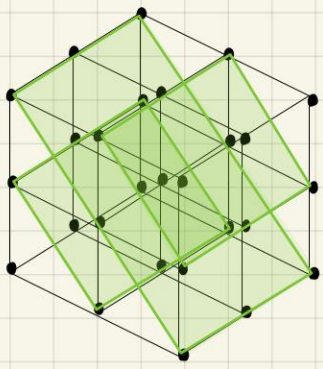
$$\rightarrow e^{i\,\underline{G}\cdot\underline{K}} = e^{i\,\underline{K}\cdot\underline{R}} \longrightarrow \boxed{\underline{G} = \underline{R}}$$

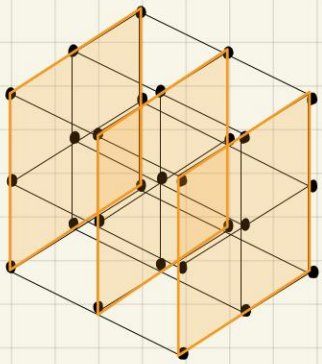
So the reciprocal of the reciprocal lattice is the original B.L.

LATTICE PLANES

Given a B.L. a lattice plane is defined to be any plane containing at least 3 non collinear Bravais lattice points. Because of the translational symmetry of the BL, any such plane will actually contain ∞ lattice points.

So another way to view a BL is to think it as composed by a family of lattice planes parallel and equally spaced. that fill all the space. There exist an ∞ number of families. Here some examples:





The reciprocal lattice provides a way to classify all possible families of lattice planes.

Theorem: For any family of lattice planes separated by a distance d there are ∞ reciprocal lattice vectors $\perp$ to the planes, the shortest of which has a lenght of $\frac{2\pi}{d}$ (In general we have $|K| = \frac{n\,2\pi}{d}$)

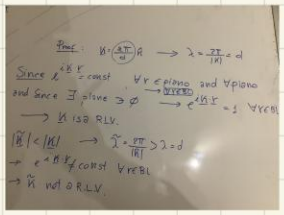
Proof:

$\rightarrow$ • Let $\hat{n}$ be a unit vector normal to the planes. Let's take $\vec{K} = \frac{2\pi\hat{n}}{d}$ Since $e^{i\vec{K}\cdot\vec{r}} = \text{const}$ in planes $\perp \vec{K}$ and has the same value in planes separated by $\lambda = \frac{2\pi}{K} = d$, and since one plane contains the B.L

point $r=0$, $e^{iK\cdot r}=1$ $\forall r=R\in BL$ $\longrightarrow$ K is a reciprocal lattice vector.

K is moreover the shortest reciprocal lattice vector. Infact for any $|\tilde{K}|<|K|$ will give a wavelenght $\tilde{\lambda}>\frac{2\pi}{K}=d$. Such a plane wave cannot satisfy $e^{i\tilde{K}\cdot r}=cost$ $\forall \underline{r}=\underline{R}\in BL$ $\longrightarrow$ $e^{i\underline{K}\cdot\underline{r}}\neq^{K}1$ $\forall \underline{r}=\underline{R}\in BL$ $\longrightarrow$ $\tilde{K}$ is not a reciprocal lattice vector

← Ashcroft (pag 113)



MILLER INDICES (h,K,ℓ)

The Miller-indices of a lattice plane are the coordinates of the shortest reciprocal lattice vector normal to that plane (with respect to a specified set of primitive reciprocal lattice vectors.)

$$\longrightarrow \quad \underline{K}=h\underline{b_1}+K\underline{b_2}+\ell\underline{b_3} \qquad |K|=\frac{2\pi}{d}$$

The condition such that this is the shortest is that h,K,ℓ cannot have common factor (coprime).

(h,K,ℓ) have a geometrical interpretation in the direct lattice. $\longrightarrow$ useful to identify directions

Let's consider the plane $\underline{K}\cdot\underline{r}=A$. It intersect the axes in $x_i\underline{a_i}$, where x_i is determined by the condition:

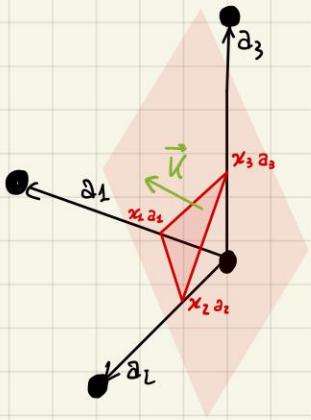
$$\underline{K}\cdot(x_i\underline{a_i})=A$$

$$\longrightarrow (h\underline{b_1}+K\underline{b_2}+\ell\underline{b_3})\cdot x_1\underline{a_1}=A \quad\longrightarrow\quad 2\pi h x_1=A$$

$$(h\underline{b_1}+K\underline{b_2}+\ell\underline{b_3})\cdot x_2\underline{a_2}=A \quad\longrightarrow\quad 2\pi K x_2=A$$

$$(h\underline{b_1}+K\underline{b_2}+\ell\underline{b_3})\cdot x_3\underline{a_3}=A \quad\longrightarrow\quad 2\pi \ell x_3=A$$

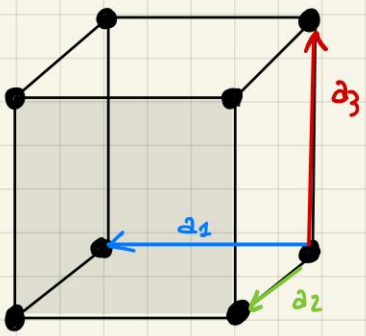
$$\longrightarrow x_1=\frac{A}{2\pi h}\ ;\ x_2=\frac{A}{2\pi K}\ ;\ x_3=\frac{A}{2\pi\ell}$$



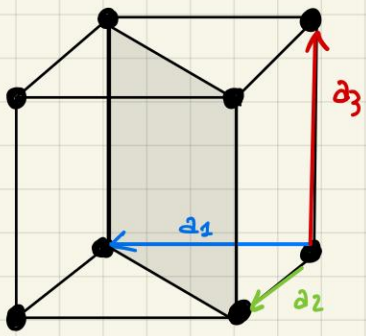
The shaded plane can be a portion of the plane in which the points of the lattice plane lie or any plane parallel to the lattice plane.

$$h:K:\ell=\frac{1}{x_1}:\frac{1}{x_2}:\frac{1}{x_3} \qquad \text{eg.} \quad \frac{h}{K}=\frac{x_2}{x_1}\ ;\ \frac{h}{\ell}=\frac{x_3}{x_1}$$

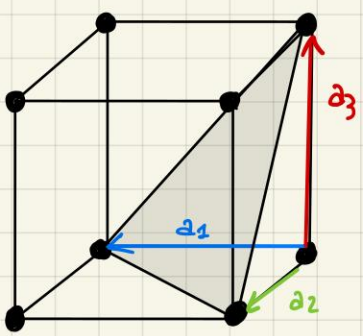
Example: cubic lattice



Il piano è ⊥ a a_1 e a_3 → (0,1,0)



(1,1,0)



(1,1,1)

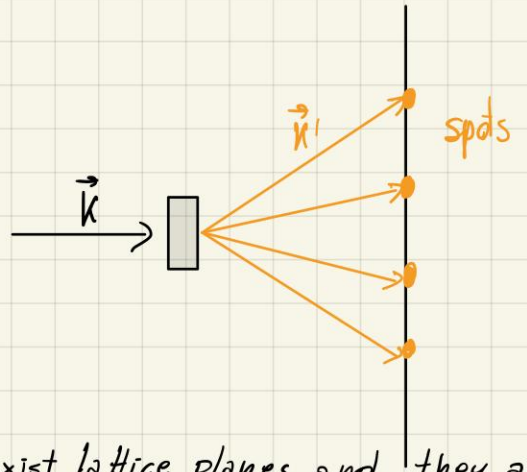
DETERMINATION OF CRYSTAL STRUCTURE BY X-RAYS SCATTERING

Why X-rays? Typical distances in a crystal are $\sim 10^{-10}\,m = 1\,\text{Å}$

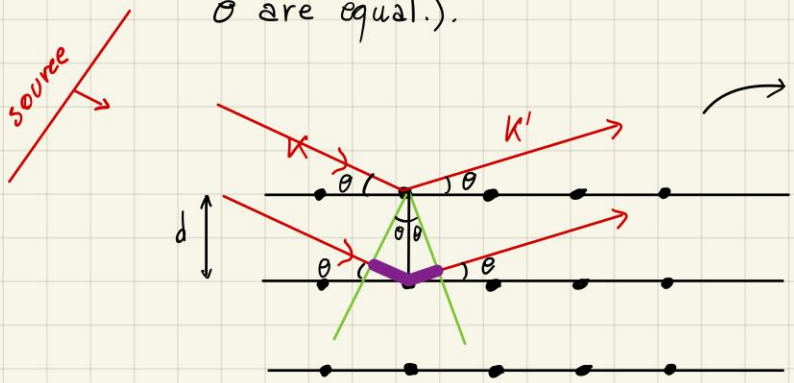
$\rightarrow \lambda_{rad} = 1\,\text{Å} \qquad \hbar\omega = \frac{c}{\lambda}h = \frac{hc}{10^{-10}\,m} \simeq 12{,}3 \cdot 10^3\,eV \rightarrow$ X-rays

BRAGG - THEORY

In 1913 Bragg found that crystals gave characteristic patterns of reflected X-radiation., for certain defined wavelenghts and incident directions, formed by intense peaks.



Assumption : there exist lattice planes and they act as perfect mirror (the angles θ are equal.).

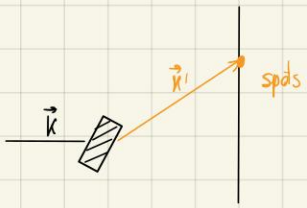


→ these 2 rays can interfer in a costructive or destructive manner depending on the path difference. $= 2d\sin\theta$

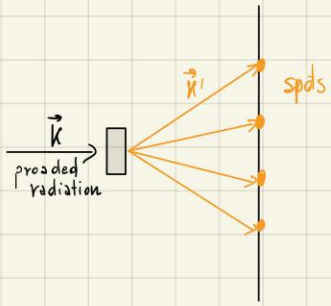
To interfere costructively this path difference must be an integer number of wavelenghts

$$2d\sin\theta = n\lambda$$

So rotating the apparatus we find for $\theta_n = \arcsin\left(\frac{n\lambda}{2d}\right)$ the associate spot.



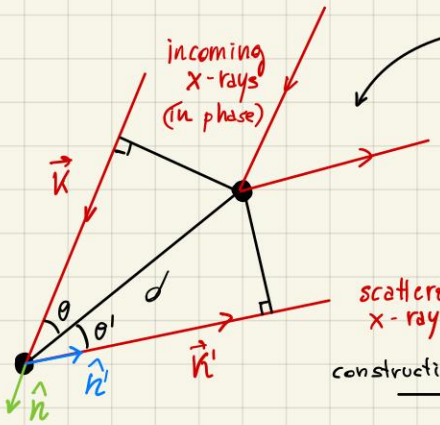
For a "white radiation" we can see many different spots.



VON - LAUE - THEORY

$$\begin{cases} \vec{K} = \frac{2\pi}{\lambda}\hat{n} \\ \vec{K}' = \frac{2\pi}{\lambda}\hat{n}' \end{cases}$$

it does not require any particular plane



$$d\cos\theta + d\cos\theta' = \vec{d}\cdot(\hat{n}-\hat{n}')$$

$$\frac{2\pi}{\lambda}(d\cos\theta + d\cos\theta') = \frac{2\pi}{\lambda}\vec{d}\cdot(\hat{n}-\hat{n}')$$

$$\frac{2\pi}{\lambda}(d\cos\theta + d\cos\theta') = \vec{d}\cdot(\vec{K}-\vec{K}')$$

constructive int. ⟶ $\frac{2\pi}{\lambda}(m\lambda) = \vec{d}\cdot(\vec{K}-\vec{K}')$

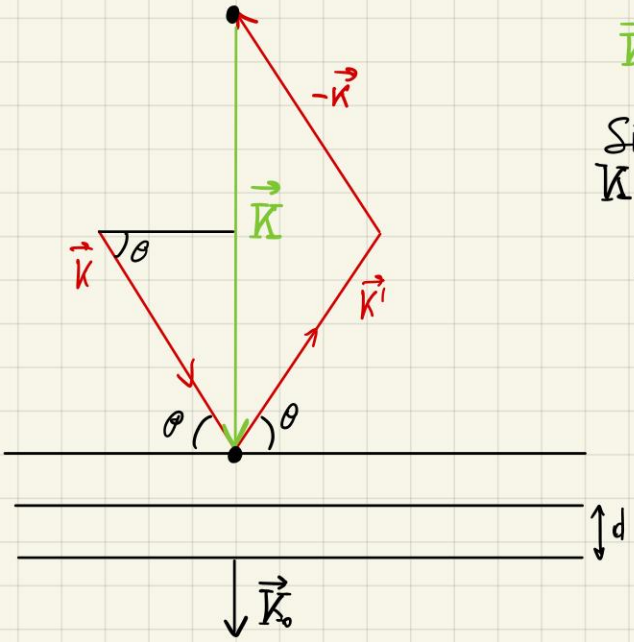
We observe that $\vec{d}$ is a generic vector of my B.L. So we can write:

$$\vec{R}\cdot(\vec{K}-\vec{K}') = 2\pi m$$

$\Longrightarrow$ $\vec{K}-\vec{K}'$ is a reciprocal lattice vector (since satisfy $e^{i(\vec{K}-\vec{K}')\cdot\vec{R}} = 1$

The Von Laue condition for constructive int. is then: $\boxed{\Delta\vec{K} = (\vec{K}-\vec{K}') = \vec{K}}$

Let's show that BRAGG'S THEORY ≡ VON LAUE THEORY



$$\vec{K} = \vec{K}-\vec{K}'$$

Since K_0 is the shortest vector K has to be a multiple of K_0

$$\vec{K} = n\vec{K}_0 \longrightarrow |\vec{K}| = n|\vec{K}_0| = n\frac{2\pi}{d}$$

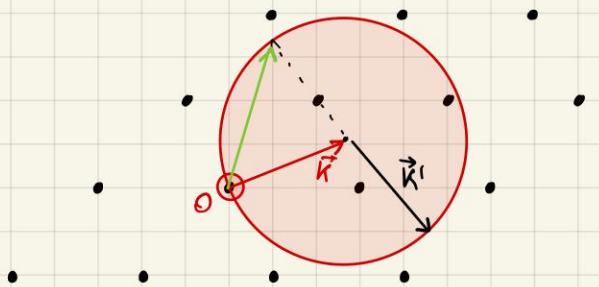
$$2|\vec{K}|\sin\theta = \frac{2\pi n}{d}$$

$$\frac{2\pi}{\lambda}\sin\theta = \frac{\pi n}{d}$$

$\longrightarrow$ $\boxed{2d\sin\theta = n\lambda}$ ✓

How can experimentally exploit all of this?

Let's take a R.L.:

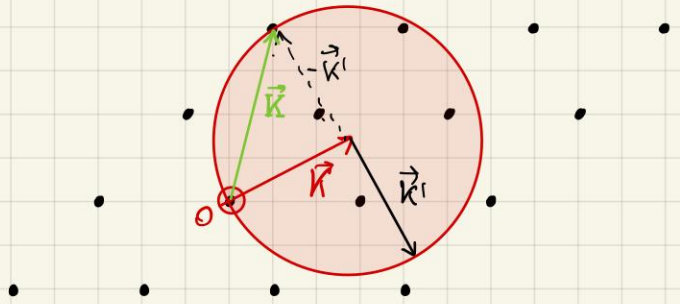


incoming x-ray ↓ outcoming x-ray ↓

Von-Laue: $(\vec{K}-\vec{K}') = K$

However I choose K', there is no point that satisfies the condition (since there are no points of the R.L. on the circle)

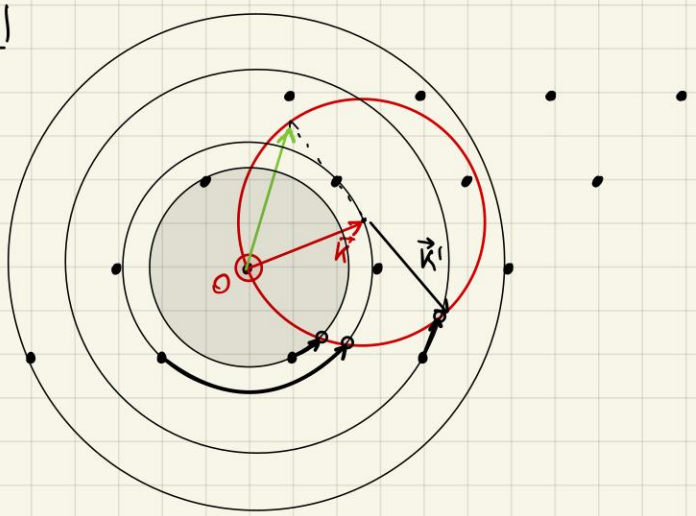
If there's a point of R.L. on the circle I can satisfy the condition



This means that the Von Laue condition is not always satisfy!

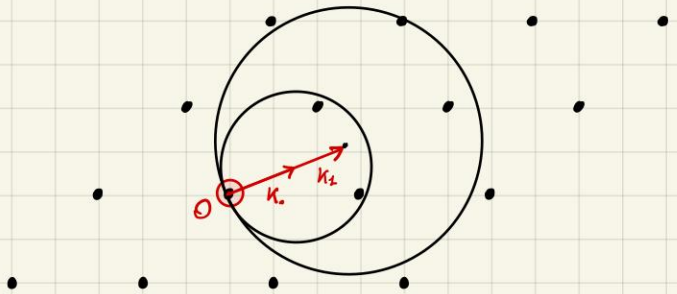
SOLUTION:

1. Rotate the crystal



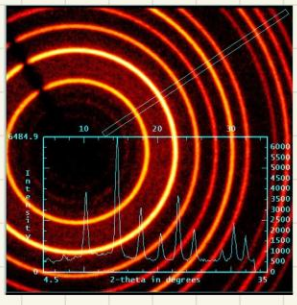
2. USING "WHITE" RADIATION

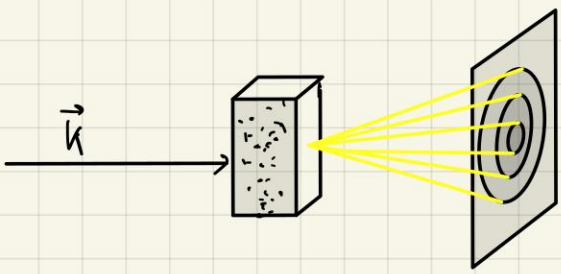
- $\lambda = \frac{2\pi}{|K|}$. If I have $\Delta\lambda \rightarrow \Delta K \rightarrow$ there is a set of circles



3. POWDER METHOD

Forming a powder of micro-crystals → all oriented in all possible directions

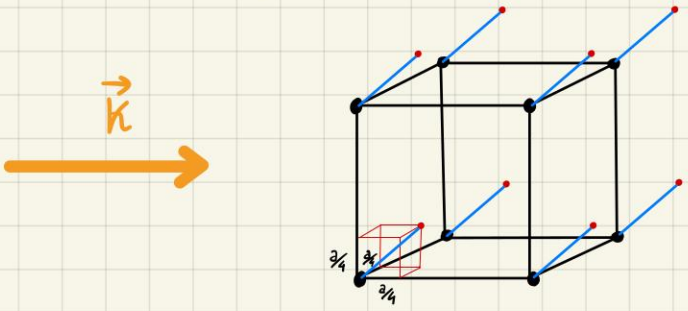




each micro-crystal oriented in a specific way contributes on a certain circle. From the distance between each circle we infer the structure of the BL.

STRUCTURE FACTOR

Let's consider the following biatomic crystal



$$d_1 = (0,0,0)$$

$$d_2 = \left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$$

Let's irradiate now this crystal with x-ray. The X-ray which comes is scattered by both atoms! (not only 1 atom) and I should keep this into account.
The answer of this kind of problem is given by the so called structure factor of the entire crystal.
The radiation scattered will come with a phase which depends on the different path between atom 1 and atom 2. The different path dypends on the distance between the 2 atoms and this structure factor is given by:

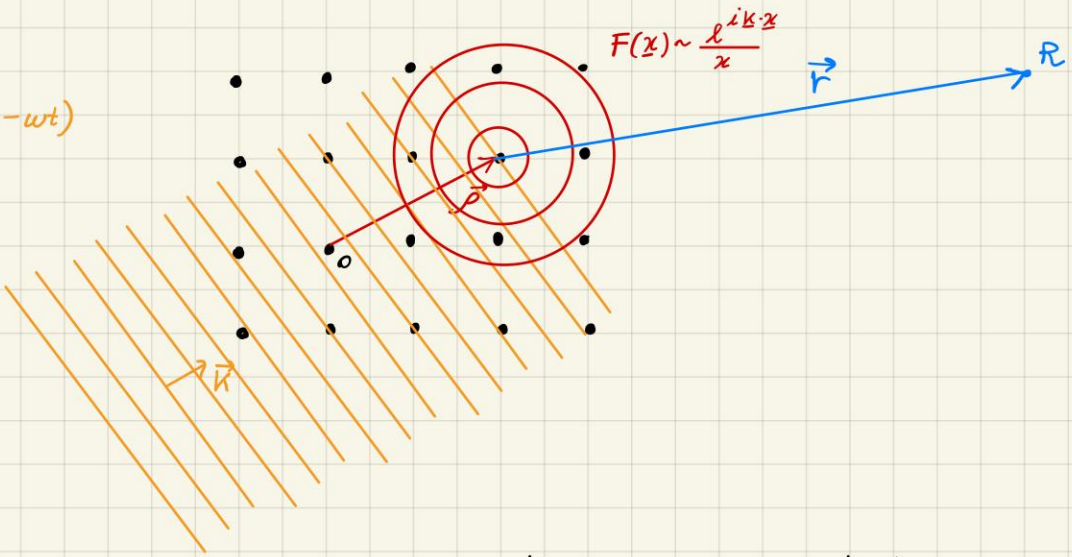
$$S = \sum_{j=1}^{2} e^{i \underline{K} \cdot d_j} = \left[1 - e^{i \underline{K} \cdot \underline{d}_2}\right]$$

So the structure factor is a modulation of the amplitude due to the interference (superposition) of the X-rays scattered from atom 1 and 2.

Another way to calculate the Von-Laue condition

Let's take a B.L. Consider 1 atom which I take as my origin, and I call ρ all the BL vectors which from O go into all the points of my BL. Consider a x-ray plane wave incidents to this BL. with a wave vector $\underline{K}$.

$$F(\underline{x}) = F_0 e^{i(\underline{K} \cdot \underline{x} - \omega t)}$$

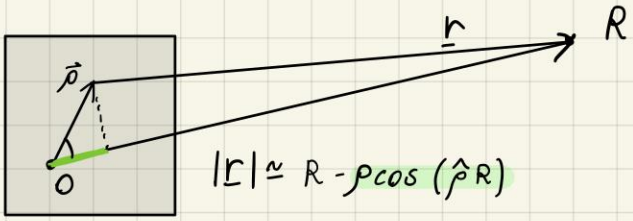


Let's call with $\underline{r}$ the vector which connects the atom in $\underline{\rho}$ to the position in R where I measure the scattered radiation.
The radiation which arrives in $\vec{\rho}$, it arrives with a phase given by $e^{i \underline{K} \cdot \underline{\rho}}$. Because when the radiation arrives in O. has to go on by this amount of phase in order to inpinch the atom in ρ
The scattered radiation is a spherical wave. So in R the intensity of the radiation is given by

$$I(R) = F_0 e^{i \underline{K} \cdot \underline{\rho}} \cdot \frac{e^{i \underline{K} \cdot \underline{r}}}{r}$$

↑ incoming plane wave ↑ outcoming plane wave

Now we observe that, if $|\underline{r}| \gg$ typical distances of the crystal



So the radiation in R can be approximated as:

$$I(R) \simeq \frac{F_0}{R}\, e^{i\left(\underline{K}\cdot\underline{\rho} + K\left(R - \rho\cos\left(\hat{\rho R}\right)\right)\right)}$$

Now in order to get the **total amplitude** we should integrate on all the volume of the crystal.

$$I_{tot} = \frac{e^{iKR}}{R}\int_V dV \cdot n(\rho) \cdot e^{i\left(\underline{K}\cdot\underline{\rho} - K\rho\cos\left(\hat{\rho R}\right)\right)}$$

($n(\rho)$: density of atoms in ρ; $\underline{K}$: 'K' in the direction of ρ; K: 'K' in the direction of ρ)

$$= \frac{e^{iKR}}{R}\int_V dV \cdot n(\rho) \cdot e^{i\left(\underline{K}-\underline{K}'\right)\cdot\underline{\rho}}$$

However our crystal are not infinitesimaly homogeneos $\longrightarrow \int \to \sum$

$$\longrightarrow I_{tot} \propto \sum_{\rho \in BL} e^{i\left(\underline{K}-\underline{K}'\right)\cdot\underline{\rho}} \qquad \text{where } \rho = m\underline{a}_1 + n\underline{a}_2 + p\underline{a}_3 \quad (n,m,p \in \mathbb{Z})$$

$$= \sum_{m,n,p} e^{-i\,\Delta\underline{K}\cdot\left(m\underline{a}_1 + n\underline{a}_2 + p\underline{a}_3\right)} \qquad \left(\text{we are going to see that } \Delta\underline{K} \text{ is a RL vector}\right)$$

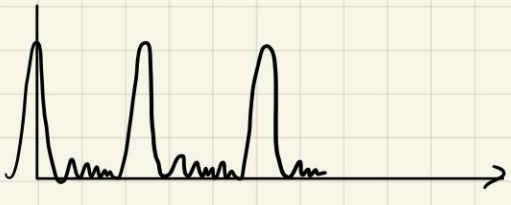
$$= \left(\sum_m e^{-i\,\Delta\underline{K}\cdot\underline{a}_1}\right)^m \cdot \left(\sum_n e^{-i\,\Delta\underline{K}\cdot\underline{a}_2}\right)^n \cdot \left(\sum_p e^{-i\,\Delta\underline{K}\cdot\underline{a}_3}\right)^p$$

Each one of these three pieces can be written as:

$$\left(\sum_{m=0}^{M-1} e^{-i\,\Delta\underline{K}\cdot\underline{a}_1}\right)^m = \frac{1 - e^{-i\,\Delta\underline{K}\cdot\underline{a}_1 M}}{1 - e^{-i\,\Delta\underline{K}\cdot\underline{a}_1}} = \frac{e^{-i\frac{M}{2}\underline{a}_1\cdot\Delta\underline{K}}}{e^{-i\frac{1}{2}\left(\underline{a}_1\cdot\Delta\underline{K}\right)}}\left(\frac{e^{i\frac{M}{2}\underline{a}_1\cdot\Delta\underline{K}} - e^{-i\frac{M}{2}\underline{a}_1\cdot\Delta\underline{K}}}{e^{i\frac{1}{2}\underline{a}_1\cdot\Delta\underline{K}} - e^{-i\frac{1}{2}\underline{a}_1\cdot\Delta\underline{K}}}\right)$$

$$= \frac{e^{-i\frac{M}{2}\underline{a}_1\cdot\Delta\underline{K}}}{e^{-i\frac{1}{2}\left(\underline{a}_1\cdot\Delta\underline{K}\right)}}\left(\frac{\sin\left(\frac{M}{2}\cdot\underline{a}_1\cdot\Delta\underline{K}\right)}{\sin\left(\frac{1}{2}\cdot\underline{a}_1\cdot\Delta\underline{K}\right)}\right)$$

$$\longrightarrow A^2 \sim \frac{\sin^2\left(\frac{M}{2}\cdot\underline{a}_1\cdot\Delta\underline{K}\right)}{\sin^2\left(\frac{1}{2}\cdot\underline{a}_1\cdot\Delta\underline{K}\right)} \xrightarrow{\text{plot}}$$



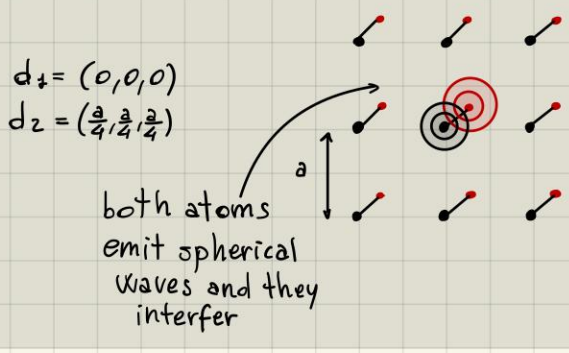
The peaks $(I = M^2)$ correspond to the conditions:

$$\begin{cases} \underline{a}_1 \cdot \Delta\underline{K} = 2\pi q \\ \underline{a}_2 \cdot \Delta\underline{K} = 2\pi \ell \\ \underline{a}_3 \cdot \Delta\underline{K} = 2\pi s \end{cases} \longrightarrow \Delta\underline{K} = q\underline{b}_1 + \ell\underline{b}_2 + s\underline{b}_3 \longrightarrow \Delta\underline{K} \text{ is a R.L.V.}$$

N.B. the total intensity is given by $I = M^2 \cdot M^2 \cdot M^2 = M^6$

EX: BIATOMIC CRYSTAL

Let's consider a biatomic lattice (the unit cell contains 2 atoms)



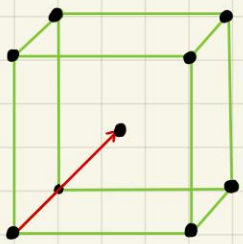
$$\longrightarrow I = \left|A \cdot \sum_{j=1}^{2} \ell^{i(\underline{K}\cdot d_j)}\right|^2 = \left|A\left(1 + \ell^{i\underline{K}\cdot d_2}\right)\right|^2 = |A|^2 |S_K|^2$$

→ the intensity is modulated by the structure factor.

EX: BCC = SC + BASIS

Let's consider a BCC treated as a SC + basis:

$d_1 = (0,0,0)$
$d_2 = (a/2, a/2, a/2)$



I can interpret the intensity of the scattered light by the BCC as the intensity of the scatterd light by a simple cubic + basis

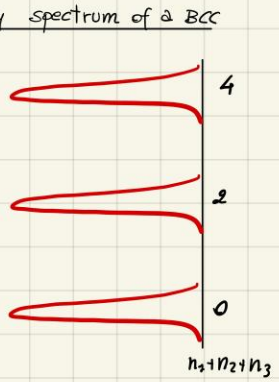
$$\longrightarrow I_{BCC} = I_{SC} \cdot |S_K|^2$$

Intensity spectrum of a SC.

$\times |S_K|^2$ →

So the S_K must cancel out the "odd" peaks and double the intensity of the "even" peaks

Intensity spectrum of a BCC



$$S_K = \sum_{j=1}^{2} \ell^{i\underline{K}\cdot d_j} = 1 + \ell^{i\frac{a}{2}\underline{K}\cdot(\hat{x}+\hat{y}+\hat{z})}$$

where K are the R.L.V. of a S.C.

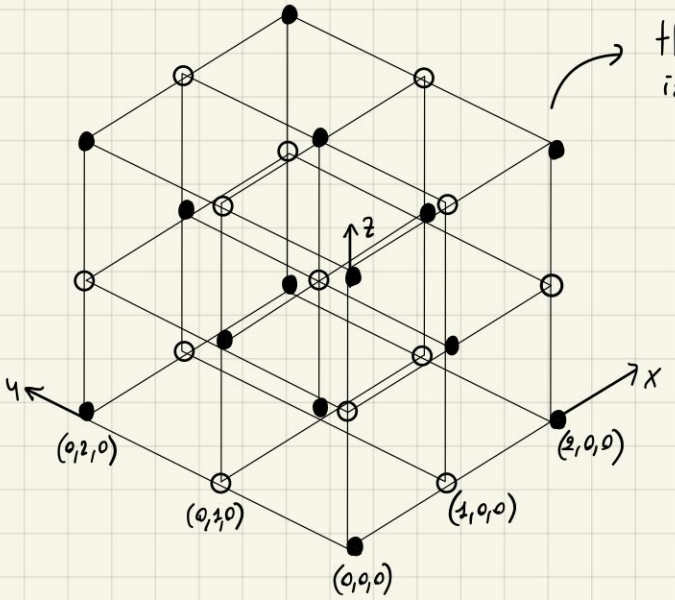
$$K_{SC} = \frac{2\pi}{a}\left(n_1\hat{x} + n_2\hat{y} + n_3\hat{z}\right)$$

$$\longrightarrow \boxed{S_K = 1 + \ell^{i\pi(n_1+n_2+n_3)}}$$

So the amplitude is given by: $A_{BCC} = A_{SC} \cdot S_K = A_{SC}\left(1 + \ell^{i\pi(n_1+n_2+n_3)}\right)$
and we notice that if:

$$\begin{cases} n_1+n_2+n_3 \text{ is even} \longrightarrow S_K = 2 & \text{(constructive interference)} \\ n_1+n_2+n_3 \text{ is odd} \longrightarrow S_K = 0 & \text{(destructive interference)} \end{cases}$$

This procedure converts the simple cubic reciprocal lattice into the face-centered cubic structure that we would have had if we had treated the body-centered cubic direct lattice as a B.L. rather than a lattice with a basis.



the points where $n_1+n_2+n_3$ is odd are invisible

↓

FACE CENTERED CUBIC

Question: suppose now to have 2 different ions: A and B

Now there is no reason to assume that the spherical plane wave intensities from A and B are the same. Infact A and B have different internal structure and then the incident x-ray has a difference response → $S_K = f_A - f_B$ ($n_1+n_2+n_3$ odd) not ϕ!

Infact in general for a polyatomic crystal:

$$\longrightarrow \quad S_K = \sum_{j=1}^{n} f_j(K)\, e^{iK\cdot d_j}$$

where f_K is the atomic form factor determined by the internal structure of the ion that occupies position d_j.

$f_j(K)$ is determined by the $\mathcal{F}(\rho_j(r))$ (Fourier transform of electronic charge distribution)

$$\longrightarrow \quad f_j(K) = -\frac{1}{e}\int d^3r\, e^{i\underline{K}\cdot\underline{r}}\,\rho_j(\underline{r})$$

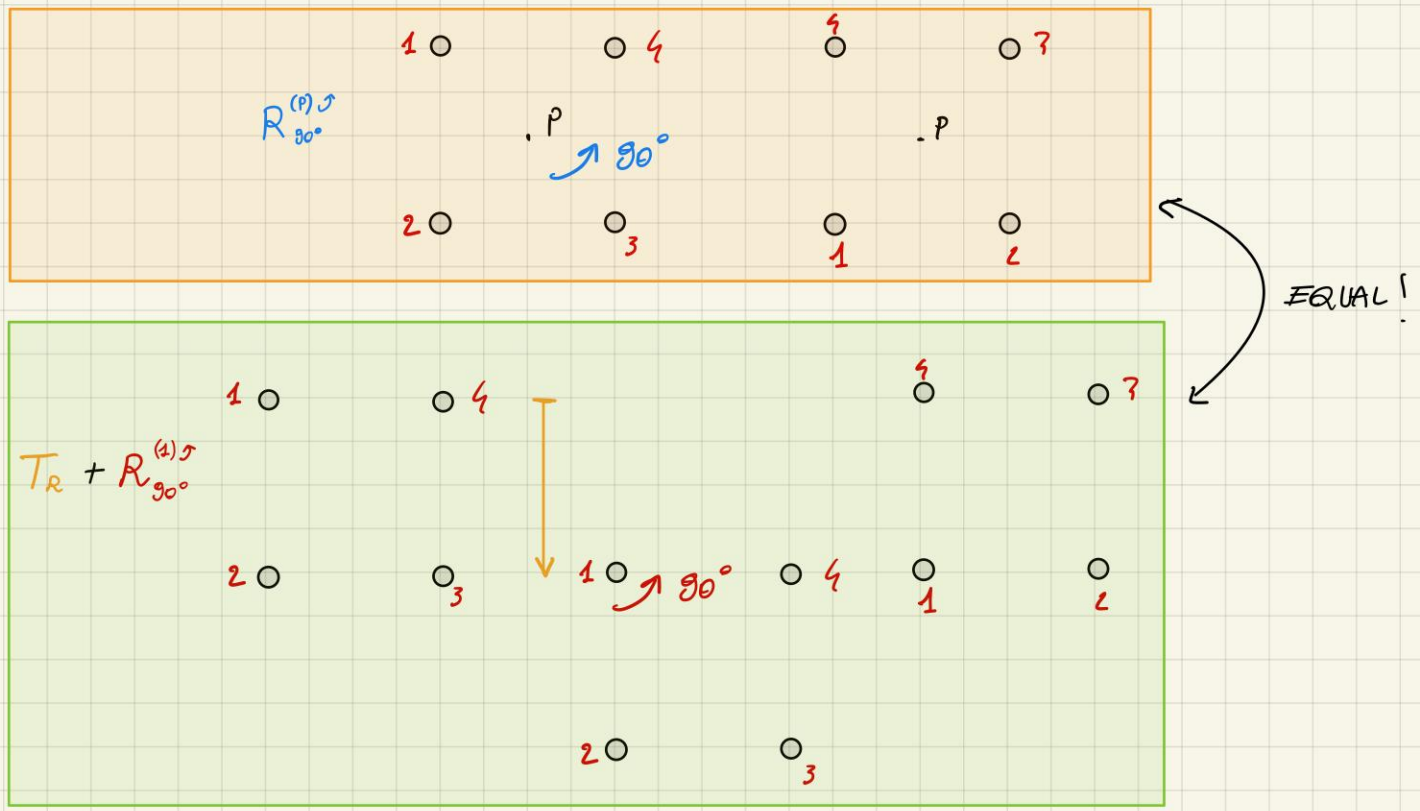
CLASSIFICATION OF BRAVAIS LATTICES AND CRYSTAL STRUCTURE

From the point of view of symmetry a BL is characterized by the specification of all rigid operations that take the lattice into itself. The set of this operations is called: **symmetry group of the BL.**

$$\text{Symm Group BL} = \{\text{translations, rotations, reflection, inversions}\}$$

Any symmetry operation of a BL can be computed as a translation T_R (trough a lattice vector R) + a rigid operation leaving at least one lattice point fixed.

Example:



$$\longrightarrow \boxed{R^{(P)}_{90°} = T_R + R^{(1)}_{90°}}$$

THE SEVEN CRYSTAL SYSTEM

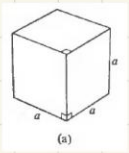
When examining non-translational symmetries one often considers *not* the entire Symm Group BL but only the operations that leave a particular point fixed.
This subset of Symm Group BL is called **point group** of the BL.
There exists only 7 distinct **point groups** that a BL can have.

⟶ Any crystal structure belongs to **one** of **seven crystal systems** depending on which of these point groups is the point group of the BL.

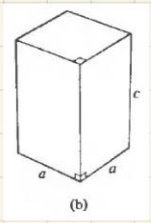
For each of the 7 point group we can identify a number of different Symm Group BL
In total it turns out that we have 14 different Symm Group BL ⟶ 14 different kinds of BLs.

Enumeration of the Seven Crystal System and Fourteen BLs.

CUBIC (3) : it contains those BL whoose point group is just the symmetry group of a cube.
3 BL with non-equivalent space groups have the cubic point group : SC, BCC, FCC.



TETRAGONAL (2): it is obtained stretching along a direction (c-axis) a SC or a BCC (we'll se BCC stretched = FCC stretched). The point roup is the tetragonal group.
Stretching a SC → simple tetragonal ; Stretching a BCC (or FCC) → centered tetragonal



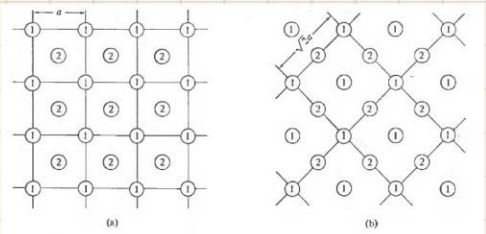
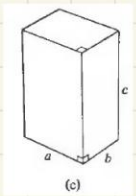
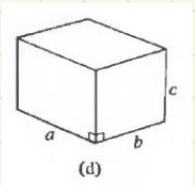


Figure 7.4
Two ways of viewing the same centered tetragonal Bravais lattice. The view is along the c-axis. The points labeled 1 lie in a lattice plane perpendicular to the c-axis, and the points labeled 2 lie in a parallel lattice plane a distance $c/2$ away. In (a) the points 1 are viewed as a simple square array, stressing that centered tetragonal is a distortion of body-centered cubic. In (b) the points 1 are viewed as a centered square array, stressing that centered tetragonal is also a distortion of face-centered cubic.

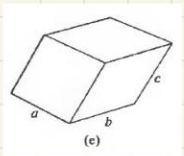
ORTHORHOMBIC (4) : it is obtained stretching a tetragonal lattice along 1 axis (simple-centered-orthorhombic) or along one set of parallel lines fig 7.4(a) (body-centered-orthorhombic) or along the set of parallel lines fig 7.4(b) (face-centered-orthorhombic) a square diagonal (base-centered orthorombic). The point group is called orthorhombic group.



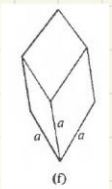
MONOCLINIC (2): it is obtained by distorting the rectangular faces, of an orthorhombic lattice, perpendicular to c-axis. into parallelograms. The point group is called monoclinic group.
Distorting a simple-orthorombic → simple monoclinic.
Distorting a face-centered or body centered orthorhombic → centered monoclinic.



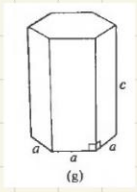
TRICLINIC (1) : it is obtained by distorting the c-axis of a monoclinic lattice is such a way it is not longer perpendicular to the faces. → creating the triclinic Bravais Lattice.



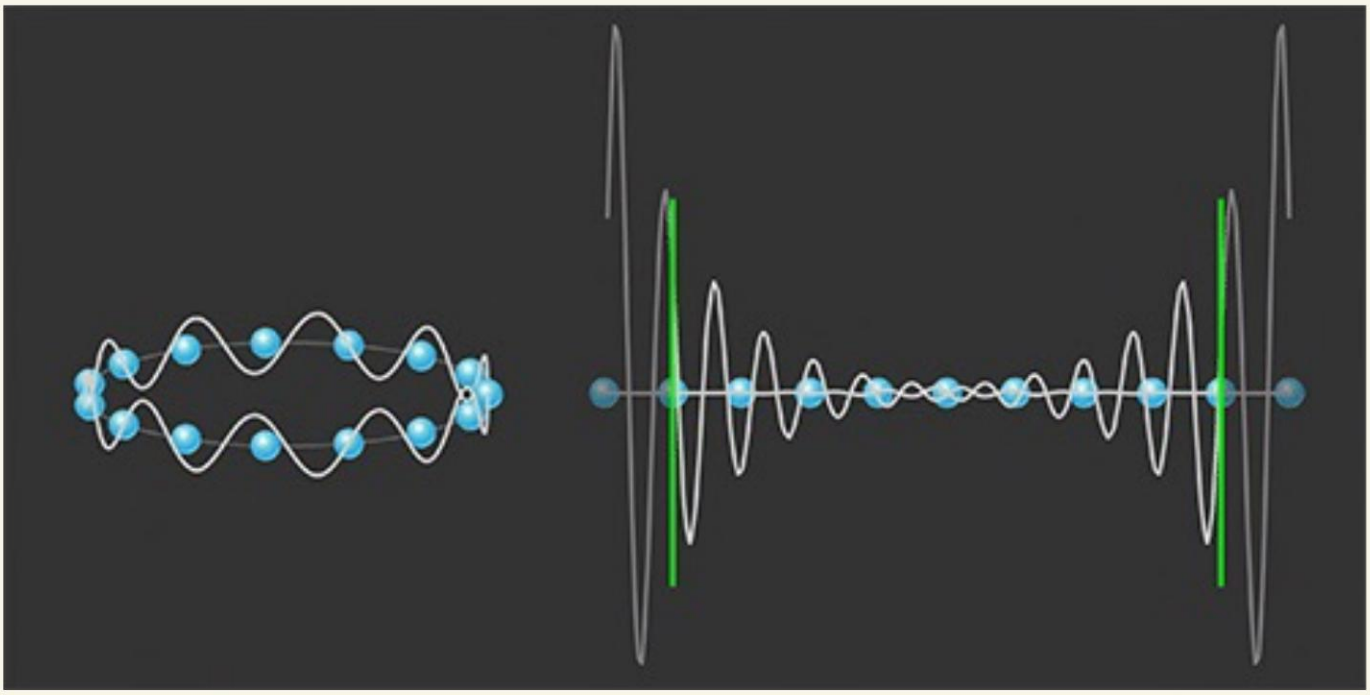
TRIGONAL (1) : the trigonal point group describes the symmetries of the object created by stretching a cube along a body diagonal → trigonal Bravais Lattice



HEXAGONAL (1) the hexagonal point group is the symmetry group of a right prism with a regular exagon as base → simple hexagonal Bravais Lattice.



Cap. 2
PROPERTIES OF ELECTRONS INSIDE A LATTICE



PROPERTY OF ELECTRONS INSIDE A LATTICE

We now that ions are sorrounded by electrons. Since the ions in a perfect crystal are arranged in a regular periodic way the electrons feel a periodic potential $U(r)$ (with the periodicity of the BL.

$$U(r+R) = U(r)$$

Of course electrons are charged objects and then they interact each other. → so we should consider also e^--e^- interaction. (very though problem : it has not symmetries)
There are various simplifications:

- Landau theory (Fermi liquids) :

  the e^--e^- interaction is important, however since they are fast, there is a sort of self screening. Then near the Fermi surface the electrons behave as free electrons.

  ↓

  this is why in the metals many internal properties (conductivity ...) are very similar to the ones deduced under the free-e^- hypothesis.

So, it is meaningfull to treat in this course electrons as non interacting objects with themselves. ⟶ not e^--e^- interaction.

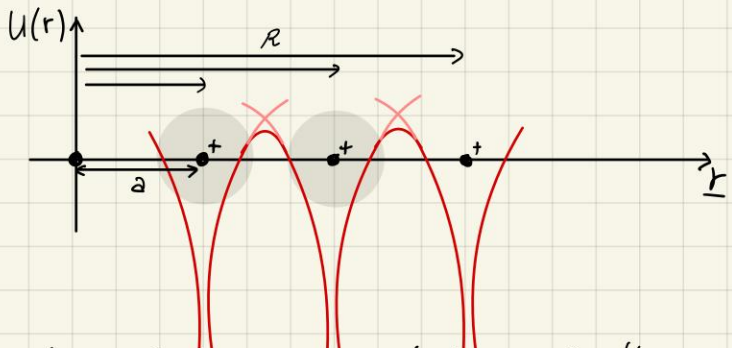
Furthermore, due to the thermal energy, the ions oscillate! So there is always a temperature-dependend probability to find misplaced ions that destroy the perfect translational symmetry ⟶ ions are not stationary but continually undergo thermal vibrations about their equilibrium positions.
(This has the consequence to the impossibility to have an ∞ conductivity of metals).

The idea is to divide the problem in 2 parts:

1) Frozen ions → the crystal is perfect
2) The deviations from perfect periodicity treated as small perturbations

THE PERIODIC POTENTIAL

Qualitatively a typical crystalline potential migh be :



The Shrödinger equation for a single electron in this potential is

$$H\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(r)\right]\psi = \varepsilon\psi$$

BLOCH'S THEOREM

Theorem: The eigenstates ψ of $\left[-\frac{\hbar^2}{2m}\nabla^2 + U(r)\right]\psi = \varepsilon\psi$, where $U(r+R) = U(r)$, for all R can be chosen to have the form of a plane wave times a function with the periodicity of the B-L.

1st relation: $\boxed{\psi_{n\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_{n\underline{k}}(r)}$ where $u_{n\underline{k}}(r+R) = u_{n\underline{k}}(r)\ \forall R \in BL$.

2nd equivalent relation: This last 2 equations imply that $\boxed{\psi_{n\underline{k}}(\underline{r}+\underline{R}) = e^{i\underline{k}\cdot\underline{R}}\,\psi_{n\underline{k}}(\underline{r})}$

FIRST PROOF: $\psi_{n\underline{k}}(\underline{r}+\underline{R}) = e^{i\underline{k}\cdot\underline{R}}\,\psi_{n\underline{k}}(\underline{r})$

$\forall R \in BL$ we can define a traslational operator T_R such that:

$$T_R f(\underline{r}) = f(\underline{r}+\underline{R}) \qquad (f \text{ any function})$$

Since H is periodic (due to $U(r) = U(r+R)$) we have:

$$T_R H\psi = H(r+R)\psi(r) = H(r)\psi(r+R) = H T_R\psi$$

$$\longrightarrow T_R H\psi = H T_R\psi \qquad \rightarrow [T_R, H] = 0$$

Moreover the result of two successive translations does not depend on the order:

$$T_R T_{R'}\psi(r) = T_{R'}T_R\psi(r) = \psi(r+R+R')$$

$$\longrightarrow T_R T_{R'} = T_{R'}T_R = T_{R+R'}$$

It's possible to check that T forms a group (abelian group). Since $[T_R, H] = 0$ the eigenstates of $\mathcal{H}$ can be chosen to be simultaneous eigenstates of all the T_R.

$$H\psi = \varepsilon\psi$$

$$T_R\psi = c(R)\psi$$

the eigenvalues $c(R)$ of T_R satisfy the following condition. Since $T_R T_{R'} = T_{R+R'}$:

$$\begin{cases} T_{R'}T_R\,\psi = c(R)\,T_{R'}\psi = c(R)c(R')\psi \\ T_{R'}T_R\,\psi = T_{R'+R}\psi = c(R+R')\psi \end{cases} \longrightarrow c(R+R') = c(R)\,c(R')$$

Now let a_i be 3 primitive vectors for the B.L. We can always write $c(\underline{a}_i)$ in the form:

$$\longrightarrow c(\underline{a}_i) = e^{2\pi i x_i} \qquad (x_i \text{ chosen})$$

If $R \in BL$: $R = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3$, then:

$$c(R) = c(a_1)^{n_1}\, c(a_2)^{n_2}\, c(a_3)^{n_3}$$

But this is equivalent to:

$$c(R) = e^{i \underline{K} \cdot \underline{R}}$$

where:

$$\underline{K} = x_1 \underline{b}_1 + x_2 \underline{b}_2 + x_3 \underline{b}_3 .$$

because:

$$c(R) = e^{2\pi i (x_1 \underline{b}_1 + x_2 \underline{b}_2 + x_3 \underline{b}_3)(n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3)} = e^{2\pi i (x_1 n_1 + x_2 n_2 + x_3 n_3)} = c(a_1)^{n_1} \cdot c(a_2)^{n_2} \cdot c(a_3)^{n_3}$$

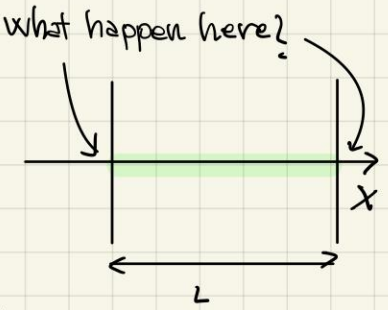
b_i are the R.L.V. (such that $\underline{b}_i \cdot \underline{a}_j = 2\pi \delta_{ij}$). So we have shown that we can choose the eigenstates ψ of H such that for every $R \in BL$

$$T_R \psi = \psi(\underline{r} + \underline{R}) = c(\underline{R}) \psi = e^{i \underline{K} \cdot \underline{R}} \psi(\underline{r})$$

□

BORN - VON KARMAN BOUNDARY CONDITION

What is K? How to determine it?



To continue we have to impose a boundary condition for the wave function. It will be not relevant to exploit the internal physical properties inside the system, it's useful to fix it only for computational purposes. The natural choice is:

PERIODIC BOUNDARY CONDITION (Born Von-Karman boundary condition)

In the Bravais lattice L is an integral multiple of the lattice constant a ⟶ so we don't work with a box of size L (as in the QM problem of an e^- inside a box) but with a box commesurable with a primitive cell. So we translate the P.B. condition to a lattice as:

$$\psi(\underline{r} + N_i \underline{a}_i) = \psi(\underline{r}) \qquad i = 1,2,3 \qquad \begin{cases} \underline{a}_i = \text{primitive vectors} \\ N_i = \text{integers} \end{cases}$$

Applying the Bloch-theorem to this boundary condition we obtain:

$$\psi_{nK}(\underline{r} + N_i \underline{a}_i) = e^{i N_i \underline{K} \cdot \underline{a}_i} \psi_{nK}(\underline{r}) \qquad i = 1,2,3,$$

which implies that:

$$e^{i N_i \underline{K} \cdot \underline{a}_i} = 1 \qquad i = 1,2,3$$

So since $K = x_1 b_1 + x_2 b_2 + x_3 b_3$ we have: $(a_i b_j = 2\pi \delta_{ij})$

$$e^{2\pi i N_i x_i} = 1 \longrightarrow x_i = \frac{m_i}{N_i} \qquad m_i \in \mathbb{Z}$$

So the general form for $\underline{K}$ is:

$$\boxed{\underline{K} = \sum_{i=1}^{3} \frac{m_i}{N_i} \underline{b}_i} \quad (*)^1$$

Observation: if there were not $N_i \to k$ was a R.L.V.

It follows that the volume Δk of k-space (for allowed value of $\underline{k}$) is the volume of a parallelepiped of edge b_i/N_i:

$$\underline{\underline{\Delta k}} = \frac{b_1}{N_1} \cdot \left(\frac{b_2}{N_2} \times \frac{b_3}{N_3} \right)$$

(volume of the Brillouin zone; # tot of unit cells to form my macro crystal $\to N$)

However the volume of the B.Z is:

$$V(B.Z.) = \frac{2\pi}{v} = \frac{2\pi}{V/N}$$

(v: volume of the unit cell (Wigner Seiz cell))

$$\longrightarrow \underline{\underline{\Delta k}} = \frac{2\pi}{V/N} \cdot \frac{1}{N} = \frac{2\pi}{V}$$

SECOND PROOF OF THE BLOCH THEOREM

We start saying that every function can be expanded obeying the Born-von Karman condition in the set of all plane waves that satisfy the boundary condition and hence with a wave vector q in the form $(*)^2$.

$$\psi(\underline{r}) = \sum_q e^{i\underline{q}\cdot\underline{r}} \cdot c_q$$

Because $U(\underline{r})$ is periodic in the lattice, its plane wave expansion will only contains plane waves with the periodicity of the lattice and therefore with
$\underline{q}$: reciprocal lattice vector.

$$U(\underline{r}) = \sum_K e^{i\underline{K}\cdot\underline{r}} \cdot U_K$$

where U_K are obtained by the $\mathcal{FT}$ of $U(\underline{r})$

$$U_K = \frac{1}{v} \int_{cell} d\underline{r}\, U(\underline{r})\, e^{-i\underline{K}\cdot\underline{r}}$$

Properties of U_K:

i) Since $U(r)$ is real $\quad U_{-K} = U_K^*$

ii) If the crystal is symmetric under parity $\longrightarrow \quad U_K = U_{-K} = U_K^*$

If we replace the expansions of $U(\underline{r})$ and $\psi(\underline{r})$ into the Shrödinger equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\underline{r}) \right] \psi = \varepsilon \psi$$

- $-\frac{\hbar^2}{2m}\nabla^2\psi = \sum_q \frac{\hbar^2}{2m} q^2 C_q e^{i\underline{q}\cdot\underline{r}}$

- $U(\underline{r})\psi = \left(\sum_{\underline{K}} e^{i\underline{K}\cdot\underline{r}} \cdot U_{\underline{K}}\right)\cdot\left(\sum_q e^{i\underline{q}\cdot\underline{r}} \cdot C_q\right) = \sum_{\underline{K},q} U_{\underline{K}} C_q e^{i(\underline{K}+\underline{q})\cdot\underline{r}} \overset{\underline{q}' = \underline{q}+\underline{K}}{=} \sum_{\underline{K},\underline{q}'} U_{\underline{K}} C_{\underline{q}'-\underline{K}} e^{i\underline{q}'\cdot\underline{r}}$

$$\longrightarrow \sum_q e^{i\underline{q}\cdot\underline{r}}\left[\left(\frac{\hbar^2}{2m}q^2 - \varepsilon\right)C_q + \sum_{\underline{K}} U_{\underline{K}} C_{q-\underline{K}}\right] = 0$$

Since $e^{i\underline{q}\cdot\underline{r}}$ $\forall\, q$ are linear indipendent, this expression is equal to ϕ iff:

$$\boxed{\left(\frac{\hbar^2}{2m}q^2 - \varepsilon\right)C_q + \sum_{\underline{K}} U_{\underline{K}} C_{q-\underline{K}} = 0}$$

It is convenient to write q in the form $\underline{q} = \underline{\kappa} - \underline{G}$ where $\underline{G}$ is a reciprocal lattice vector chosen so that $\underline{\kappa}$ lies in the 1st Brillouin Zone.

$$\longrightarrow \left(\frac{\hbar^2}{2m}q^2 - \varepsilon\right)C_{\underline{\kappa}-\underline{G}} + \sum_{\underline{K}} U_{\underline{K}} C_{\underline{\kappa}-\underline{K}-\underline{G}} = 0$$

If we make the change of variables $\underline{K} \longrightarrow \underline{K}-\underline{G}$

$$\longrightarrow \boxed{\left(\frac{\hbar^2}{2m}q^2 - \varepsilon\right)C_{\underline{\kappa}-\underline{G}} + \sum_{\underline{K}} U_{\underline{K}-\underline{G}} C_{\underline{\kappa}-\underline{K}} = 0} \quad (*)^1$$

This equation is just the restatement of the Shrödinger equation in momentum space.

For fixed $\underline{\kappa}$ in the 1st B.Z. the set of equations $\forall\, G$ couples the coefficients C_κ, $C_{\kappa-G_1}$, $C_{\kappa-G_2}$, ... whose wave vector differ from $\underline{\kappa}$ by a R.L.V $\underline{G}_i$.

Thus the original problem has separated into N independent problems: one for each $\underline{\kappa}$ in the 1st B.Z.
Each such problem has solution that are superpositions of plane waves containing only the wave vector $\underline{\kappa}$ and wave vectors differing from $\underline{\kappa}$ by a R.L.V.

$$\longrightarrow \psi_{\underline{\kappa}}(\underline{r}) = \sum_{\underline{G}} C_{\underline{\kappa}-\underline{G}}\, e^{i(\underline{\kappa}-\underline{G})\cdot\underline{r}}$$

but:

$$\sum_{\underline{G}} C_{\underline{\kappa}-\underline{G}}\, e^{i(\underline{\kappa}-\underline{G})\cdot\underline{r}} = e^{i\underline{\kappa}\cdot\underline{r}} \sum_{\underline{G}} C_{\underline{\kappa}-\underline{G}}\, e^{-i\underline{G}\cdot\underline{r}} \equiv e^{i\underline{\kappa}\cdot\underline{r}} \cdot u_{\underline{\kappa}}(\underline{r})$$

$$\longrightarrow \boxed{\psi_{\underline{\kappa}}(\underline{r}) = e^{i\underline{\kappa}\cdot\underline{r}} \cdot u_{\underline{\kappa}}(\underline{r})} \qquad \square$$

GENERAL REMARKS ABOUT BLOCH THEOREM

1. Bloch's theorem introduces a wave vector $\underline{K}$ which plays the same role of the $\underline{k}$ in the problem of the free electron in the Sommerfield theory. However although the free electron wave vector is simply $\underline{p}/\hbar$ where $\underline{p}$ is the momentum of the electron, in the Bloch case $\underline{K} \not\propto \underline{p}$.
This is due to the fact that H does not have a complete translational invariance in the presence of a non constant potential and therefore its eigenstates will be not simultaneus eigenstates of the momentum operator. $\underline{p} = -i\hbar\underline{\nabla}$. Infact:

$$-i\hbar\underline{\nabla}\psi_{n,\underline{K}} = -i\hbar\underline{\nabla}\left(e^{i\underline{K}\cdot\underline{r}}u_{n,\underline{K}}(\underline{r})\right) = \hbar\underline{K}\psi_{n\underline{K}} - i\hbar e^{i\underline{K}\cdot\underline{r}}\underline{\nabla}u_{n,\underline{K}}(\underline{r})$$

$\longrightarrow$ $\psi_{n,K}$ is not an eigenstate of $\underline{p}$.

Neverthless, $\hbar K$ is Know as crystal momentum of the electron, to enphasize similarity. An intuitive understanding of $\underline{K}$ will come when we'll consider the response of Bloch electrons to externally applied EM fields.

2.1) Let's take a Bloch-wave: $\psi(\underline{r}) = e^{i\underline{K}\cdot\underline{r}}u_{\underline{K}}(\underline{r})$ where $\underline{K}$ is fixed. Substituting $\psi(\underline{r})$ in the Shrödinger equation we find the equation for $u_{\underline{K}}(\underline{r})$

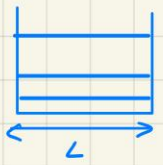
$$H_K u_K(\underline{r}) = \varepsilon_u u_K(\underline{r})$$

$$\boxed{\left[\frac{\hbar^2}{2m}\left(-i\underline{\nabla} + \underline{K}\right)^2 + U(\underline{r})\right]u_{\underline{K}} = \varepsilon_K u_K}$$

with the constrain given by the P.B.C.:

$$\boxed{u_K(\underline{r}) = u_K(\underline{r} + \underline{R})}$$

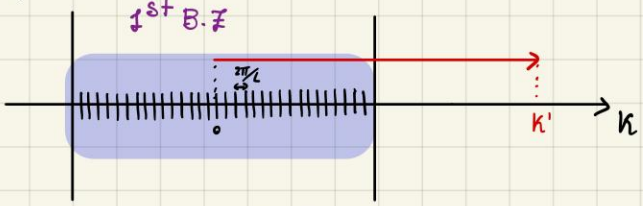
Because of the P.B.C. we can think this as an eigenvalue problem restricted to a single primitive cell of the crystal. Since this problem is set in a fixed finite volume we expect to find an infinite family of solutions with discretely spaced eigenvalues $\varepsilon_n(K)$. As in the problem of the free particle in a box.



$K = \frac{2\pi}{L}n$

$\rightarrow \varepsilon_n \sim n^2$

2.2) Let's go in the momentum space:



$\longrightarrow$ Any K' can be rewritten as $\underline{K}' = \underline{K} + \underline{G}$

$$\longrightarrow \psi_{nK'}(\underline{r}+\underline{R}) = e^{i\underline{K}'\underline{R}}\psi_{nK'}(\underline{r})$$

$$= e^{i\underline{K}\cdot\underline{R}}e^{i\underline{G}\cdot\underline{R}}\psi_{nK'}(\underline{r}) =$$

$$= 1 \text{ by definition of R.L.V.}$$

$$= e^{i\underline{K}\cdot\underline{R}}\,\psi_{nK'}(\underline{r}) =$$
$$= e^{i\underline{K}\cdot\underline{R}}\,\psi_{nK'}(\underline{r}+\underline{R})$$

$$\rightarrow \boxed{\psi_{nK'}(\underline{r}+\underline{R}) = e^{i\underline{K}\cdot\underline{R}}\,\psi_{nK'}(\underline{r}+\underline{R})}$$

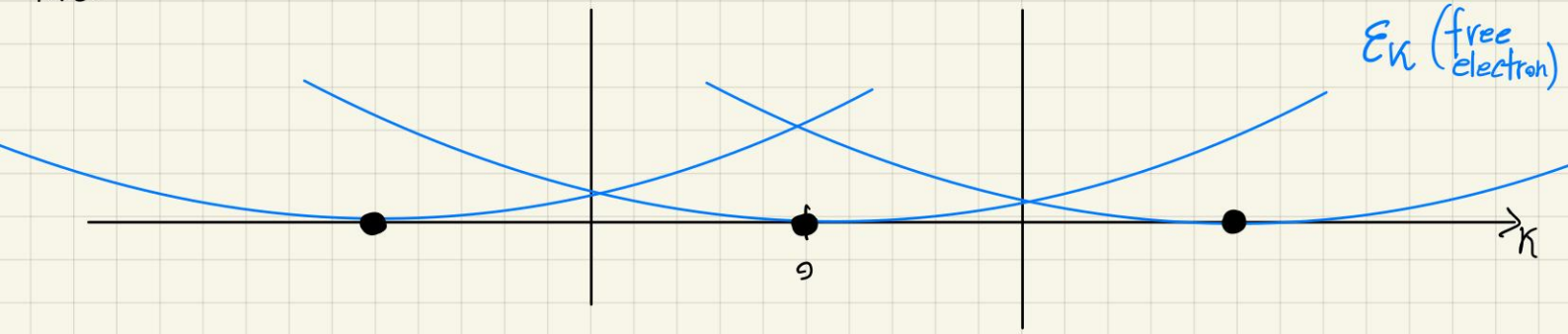
Reformulation of the Bloch theorem for $\psi_{nK'}$

This means that: $\boxed{\psi_{nK} = \psi_{nK'}}$: the info stored in the 1st BZ is equal the info in any other BZ.

And this means that if I translate all by a RLV : $\underline{G}$ nothing changes in (*)²

$$\rightarrow \begin{cases} \psi_{nK}(\underline{r}) = \psi_{n(K+G)}(\underline{r}) \\ \mathcal{E}_n(K) = \mathcal{E}_n(K+G) \end{cases}$$

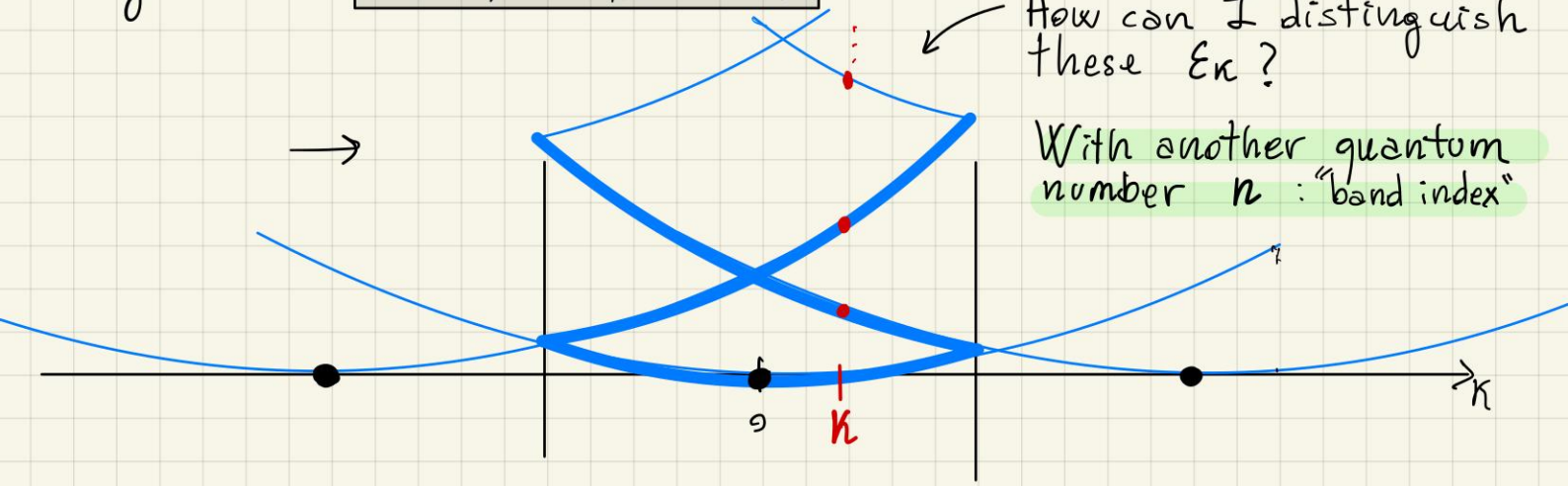
This leads to a description of the energy levels of an electron in a periodic potential in terms of a family of $\mathcal{E}_n(K)$, each with the periodicity of the R.L.



Using that: $\boxed{\mathcal{E}_n(K) = \mathcal{E}_n(K+G)}$

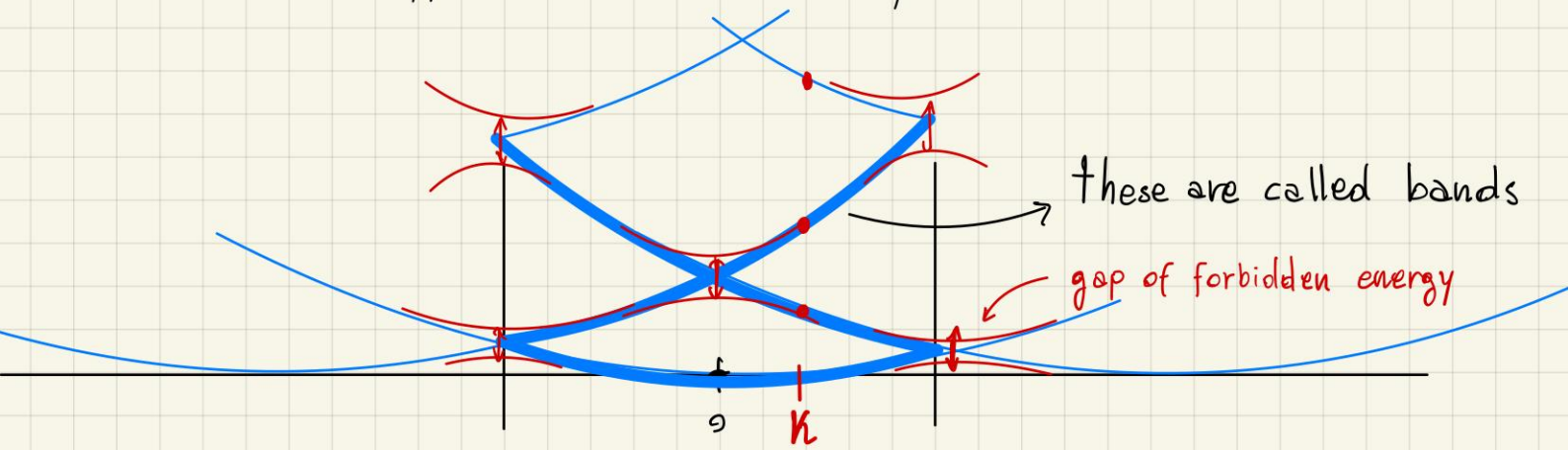
How can I distinguish these $\mathcal{E}_K$?

With another quantum number n : "band index"



What happen if I add a perturbation?

Whenever I put a perturbation it's quite usual to lift the degeneracy!
This is what will happen when we'll add a perturbation:

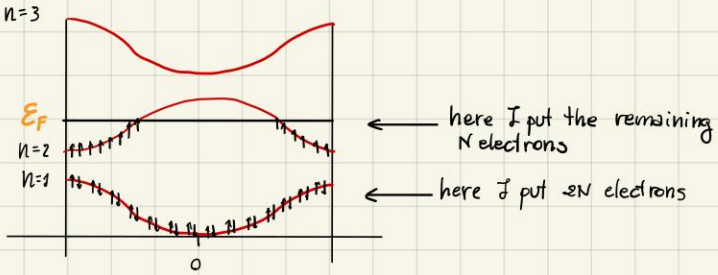


This is very important to understand why some materials are conducting materials and others insulating materials.

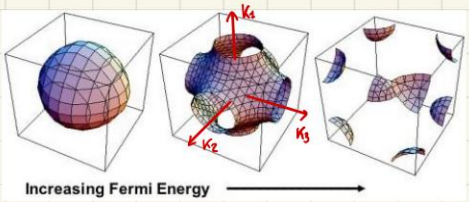
- Solid with band gaps $\gg K_B T_{amb}$ $\longrightarrow$ insulators
- Solid with band gap $\sim K_B T_{amb}$ $\longrightarrow$ intrinsic semiconductor

THE FERMI SURFACE

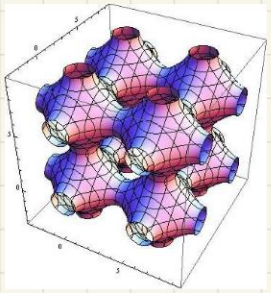
For each band we have in total N K states which can host 2 electrons. So in total we have $2N$ free slots for each band.
A certain number of bands may be completely filled while all others remaining empty. For example if I have Li^3 $(1s^2 2s^1)$ $\longrightarrow$ $3N$ total electrons



Like in this example a number of bands may be partially filled. The energy of the highest occupied level is called Fermi energy.
For each partially filled band there will be a surface in K-space separating the occupied from the unoccupied levels. The set of all such surfaces is called Fermi surface.
The parts of the Fermi surface, due to the single partially filled bands, are called branches
Analytically the branch of the Fermi surface in the nth band is that surface in K space determined by $\varepsilon_n(K) = \varepsilon_F$

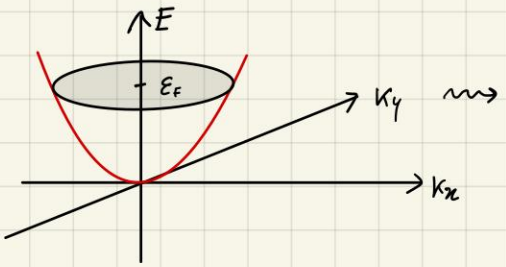


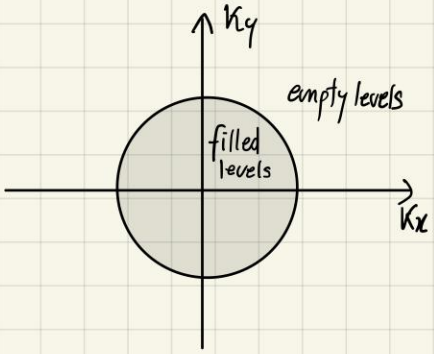
Since $\varepsilon_n(K)$ are periodic in the R.L. the solution to this problem $\forall n$ is a K-space surface with the periodicity of R.L.



Example / reminder of Fermi surfaces applied to free electron

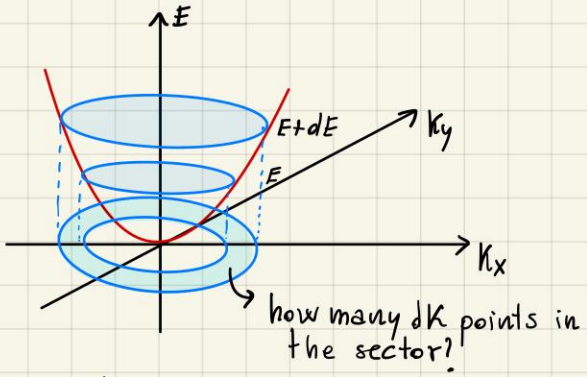
$$\varepsilon(K) = \frac{\hbar^2}{2m}(K_x^2 + K_y^2) \longrightarrow$$





DENSITY OF STATES

Idea (in the free electron case):



One most often calculate quantities that are weighted sums over the e⁻ levels of various one-e⁻ properties. Such quantities are in the form:

$$Q = 2 \sum_{n,K} Q_n(K)$$

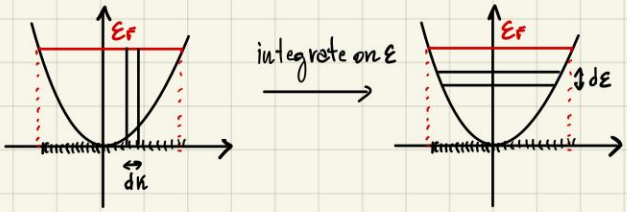
which $\forall n$ the sum is over all the allowed K giving physically distinct levels. In the limit of large crystal the allowed K get very close togheter and the sum may be replaced with an integral. Since the volume of each K point is $\Delta K = \frac{(2\pi)^3}{V}$:

$$Q = 2 \sum_{n,K} Q_n(K) \cdot \frac{\Delta K}{\Delta K} = 2 \sum_{n,K} Q_n(K) \frac{V}{(2\pi)^3} \Delta K$$

$$\longrightarrow \frac{Q}{V} = 2 \sum_{n,K} \frac{\Delta K}{(2\pi)^3} Q_n(K) \longrightarrow \lim_{V\to\infty} \frac{Q}{V} = \boxed{2 \sum_n \int_{\text{primitive cell volume}} \frac{d^3K}{(2\pi)^3} Q_n(K) \equiv q}$$

If $Q_n(K)$ depends on n and K only through the energy $\varepsilon_n(K)$ then we can define the density of levels per unit volume $g(\varepsilon)$ such that:

$$\boxed{q = \int d\varepsilon \; g(\varepsilon) Q(\varepsilon)}$$



Comparing the 2 relations we get:

$$\boxed{g(\varepsilon) = \sum_n g_n(\varepsilon)}$$

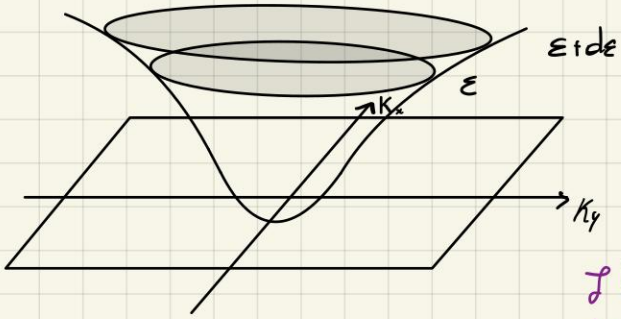
where $g_n(\varepsilon)$ is the density of levels in the nth band:

$$g_n(\varepsilon) = \int_{\text{primitive cell volume.}} \frac{d^3k}{4\pi^3}\, \delta(\varepsilon - \varepsilon_n(k))$$

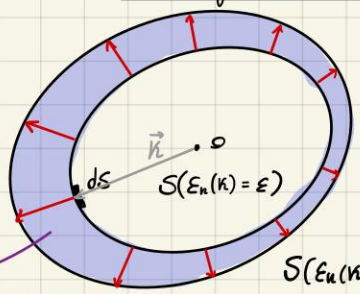
or equivalently:

$$g_n(\varepsilon)d\varepsilon = \frac{2}{V} \times \left(\begin{array}{l} \#\text{ of allowed } k \text{ in the } n^{th} \text{ band in} \\ \text{the energy interval } \varepsilon, \varepsilon+d\varepsilon \end{array} \right) = 2\int \frac{d^3k}{(2\pi)^3} \times \begin{cases} 1 & \varepsilon \le \varepsilon_n(k) \le \varepsilon + d\varepsilon \\ \phi & \text{otherwise} \end{cases}$$

How to rewrite $g_n(\varepsilon)$ in a more computable way?



more general situation



I have to count how many k points are there $\delta k(\underline{k})$

→ in each k point the dir. ⊥ to S_ε is different and the lenght is different.

$$\longrightarrow g_n(\varepsilon)d\varepsilon = \int_{S_n(\varepsilon_n=\varepsilon)} \frac{dS}{4\pi^3}\, \delta k(\underline{k})$$

Remind:

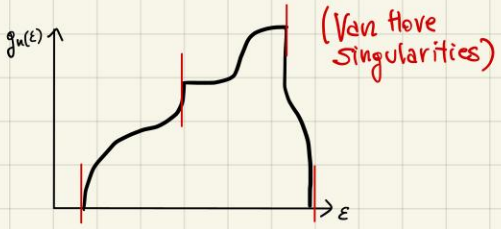
$$\varepsilon(k+dk) = \varepsilon(k) + \vec{\nabla}\varepsilon \cdot d\vec{k}$$
$$\varepsilon + d\varepsilon = \varepsilon + \nabla\varepsilon \cdot \delta k(\vec{k})$$

How to determine $\delta k(\underline{k})$?

$$\varepsilon + d\varepsilon = \varepsilon + |\nabla\varepsilon_n(k)| \cdot \delta k(\underline{k}) \longrightarrow \boxed{\delta k(\underline{k}) = \frac{d\varepsilon}{|\nabla\varepsilon_n(k)|}}$$

$$\longrightarrow g_n(\varepsilon)d\varepsilon = \left[\int_{S_n(\varepsilon_k=\varepsilon)} \frac{dS}{4\pi^3} \frac{1}{|\nabla\varepsilon_n(k)|} \right] d\varepsilon$$

$$\longrightarrow \boxed{g_n(\varepsilon) = \int_{S_n(\varepsilon_k=\varepsilon)} \frac{dS}{4\pi^3} \frac{1}{|\nabla\varepsilon_n(k)|}}$$



Because $\varepsilon_n(k)$ is periodic, bounded above and below there must be values of k in each primitive cell in which $|\nabla\varepsilon_n(k)| = 0$. → then the integrand diverges. It can be shown that such singularities, in 3-dim, are integrable. However $\frac{dg_n}{d\varepsilon} \to \infty$ (Van Hove singularities).

Example: free electron case

$$\varepsilon(k) = \frac{\hbar^2k^2}{2m} = \varepsilon \qquad |\nabla_k\varepsilon_n(k)| = \frac{\hbar^2k}{m} = \text{const} \qquad ; \qquad dS = 4\pi k\, dk$$

$$\longrightarrow g(\varepsilon) = \int_{S(\varepsilon_k=\varepsilon)} \frac{dS}{4\pi^3} \frac{1}{|\nabla\varepsilon_n(k)|} = \frac{4\pi}{4\pi^3} \int_0^{\frac{\sqrt{2m\varepsilon}}{\hbar}} dk\, k \cdot \frac{m}{\hbar^2 k} = \frac{m}{\hbar^2\pi^2} \frac{\sqrt{2m\varepsilon}}{\hbar}$$

Cap. 3
ELECTRONS IN A WEAK PERIODIC POTENTIAL

Almost all the metals are often referred to as "nearly free electron" metals. because the starting point of their description is the Sommerfield free electron gas, modified by the presence of a weak periodic potential. In this chapter we'll describe some features of band structure from the "almost free electron" point of view.

There are 2 fundamental reasons why the conduction bands of these metals should be so free-electron like, so 2 fundamental reasons why the strong interaction of the conduction electrons with each others and with the positive ions can have the effect of a weak potential:

1) e^--ions interaction is stronger at small separations, but the conduction electrons are forbidden from entering the immediate neighbourhood of the ions because this region is already occupied by the core electrons.

2) The fast mobility of the conduction electrons implies a sort of screening effect for the potential.

$$U(r) = \sum_{G \in RLV} C_G e^{iGr} \ll \varepsilon(K) = \frac{\hbar^2 K^2}{2m}$$

We know that for a fixed k the Bloch wave is:

$$\psi_k(r) = \sum_K c_{k-K} e^{i(k-K)\cdot r}$$

and for each vector K there is an equation:

$$\left[\frac{\hbar^2}{2m}(k-K)^2 - \varepsilon\right] c_{k-K} + \sum_{K'} U_{K'-K}\, c_{k-K'} = 0$$

In the free electron case all the Fourier components $U_K = 0 \ \forall K$ so the equation becomes:

$$\left(\varepsilon^\circ_{k-K} - \varepsilon\right) c_{k-K} = 0 \qquad \text{where we defined:} \qquad \varepsilon^\circ_q \equiv \frac{\hbar^2}{2m} q^2$$

this equation tells us that:

$$\boxed{c_{k-K} = 0} \quad \text{or} \quad \boxed{\varepsilon = \varepsilon^\circ_{k-K}}$$

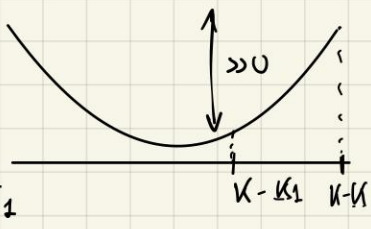
For the second relation we have two cases:

1) it is true only for a single K. : $\varepsilon = \varepsilon^\circ_{k-K}$ (no degeneracy)
   ⟶ for that k the only coeff $\neq 0$ is $c_{k-k} \neq 0$
2) it is true for a group of R.L.V. $K_1 \dots K_m$: $\varepsilon = \varepsilon^\circ_{k-K_1} = \dots = \varepsilon^\circ_{k-K_m}$ (m degeneracy)
   ⟶ for that k the only coeff $\neq 0$ are $c_{k-K_1}, c_{k-K_2} \dots, c_{k-K_m} \neq 0$

Now we want to see what happen if $U_K \neq 0$ but very small. The analysis still divides into two cases: non degenerate and (quasi) degenerate case. "Quasi" because in this case we say that 2 energy levels are equal aside from terms of order U.

CASE 1 (non degenerate case):
Fix k and consider a particular R.L.V. K_1 such that:

$$\left|\varepsilon^\circ_{k-K_1} - \varepsilon^\circ_{k-K}\right| \gg U \qquad \text{for fixed } k \text{ and } \forall K \neq K_1$$



We want to investigate the effect of this small potential on that free electron <u>level</u> given by:

$$\mathcal{E} = \mathcal{E}^{\circ}_{k-K_1} \qquad c_{k-K_1} \neq 0 \qquad (c_{k-K} = o(U) \simeq 0 \quad \forall\, K \neq K_1)$$

↳ Wait! How we know that? Because $U(r) = \sum U_K e^{iKr}$ where $U_K = \sum_K c_{k-K} e^{iK\cdot r} \longrightarrow c_{k-K} \sim o(U)$

So, the equation to consider for c_{k-K_1} is:

1) $$(\mathcal{E} - \mathcal{E}^{\circ}_{k-K_1})\, c_{k-K_1} = \cancel{U_0 c_{k-K_1}} + \sum_{K \neq K_1} U_{K-K_1}\, c_{k-K}$$

because we fix $U_0 = 0$ (since the potential is defined aside from a constant)

Then the equation for all c_{k-K} with $K \neq K_1$ is: (for all the others $K \neq K_1$)

$$(\mathcal{E} - \mathcal{E}^{\circ}_{k-K})\, c_{k-K} = \sum_{K'} U_{K'-K}\, c_{k-K'}$$

2) $$(\mathcal{E} - \mathcal{E}^{\circ}_{k-K})\, c_{k-K} = U_{K_1-K}\, c_{k-K_1} + \sum_{K' \neq K_1} U_{K'-K}\, c_{k-K'}$$

$$\longrightarrow \quad c_{k-K} = \frac{U_{K_1-K}\, c_{k-K_1}}{(\mathcal{E} - \mathcal{E}^{\circ}_{k-K})} + \sum_{K' \neq K_1} \frac{U_{K'-K}\, c_{k-K'}}{(\mathcal{E} - \mathcal{E}^{\circ}_{k-K})}$$

($U_{K_1-K}\, c_{k-K_1}$: $\sim o(1)$; $(\mathcal{E} - \mathcal{E}^{\circ}_{k-K}) \gg U$; $\sim o(U)$ — $U_{K'-K}\, c_{k-K'}$: $\sim o(U)$; $(\mathcal{E} - \mathcal{E}^{\circ}_{k-K}) \gg U$; $\sim o(U^2)$)

So we found that the correction to c_{k-K}, in the zone far away from the quasi degeneracy point, is of the order of $o(U^2)$:

$$c_{k-K} = \frac{U_{K_1-K}\, c_{k-K_1}}{(\mathcal{E} - \mathcal{E}^{\circ}_{k-K})} + o(U^2)$$

Placing this into the first equation we get:

$$(\mathcal{E} - \mathcal{E}^{\circ}_{k-K_1})\, c_{k-K_1} = \sum_{K \neq K_1} \frac{U_{K-K_1}\, U_{K_1-K}}{(\mathcal{E} - \mathcal{E}^{\circ}_{k-K})}\, c_{k-K_1} + \sum_{K \neq K_1} \sum_{K' \neq K_1} U_{K-K_1}\, \frac{U_{K'-K}\, c_{k-K'}}{(\mathcal{E} - \mathcal{E}^{\circ}_{k-K})}$$

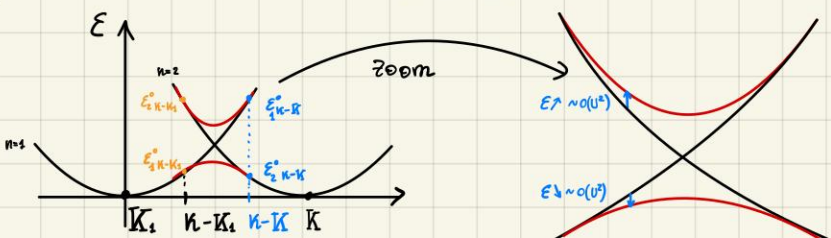
$$(\mathcal{E} - \mathcal{E}^{\circ}_{k-K_1})\, \cancel{c_{k-K_1}} = \sum_{K \neq K_1} \frac{U_{K-K_1}\, U_{K_1-K}}{(\mathcal{E} - \mathcal{E}^{\circ}_{k-K})}\, \cancel{c_{k-K_1}} + o(U^3)$$

Thus $\mathcal{E}$ differs from $\mathcal{E}^{\circ}_{k-K_1}$ by terms of order $o(U^2)$ To solve the equation for $\mathcal{E}$ to this order is therefore suffices to replace the $\mathcal{E}$ on the rhs at the 1st order with $\mathcal{E} \simeq \mathcal{E}^{\circ}_{k-K_1}$.

$$\longrightarrow \quad \boxed{\mathcal{E} \simeq \mathcal{E}^{\circ}_{k-K_1} + \sum_{K \neq K_1} \frac{|U_{K-K_1}|^2}{(\mathcal{E}^{\circ}_{k-K_1} - \mathcal{E}^{\circ}_{k-K})} = \mathcal{E}^{\circ}_{k-K_1} + o(U^2)}$$

This equation asserts that for every $\mathcal{E}^{\circ}_{k-K}$ below $\mathcal{E}^{\circ}_{k-K_1}$ contributes a term that raises the value of $\mathcal{E}$, while every levels that lies above $\mathcal{E}^{\circ}_{k-K_1}$ contributes a term that lowers the value of $\mathcal{E}$.

$$\begin{cases} \text{if} \quad \mathcal{E}^{\circ}_{n\,k-K_1} > \mathcal{E}^{\circ}_{n\,k-K} & \mathcal{E} \nearrow \\ \text{if} \quad \mathcal{E}^{\circ}_{n\,k-K_1} < \mathcal{E}^{\circ}_{n\,k-K} & \mathcal{E} \searrow \end{cases}$$



CASE 2: (quasi) degenerate case

Suppose the value of κ is such that there are m R.L.V. $K_1, \dots, K_m$ with:

$$\varepsilon^{\circ}_{\kappa-K_1} \simeq \dots \simeq \varepsilon^{\circ}_{\kappa-K_m} \qquad (\simeq \text{ within } o(U))$$

and then:

$$|\varepsilon^{\circ}_{\kappa-K} - \varepsilon^{\circ}_{\kappa-K_i}| \gg U \qquad \forall i = 1,\dots,m \;,\; K \neq K_1,\dots,K_m$$

In analogy from the previous case we write the equation for $c_{\kappa-K_i}$

$$(\varepsilon - \varepsilon^{\circ}_{\kappa-K_i})\, c_{\kappa-K_i} = \sum_{j=1}^{m} U_{K_j-K_i}\, c_{\kappa-K_j} + \sum_{K\neq K_1,\dots,K_m} U_{K-K_i}\, c_{\kappa-K} \qquad i = 1,\dots,m$$

and the equation for the others $c_{\kappa-K}$ with $K \neq K_1 \dots K_m$

$$(\varepsilon - \varepsilon^{\circ}_{\kappa-K})\, c_{\kappa-K} = \sum_{j=1}^{m} U_{K_j-K}\, c_{\kappa-K_j} + \sum_{K'\neq K_1,\dots,K_m} U_{K'-K}\, c_{\kappa-K'} \qquad K \neq K_1,\dots K_m$$

$$c_{\kappa-K} = \frac{1}{(\varepsilon - \varepsilon^{\circ}_{\kappa-K})}\left(\sum_{j=1}^{m} U_{K_j-K}\, c_{\kappa-K_j} + \sum_{K'\neq K_1,\dots,K_m} U_{K'-K}\, c_{\kappa-K'}\right)$$

($c_{\kappa-K_j} \sim o(1)$; $U_{K'-K} \sim o(U)$; $c_{\kappa-K'} \sim o(U^2)$)

$$c_{\kappa-K} = \frac{1}{(\varepsilon - \varepsilon^{\circ}_{\kappa-K})}\left(\sum_{j=1}^{m} U_{K_j-K}\, c_{\kappa-K_j}\right) + o(U^2)$$

Placing this into the 1st equation we get:

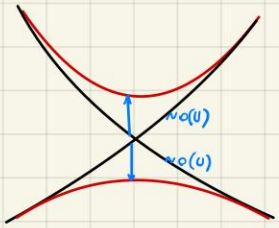
$$(\varepsilon - \varepsilon^{\circ}_{\kappa-K_i})\, c_{\kappa-K_i} = \sum_{j=1}^{m} U_{K_j-K_i}\, c_{\kappa-K_j} + \sum_{j=1}^{m}\left(\sum_{K\neq K_1,\dots,K_m} \frac{U_{K-K_i}\, U_{K_j-K}}{(\varepsilon - \varepsilon^{\circ}_{\kappa-K})}\, c_{\kappa-K_j}\right) + o(U^3)$$

($U_{K_j-K_i} \sim o(U)$; $c_{\kappa-K_j} \sim o(1)$; $U_{K-K_i}\, U_{K_j-K} \sim o(U^2)$; $\frac{1}{(\varepsilon - \varepsilon^{\circ}_{\kappa-K})} \sim o(1)$)

$$\longrightarrow (\varepsilon - \varepsilon^{\circ}_{\kappa-K_i})\, c_{\kappa-K_i} = \sum_{j=1}^{m} U_{K_j-K_i}\, c_{\kappa-K_j} + o(U^2)$$

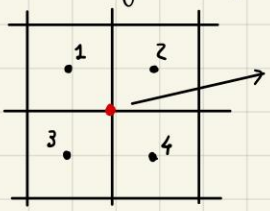
$$\longrightarrow \boxed{\varepsilon = \varepsilon^{\circ}_{\kappa-K_i} + \sum_{j=1}^{m} \frac{U_{K_j-K_i}\, c_{\kappa-K_j}}{c_{\kappa-K_i}} = \varepsilon^{\circ}_{\kappa-K_i} + o(U)}$$

($c_{\kappa-K_j} \sim o(1)$; $c_{\kappa-K_i} \sim o(1)$; $U_{K_j-K_i} \sim o(U)$)



ENERGY LEVELS NEAR A SINGLE BRAGG PLANE (for m=2)

In general we can have a degeneracy of order $m \geq 2$. For example:



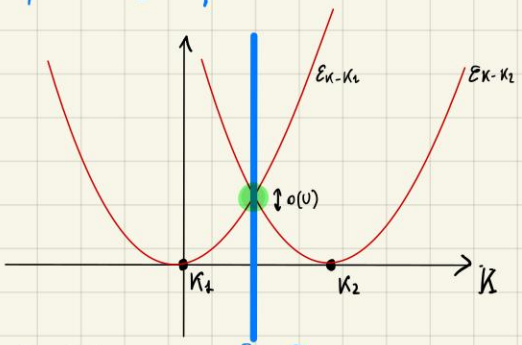
If I sit here, due to the symmetry, there are 4 bands with the same energy ($m=4$)

Now we want treat the simplest and most important example of $m=2$. This means that we work only with 2 equations:

$$\begin{cases} (\mathcal{E} - \mathcal{E}^{\circ}_{k-K_1})\, C_{k-K_1} = U_{K_2-K_1}\, C_{k-K_2} \\ (\mathcal{E} - \mathcal{E}^{\circ}_{k-K_2})\, C_{k-K_2} = U_{K_1-K_2}\, C_{k-K_1} \end{cases}$$

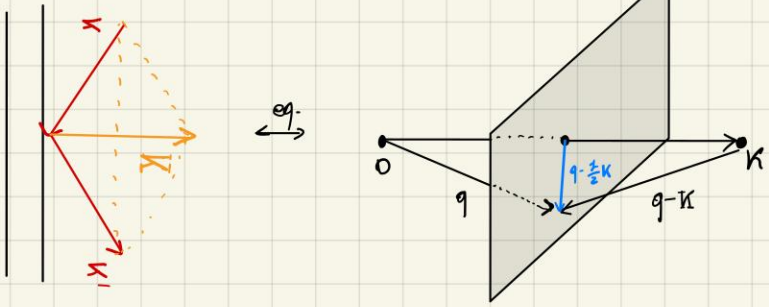
This is an homogeneus system! In order to have a non trivial solution we have to impose that det (coeff. matrix) = 0.
Before that it's convenient to write $k-K_1 \equiv q$, $K_2-K_1 \equiv K$; $k-K_2 \equiv q-K$

$$\begin{cases} (\mathcal{E} - \mathcal{E}^{\circ}_{q})\, C_{q} = U_{K}\, C_{q-K} \\ (\mathcal{E} - \mathcal{E}^{\circ}_{q-K})\, C_{q-K} = U_{-K}\, C_{q} \end{cases}$$



We have that $\mathcal{E}^{\circ}_{q} \simeq \mathcal{E}^{\circ}_{q-K}$ and $|\mathcal{E}^{\circ}_{q} - \mathcal{E}^{\circ}_{q-K'}| \gg U$ for $K' \neq K$

$\mathcal{E}^{\circ}_{q}$ is equal to $\mathcal{E}^{\circ}_{q-K}$ for some K only when $|q| = |q-K|$. This means that q must lie on the Bragg plane:



So if $|q| = |q-K|$ q lie in the Bragg plane determined by K.
(This implies that $q - \frac{1}{2}K$ is parallel to the plane)

Then saying that $\mathcal{E}^{\circ}_{q} \simeq \mathcal{E}^{\circ}_{q-K}$ and $|\mathcal{E}^{\circ}_{q} - \mathcal{E}^{\circ}_{q-K'}| \gg U$ for $K' \neq K$ have the geometric significance of requiring q to be close to a Bragg plane (but not close to a place where two or more Bragg planes intersect).

Therefore the case of 2 nearly degenerate levels applies to an electron whose wave vector satisfies very nearly the condition for a single Bragg scattering (wave vector must lies on a Bragg plane)
For the general case of m-degeneracy can occur many simultaneous Bragg reflection.
We conclude that a weak periodic potential has its major effects on only those free electron levels whose wave vectors are close to ones at which Bragg reflection can occur

Let's find the non trivial solution of our problem.

$$\xrightarrow{\text{n.b. } U_{-K}=U_K^*} \begin{vmatrix} \varepsilon-\varepsilon_q^\circ & -U_K \\ -U_K^* & \varepsilon-\varepsilon_{q-K}^\circ \end{vmatrix} = 0$$

$$\longrightarrow \quad (\varepsilon-\varepsilon_q^\circ)(\varepsilon-\varepsilon_{q-K}^\circ) - |U_K|^2 = 0$$

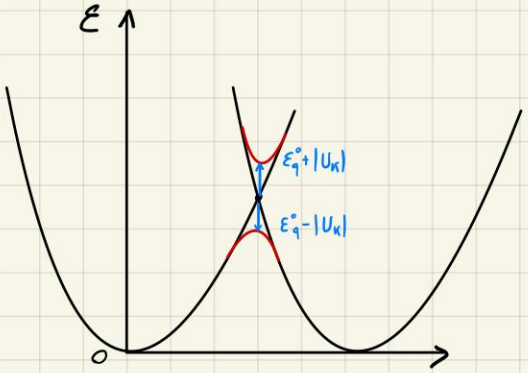
$$\varepsilon^2 - \varepsilon\left(\varepsilon_{q-K}^\circ + \varepsilon_q^\circ\right) + \varepsilon_q^\circ \varepsilon_{q-K} - |U_K|^2 = 0$$

$$\boxed{\varepsilon = \frac{1}{2}\left(\varepsilon_q^\circ + \varepsilon_{q-K}^\circ\right) \pm \frac{1}{2}\sqrt{\left(\varepsilon_q - \varepsilon_{q-K}\right)^2 + 4|U_K|^2}}$$

These two roots give the dominant effect of the periodic potential on the energies of the two free electron levels ε_q° and ε_{q-K}° when q is close to the Bragg plane determined by K.

For points exactly on the Bragg's plane $\varepsilon_q^\circ = \varepsilon_{q-K}^\circ$. Hence:

$$\boxed{\varepsilon = \varepsilon_q^\circ \pm |U_K|}$$



Now when q lies on a single Bragg plane we may also identify the form of the wavefunction corresponding to the two solutions $\varepsilon = \varepsilon_q^\circ \pm |U_K|$

Now, remember that $(\varepsilon-\varepsilon_q^\circ)\,c_q = U_K\, c_{q-K}$:

If $U_K > 0$ $\quad \varepsilon-\varepsilon_q^\circ = \pm U_K \longrightarrow \pm U_K c_q = U_K c_{q-K} \longrightarrow c_q = \pm c_{q-K}$

If $U_K < 0$ $\quad \varepsilon-\varepsilon_q^\circ = \mp U_K \longrightarrow \mp U_K c_q = U_K c_{q-K} \longrightarrow c_q = \mp c_{q-K}$

$$\boxed{c_q = \pm c_{q-K}\cdot \text{sign}(U_K)}$$

We know that:

$$\psi(\underline{r}) = \sum_K e^{i(K-K)r}\, c_{K-K} \simeq c_q e^{iqr} + c_{q-K}\, e^{i(q-K)r}$$

Suppose for ex. $U_K > 0$

$$\longrightarrow \quad \psi(\underline{r}) = c_q e^{iqr} \pm c_q e^{i(q-K)r} = 2i c_q\, e^{iqr} e^{-i\frac{K}{2}r}\left[\frac{e^{i\frac{K}{2}r} \pm e^{-i\frac{K}{2}r}}{2i}\right]$$

$$\longrightarrow \quad \boxed{\psi(\underline{r}) \simeq 2 c_q\, e^{i\left(q-\frac{K}{2}r\right)} \times \begin{cases} \cos\left(\frac{K}{2}r\right) \\ i\sin\left(\frac{K}{2}r\right) \end{cases}}$$

Cap. 4
TIGHT-BINDING METHOD

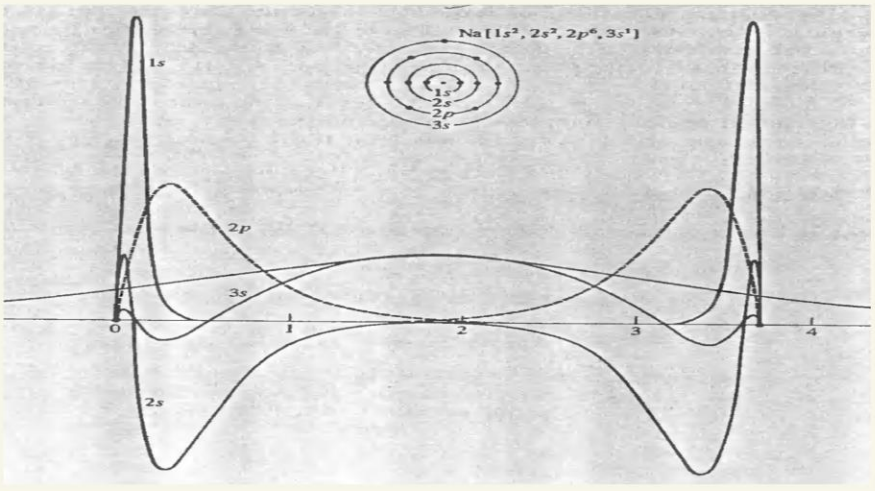
In Chapter 9 we calculated electronic levels in a metal by viewing it as a gas of nearly free conduction electrons, only weakly perturbed by the periodic potential of the ions. We can also take a very different point of view, regarding a solid (metal or insulator) as a collection of weakly interacting neutral atoms. As an extreme example of this, imagine assembling a group of sodium atoms into a body-centered cubic array with a lattice constant of the order of centimeters rather than angstroms. All electrons would then be in atomic levels localized at lattice sites, bearing no resemblance to the linear combinations of a few plane waves described in Chapter 9.

If we were to shrink the artificially large lattice constant of our array of sodium atoms, at some point before the actual lattice constant of metallic sodium was reached we would have to modify our identification of the electronic levels of the array with the atomic levels of isolated sodium atoms. This would become necessary for a particular atomic level, when the interatomic spacing became comparable to the spatial extent of its wave function, for an electron in that level would then feel the presence of the neighboring atoms.

The actual state of affairs for the 1*s*, 2*s*, 2*p* and 3*s* levels of atomic sodium is shown in Figure 10.1. The atomic wave functions for these levels are drawn about two nuclei separated by 3.7 Å, the nearest-neighbor distance in metallic sodium. The overlap of the 1*s* wave functions centered on the two sites is utterly negligible, indicating that these atomic levels are essentially unaltered in metallic sodium. The overlap of the 2*s*- and 2*p*-levels is exceedingly small, and one might hope to find levels in the metal very closely related to these. However, the overlap of the 3*s*-levels (which hold the atomic valence electrons) is substantial, and there is no reason to expect the actual electronic levels of the metal to resemble these atomic levels.

The *tight-binding approximation* deals with the case in which the overlap of atomic wave functions is enough to require corrections to the picture of isolated atoms, but not so much as to render the atomic description completely irrelevant. The approximation is most useful for describing the energy bands that arise from the partially filled *d*-shells of transition metal atoms and for describing the electronic structure of insulators.

Quite apart from its practical utility, the tight-binding approximation provides an instructive way of viewing Bloch levels complementary to that of the nearly free electron picture, permitting a reconciliation between the apparently contradictory features of localized atomic levels on the one hand, and free electron-like plane-wave levels on the other.



GENERAL FORMULATION

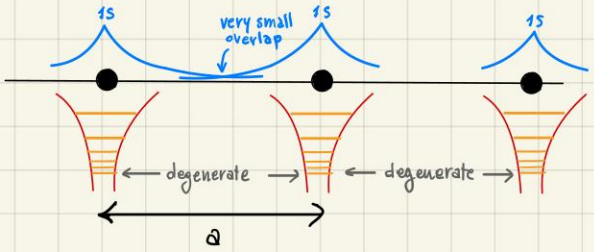
Let's image we have that the crystal (Bloch) Hamiltonian is described by:

$$H = H_{at} + \Delta U(r)$$

H_{at}: atomic Hamiltonian; $\Delta U(r)$: small correction

and we know the solution to the atomic problem ($\Delta U(r) = 0$.)

$$H_{at}\,\psi_n(r) = E_n\,\psi_n(r)$$



The atoms are so far apart that they influence very little to each other. So the potential is the atomic potential + perturbation ΔU

We can think of the lattice as a set of non interacting ions and impose the periodicity (without ΔU). Since I know the solution of the atomic potential, I know the atomic levels and the atomic eigenfunctions. These eigenfunctions however have a problem: they are not in the Bloch form. The idea is to take a linear combination of degenerate states to form a Bloch wave

Guess: ★ $$\psi_{n\underline{k}}(\underline{r}) = \sum_{\underline{R}'} e^{i\underline{k}\cdot\underline{R}'}\,\psi_n(\underline{r}-\underline{R}')$$ → N linear combinations

$\underline{R}'$: B.L. vectors; $\psi_n(\underline{r}-\underline{R}')$: atomic wavefunctions centered in each B.L. points (with same energy)

Let's show if this is in the form of Bloch (applying the translational operator):

$$\psi_{n\underline{k}}(\underline{r}+\underline{R}) = \sum_{\underline{R}'} e^{i\underline{k}\cdot\underline{R}'}\,\psi_n(\underline{r}-(\underline{R}'-\underline{R})) \overset{\underline{R}''=\underline{R}'-\underline{R}}{=} \sum_{\underline{R}''} e^{i\underline{k}\cdot(\underline{R}+\underline{R}'')}\,\psi_n(\underline{r}-\underline{R}'')$$

$$= e^{i\underline{k}\cdot\underline{R}} \sum_{\underline{R}''} e^{i\underline{k}\cdot\underline{R}''}\,\psi_n(\underline{r}-\underline{R}'') = e^{i\underline{k}\cdot\underline{R}}\,\psi_{n\underline{k}}(\underline{r}) \rightarrow \text{Bloch functions!}$$

Let's include the perturbation. We started from a situation where atoms are so far apart that they do not influence each other. Now we take these atoms and we bring them closer and closer each other. Of course ★ is not longer a solution
We want to write $\psi(r)$, solution with the presence of ΔU, in analogy to the previous relation as:

$$\psi_{\underline{k}}(\underline{r}) = \sum_{\underline{R}} e^{i\underline{k}\cdot\underline{R}}\,\underbrace{\phi(\underline{r}-\underline{R})}_{\text{Wanier function}}$$

with a suitable choice of $\phi(\underline{r}-\underline{R})$. Since the atoms are getting closer and closer, the orbitals start to mix each other! So my trial function is a linear combination of atomic orbitals: (LCAO)

$$\phi(\underline{r}) = \sum_m b_m\,\psi_m(\underline{r})$$

We can demostrate that a Bloch wave function can be always seen as a linear combination of wave functions centered at different B.L. sites. (Wanier theorem)

Now we should apply this $\psi(\underline{r})$ to $H_{at} + \Delta U$ and find that it is the correct solution and solve the eigenvalue problem:

$$(H_{at} + \Delta U)\,\psi(\underline{r}) = \mathcal{E}_{\underline{\kappa}}\,\psi(\underline{r})$$

where

$$\psi_{\underline{\kappa}}(\underline{r}) = \sum_{\underline{R}} e^{i\underline{\kappa}\cdot\underline{R}} \sum_{n} b_n\,\psi_n(\underline{r}-\underline{R})$$

We note that in this eigenvalue problem the only unknown quantities are the b_m coefficients, assuming knowed all the ψ_m. So the idea is to transform the eigenvalue problem in a linear problem with b_m as unknown quantities.

$$(H_{at} + \Delta U)\,\psi(\underline{r}) \times \psi_m^*(\underline{r}) = \mathcal{E}_{\underline{\kappa}}\,\psi(\underline{r}) \times \psi_m^*(\underline{r})$$

Integrate $\int d^3r$ $\longrightarrow$

$$\int d^3r\,\psi_m^*(\underline{r})\left[(E_m - \mathcal{E}_{\underline{\kappa}}) + \Delta U(\underline{r})\right] \sum_{\underline{R}}\sum_{n} e^{i\underline{\kappa}\cdot\underline{R}}\, b_n\,\psi_n(\underline{r}-\underline{R}) = 0$$

In general this is a very complicated problem. However we use the idea of tight binding: electrons tightly bind to the nuclei and small $\Delta U(r)$ correction.
Let's enforce this. First of all we can split for simplicity

$$\sum_{\underline{R}} = \Big|_{\underline{R}=0} + \sum_{\underline{R}\neq 0}$$

because the atomic ψs are orthogonal to each other when they refer to the same atom; when they refer to different atoms they are no longer orthogonals.

in $R=0$ $\longrightarrow$ $\int d^3r\,\psi_m^*(\underline{r})\,\psi_n(\underline{r})\,d^3\underline{r} = \delta_{nm}$

Then:

$$(E_m - \mathcal{E}_{\underline{\kappa}})\,b_m + (E_m - \mathcal{E}_{\underline{\kappa}}) \sum_{\underline{R}\neq 0}\sum_{n} b_n\, e^{i\underline{\kappa}\cdot\underline{R}} \int \psi_m^*(\underline{r})\,\psi_n(\underline{r}-\underline{R})\,d^3r + \sum_{n} b_n \int \psi_m^*(\underline{r})\,\Delta U(\underline{r})\,\psi_n(\underline{r})\,d^3r +$$

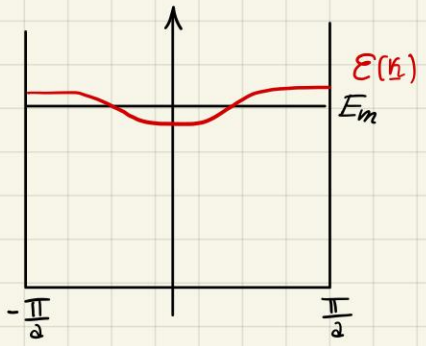
$\int \psi_m^*(\underline{r})\,\psi_n(\underline{r}-\underline{R})\,d^3r$: overlap of wavefunctions on different atoms. It's small because ψ decays exp.

$\Delta U(\underline{r})$: it's small by construction

$$+ \sum_{R\neq 0} e^{i\underline{\kappa}\cdot\underline{R}} \sum_{n} b_n \int \psi_m^*(\underline{r})\,\Delta U(\underline{r})\,\psi_n(\underline{r}-\underline{R})\,d^3r = 0$$

$\psi_m^*(\underline{r})\,\Delta U(\underline{r})\,\psi_n(\underline{r}-\underline{R})$: very small due to the presence of ΔU and of the tiny overlap between ψ.

So this implies that even $(E_m - \mathcal{E}_{\underline{\kappa}})\,b_m$ must be small, and this is true only if b_m is small or $E_m - \mathcal{E}_{\underline{\kappa}}$ is small. Thi first case is the trivial one, an hence: $E_m - \mathcal{E}_{\kappa}$ must be small, which means that $\mathcal{E}(\kappa)$ must be close to an atomic level E_m.



What are the possibilities?

- The level is a single degenerate level e.g. 1s and all the other levels are far away in energy from this level. The general problem reduces to a single equation (1x1 problem) giving an explicit expression for the energy of the band arising from this s-level (s band).

- If we are interested in bands arising from atomic p-level, which is triply degenerate, then the general problem would give a set of three homogeneous equations, whos eigenvalue would give the $\mathcal{E}(\underline{k})$ for the three p-bands, and $b(\underline{k})$ would give the appropriate linear combination of atomic p-levels making up ϕ at the various k's in the B.Z.

- If we are interested to d-bands we have to solve a 5×5 secular problem etc.

APPLICATION TO AN S-BAND ARISING FROM A SINGLE ATOMIC S-LEVEL

$$(E_s - \mathcal{E}_{\underline{k}})\,b_s + (E_s - \mathcal{E}_{\underline{k}}) \sum_{\underline{R}\neq 0} b_s\, e^{i\underline{k}\cdot\underline{R}} \int \psi_s^*(\underline{r})\,\psi_s(\underline{r}-\underline{R})\,d^3r + b_s \int \psi_s^*(\underline{r})\,\Delta U(\underline{r})\,\psi_s(\underline{r})\,d^3r + \sum_{\underline{R}\neq 0} e^{i\underline{k}\cdot\underline{R}}\, b_s \int \psi_s^*(\underline{r})\,\Delta U(\underline{r})\,\psi_s(\underline{r}-\underline{R})\,d^3r = 0$$

$$\longrightarrow \quad \mathcal{E}_{\underline{k}} = E_s + \frac{\int \psi_s^*(\underline{r})\,\Delta U(\underline{r})\,\psi_s(\underline{r})\,d^3r + \sum_{\underline{R}\neq 0} e^{i\underline{k}\cdot\underline{R}} \int \psi_s^*(\underline{r})\,\Delta U(\underline{r})\,\psi_s(\underline{r}-\underline{R})\,d^3r}{1 + \sum_{\underline{R}\neq 0} e^{i\underline{k}\cdot\underline{R}} \int \psi_s^*(\underline{r})\,\psi_s(\underline{r}-\underline{R})\,d^3r}$$

So we see tha this band correction is due to the fact that the atoms that are close enough have overlapping orbitals and since this orbitals overlap (a little bit) an electron can jump from an atom to the other. and when it jumps it can move across the crystal and form a band

$$\beta = -\int d^3r\, \psi_s^*(\underline{r})\,\Delta U(\underline{r})\,\psi_s(\underline{r})$$: SHIFT INTEGRAL : it shift the band

$$\gamma(R) = -\int d^3r\, \psi_s^*(\underline{r})\,\Delta U(\underline{r})\,\psi_s(\underline{r}-\underline{R})$$: TRANSFER INTEGRAL : probability to transfer an electron to a site to an other. The band dispersion would not be possible without $\gamma(\underline{R})$

$$\alpha(R) = \int d^3r\, \psi_s^*(\underline{r})\,\psi_s(\underline{r}-\underline{R})$$: OVERLAP INTEGRAL : overlap between ψ_s's of different sites

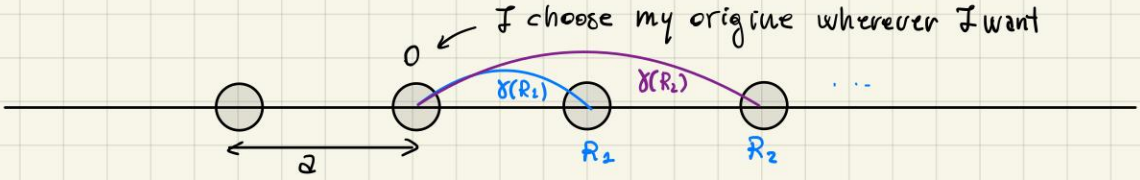
Why this choice of sign? Because usually $\Delta U(r) < 0$ and with the minus sign $\beta, \gamma > 0$. In general this is not true: we can be in a situation where the orbital has not a given sign e.g. p-orbital (has 2 lobes 1 positive and one negative)

$$\longrightarrow \varepsilon_{\underline{k}} = E_s - \frac{\beta + \sum_{\underline{R}\neq 0} \gamma(\underline{R}) e^{i\underline{k}\cdot\underline{R}}}{1 + \underbrace{\sum_{\underline{R}\neq 0} \alpha(\underline{R}) e^{i\underline{k}\cdot\underline{R}}}_{\ll 1}} \simeq \boxed{E_s - \beta - \sum_{\underline{R}\neq 0} \gamma(\underline{R}) e^{i\underline{k}\cdot\underline{R}}}$$

Now we can see the meaning of these quantities:

- β is a rigid shift of the band. If $\beta > 0$ $\varepsilon(\underline{k})$ is shifted down respect to E_s So my band is not centered around E_s but around $E_s - \beta$
- the 3rd piece is the k dependence part that gives the form of a curve to my $\varepsilon(k)$

Let's take a 1-dimensional crystal of s-orbitals.



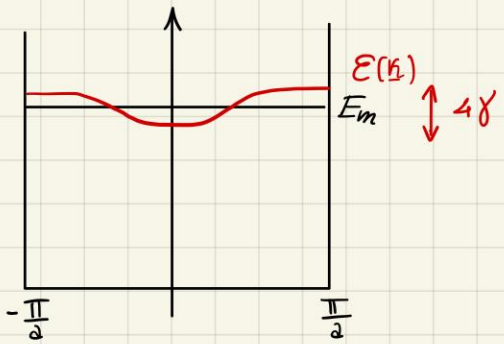
We expect that if $\gamma(R_1)$ is small $\gamma(R_n)$ is smaller $(n>1)$. Then is very usual to limit this sum to the nearest neighbours atoms.

$$\longrightarrow \varepsilon(\underline{k}) \simeq E_s - \beta - \sum_{n.n.} \gamma(\underline{R}) e^{i\underline{k}\cdot\underline{R}} = E_s - \beta - \left[\gamma(+a) e^{ika} + \gamma(-a) e^{-ika}\right]$$

However since $\psi_s(-\underline{R}) = \psi_s(\underline{R})$, because it is an s orbital, and since $\Delta U(\underline{R}) = \Delta U(-\underline{R})$ because of the translational invariance of the lattice, $\gamma(\underline{R}) = \gamma(-\underline{R})$.

$$\gamma(a) = \gamma(-a) \equiv \gamma$$

$$\longrightarrow \boxed{\varepsilon(\underline{k}) \simeq E_s - \beta - 2\gamma\cos(ka)}$$



OBSERVATION

Since the electron wavefunction in a tight binding band changes only by the phase factor $e^{i\underline{k}\underline{R}}$ as ones moves from one cell to another at distance $\underline{R}$, the probability to find it in a cell or in another one is equal.

WANNIER THEOREM

The Bloch functions for any band can be always written in the form

$$\psi_{n\underline{k}}(\underline{r}) = \sum_{\underline{R}} e^{i\underline{k}\cdot\underline{R}} \cdot \varphi_n(\underline{r}-\underline{R})$$

↑ Wannier functions

Proof: Since $\psi_{n\underline{k}}(\underline{r})$ is periodic (in the reciprocal space) it can be expanded in a Fourier series:

$$\psi_{n\underline{k}}(\underline{r}) = \sum_{\underline{R}\in BL} f_n(\underline{r},\underline{R})\, e^{i\underline{k}\cdot\underline{R}}$$

The Fourier coefficients by definition are:

$$f_n(\underline{r},\underline{R}) = \frac{1}{v_{1^{st}BZ}} \int d^d\underline{k}\; e^{-i\underline{k}\cdot\underline{R}}\, \psi_{n\underline{k}}(\underline{r})$$

Now let's calculate $f_n(\underline{r}+\underline{R}_0\,;\,\underline{R}+\underline{R}_0)$ (shift of $\underline{R}_0$):

$$f_n(\underline{r}+\underline{R}_0,\underline{R}+\underline{R}_0) = \frac{1}{v_{1^{st}BZ}} \int d^d\underline{k}\; e^{-i\underline{k}\cdot(\underline{R}+\underline{R}_0)}\, \psi_{n\underline{k}}(\underline{r}+\underline{R}_0)$$

but since $\psi_{n\underline{k}}$ is a Bloch wave function $\psi_{n\underline{k}}(\underline{r}+\underline{R}_0) = e^{i\underline{k}\cdot\underline{R}_0}\psi_{n\underline{k}}(\underline{r})$

$$\longrightarrow f_n(\underline{r}+\underline{R}_0,\underline{R}+\underline{R}_0) = \frac{1}{v_{1^{st}BZ}} \int d^d\underline{k}\; e^{-i\underline{k}\cdot(\underline{R}+\underline{R}_0)}\, e^{i\underline{k}\cdot\underline{R}_0}\, \psi_{n\underline{k}}(\underline{r}) =$$

$$= \frac{1}{v_{1^{st}BZ}} \int d^d\underline{k}\; e^{-i\underline{k}\cdot\underline{R}}\, \psi_{n\underline{k}}(\underline{r}) = f_n(\underline{r},\underline{R})$$

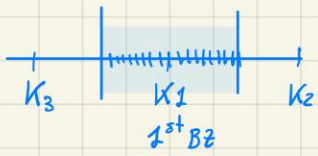
Then we prove that:

$$f_n(\underline{r},\underline{R}) = f(\underline{r}+\underline{R}_0,\underline{R}+\underline{R}_0) \longrightarrow \boxed{f_n(\underline{r}-\underline{R})} \longrightarrow \boxed{\psi_{n\underline{k}}(\underline{r}) = \sum_{\underline{R}} e^{i\underline{k}\cdot\underline{R}} \cdot f_n(\underline{r}-\underline{R})}$$

□

COROLLARY: IF $\underline{R}=0$: $\varphi_n(\underline{r}) = \frac{1}{v_{1^{st}BZ}} \int d^d\underline{k}\; \psi_{n\underline{k}}(\underline{r})$ (average on the $1^{st}BZ$ of $\psi(r)$

$$\psi_{nk}(r) = \sum_R e^{ikR} f_n(R,r)$$ ← Wannier function



The idea is to define $f_n(R,r) = \frac{1}{v_{1^{st}BZ}} \int_{BZ} dk\, e^{-iRk} \psi_{nk}(r)$

- The 1st thing to prove is that $f_n(R,r) = f_n(R-r)$

I shift $\begin{cases} r \to r+R_0 \\ R \to R+R_0 \end{cases}$ $\longrightarrow$ $f(r+R_0, R+R_0) = \frac{1}{v_0} \int dk\, e^{-i(R+R_0)k} \psi_{nk}(r+R_0)$

But since $\psi_{nk}(r+R_0) = e^{ikR_0} \psi_{nk}(r)$ (ψ_{nk} is a Bloch function)

$\longrightarrow f(r+R_0, R-R_0) = \frac{1}{v_0} \int dk\, e^{-i(R+R_0)k} e^{ikR_0} \psi_{nk}(r) = f_n(r,R)$

$\longrightarrow f_n(r,R) = f_n(r-R)$ □

- The Wannier functions are orthogonal

$$\delta_{nm}\delta_{RR'} = \int dr\, \phi_n^*(r-R)\phi_m(r-R') = \int dr \int \frac{dk}{v_0} \int \frac{dk'}{v_0} e^{ikR} \psi_{nk}^*(r-R) e^{ik'R'} \psi_{nk'}(r-R') =$$

$$= \frac{1}{v_0^2} \int dk \int dk'\, e^{ikR} e^{-ik'R'} \int dr\, \psi_{nk}^*(r-R)\psi_{mk'}(r-R') =$$

$R' = R + \tilde{R} \to \psi_{mk'}(r-R-\tilde{R}) = e^{ik'\tilde{R}} \psi_{mk'}(r-R)$

$$= \frac{1}{v_0^2} \int dk \int dk'\, e^{ikR} e^{-ik'R'} e^{ik'R'} e^{-ik'R} \int dr\, \psi_{nk}^*(r-R)\, \psi_{mk'}(r-R)$$

↑ scalar product of two Bloch states

Since 2 Bloch states are independent (because they have different quantum numbers) so:

$$= \frac{1}{v_0^2} \int dk \int dk'\, e^{ikR} e^{-ik'R'} e^{ik'R'} e^{-ik'R} \delta_{nm}\delta_{kk'} =$$

$$= \frac{1}{v_0^2} \int dk\, e^{i(R-R')k} \delta_{nm} = \delta(R-R')\delta_{nm}$$ □

Electron's velocity

Another definition of the Bloch function, we know is:

$\psi_{nk}(r) = e^{ik\cdot r} u_{nk}(r)$ where $u_{nk}(r) = u_{nk}(r+R)$

We know that:

$$\frac{\hbar}{i}\nabla\psi_{nk}(r) = \frac{\hbar}{i}\nabla(e^{ik\cdot r}u_{nk}(r)) = \hbar k\, \psi_{nk}(r) + \frac{\hbar}{i} e^{ik\cdot r} \nabla u_{nk}(r)$$

$\longrightarrow -i\hbar\nabla$ is not a momentum $\to$ quasimomentum.

$$H_k u_{nk}(r) = \left(+\frac{\hbar^2}{2m}\left(-i\nabla + k\right)^2 + U(r)\right) u_{nk}(r) = \varepsilon_{nk}\, u_{nk}(r)$$

Now, let's take a small variation of k $\quad k+q$ and let's compute $\varepsilon_n(\underline{k}+\underline{q})$ (Taylor expansion)

$$\varepsilon_n(\underline{k}+\underline{q}) = \varepsilon_n(\underline{k}) + \sum \frac{\partial \varepsilon_n(k)}{\partial k_i} q_i + \frac{1}{2}\sum_{i,j} \frac{\partial^2 \varepsilon_n(k)}{\partial k_i \partial k_j} q_i q_j + o(q^2)$$

$$H_{k+q} = +\frac{\hbar^2}{2m}\left(-i\nabla + k + q\right)^2 + U(r) =$$

$$= H_k + \frac{\hbar^2 q^2}{2m} + \frac{\hbar^2}{m}\, q \cdot \left(\frac{1}{i}\nabla + k\right) \quad \checkmark$$

We know that in perturbation theory: $H = H_0 + V$

$$\varepsilon_n = \varepsilon_n^0 + \int dr\, \psi_n^* V \psi_n + \sum_{n' \neq n} \frac{\left|\int dr\, \psi_n^* V \psi_{n'}\right|^2}{\varepsilon_n^0 - \varepsilon_{n'}^0}$$

Then applying this to the previous Hamiltonian

$$\sum_i \frac{\partial \varepsilon_n(k)}{\partial k_i} q_i = \sum_i \int d\underline{r}\, u_{nk}^*(\underline{r}) \frac{\hbar^2}{m}\left(\frac{1}{i}\nabla + k\right)_i q_i\, u_{nk}(r) =$$

$$= \sum_i \int d\underline{r}\; e^{-ikr}\, u_{nk}^*(\underline{r}) \frac{\hbar^2}{m}\, e^{ikr} \left(\frac{1}{i}\nabla + k\right)_i q_i\, u_{nk}(r) =$$

$$= \frac{\hbar}{m}\sum_i \int d\underline{r}\, \psi_{nk}^*(\underline{r})\, \frac{\hbar}{i}\nabla_i\, \psi_{nk}(\underline{r})\, q_i =$$

$$\longrightarrow \quad \frac{\partial \varepsilon_n(k)}{\partial k_i} = \frac{\hbar}{m}\int d\underline{r}\, \psi_{nk}^*(\underline{r}) \left(\frac{\hbar}{i}\nabla\right) \psi_{nk}(\underline{r})$$

$$\longrightarrow \quad \boxed{\frac{1}{\hbar}\frac{\partial \varepsilon_{nk}}{\partial k_i} = \langle v_i \rangle}$$

So the velocity of the electron is the gradient of the band (respect to k) divided by $\hbar$.

Why not use the Fermi surface in the tight-binding model?

By convention, the Fermi surface separates filled from empty states, *where these are infinitesimally close* – that is, where the boundary falls in the middle of a band. If the boundary (the Fermi level) instead falls in a band gap, we say that a material has no Fermi surface. Thus one definition of a metallic conductor is "a solid with a Fermi surface".

In the NFE model, there are only very small band gaps, which are treated as perturbations to the free electron gas, and there will always be a Fermi surface. On the other hand, in the tight-binding approximation, there are large gaps between bands, and if (as in this case) we have a filled band, there will be no Fermi surface.

Why don't they give the same answer?

Ultimately these two models are approaching the same place from opposite directions: the NFE model says that solids are basically metals, with some small perturbations that could make them insulators, and the TB model says that solids are basically insulators, with some small perturbations that could make them metals. You could think of them like the Taylor series for the same function expanded about different points. They're both approximations to the same thing, but that doesn't mean they have to agree with one another – each is better than the other in different regions.

In order to decide which model is more appropriate for a real system, we'd need to get more quantitative. In the NFE model, this would mean specifying the weak periodic potential (or, more specifically, its Fourier components). In the TB model, it would mean introducing more orbitals and being precise about their overlap.

Given quantitative values for each model, it is indeed possible for them to predict the same bands and therefore the same behaviour. But with as little information as you were given in this problem, we can't go any further than the worked solution that you gave – including the fact that the models give different predictions.

Cap. 5
DYNAMICS OF THE ELECTRONS INSIDE A CRYSTAL

ELECTRICAL CONDUCTIVITY IN A METAL in the DRUDE MODEL

The current density is related to Electric field via an object, that in general is a tensor, called conductivity. σ

$$\boxed{\underline{j} = \sigma \underline{E}}$$

where the current density is defined as:

$$\boxed{\underline{j} = (-e)\, n \cdot \langle \underline{v} \rangle}$$

where $\langle \underline{v} \rangle = \underline{v}_0 - \left\langle \frac{e\underline{E}t}{m} \right\rangle = -\frac{e}{m}\underline{E}\cdot\tau$

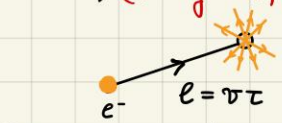
- $\langle \underline{v} \rangle$: average statistic velocity
- $\underline{v}_0$: average velocity inside the metal (in absence of $\underline{E}$)
- τ: average time between 2 collisions (between e^- and ions)

$$\longrightarrow \boxed{\sigma = \frac{n e^2}{m}\tau}$$ Standard Drude formula for the conductivity

What are the assumption of this model?

- No $e^- - e^-$ interaction (free particle) (Wrong assumption)
- The e^- can collide with the ions of the crystal. The collisions are instantaneous and each time they collide they scatter in a random uniform direction. (because ions are much heavier) (Wrong assumption)

$$\begin{cases} \frac{dt}{\tau} : \text{probability of collision between } [t, t+dt] \\ \left(1 - \frac{dt}{\tau}\right) : \text{probability of no collision between } [t, t+dt] \end{cases}$$



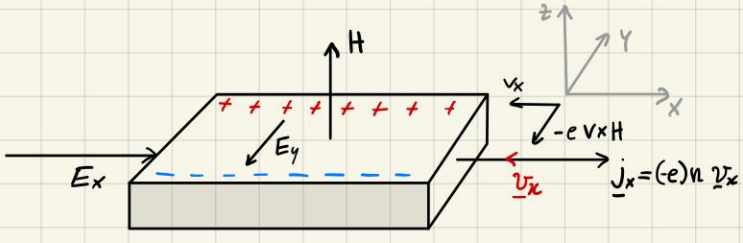
if I make a super cleaner crystal working at low T (for lesser vibrations) $\tau_{exp} \gg$ $\rightarrow \ell \gg 10\,\text{Å}$ How is it possible?!

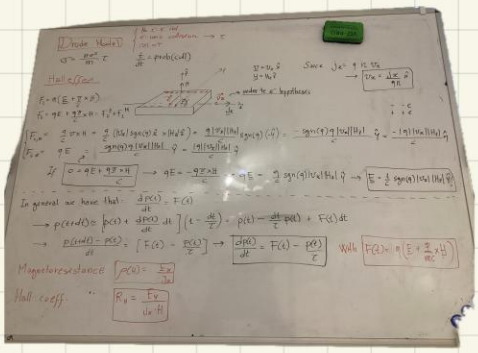
- The scale of the velocity is determined by the temperature $|v| \sim T$ (Wrong assumption)
  It's wrong because the electrons are not classical particles and $|v| \sim T$ it is not true at low energy scale.
  With this wrong assumption, if we assome $\ell \sim 1\text{-}10\,\text{Å}$ (wrong assumption) we get apparently and erroneously a value of τ not so different from the experimental result of $\tau \sim 10^{-14}\,s$. (obtaining an apparent agreement).

We know that e^- do not hit ions : they are in a stationary Bloch state, they feel the periodic potential of the ions. If there was an impurity (e.g. a missing atom) or the temperature is too high and it induces thermal vibrations, the symmetry of the B.L. can be broken and this can induces possible scattering.

HALL EFFECT AND MAGNETORESISTANCE

The Hall effect is the oboervation of a potential difference ΔV in the transversal direction in a conductor got through a current in the longitudinal direction in a perpendicular magnetic field.





The force excerts by $\underline{H}$ on the electrons is : $\boxed{\underline{F}(t) = -\frac{e}{c}\underline{v} \times \underline{H}}$

As in the figure we choose $\underline{v} = v_x \hat{x}$; $\underline{H} = H_z \hat{z}$ $\longrightarrow$ $\underline{F}(t) = -\frac{e}{c} v_x H \hat{y}$

With a certain time the accomulated charge is such that the Lorentz force is compensated by the new electric field generated in the y direction.

$\longrightarrow$ $q\underline{E} = -\frac{q}{c} v_x H \hat{y}$ $\longrightarrow$ $\boxed{\underline{E} = -\frac{v_x}{c} H \hat{y}}$ $\longrightarrow$ Voltage $\Delta V \neq 0$

In this way electrons will move only along $\hat{x}$. $\longrightarrow$ only $j_x \neq 0$ $(j_y = 0)$

We can define two quantities of interest:

1) The magnetoresistance: $\boxed{\rho(H) = \frac{E_x}{j_x}}$ (tendency of a material to change the value of its electrical res.)

2) The Hall coefficient: $\boxed{R_H = \frac{E_y}{j_x \cdot H}}$ (characteristic of the material, well measurable)

The force is in general $\frac{dp(t)}{dt} = F(t)$ $\longrightarrow$ $dp(t) = F(t)\,dt$

$\longrightarrow$ $p(t+dt) = \left[p(t) + F(t)\,dt + o(dt^2)\right]\left(1 - \frac{dt}{\tau}\right) \simeq p(t) - \frac{dt}{\tau} p(t) + F(t)\,dt$ $\longrightarrow$ $\boxed{\frac{dp}{dt} = F(t) - \frac{1}{\tau} p(t)}$

- $F(t)\,dt$: variation of the p(t) due to the force
- $\left(1 - \frac{dt}{\tau}\right)$: prob. of no collision (we can be sure that the e^- is not collided with any ions) (where the Drude model enters)
- $\frac{1}{\tau} p(t)$: it acts like a friction coefficient

To calculate them we firstly find j_x and j_y in the presence of an $\underline{E}$ with generic E_x and E_y and in presence of $\underline{H}$ in the $\hat{z}$ axis. The force acting of each electron is $\underline{F} = -e\left(\underline{E} + \frac{\underline{v}}{c} \times \underline{H}\right)$

$$\frac{d\underline{p}}{dt} = -e\left(\underline{E} + \frac{\underline{p}}{mc} \times \underline{H}\right) - \frac{\underline{p}}{\tau} \qquad \text{n.b. } \underline{j}(t) = -en\underline{v}(t) = \frac{-ne}{m}\underline{p}(t)$$

$\longrightarrow$

$$\begin{cases} 0 = \left(-eE_x + \left(\frac{eH}{mc}\right)p_y - \frac{p_x}{\tau}\right) \times \left(\frac{-en\tau}{m}\right) \\ 0 = \left(-eE_y + \left(\frac{eH}{mc}\right)p_x - \frac{p_y}{\tau}\right) \times \left(\frac{-en\tau}{m}\right) \end{cases} \qquad \begin{cases} \sigma E_x + (\omega_c \tau) j_y - j_x = 0 \\ \sigma E_y + (\omega_c \tau) j_x - j_y = 0 \end{cases}$$

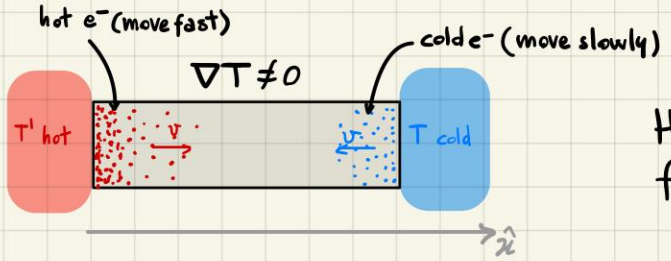
Since we want to be in a stationary state where theres current only along $\hat{x}$ and not along $\hat{y}$, $j_y = 0$

$\longrightarrow$ $\begin{cases} j_x = \sigma E_x \\ \sigma E_y = j_x(-\omega_c \tau) \end{cases}$ $\longrightarrow$ $\boxed{\rho(H) = \frac{1}{\sigma}}$ (it does not depend on H) (quite correct for some metals)

$\boxed{R_H = \frac{E_y}{H j_x} = -\frac{1}{nec}}$ (just a constant, characteristic of the material)

R_H can be tested experimentally. The mistery is that in some metals $R_H < 0$ (which confirms that the electrons are the carriers of the current) and in some metals $R_H > 0$ (which means that an hypothetical positive charge particle carries the current.
This was a real problem even for the updated version of Drude : Sommerfeld model.

HEAT CONDUCTION IN A METAL



How the heat is carried from the left to the right?

Heat current : $j_q = -\kappa \frac{dT}{dx}$

κ ↑ heat conductivity

In the hot region e^- move to the right $\quad x = vt$
In the cold region e^- move to the left $\quad x = -vt$

$$\longrightarrow \quad j_q^{eq} = \frac{n}{2} v\, \varepsilon\left(T(x-v\tau)\right) + \frac{n}{2}(-v)\,\varepsilon\left(T(x+v\tau)\right)$$

↑ half of tot e^- ; ↑ energy carried by hot electrons

If we assume that $\ell = v\tau \ll L \sim o(\nabla T)$ (scattering lenght ≪ thermal variation lenght scale) we can expand j_q^{eq} at the point x

$$j_q^{eq} = \cancel{\frac{n}{2} v\,\varepsilon(T(x))} - \cancel{\frac{n}{2} v\,\varepsilon(T(x))} + \frac{n}{2} v \frac{d\varepsilon}{dT}\frac{dT}{dx}(-v\tau) \times 2$$

$$j_q^{eq} = n v^2 \tau \frac{d\varepsilon}{dT}\left(\frac{-dT}{dx}\right)$$

Now $\quad \langle v_z^2 \rangle = \langle v_y^2 \rangle = \langle v_x^2 \rangle = \frac{\langle v^2 \rangle}{3} \quad \longrightarrow \quad j_q^{eq} = -\frac{N}{V} v_x^2 \tau \frac{d\varepsilon}{dT} \nabla T = -\frac{1}{3}\langle v^2 \rangle \tau\, c_v \nabla T$

$$\longrightarrow \boxed{j_q^{eq} = -\frac{\langle v^2 \rangle}{3} \tau\, c_v \nabla T} \qquad \boxed{\kappa = \frac{\langle v^2 \rangle}{3} \tau\, c_v = \frac{1}{3} \ell v c_v} \quad \text{heat conductivity}$$

Dividing the thermal conductivity by the electrical conductivity :

$$\frac{\kappa}{\sigma} = \frac{\frac{\langle v^2 \rangle}{3} \cancel{\tau}\, c_v}{\frac{ne^2}{m}\cancel{\tau}} = \frac{1}{3}\frac{\langle v^2 \rangle m c_v}{ne^2}$$

It was natural for Drude to apply the classical ideal gas laws in evaluating c_v and $\langle v^2 \rangle$

$$c_v = \frac{3}{2} n k_B \quad ; \quad \frac{1}{2} m v^2 = \frac{3}{2} k_B T \longrightarrow v^2 = \frac{3 k_B T}{m}$$

$$\longrightarrow \frac{\kappa}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 \quad \sim \text{Wiedmann - Franz equation}$$

$$\longrightarrow \boxed{\frac{\kappa}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2} \simeq 2{,}22 \cdot 10^{-8} \frac{W\Omega}{K^2} = 2 \times \text{exp. result} \quad \text{Fortuitous agreement}$$

Two huge mistakes compensated each others giving a fortuitous agreement.

The main problem of Drude theory is that when I have a very clean material the σ_{exp} starts to become higher and then τ_{exp} becomes higher too. This means that even assuming a small velocity $\ell = |v|\tau$ can be higher than 10 Å How is it possible? The distance between 2 ions must be unchanged!

The main issue of Drude theory was the assumption of electrons as classical particles : then the estimation of $|v|$ and c_v was not correct.
The solution to this pozzle is due by the Sommerfeld model.

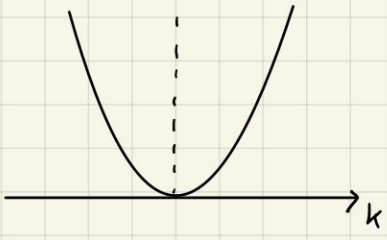
SOMMERFELD MODEL

The Sommerfeld model takes into account that electrons are Fermionic quantum particles. The key point is that they have to satisfy the Pauli principle, then we can put at most 2 electrons (1 spin up, 1 spin down) per quantum state therefore we have to fill sequentially the levels which have an ever higher energy Then we have a large Kinetic energy scale for the fermions (eg for typical metals ~ 1-10 eV) Then we observe that $|v| \sim T$ is too underestimated (because we understand it was neglected the fermionic character of the electrons)

$$\mathcal{E}_{\underline{K}} = \frac{\hbar^2 K^2}{2M}$$

$$\underline{v} = \frac{\underline{p}}{m} = \frac{\hbar \underline{K}}{m} = \frac{1}{\hbar}\frac{\partial \mathcal{E}_K}{\partial \underline{K}} \qquad \underline{p} = \hbar \underline{K}$$

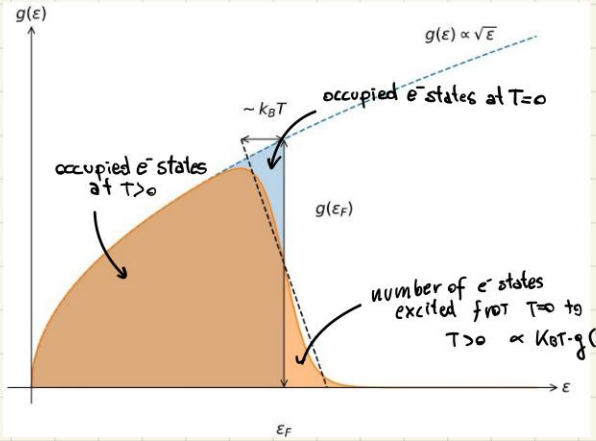
$$\psi_{\underline{K}} = \frac{1}{\sqrt{V}} e^{i \underline{K}\cdot \underline{r}} \quad : \text{plane waves}$$



$K \in [-\infty, +\infty] \quad \Delta K = \frac{2\pi}{L}$

(n.b. In Bloch's model $K \in 1^{st}BZ \quad \Delta K = \frac{2\pi}{L}$)

At the same time the estimation of c_v was too much overestimated because at $T \to 0K$ the c_v has to vanish otherwise we cannot satisfy the 3rd principle of thermodynamics (the entropy $S \to 0$ for $T \to 0$)
This is indeed true for fermionic particles since $c_v \sim T$. Infact if we give some heat to our sample (to see how its temperature has changed as an effect of the internal energy changing) the extra energy can be accepted only by electrons near the Fermi energy because only them have near empty states. How many electrons can acquire energy? Only them that are in a shell of order T around the Fermi level, so the # of e^- which can accept energy is of order T. Therefore when I give an energy of order $k_B T$ the total amount of energy ΔU which can I give to my system is of order $\sim T^2$ and then $c_v \sim T$.
In conclusion $c_v \sim T$ is a consequence of the Pauli principle too. (See figure below)



For a much accurate treatment: we know $\mathcal{E}(K) = \frac{\hbar^2 K^2}{2m}$

$$D(\mathcal{E}) = 2\int \frac{ds}{(2\pi)^3}\frac{1}{|\nabla \mathcal{E}(K)|} = \int \frac{ds}{4\pi^3}\frac{m}{\hbar^2 K} = \int_0^{\frac{\sqrt{2m\mathcal{E}}}{\hbar}} dK \frac{4\pi K^2}{4\pi^3}\frac{m}{\hbar^2 K} = \frac{m}{\hbar^2 \pi^2}\frac{\sqrt{2m\mathcal{E}}}{\hbar} \sim \sqrt{\mathcal{E}}$$

$$U = \int_{-\infty}^{+\infty} d\mathcal{E}\, \mathcal{E}\, D(\mathcal{E})\frac{1}{e^{\beta\mathcal{E}}-1} \underset{\beta\to\infty\ (T\to 0)}{\sim} U_0 + T^2$$

↑ Sommerfeld expansion

$$C_v = \frac{\partial U}{\partial T} \sim T$$

In conclusion Drude theory was wrong, Sommerfeld theory gave great improvement but he still couldn't explain R_H (<0 or >0). Moreover it is strange to consider electrons as free particles in an environment full of ions. why the e^- do not scatter with them?

The last update is the so called Semiclassical theory of Bloch electrons.

SEMICLASSICAL MODEL OF BLOCH ELECTRONS DYNAMICS

In the hystory of "Condensed Matter Physics" there are three attempts to describe physics of the electrons in a crystal:

1) **DRUDE MODEL**: In this model electrons in a solid are a gas of Boltzmann particles. (equipartition theorem, roughly estimation of c_v). By the ratio of $\frac{\sigma_{electrical}}{\sigma_{thermal}}$ the fact that he was wrong almost canceled except for a factor of 2, so at the beginning some people though that Drude's theory was correct (only wrong by a factor of 2). No Quantum Mechanics.

2) **SOMMERFELD MODEL**: This model takes into account Quantum Mechanics but the gas is considered as a free-electron gas $\longrightarrow$ Free Fermionic Gas.

$$\mathcal{E}_{\underline{k}} = \frac{\hbar^2 k^2}{2M} \; ; \; \underline{p} = \hbar \underline{k} \; ; \; \underline{v} = \frac{\underline{p}}{m} = \frac{\hbar \underline{k}}{m} = \frac{1}{\hbar} \frac{\partial \mathcal{E}_{\underline{k}}}{\partial \underline{k}} \; ; \quad \psi_{\underline{k}} = \frac{1}{\sqrt{V}} e^{i \underline{k} \cdot \underline{r}}$$

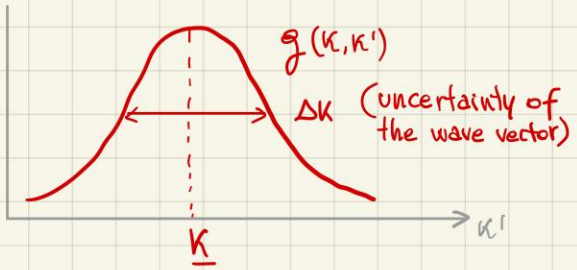
Problem: it does not explain why there are metals and insulators. Infact a system explained in this way behaves always like a metal.

3) **BLOCH'S MODEL**: This model, as we know, join the Quantum Mechanics with the lattice theory. Then it treats the electrons like a fermionic gas in a periodic potential (not free).

$$\mathcal{E}_{\underline{k},n} \text{ (bands separated by gaps)} \; ; \; \underline{p} \neq \hbar \underline{k} \; ; \; \underline{v}_{n\underline{k}} = \frac{1}{\hbar} \frac{\partial \mathcal{E}_{n\underline{k}}}{\partial \underline{k}} \; ; \quad \psi_{n\underline{k}}(\underline{r}) = u_{n\underline{k}}(\underline{r}) e^{i \underline{k} \cdot \underline{r}}$$

Whenever I think of an electron moving in a crystal I should not think of an e^- as being in an eigenstate of the Bloch Hamiltonian, because in an eigenstate nothing depends on time because they are stationary states. If an electron travel along a crystal we have to think of this e^- described by wave pocket, ie. linear combination of Bloch waves functions, with different wavevectors, which, since they are eigenfunctions, evolve as $e^{-i \mathcal{E}_{nk'} t} \psi_{nk'}$:

$$\psi_n(\underline{k}, \underline{r}, t) = \sum_{\underline{k}'} \underbrace{g(\underline{k}, \underline{k}')}_{\text{e.g. Gaussian (for a Gaussian W.P.)}} \psi_{nk'}(\underline{r}) e^{\frac{-i \mathcal{E}_{nk'} t}{\hbar}}$$



We want to assign the k-vector to the wavepacket with a small uncertainty. For example if $\Delta k \sim \frac{\pi}{a} \longrightarrow \underline{k}$ is practically completly undetermined. Then we want $\Delta k \ll \frac{\pi}{a}$

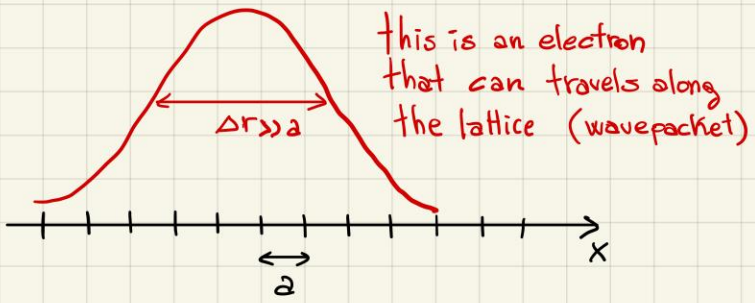
N.B. I'm fixing the index band n (I cannot promote e^- to a band to another: low energy processes)

Let's expand for $k' \approx k \longrightarrow k' \approx k + (k' - k) = k + \Delta k$ (assuming that $g(k,k')$ is peaked around $\underline{k}$)

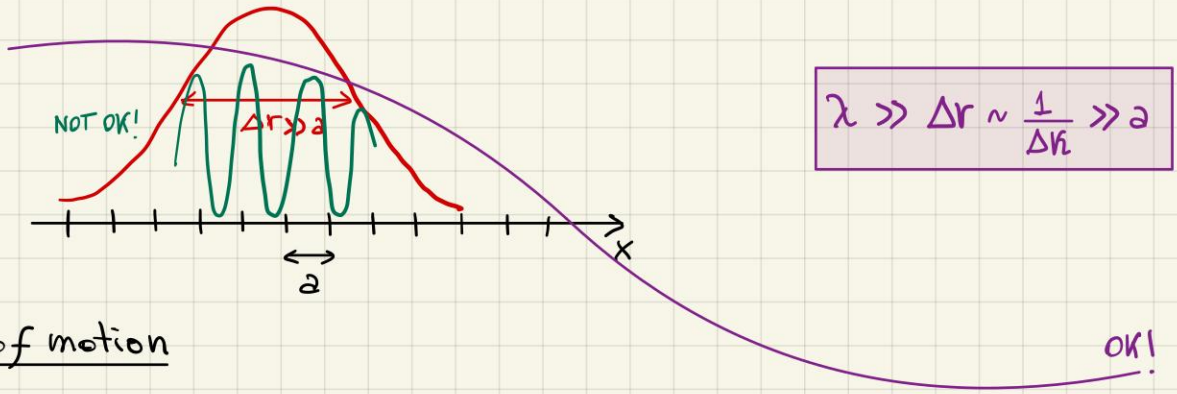
$$\psi_{nk'} = u_{nk'}(\underline{r}) \cdot e^{i \left(\underline{k}' \cdot \underline{r} - \frac{\mathcal{E}_{nk'} t}{\hbar} \right)} \approx u_{n\underline{k}}(\underline{r}) e^{i \left(\underline{k} \cdot \underline{r} - \frac{\mathcal{E}_{n\underline{k}} t}{\hbar} \right)} e^{i (\underline{k}' - \underline{k}) \left[\underline{r} - \frac{1}{\hbar} \frac{\partial \mathcal{E}_{n\underline{k}}}{\partial \underline{k}} t \right]}$$

$$\longrightarrow \psi_n(\underline{k}, \underline{r}, t) \approx u_{n\underline{k}}(\underline{r}) \cdot e^{i \left(\underline{k}' \cdot \underline{r} - \frac{\mathcal{E}_{nk'} t}{\hbar} \right)} \sum_{\underline{k}'} g(\underline{k}, \underline{k}') e^{i (\underline{k}' - \underline{k}) \left[\underline{r} - v_{n\underline{k}} \cdot t \right]}$$

Let's take a lattice with spacing a. Since we asked that $\Delta k \ll \frac{\pi}{a}$ it means that $\Delta r \gg a$ $(\Delta r \Delta k \sim 1)$



A way to probe the properties of an electron in a crystal is to apply an external E.M. field. Since the particle is not point like but it's spread with some Δr, the field cannot vary to fast on the scale Δr. Then the wave lenght of the field will be much larger of $\Delta r \longrightarrow \lambda \gg \Delta r$



$$\lambda \gg \Delta r \sim \frac{1}{\Delta k} \gg a$$

Equations of motion

$$\begin{cases} \dot{\underline{r}} = \underline{v}_{n\underline{k}} = \frac{1}{\hbar}\frac{\partial \varepsilon_{n\underline{k}}}{\partial \underline{k}} \\ \hbar \dot{\underline{k}} = -e\left[\underline{E}(\underline{r},t) + \frac{\underline{v}_{n\underline{k}}}{c} \times \underline{H}(\underline{r},t)\right] \longrightarrow \text{the rate of change of } \underline{k} \text{ is } \propto \text{ to the force} \\ \qquad\qquad \text{(if } F=0 \rightarrow \underline{k} \text{ would be a good quantum number)} \\ n = \text{const of motion (not interband processes)} \longrightarrow \text{weak e.m. field} \end{cases}$$

What are the values of E and H in order to have $n \neq$ const?

ELECTRIC BREAKDOWN $\quad eE_a \lesssim \frac{\varepsilon_{gap}^2}{\varepsilon_F}$ (typically $eE_a \sim 10^{-10}$ eV) $\longrightarrow \varepsilon_{gap} \sim 10^{-5}$ eV

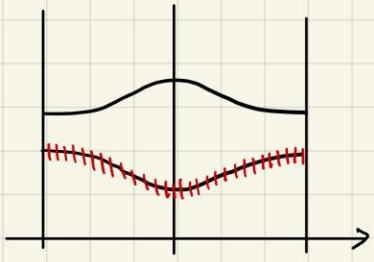
MAGNETIC BREAKDOWN $\quad \hbar\omega_c = \hbar\frac{eH}{mc} \lesssim \frac{\varepsilon_{gap}^2}{\varepsilon_F}$ (typically $\hbar\omega_c = 10^{-1}$ eV) $\longrightarrow \varepsilon_{gap} \sim 10^{-2}$ eV

What are the conclusion implied by those equations?

1st statement: FILLED (AND EMPTY) BANDS ARE INERT

A filled band does not play any role in the dynamics (under the assumption tha $n = \text{const}$).

- Current density (in a lattice)



$$\underline{j} = (-e)n\cdot\underline{v} \xrightarrow{\text{lattice}} \underline{j} = (-e)\cdot 2\int_{1^{st}BZ}\frac{dk}{(2\pi)^3}\underline{v}_{n\underline{k}} = 0$$

2: spin degeneracy; $\underline{v}_{n\underline{k}} = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k}$

Since v_{nk} is the derivative of a periodic function $\varepsilon(k) = \varepsilon(k+G)$ The integrating from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$ we get 0. ★

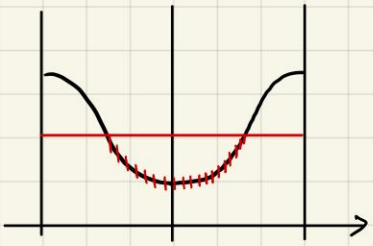
- Heat density

$$\underline{j}_\varepsilon = 2\int_{1^{st}BZ}\frac{dk}{(2\pi)^3}\underline{v}_{n\underline{k}}\,\varepsilon_{n\underline{k}} = 0 \quad \text{(For the same reason)}$$

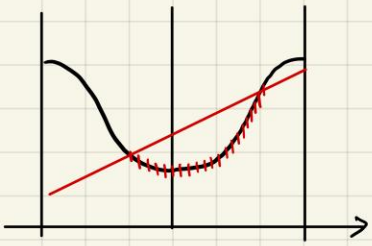
$\longrightarrow$ WE CAN IGNORE EMPTY AND FILLED BANDS

2nd STATEMENT — THE ONLY INTERESTING BANDS (THAT INVOLVE THE e^- IN A CRYSTAL) ARE THE PARTIALLY FILLED BANDS

Of course we need an e.m. field! Infact if we do not perturb the system we have as many electrons going forward as we have electrons going backward $\longrightarrow$ symmetry $\longrightarrow j=0$

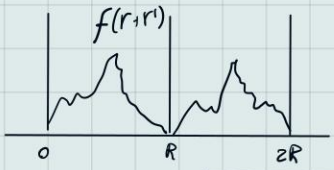


If we perturb an E.M. field on a metal at equilibrium I will have some more electrons in one direction than I have in the other and then in the presence of an electric field the average current will be not zero $j \neq 0 \longrightarrow$ there is non-zero drift velocity



Theorem : (to prove ★)

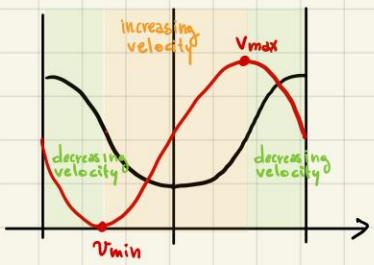
$$I(r') = \int_{\text{Prim. cell}} dr\, f(r+r') \quad \text{where } f \text{ is repeated periodically}$$



$$\nabla_{r'} I(r') = \int_{\text{cell}} dr\, \nabla_{r'} f(r+r') = \int dr\, \nabla_r f(r+r') = 0 \longrightarrow \boxed{\int_{\text{Cell}} dr\, \nabla f(r) = 0}$$

Motion of Bloch electrons in a constant E field

$$\begin{cases} \hbar \dot{k} = -e\,\underline{E} \longrightarrow \underline{k}(t) = \underline{k}(0) - \dfrac{e\underline{E}}{\hbar} t \\ v_{n\underline{k}(t)} = \dfrac{1}{\hbar} \dfrac{\partial E_k}{\partial \underline{k}} \quad \text{(periodic function of } \underline{k}) \end{cases}$$



Seems tha a constant E field should create an alternating current but this is never been observed. We indeed observe a constant drift velocity. Why? Because we have the balancing of two forces : one is the force of the E field and the other is the force exerted by some other d.o.f. that act like a friction. This friction is not due by the ions because a periodic potential is not able to exert a friction. but it can be exist by two causes :

1) defects in the crystal (a missing atom somewhere) (dominant at low temperature)
2) At high temperature the vibration of the crystal (implies that the periodicity is true only on an average) produces an effective friction.

So this equation is correct if we neglet "collisions". If in a crystal there are collisions, these collisions will bring our electron to a steady state where the equation is not true anymore.

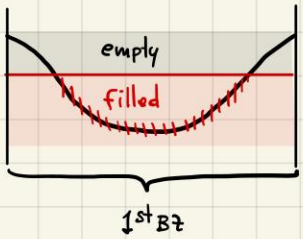
HOLES

Let's show that occupied states behave as electrons and unoccupied ones as positrons (holes). We observed that:

$$\underline{j} = (-e)\cdot 2\int_{1^{st}BZ} \frac{d\underline{k}}{(2\pi)^3} v_{n\underline{k}} = 0 \qquad \text{(because of the periodicity)}$$

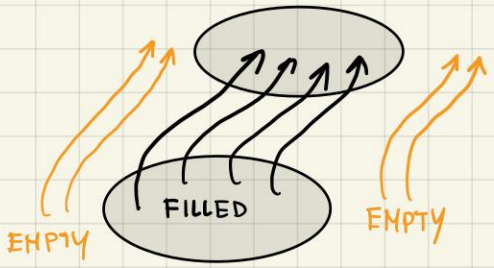
Now imagine to have a partially filled band (there are also empty states). Then:

$$0 = \int_{1^{st}BZ} = \int_{filled} + \int_{empty} \longrightarrow \int_{filled} = -\int_{empty}$$



$$\longrightarrow \quad \underline{j} = (-e)\cdot 2\int_{filled} \frac{d\underline{k}}{(2\pi)^3} v_{n\underline{k}} = e\cdot 2\int_{empty} \frac{d\underline{k}}{(2\pi)^3} v_{n\underline{k}}$$

So we can interpret the empty states as producing a current with a charge $+e$. Those empty states are called **holes** (or **positrons**). Even if the true carriers are the electrons we can consider the current to be carried by fictitious particles e^+ that fill the empty levels.
Of course since the total # of e^- is fixed if an empty state becomes occupied the dd occupied state becomes empty; then any evolution of my Bloch's electrons is an evolution where filled states evolve into other filled states and empty states evolve into other empty states.



Relation between force and acceleration

$$\underbrace{\hbar\dot{\underline{k}}}_{\parallel F}\cdot\underbrace{\underline{a}}_{\parallel \frac{F}{m}} = \hbar\dot{\underline{k}}\cdot\dot{\underline{v}} = \dot{\underline{k}}\cdot\frac{d}{dt}\left[\frac{\partial\varepsilon_{n\underline{k}}}{\partial\underline{k}}\right] = \sum_{\alpha=1,2,3}\dot{k}_\alpha\frac{d}{dt}\frac{\partial\varepsilon_{n\underline{k}}}{\partial k_\alpha} = \sum_{\substack{\alpha=1,2,3\\ \beta=1,2,3}}\underbrace{(\hbar\dot{k}_\alpha)}_{\parallel F}\underbrace{\frac{1}{\hbar^2}\frac{\partial^2\varepsilon_{n\underline{k}}}{\partial k_\alpha\partial k_\beta}}_{\uparrow \frac{1}{m}}\underbrace{(\hbar\dot{k}_\beta)}_{\parallel F} \quad \bigstar$$

$$\boxed{M^{-1}_{\alpha\beta} = \frac{1}{\hbar^2}\frac{\partial^2\varepsilon_{n\underline{k}}}{\partial k_\alpha\partial k_\beta}}$$ Inverse Mass tensor (symmetric and 3×3)

The relation $\bigstar$ shows that in a crystal $\underline{F}$ and $\underline{a}$ are not necessarily $\parallel$ and that the proportional factor is a 3×3 tensor; this implies that a force along a direction can produce an acceleration along another one.

We observe that: $\pm M^{-1}_{\alpha\beta} = \pm\frac{1}{\hbar^2}\frac{\partial^2\varepsilon_{n\underline{k}}}{\partial k_\alpha\partial k_\beta}$

- $-$ $\underline{k}$ near a band max (negative curvature)
- $+$ $\underline{k}$ near a band min (positive curvature)

$$\longrightarrow \quad \underline{a} = \pm M^{-1}\underline{F} = \pm M^{-1}\hbar\dot{\underline{k}} \longrightarrow \boxed{M\underline{a} = \pm\underline{F} = \pm(-e)\left[\underline{E} \pm \frac{\underline{v}}{c}\times\underline{H}\right]}$$ equation of motion (describe both e^- and holes)

If we expand near a minimum or the maximum the dispersion relation we find a parabola, then the m^{-1}_{ij} will be a diagonal matrix with eigenvalues $\pm m_1^{-1}, \pm m_2^{-1}, \pm m_3^{-1}$ on the 3 principal axes

$$\begin{pmatrix} \pm m_1^{-1} & & \\ & \pm m_2^{-1} & \\ & & \pm m_3^{-1} \end{pmatrix} \longrightarrow \varepsilon_{n\underline{k}} = + \left(\frac{\hbar k_1^2}{2m_1} + \frac{\hbar^2 k_2^2}{2m_2} + \frac{\hbar^2 m_3^2}{2m_3}\right)$$  or $\varepsilon_{n\underline{k}} = -\left(\frac{\hbar k_1^2}{2m_1} + \frac{\hbar^2 k_2^2}{2m_2} + \frac{\hbar^2 k_3^2}{2m_3}\right)$ 

I can treat holes as states with negative mass, or equivalently states with positive mass and negative energy (and hence positive charge).

It is easy to see that $\underline{v}_{n\underline{k}} = \frac{1}{\hbar}\frac{\partial \mathcal{E}}{\partial \underline{k}}$ is in the opposite direction of the electrons.

The if I apply a force along one principal axis the $\vec{a}$ of the e^- will be // to the $\vec{F}$ (if +) and antiparallel (if −). For the holes will be // (if −) and antiparallel (if +)

Cap. 6
THEORY OF HARMONIC CRYSTAL

CLASSICAL THEORY OF HARMONIC CRYSTALS

We described crystals as made of fixed atoms using the BL formalism. But this is an ideal description since atoms are made of nuclei and electrons that oscillate.
I can think a crystal as a "huge molecule" and so describe their dynamic with the quantum mechanics: approx of B.O. : e^- much faster than nuclei (since are more lighter) $\longrightarrow$ solve electronic problem assuming steady nuclei and then the energy E_e of the electron problem act as an effective potential for the nuclei motion

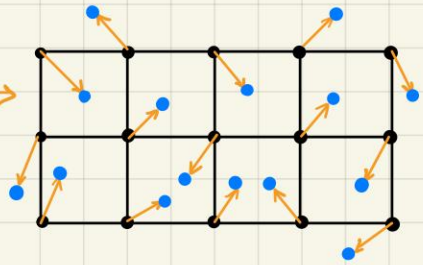
The nuclei so move in an effective potential: at g.state all the nuclei are at eq position (minimum). If we excite the system (i.e. increase T) they oscillate around the eq position.

We'll introduce a classical theory to describe the oscillations in a crystal based on the harmonic approximation and then we'll quantize it obtaining quanta: phonons. (quanta of sounds)

HARMONIC APPROXIMATION

Let's start with a a crystal described by a BL(R) (equilibrium case) If I raise T, before crystal melts, all nuclei in the site can move and we can find them on a displaced position.

$|u| \ll a$, otherwise liquid phase is more stable than solid (crystal melts)



● : ground-state
● : displacement $|u|$
● : nuclei after oscillation

$$\longrightarrow \quad \underline{r}(R) = \underline{R} + \underline{u}(R)$$

$\underline{u}(R)$ → displacement (discrete field)

The potential energy of the nuclei:

$$U = \frac{1}{2}\sum_{\underline{R},\underline{R}'} \phi(\underline{r}(R)-\underline{r}(R')) = \frac{1}{2}\sum_{\underline{R},\underline{R}'} \phi(\underline{R}-\underline{R}'+\underline{u}(R)-\underline{u}(R')) \simeq \text{(expand around eq. pos)}$$

$\downarrow$ all possible pairs

$$\simeq \frac{1}{2}\sum_{\underline{R},\underline{R}'} \phi(\underline{R}-\underline{R}') + \frac{1}{2}\sum_{\underline{R},\underline{R}'} \underbrace{(\nabla\phi)}_{=0}\cdot(\underline{u}(R)-\underline{u}(R')) + \frac{1}{4}\sum_{\underline{R},\underline{R}'}\left[(\underline{u}(R)-\underline{u}(R')\nabla\right]^2\phi\Big|_{u=0} + \cancel{O(u^3)}$$

$$\longrightarrow U = \frac{1}{2}\sum_{\underline{R},\underline{R}'}\phi(\underline{R}-\underline{R}') + \frac{1}{4}\sum_{\underline{R},\underline{R}'}\sum_{\mu,\nu=(x,y,z)}(u_\mu(R)-u_\mu(R'))\,\phi_{\mu\nu}\,(u_\nu(\underline{R})-u_\nu(\underline{R}')) \quad \text{where} \quad \phi_{\mu\nu} = \left(\frac{\partial^2\phi}{\partial r^\mu \partial r^\nu}\right)_{u=0} \quad (1)$$

We can change the variable $R-R' \equiv R''$, and notice that:

$$\sum_{\underline{R},\underline{R}'} f(R-R') = \sum_{\underline{R},\underline{R}''} f(R'') = N\sum_{R''} f(R'')$$

$$\longrightarrow U = \underbrace{\frac{N}{2}\sum_{\underline{R}}\phi(\underline{R})}_{U_{eq}} + \underbrace{\frac{1}{2}\sum_{\underline{R},\underline{R}'}\sum_{\mu,\nu=(x,y,z)} D_{\mu\nu}(\underline{R}-\underline{R}')\,u_\mu(\underline{R})\,u_\nu(\underline{R}')}_{U_{harmonic}} \quad (2)$$

N = # lattice sites

$D_{\mu\nu}(\underline{R}-\underline{R}')$ → Dynamical matrix

We can find $D_{\mu\nu}(\underline{R}-\underline{R}')$ by comparison. Let's start from the 2nd piece in ①

$$\frac{1}{4}\sum_{\underline{R},\underline{R}'}\sum_{\mu,\nu}\phi_{\mu\nu}(\underline{R}-\underline{R}')\left[u_\mu(\underline{R})u_\nu(\underline{R})+u_\mu(\underline{R}')u_\nu(\underline{R}')-u_\mu(\underline{R})u_\nu(\underline{R}')-u_\mu(\underline{R}')u_\nu(\underline{R})\right]=$$

We can see $\phi(\underline{R}-\underline{R}')=\phi(\underline{R}'-\underline{R})$ (it depends only by the distance between them). Therefore:

$$=\frac{1}{2}\sum_{\underline{R},\underline{R}'}\sum_{\mu,\nu}\phi_{\mu\nu}(\underline{R}-\underline{R}')\left[u_\mu(R)u_\nu(R)-u_\mu(R)u_\nu(R')\right]=$$

Now we see that:

$$\sum_{\underline{R},\underline{R}'}\sum_{\mu,\nu}u_\mu(R)\,\phi_{\mu\nu}(\underline{R}-\underline{R}')\,u_\nu(R)\overset{\underline{R}''=\underline{R}-\underline{R}'}{=}\sum_{\underline{R}}\left(\sum_{R''}\phi(R'')\right)u_\mu(R)\,u_\nu(R)=\sum_{\underline{R},\underline{R}'}\left(\sum_{R''}\phi(R'')\right)u_\mu(R)\,u_\nu(R')\,\delta(R-R')$$

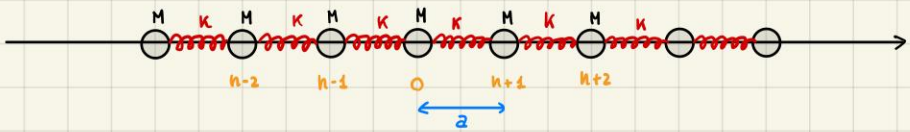
$$\longrightarrow\quad=\frac{1}{2}\sum_{\underline{R},\underline{R}'}\sum_{\mu,\nu}u_\mu(\underline{R})\left[\left(\sum_{R''}\phi(R'')\right)\delta(\underline{R}-\underline{R}')-\phi_{\mu\nu}(\underline{R}-\underline{R}')\right]u_\nu(\underline{R}')$$

By comparing this result with ② I get:

$$\boxed{D_{\mu\nu}(\underline{R}-\underline{R}')=\sum_{R''}\phi_{\mu\nu}(R'')\,\delta(\underline{R}-\underline{R}')-\phi_{\mu\nu}(\underline{R}-\underline{R}')}\qquad\text{Dynamical matrix}$$

Thanks to harmonic approx. we can describe the system as independent normal modes. To solve the normal modes problem we find the eigen values of $D_{\mu\nu}$ and it's simple using FT.

TOY MODEL 1D: SPRINGS AND BALLS



When an ion is excited it oscillates transferring its motion to all other atoms : motion of one ion is not a normal mode. The vibration in this case is longitudinal

Because we want to study the dynamic of the ion we use the displacement from the origin with a time dependence $u_n(t)$

$$U=U_{eq}+\frac{1}{2}K\sum_n(u_{n+1}-u_n)^2\qquad:\ \text{POTENTIAL ENERGY of the system}$$

$$K=\frac{1}{2}\sum_n M\dot{u}_n^2\qquad:\ \text{KINETIC ENERGY of the system}$$

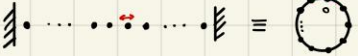
The Lagrangian $L=K-U$

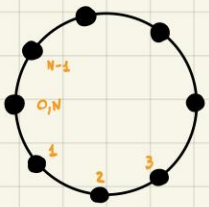
$$\longrightarrow\quad L=\frac{M}{2}\sum_n\dot{u}_n^2-\frac{K}{2}\sum_n(u_{n+1}-u_n)^2\longrightarrow\frac{d}{dt}\frac{\partial L}{\partial\dot{u}_n}=\frac{\partial L}{\partial u_n}\qquad\text{eq. of motion } n=1,\dots,N$$

$$\longrightarrow\quad M\ddot{u}_n=K(u_{n+1}-u_n)-K(u_n-u_{n-1})\longrightarrow M\ddot{u}_n=-K(2u_n-u_{n+1}-u_{n-1})$$

The lattice is not infinite : it has borders. This means that we need to fix the boundary condition.

1) Fixed B.C. : the solutions are standing waves (not propagating). The real B.C. but the more complex.
2) P.B.C : the solution are propagating waves. We can think our chain as a circle : $u_0=u_N\rightarrow u_{N+\mu}=u_\mu$. (not physical, however if we are far away from the ends of the crystal there is no much difference between what the ion does in the case of standing or travelling waves





$u_{N+\mu} = u_\mu$

P.B.C. or Born-Von Karman boundary condition

We want to solve the equation in the P.B.C. This means that we're looking for travelling waves solution:

$$u_n(t) = A e^{i(qna - \omega t)} \qquad \text{where } r = na \text{ is the distance of the } n^{th} \text{ ion to O.}$$

Using the P.B.C. $u_0 = u_N \ \forall t \rightarrow A e^{-i\omega t} = A e^{iqNa} e^{-i\omega t} \rightarrow 1 = e^{iqNa}$

$$\longrightarrow qNa = 2\pi n \longrightarrow \boxed{q = \frac{2\pi}{a}\frac{n}{N}} \qquad n = 1, \dots, N \longrightarrow$$

N normal modes
the # of solution of the travelling waves is the # of dof

q is a discret set of wave vectors. Since $q = \frac{2\pi}{a}\frac{n}{N}$ they all live in the 1st B.Z. (w.s. cell in R.L)
Moreover they are very dense $\Delta q = \frac{2\pi}{aN}$

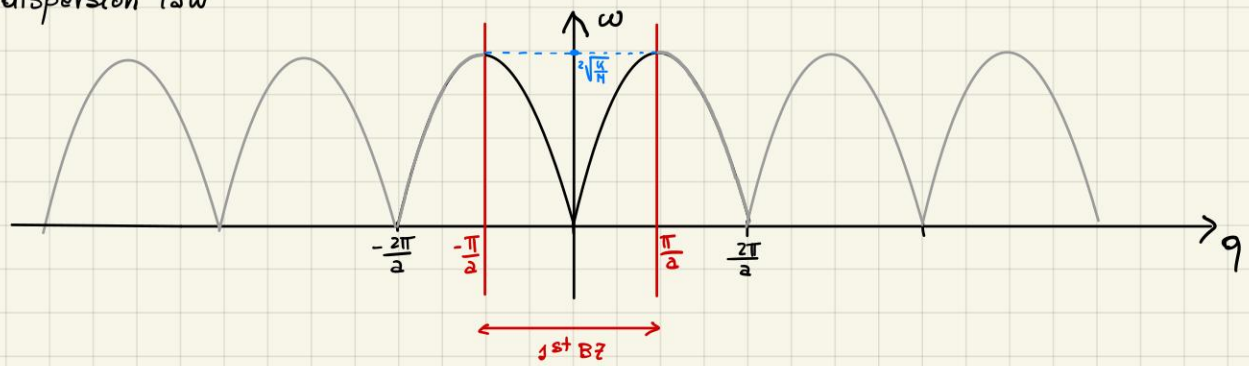
($\frac{1}{a}$ = size of 1st BZ)

$$\longrightarrow -\omega^2 M A e^{i(qna - \omega t)} = -AK\left(2 - e^{iqa} - e^{-iqa}\right) e^{i(qna - \omega t)}$$

$$\longrightarrow -\omega^2 MA = -2K(1 - \cos(qa))A \qquad (A=0 \text{ is the trivial case, assume } A \neq 0)$$

$$\longrightarrow \omega^2 = \frac{2K}{M}(1 - \cos(qa)) = \frac{4K}{M}\sin^2\left(\frac{qa}{2}\right) \longrightarrow \boxed{\omega(q) = 2\sqrt{\frac{K}{M}}\left|\sin\left(\frac{qa}{2}\right)\right|}$$ Dispersion law $\omega(q)$

The disturbance can propagates across my lattice iff the frequency ω and q are related by this dispersion law



As we said q is a discrete set and hence $\omega(q)$ is a discrete function. However because of $N \gg 1$ ($N \sim N_A$) the set is really dense. Thus in the R. space we draw $\omega(q)$ continuosly and because of the PBC we consider only the 1st B.Z.

When q is small compared with $\frac{\pi}{a}$ (i.e. $\lambda \gg a$) I get that ω is linear in q:

$$\omega(q) \simeq 2\sqrt{\frac{K}{M}}\frac{|q|a}{2} = a\sqrt{\frac{K}{M}}|q| \qquad \text{(dispersion relation for audible sound } \lambda \gg a)$$

This is the case of ordinary sound waves (if ω is linear in q, group and phase velocity are the same and indipendendent by the frequency). So, given $c_s = \frac{\omega}{q}$

$$c_s = \sqrt{\frac{K}{M}}a = \sqrt{\frac{Ka}{M/a}} = \sqrt{\frac{\tau}{\mu}}$$

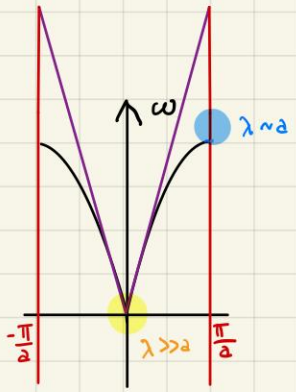
τ ← string tension; μ ← linear density

VELOCITY OF SOUNDS

$\sqrt{\frac{K}{M}}$: microscopic properties (M: mass of 1 atom, K: el. const between 2 atoms)

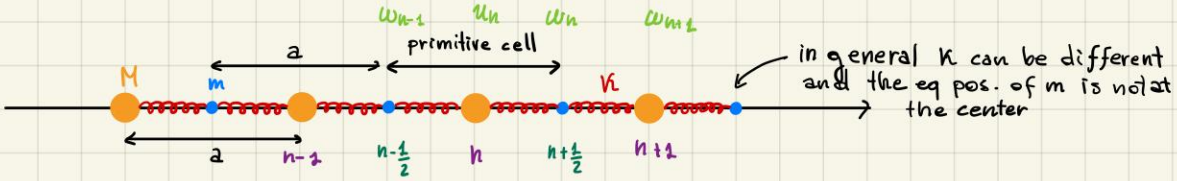
$\sqrt{\frac{\tau}{\mu}}$: macroscopic properties (elastic theory)

In conclusion from $\lambda \gg a$ (small q) ω is linear with q and then sound propagates according the elasticity theory. However if we increase q $\omega(q)$ becomes flat at the borders. because of the periodicity, in this case $\omega(q)$ is the dispersion relation for sound that we cannot hear $\lambda \sim a \rightarrow \omega$ very high



Until now we're describing oscillation classically. When we'll quantize we'll have a field whose quanta are the phonons. These quanta must obey the Bose statistic since in order to hear sound I must have a lot of them → so they should be able to occupy the same quantum state. (Analogy to seeing light → we need a lot of photons)
So as the E.M. field is a coherent state of many photons, sound is a coherent state of many phonons.

HARMONIC VIBRATIONS IN A LATTICE WITH A BASIS.



Both M and m are BL. But toghether are a BL + basis (2 atom basis).
Let: u_n be the displacement of N atoms. M are located in: $R_N = na + u_n$
Let: w_n be the displacement of m atoms. m are located in: $R_m = \left(n+\frac{1}{2}\right)a + w_n$

Then:

$$K = \sum_n \left(\frac{M}{2}\dot{u}_n^2 + \frac{m}{2}\dot{w}_n^2\right) \qquad \text{KINETIC ENERGY of the system}$$

$$U = \frac{1}{2}K \sum_n \left[\left(u_n - w_n\right)^2 + \left(u_n - w_{n-1}\right)^2\right] \qquad \text{POTENTIAL ENERGY of the system}$$

Equation of motion:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{u}_\ell} = \frac{\partial L}{\partial u_\ell} \quad ; \quad \frac{d}{dt}\frac{\partial L}{\partial \dot{w}_\ell} = \frac{\partial L}{\partial w_\ell} \qquad \ell = 1,2,\dots$$

$$\longrightarrow \begin{cases} M\ddot{u}_\ell = -K\left(u_\ell - w_\ell + u_\ell - w_{\ell+1}\right) = -K\left(2u_\ell - w_\ell - w_{\ell-1}\right) \\ m\ddot{w}_\ell = -K\left(w_\ell - u_\ell + w_\ell - u_{\ell+1}\right) = -K\left(2w_\ell - u_\ell - u_{\ell+1}\right) \end{cases}$$

I look for travelling waves solutions imposing P.B.C.

$$\begin{cases} u_n = A\, e^{i(qna - \omega t)} \\ w_n = B\, e^{i(qna - \omega t)} \end{cases}$$

(travelling waves are indipendent from the basis)

$$\longrightarrow \begin{cases} M(-i\omega)^2 A = -K\left(2A - B - B\, e^{-iqa}\right) \\ m(-i\omega)^2 B = -K\left(2B - Ae^{iqa} - A\right) \end{cases} \longrightarrow \begin{cases} \left(2K - \omega^2 M\right)A - K\left(1 + e^{-iqa}\right)B = 0 \\ \left(2K - \omega^2 m\right)B - K\left(1 + e^{iqa}\right)A = 0 \end{cases}$$

We look for non trivial solutions. I.e. det=0:

$$\begin{vmatrix} 2K - M\omega^2 & -K(1+e^{-iqa}) \\ -K(1+e^{iqa}) & 2K - m\omega^2 \end{vmatrix} = 0 \longrightarrow \text{(Must be hermitian)}$$

$$\longrightarrow \quad (2K - M\omega^2)(2K - m\omega^2) - K^2(2 + e^{iqa} + e^{-iqa}) = 0$$
$$(2K - M\omega^2)(2K - m\omega^2) - 2K^2(1 + \cos(qa)) = 0$$

TIP: Before solving the eq. check for sound modes: $q=0 \leftrightarrow \omega = 0$. If eq. obeys it then we can proceed.

$$\longrightarrow \quad \left(\frac{2K}{M} - \omega^2\right)\left(\frac{2K}{m} - \omega^2\right) - \frac{4K^2}{Mm}\cos^2\left(\frac{ka}{2}\right) =$$
$$= \omega^4 - 2\left(\frac{K}{m} + \frac{K}{M}\right)\omega^2 + \frac{4K^2}{Mm}\left(1 - \cos^2\left(\frac{qa}{2}\right)\right) =$$
$$= \omega^4 - 2K\left(\frac{1}{m} + \frac{1}{M}\right)\omega^2 + \frac{4K^2}{Mm}\sin^2\left(\frac{qa}{2}\right) = 0$$

$$\longrightarrow \quad \omega^2 = \underbrace{K\left(\frac{1}{M} + \frac{1}{m}\right)}_{\bar{\Omega}^2} \pm \sqrt{K^2\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4K^2}{Mm}\sin^2\left(\frac{qa}{2}\right)}$$

$$\downarrow$$

$$\min: \ \frac{K^2}{M^2m^2}(m+N)^2 - \frac{4K^2}{Mm} > 0 \quad \text{(always positive)}$$

The solutions are real and positive:

$$\omega^2 = \bar{\Omega}^2 \pm \sqrt{\bar{\Omega}^4 - \frac{4K^2}{Mm}\sin^2\left(\frac{qa}{2}\right)} = \bar{\Omega}^2\left[1 \pm \sqrt{1 - \frac{4K^2}{Mm\,\bar{\Omega}^4}\sin^2\left(\frac{qa}{2}\right)}\right]$$

(+) optical mode, (−) acoustic mode

The (−) solution goes to zero for $q \to 0$ → For small q it describes the propagation of sound in the crystal, that's why it's called acoustic mode. So for $q \to 0$ we have:

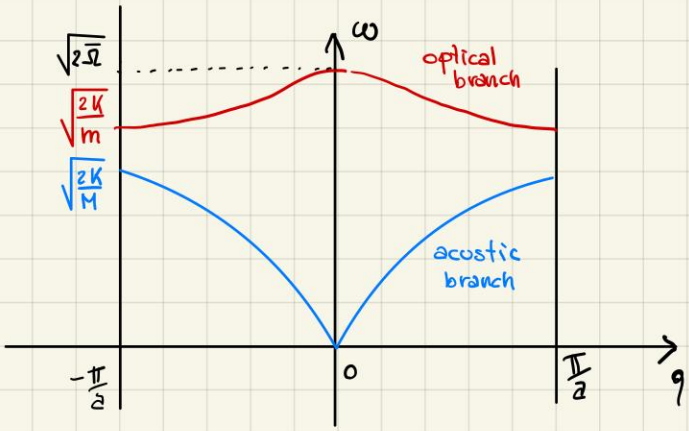
- $\omega_-^2 \simeq K\left(\frac{1}{M} + \frac{1}{m}\right)\left(1 - \sqrt{1 - \frac{4}{Mm\left(\frac{1}{M}+\frac{1}{m}\right)^2}\frac{q^2a^2}{4}}\right) \simeq$

$$\simeq K\left(\frac{1}{M} + \frac{1}{m}\right)\left(1 - 1 + \frac{q^2a^2}{2Mm\left(\frac{1}{M}+\frac{1}{m}\right)^2}\right) = \frac{Kq^2}{2(M+m)}$$

$$\longrightarrow \omega_- = \sqrt{\frac{Ka^2}{2(M+m)}}\,q = c_s q \longrightarrow c_s = \sqrt{\frac{Ka^2}{2(M+m)}}$$

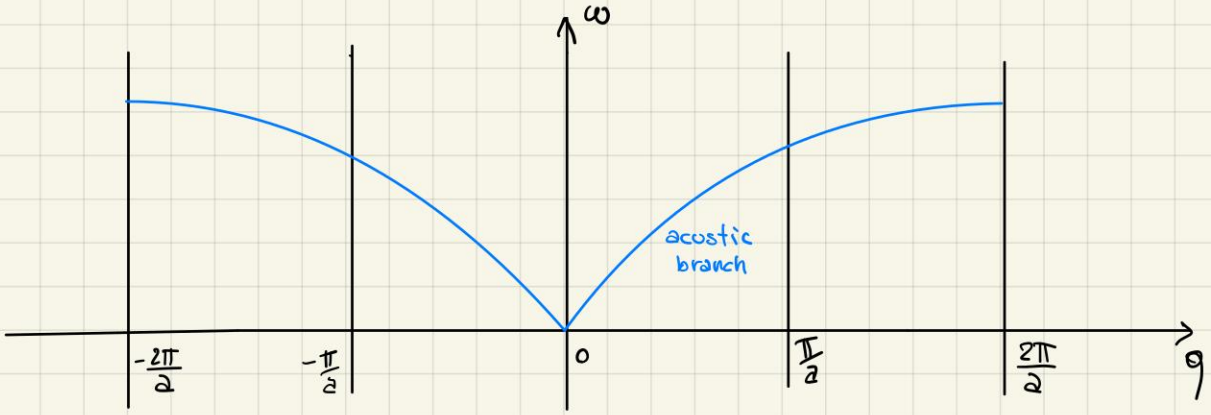
- $\omega_+^2 \simeq 2\bar{\Omega}^2 - \frac{K^2a^2}{2Mm\bar{\Omega}^2}q^2 > 0$

$$\longrightarrow \omega_+ = \sqrt{2\bar{\Omega}^2 - \frac{K^2a^2}{2Mm\bar{\Omega}^2}q^2}$$



So, for every q I have two ω, and so two travelling waves. The + solution is called optical mode because these modes, in ionic crystal can interact with EM radiation (dipole) and so are responsible for the characteristic optical behaviour of such crystals. The − solution is called acoustic mode because its dispersion at small q is $\omega = c_s q$ (characteristic of sound waves).

What happens if the 2 atoms are equal? There's no basis and the gap between branches disappears. The new displacement is $\frac{a}{2}$ therefore c_s is also the half. The 1st B.Z becomes bigger: $a \to \frac{a}{2} \xleftrightarrow{F.T.} \frac{\pi}{a} \to \frac{2\pi}{a}$
So for $m \to M$ the "basis case" tends to the "no basis case".



In conclusion in all lattices we have acoustic modes. In a BL it's the only mode we have in BL + basis we have also optical modes.

RULE
- # Sound modes is D
- # Optical modes is D(p−1)

(where p is the # of basis atoms and D the dimension)

In 1D crystal: we have 1 sound mode and p−1 optical modes
In 2D crystal: we have 2 sound modes and 2(p−1) optical modes
In 3D crystals: we have 3 sound modes (1L/2T) and 3(p−1) optical modes

The number of dof is DpN

QUANTUM THEORY OF THE HARMONIC CRYSTAL

We have the displacement classical field $\underline{u}(\underline{R},t)$. How can we quantize it?
1) We need to decompose the field in its normal modes
2) Then we can quantize the normal modes and find finally $\hat{\underline{u}}(\underline{R},t)$

In our problem we have $3Np$ normal modes (# d.o.f.). Each normal mode is characterized by each frequency which is characterized by the wave vector $\underline{q}$ and the polarization s : $\omega_s(\underline{q})$
In analogy:
- For photons $\omega_s(\underline{q}) = c|\underline{q}|$ where $s=1,2$ (only transverse)
- For phonons $\omega_s(\underline{q})$ where $s=1,2,\dots,3p$

We can write the classical Hamiltonian as:

$$\mathcal{H} = \sum_{\underline{q}}\sum_{s} \frac{1}{2}\left(P^2_{\underline{q}s} + \omega_s^2(\underline{q})\, Q^2_{\underline{q}s}\right)$$

$3pN$ indipendent harmonic oscillators (normal modes)
P: momenta of normal mode
Q: coordinate of normal mode

We know how to quantize it:

$$\hat{\mathcal{H}} = \sum_{\underline{q}}\sum_{s} \hbar\omega_s(\underline{q})\left(a^{\dagger}_{\underline{q}s}\, a_{\underline{q}s} + \frac{1}{2}\right)$$

As we said so far phonons have to be bosons. Therefore the creation and annihilation operators satisfies a commutation rule (if they had obeyed the Fermi Dirac statistic there would have been an anticommutation relation):

$$\left[a_{\underline{q}s}, a^{\dagger}_{\underline{q}'s'}\right] = \delta_{ss'}\,\delta^3(\underline{q}-\underline{q}')$$

Spectrum of the Hamiltonian

$$E = \sum_{\underline{q}}\sum_{s} \hbar\omega_s(\underline{q})\left(n_s(\underline{q}) + \frac{1}{2}\right) \equiv E_{\{n_{\underline{q}s}\}}$$

$3NP$ integers

$\underline{q}_1,\dots,\underline{q}_N$; $s_1,\dots,s_{3p}$; $N \times 3p = 3NP$

Free energy of the crystal

$$F = \ln \sum_{\{n_{\underline{q}s}\}} e^{-\beta E_{\{n_{\underline{q}s}\}}} = \ln\left[\sum_{n\,\underline{q}_1 s_1} e^{-\beta\hbar\omega_{s_1}(\underline{q}_1)\left(n_1(\underline{q}_1)+\frac{1}{2}\right)} + \dots \sum_{n\,\underline{q}_N s_{3p}} e^{-\beta\hbar\omega_{s_{3p}}(\underline{q}_N)\left(n_{3p}(\underline{q}_N)+\frac{1}{2}\right)}\right] =$$

$$= \ln \prod_{s}\prod_{\underline{q}}\left[\sum_{n,\underline{q},s} e^{-\beta\hbar\omega_s(\underline{q})\left(n_s(\underline{q})+\frac{1}{2}\right)}\right] =$$

convergent geometric series

$$= \ln \prod_{s}\prod_{\underline{q}} e^{-\frac{\beta}{2}\hbar\omega_s(\underline{q})} \sum_{n_{\underline{q}},s=0}^{\infty}\left(\underbrace{e^{-\beta\hbar\omega_s(\underline{q})}}_{<1}\right)^{n_s(\underline{q})} =$$

$$= \ln \prod_{s}\prod_{\underline{q}} \frac{e^{-\frac{\beta\hbar\omega_s(\underline{q})}{2}}}{1-e^{-\beta\hbar\omega_s(\underline{q})}} = \sum_{\underline{q},s} \ln\left(\frac{e^{-\frac{\beta}{2}\hbar\omega_s(\underline{q})}}{1-e^{-\beta\hbar\omega_s(\underline{q})}}\right)$$

$$\rightarrow \boxed{F = \sum_{\underline{q},s} \ln\left(\frac{e^{-\frac{\beta}{2}\hbar\omega_s(\underline{q})}}{1-e^{-\beta\hbar\omega_s(\underline{q})}}\right)}$$

Internal energy of the crystal

$$U = -\frac{\partial F}{\partial \beta} = \frac{\partial}{\partial \beta}\left[\sum_{\underline{q},s} \frac{\beta\hbar\omega_s(\underline{q})}{2} + \ln\left(1 - e^{-\beta\hbar\omega_s(\underline{q})}\right)\right] =$$

$$= \sum_{\underline{q},s}\left[\frac{\hbar\omega_s(\underline{q})}{2} + \frac{-e^{-\beta\hbar\omega_s(\underline{q})}(-\hbar\omega_s(\underline{q}))}{1 - e^{-\beta\hbar\omega_s(\underline{q})}}\right] =$$

$$= \sum_{\underline{q},s} \hbar\omega_s(\underline{q})\left[\frac{1}{e^{\beta\hbar\omega_s(\underline{q})} - 1} + \frac{1}{2}\right]$$

$$\longrightarrow \quad \boxed{U = \sum_{\underline{q},s} \hbar\omega_s(\underline{q})\left[\frac{1}{e^{\beta\hbar\omega_s(\underline{q})} - 1} + \frac{1}{2}\right]}$$

If I compare the internal energy and the $\langle$quantum energy$\rangle$ (thermal averaged) we get that the # of quanta quantum states is

$$\boxed{\langle n_{\underline{q}s}\rangle = \frac{1}{e^{\beta\hbar\omega_s(\underline{q})} - 1}}$$

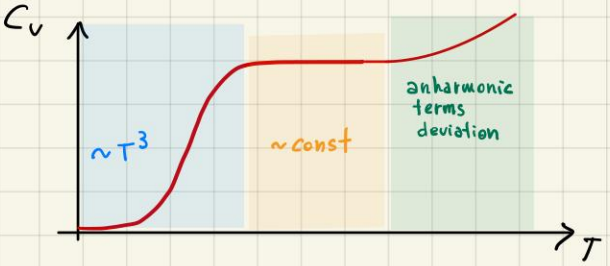
→ the thermal distribution of phonons obeies the B.E. statistic

Notice that in the above relation there's no $\mu = 0$. Since the # of phonons is not conserved we can only define their thermodynamics at equilibrium (ie # of particles fixed) which means require: $\mu = \frac{\partial F}{\partial N} = 0$

Specific heat

$$\boxed{C_V = \frac{1}{V}\frac{\partial U}{\partial T} = \frac{1}{V}\sum_{\underline{q},s} \hbar\omega_s(\underline{q})\frac{\partial}{\partial T}\left(\frac{1}{e^{\beta\hbar\omega_s(\underline{q})} - 1}\right)}$$

Experimentally:



DULONG-PETIT LAW

- In the high T limit I get the classical limit (Boltzmann distribution) ($\hbar$ disappears)

$$\beta\hbar\omega \ll 1 \longrightarrow C_V = \frac{1}{V}\sum_{\underline{q},s} \hbar\omega_s(\underline{q})\frac{\partial}{\partial T}\frac{k_B T}{\hbar\omega_s(\underline{q})} = \frac{k_B}{V}\sum_{\underline{q},s} 1 = \frac{3Np\,k_B}{V}$$

$$\longrightarrow \quad \boxed{C_V = \frac{3pN\,k_B}{V}} \quad \text{Dulong-Petit}$$

EINSTEIN MODEL

Crystal is a set of oscillators that oscillate at the same constant frequency $\omega_s(\underline{q}) = \omega_E$

$$\longrightarrow \quad \boxed{C_V = \frac{3pN}{V}\hbar\omega_E\frac{\partial}{\partial T}\frac{1}{e^{\beta\hbar\omega_E} - 1}}$$

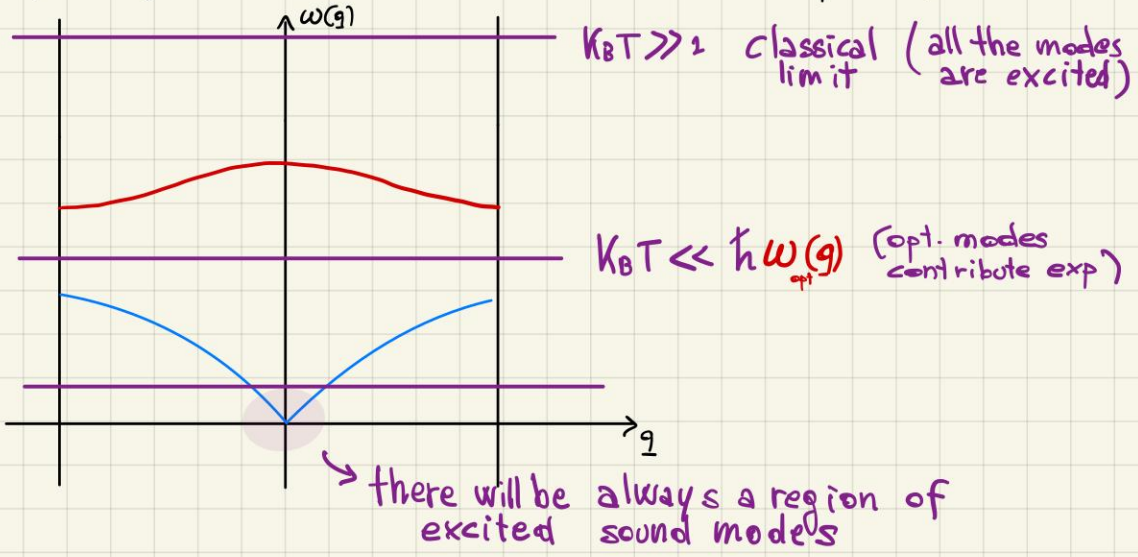
- For high T we reobtain Dulong-Petit as we should.
- In the low T limit $\frac{\hbar\omega_E}{k_B T} \gg 1$.

$$\longrightarrow \quad C_V = \frac{3pN}{V}\hbar\omega_E \frac{\partial}{\partial T} e^{-\beta\hbar\omega_E} = \frac{3pN}{V}\cdot\hbar\omega_E \frac{\hbar\omega_E}{k_B T^2} e^{-\beta\hbar\omega_E} = \frac{3pNk_B}{V}\left(\frac{\hbar\omega_E}{k_B T}\right)^2 e^{-\beta\hbar\omega_E}$$

We can define the Einstein temperature $\Theta_E = \frac{\hbar\omega_E}{k_B}$, therefore $T \ll 1 \longrightarrow \Theta_E \gg T$.

$\Theta_E \gg T$ quantum behaviour	$\longrightarrow C_V = \frac{3pNk_B}{T}\left(\frac{\Theta_E}{T}\right)^2 e^{-\frac{\Theta_E}{T}}$
$\Theta_E \ll T$ classical behaviour	$\longrightarrow C_V = 3nk_B$

We observe that C_V goes to zero exponentially but experimentally it goes to zero as $\sim T^3$. Therefore Einstein model fails to describe C_V for small T. Einstein's error lies in the assumption that all the oscillations have the same frequency.; this means that we can say that $k_B T \ll \hbar\omega$.
This is true for the optical oscillations, infact there exist a T from which $k_B T \ll \hbar\omega$ and hence cannot be excited and their contribution to C_V becomes exponentially small. For the acoustic modes instead there will be always a region under $k_B T$ and therefore C_V will have always a contribution even if small from those modes (the only solution would be take T=0 but this is impossible)



DEBYE MODEL

The Debye model consideres only the phonons in the acustic branches, so it's valid at low T. At low T the optical modes are frozen (T is lower than the lowest ω_{opt}) and therefore they do not contribute to C_V.
We know that an acostic mode has for $|q| \to 0$ has the following dispersion relation:

$$\hbar\omega_s(q) = \hbar c_s(\hat{q})|q| \qquad s = 1,2,3 \quad \text{(3 acoslic modes: 2 transersal, 1 longitudinal)}$$

($\hat{q}$: unit vector in the direction of q (in a gas there's no $\hat{q}$ dependence))

$$\longrightarrow \quad C_V = \frac{1}{V}\sum_q \sum_{s=1,2,3} \hbar c_s(\hat{q})|q| \frac{\partial}{\partial T}\left(\frac{1}{e^{\beta\hbar c_s(\hat{q})|q|} - 1}\right)$$

at sufficiently low T in order to neglet the opt. mods

Since q are discrete but very very dense we can turn $\frac{1}{V}\sum_q \to \int$

Firstly recall that due to P.B.C. the allowed wave vectors are:

$$\underline{q} = \frac{m_1}{N_1}\underline{b}_1 + \frac{m_2}{N_2}\underline{b}_2 + \frac{m_3}{N_3}\underline{b}_3 \qquad \begin{cases} 0 \le m_1 \le N_1 - 1 \\ 0 \le m_2 \le N_2 - 1 \\ 0 \le m_3 \le N_3 - 1 \end{cases} \qquad N = N_1 \cdot N_2 \cdot N_3$$

$$\longrightarrow \quad \Delta\underline{q}_1 = \frac{\underline{b}_1}{N_1} \; ; \quad \Delta\underline{q}_2 = \frac{\underline{b}_2}{N_2} \; ; \quad \Delta\underline{q}_3 = \frac{\underline{b}_3}{N_3}$$

Hence the elementary volume is $\Delta\underline{q}_1 \cdot (\Delta\underline{q}_2 \times \Delta\underline{q}_3) = \frac{1}{N_1 \cdot N_2 \cdot N_3} \cdot \underline{b}_1 \cdot (\underline{b}_2 \times \underline{b}_3) = \frac{(2\pi)^3}{N \cdot v} = \frac{(2\pi)^3}{V} \longrightarrow \frac{1}{V} = \frac{\Delta^3 q}{(2\pi)^3}$

$$\longrightarrow \quad \frac{1}{V}\sum_{\underline{q}} f(\underline{q}) = \sum_{\underline{q}} \frac{\Delta^3 q}{(2\pi)^3} f(\underline{q}) \xrightarrow[\substack{N\to\infty \\ (\text{reasonable} \\ N \sim N_A)}]{} \int_{1^{st}\,BZ} f(\underline{q}) \frac{d^3 q}{(2\pi)^3}$$

$$\longrightarrow \quad C_V = \frac{\partial}{\partial T} \sum_{s=1,2,3} \int_{1^{st}\,BZ} \frac{d^3 q}{(2\pi)^3} \hbar\, c_s(\hat{q})\,|\underline{q}|\, \frac{\partial}{\partial T}\left(\frac{1}{e^{\beta\hbar c_s(\hat{q})|\underline{q}|} - 1}\right) =$$

$$= \frac{\partial}{\partial T} \sum_{s=1,2,3} \int \frac{q^2 dq\, d\Omega}{(2\pi)^3} \frac{\hbar\, c_s(\Omega) q}{e^{\beta\hbar c_s(\Omega) q} - 1} =$$

$$= \frac{\partial}{\partial T} \sum_{s=1,2,3} \int \frac{d\Omega}{(2\pi)^3} \int_0^{\Lambda(\Omega)} dq \frac{q^3 \hbar\, c_s(\Omega)}{e^{\beta\hbar c_s(\Omega) q} - 1} \qquad \Lambda(\Omega) \leftarrow \text{certain cut-off}$$

$\longleftrightarrow$ 

$$x = \beta\hbar c_s(\Omega) q \longrightarrow dq = \frac{dx}{\beta\hbar c_s(\Omega) q} \qquad q = \frac{x}{\beta\hbar\, c_s(\Omega)}$$

$$= \frac{\partial}{\partial T} \sum_{s=1,2,3} \int \frac{d\Omega}{(2\pi)^3} \frac{\hbar\, c_s(\Omega)}{(\beta\hbar c_s(\Omega))^4} \int_0^{\beta\hbar c_s(\Omega) q} dx \frac{x^3}{e^x - 1}$$

at low T $\beta\hbar c_s(\Omega) q \to \infty$

$$= \frac{\partial}{\partial T} \sum_{s=1,2,3} \int \frac{d\Omega}{(2\pi)^3} \frac{\hbar\, c_s(\Omega)}{(\beta\hbar c_s(\Omega))^4} \int_0^{\infty} dx \frac{x^3}{e^x - 1} =$$

$$\simeq \frac{\partial}{\partial T} \left(\frac{K_B T}{\hbar}\right)^4 \frac{\hbar\,\pi^4}{15} \sum_{s=1,2,3} \int \frac{d\Omega}{(2\pi)^3} \frac{1}{c_s(\Omega)^3} \qquad \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$$

Now let's define the average sound velocity c such that:

$$\boxed{\frac{1}{c_s^3} \overset{def}{=} \frac{1}{3} \sum_{s=1,2,3} \frac{1}{4\pi} \int d\Omega \frac{1}{c_s(\Omega)^3}}$$

$$\longrightarrow \quad C_V^{Sound} = \frac{\partial}{\partial T} (K_B T)^4 \frac{1}{(\hbar c)^3} \frac{12\pi^5}{15} \frac{1}{8\pi^3} = \frac{\partial}{\partial T} \frac{\pi^2}{10} \frac{(K_B T)^4}{(\hbar c)^3} = \frac{2\pi^2}{5} K_B \left(\frac{K_B T}{\hbar c}\right)^3$$

$$\longrightarrow \quad \boxed{C_V^{Sound} = \frac{2\pi^2}{5} K_B \left(\frac{K_B T}{\hbar c_s}\right)^3} \qquad \text{Debye low T cv}$$

- C_V^{Debye} goes to zero as T^3 ✓
- Due to the presence of $\hbar$ it's a quantum phenomenon
- The velocity of sound modes appears in an average of c_s that considers that there are 3 different sound modes

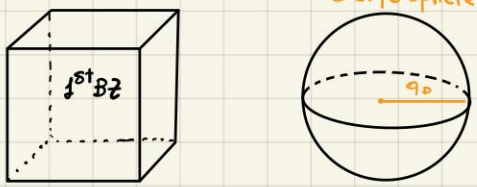
each one with different $c_s(\hat{q})$ and also that the velocity depends on the direction $c_s(\hat{q})$

The 2nd goal of Debye was to prove that if we don't approximate the cutoff we get a function that can interpolate c_v for all the low T. To solve the problem of the direction dependence of the cutoff the proposal of Debye was:

1) $c_s(\hat{q}) = c_s$ (sound velocity = average)
2) 1st BZ = SPHERE OF RADIUS q_D

Debye approximation

What is the best q_D? We impose that the 2 volume must be the same.



$$\int_{1^{st}BZ} d^3q = \frac{(2\pi)^3}{\frac{V}{N}} = (2\pi)^3 \frac{N}{V} = (2\pi)^3 n = \frac{4\pi}{3} q_D^3$$

$$\longrightarrow \quad \boxed{q_D = (6\pi^2 n)^{1/3}}$$

integral in $d\Omega$

$$\longrightarrow \quad c_v = \frac{\partial}{\partial T} \sum_s \int_0^{q_D} \frac{d^3q}{(2\pi)^3} \frac{\hbar\,\omega_s(q)}{e^{\beta\hbar\omega_s} - 1} = \frac{3 \cdot 4\pi}{(2\pi)^3} \frac{\partial}{\partial T} \int_0^{q_D} dq \frac{\hbar\, c_s q^3}{e^{\beta\hbar c_s q} - 1} =$$

$$= \frac{12\pi}{(2\pi)^3} \int_0^{q_D} dq \frac{\hbar^2 c_s^2 q^2 e^{\beta\hbar c_s q}}{e^{\beta\hbar c_s q} - 1} \frac{1}{k_B T^2} = \frac{3}{(2\pi)^2} k_B \left(\frac{k_B T}{\hbar c_s}\right)^3 \int_0^{\beta\hbar c_s q_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

We can define the Debye frequency and temperature:

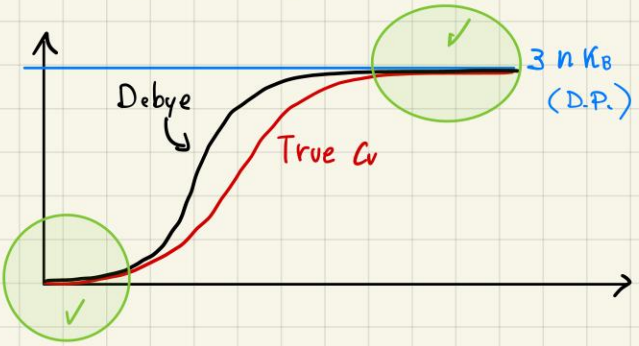
$$\boxed{\omega_D = c_s q_D} \longrightarrow \boxed{\Theta_D = \frac{\hbar\omega_D}{k_B}} \longrightarrow \beta\hbar c q_D = \frac{\hbar\omega_D}{k_B T} = \frac{\Theta_D}{T} \quad \text{(dimensionless)}$$

$$\begin{cases} T \gg \Theta_D & \longrightarrow \text{classic behaviour} \\ T \ll \Theta_D & \longrightarrow \text{quantum behaviour} \end{cases}$$

$$c_v = \frac{3}{2\pi^2} q_D^3 k_B \left(\frac{k_B T}{\hbar c_s q_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} dx \frac{x^4 e^x}{(e^x - 1)^2} = 9n k_B \left(\frac{T}{\Theta_D}\right)^3 \phi\left(\frac{T}{\Theta_D}\right)$$

$$\frac{\Theta_D}{T} \ll 1 \longrightarrow c_v = 9n k_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} dx\, x^3 \simeq \frac{9n k_B}{3} = 3n k_B \quad \checkmark$$

$$\frac{\Theta_D}{T} \gg 1 \longrightarrow c_v = 9n k_B \left(\frac{T}{\Theta_D}\right)^3 \frac{4\pi^4}{15} = \frac{12\pi^4}{5} \left(\frac{T}{\Theta_D}\right)^3 n k_B \quad \checkmark$$



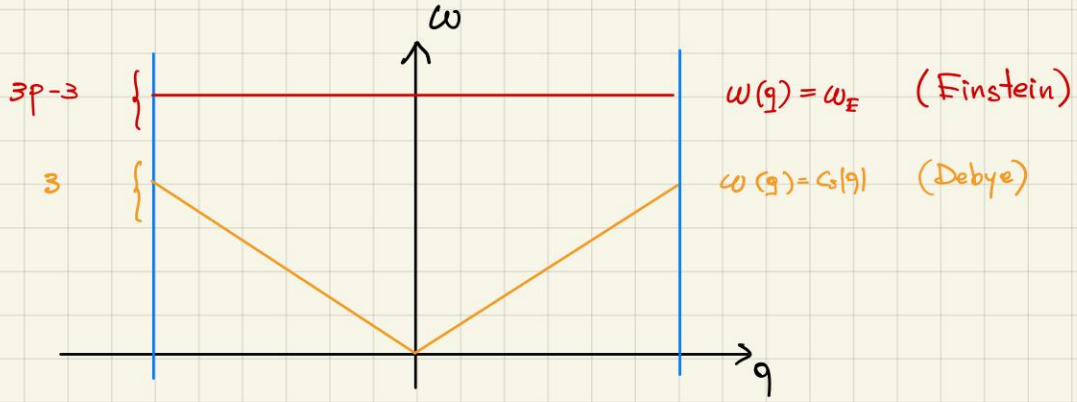
Therefore Debye model is good for low (and high T) but not in the middle because of the assumptions made are approximations.

In conclusion we discorer that the Debye model describes very well c_v^{sound} for low T, in which I take into account only the sound modes because at low T the optical modes are "frozen".

$$\begin{cases} c_v^{sound} = \frac{12\pi^4}{5} n k_B \left(\frac{T}{\Theta_D}\right)^3 \\ \omega(q) \simeq c_s |q| \qquad c_s = 12\pi \left(\sum_s \int d\Omega \, \frac{1}{c_s(\Omega)^3}\right)^{-1} \end{cases}$$

The Einsten model instead has the ability to describe c_v^{opt} considering an average ω_E as dispersion law. Their contribution as we saw goes exponentially to zero at low temperature

$$\begin{cases} c_v^{opt} = (3p-3) n k_B \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1\right)^2} \\ \omega_s^{opt}(q) = \omega_E \end{cases}$$



Useful TIPS

- $n = \frac{N}{V}$ (density of BL points and it does not care about the basis)

$$\begin{cases} \text{ex. FCC} \quad n = \frac{4}{a^3} \\ \text{ex BCC} \quad n = \frac{2}{a^3} \end{cases}$$

$\longrightarrow$ q_D is the same if I have a basis or not because n is only affected by BL points.

BORN - OPPENHEIMER APPROXIMATION

$$H = T + V$$

$$T = T_e + T_n = \sum_i \left(-\frac{\hbar^2}{2m_e}\right)\nabla_i^2 + \sum_{\alpha \in ions}\left(-\frac{\hbar^2}{2M_\alpha}\right)\nabla_\alpha^2$$

$$V(\{r_i\},\{R_\alpha\}) = \underbrace{\frac{1}{4\pi\varepsilon_0}\sum_{i,j}\frac{e^2}{|\underline{r}_i - \underline{r}_j|}}_{V_{ee}} - \underbrace{\frac{1}{4\pi\varepsilon_0}\sum_{i,\alpha}\frac{Z_\alpha e^2}{|\underline{r}_i - \underline{R}_\alpha|}}_{V_{en}} + \underbrace{\frac{1}{4\pi\varepsilon_0}\sum_{\alpha,\beta}\frac{Z_\alpha Z_\beta e^2}{|\underline{R}_\alpha - \underline{R}_\beta|}}_{V_{nn}}$$

$$\longrightarrow H(\{r_i\},\{R_\alpha\}) = T_e(r_i) + T_n(R_\alpha) + V_{ee}(r_i) + V_{en}(r_i, R_\alpha) + V_{nn}(R_\alpha) \longrightarrow \psi_E \equiv \psi_E(r_i, R_\alpha)$$

The key point of Born Oppenheimer approximation is that $m_e \ll m_{ions}$: $m_e \sim \frac{m_{ions}}{2000}$. Therefore supposing $M_\alpha \sim \infty$ the kinetic ions energy vanishes. Then the idea is :

1) Solve the electronic problem assuming freezed ions ($M_\alpha \sim \infty$) and get $E_e(\{R_\alpha\})$
2) Finally study the ions problem using as potential the E_e result

PURE ELECTRONIC PROBLEM

$$H^e(r_i;\{R_\alpha\}) = T_e(r_i) + V_{ee}(r_i) + V_{en}(r_i, R_\alpha)$$

$$H^e \psi_\varepsilon^e(r, R_\alpha) = E_\varepsilon^e(R_\alpha)\,\psi_\varepsilon^e(r_i, R_\alpha)$$

IONIC PROBLEM

$$H^n(R_\alpha) = T_n(R_\alpha) + V_{nn}(R_\alpha) + E_\varepsilon^e(R_\alpha)$$

$$H^n(R_\alpha)\,\psi_\nu^n(R_\alpha) = E_{\varepsilon\nu}\,\psi_\nu^n(R_\alpha)$$

$$\longrightarrow \boxed{\Psi_{\varepsilon\nu}(r_i, R_\alpha) = \psi_\varepsilon^e(r_i, R_\alpha)\,\psi_\nu^n(R_\alpha)}$$

We decoupled the problem

Suppose we solved the pure electronic problem:

$$(T_e + V_{ee} + V_{en})\,\psi^e(r, R) = E(R)\,\psi^e(r, R) \longrightarrow \psi^e(r, R_\alpha)\ ,\ E(R_\alpha).$$

Since $(T_e + V_{ee} + V_{en})$ does not affect of ψ^n we could insert in that equation a ψ^n :

$$(T_e + V_{ee} + V_{en})\,\psi_\varepsilon^e(r, R)\,\psi^n(R) = E_\varepsilon(R)\,\psi_\varepsilon^e(r, R)\,\psi^n(R)$$

Then if we consider the general equation:

$$(T_e + V_{ee} + V_{en} + T_n + V_{nn})\,\psi^e\psi^n = E\psi^e\psi^n$$

$$\longrightarrow (T_e + V_{ee} + V_{en})\,\psi^e\psi^n + (T_n + V_{nn})\,\psi^e\psi^n = E\psi^e\psi^n$$

$$\longrightarrow E_\varepsilon(R)\,\psi^e(r, R)\,\psi^n + (T_n + V_{nn})\,\psi^e\psi^n = E\psi^e\psi^n$$

$$\longrightarrow \boxed{[T_n + V_{nn} + E_\varepsilon(R)]\,\psi^e(r, R)\,\psi^n(R) = E\psi^e(r, R)\,\psi^n(R)}$$

I cannot simplify $\psi^e(r,R)$ because T_n has a ∇_R^2. This would be exact iff: $[T_n, \psi^e]\psi^n = 0$

$$\longrightarrow \quad T_n \psi^e \psi^n - \psi^e T_n \psi^n = 0$$

$$T_n \psi^e \psi^n = \sum_\alpha \frac{-\hbar}{2M_\alpha} \frac{\partial^2}{\partial R_\alpha^2}\left(\psi^e(r,R)\,\psi^n(R)\right) = \sum_\alpha \frac{-\hbar}{2M_\alpha} \partial R_\alpha \left(\psi^n \partial_{R_\alpha}\psi^e + \psi^e \partial_{R_\alpha}\psi^n\right) =$$

$$= \sum_\alpha \frac{-\hbar}{2M_\alpha}\, \partial_{R_\alpha}\psi^n \partial_{R_\alpha}\psi^e + \sum_\alpha \frac{-\hbar}{2M_\alpha}\, \psi^n \partial_{R_\alpha}^2 \psi^e + \sum_\alpha \frac{-\hbar}{2M_\alpha}\, \partial_{R_\alpha}\psi^e \partial_{R_\alpha}\psi^n + \sum_\alpha \frac{\hbar}{2M_\alpha} \psi^e \partial_{R_\alpha}^2 \psi^n =$$

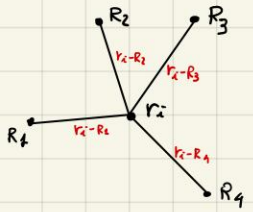
$$= \psi^e T_n \psi^n + \sum_\alpha \frac{-\hbar}{2M_\alpha}\, \psi^n \partial_{R_\alpha}^2 \psi^e + 2\sum_\alpha \frac{-\hbar}{2M_\alpha}\, \nabla_{R_\alpha}\psi^e \nabla_{R_\alpha}\psi^n$$

$$\longrightarrow \quad [T_n, \psi^e]\psi^n = \sum_\alpha \frac{-\hbar^2}{2M_\alpha}\left[\psi^n \partial_{R_\alpha}^2 \psi^e + 2\left(\nabla_{R_\alpha}\psi^e\right)\left(\nabla_{R_\alpha}\psi^n\right)\right]$$

To prove that those terms can be ignored we can see that they contribute almost nothing to the expectation value of the energy of the system in a state Ψ

- **1st term**

Since :



$$\psi_\varepsilon(r_i, R_\alpha) = \psi_\varepsilon(r_i - R_\alpha) \longrightarrow |\partial_{r_i}\psi^e(r_i - R_\alpha)| \simeq |\partial_{R_\alpha}\psi^e(r_i - R_\alpha)|$$

$$\sum_\alpha \frac{-\hbar^2}{2M_\alpha}\, \psi^n \partial_{R_\alpha}^2 \psi^e \simeq \sum_\alpha \frac{-\hbar^2}{2M_\alpha}\, \psi^n \frac{m_e}{m_e} \frac{\partial^2}{\partial r_i^2}\psi^e = -\left(\sum_\alpha \frac{m_e}{M_\alpha}\psi^n\right) \frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial r_i^2}\psi^e$$

$$\longrightarrow \int dr\, dR_\alpha\, \Psi^*(1^{st}\text{term})\Psi \propto -\frac{m_e}{M_\alpha} \int dr\, \psi^{e*} \frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial r_i^2}\psi^e \simeq 0$$

- **2nd term**

tot # of e^- = const

$$2\sum_\alpha \frac{-\hbar^2}{2M_\alpha}\left(\nabla_{R_\alpha}\psi^e\right)\left(\nabla_{R_\alpha}\psi^n\right) \longrightarrow \int dr\, dR_\alpha\, \Psi^*(2^{nd}\text{term})\Psi \propto -\int dr\, \psi^{e*} \frac{\partial}{\partial R_\alpha}\psi^e = \frac{1}{2}\frac{\partial}{\partial R_\alpha}\int dr\, \psi^{e*}\psi^e = \frac{1}{2}\frac{\partial n_e}{\partial R_\alpha} = 0$$

$$\longrightarrow \quad [T_n, \psi^e]\psi^n \simeq 0$$

$$\longrightarrow \quad \boxed{\left[T_n + V_{nn} + E_\varepsilon(R)\right]\psi^n(R) \simeq E\,\psi^n(R)}$$

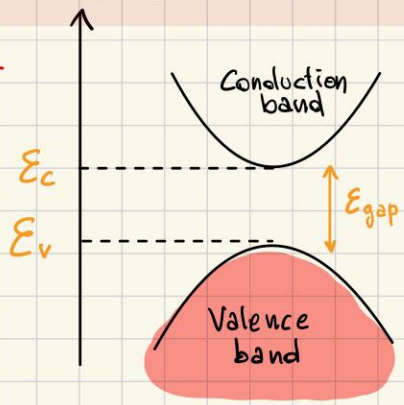
Cap. 7
THEORY OF SEMICONDUCTORS

SEMICONDUCTORS

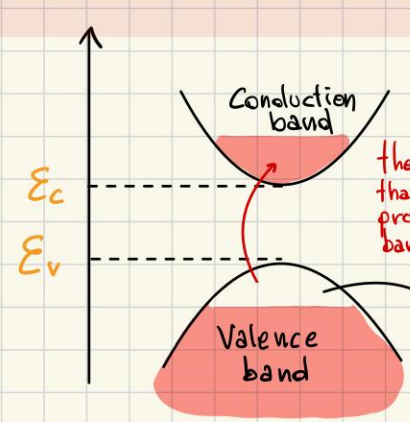
A semiconductor can be used as active element in a circuit (e.g. diode, transistors)
(passive element: resistance, inductors, capacitors)

A semiconductor is a system where I have the valence band completely filled, and the conduction band completely empty at $T=0$ and such that at $T>0$ there is a promotion and so conduction.

DIRECT GAP



If we raise $T>0$ → to a T such that $\mathcal{E}_c - \mathcal{E}_v \lesssim K_B T$

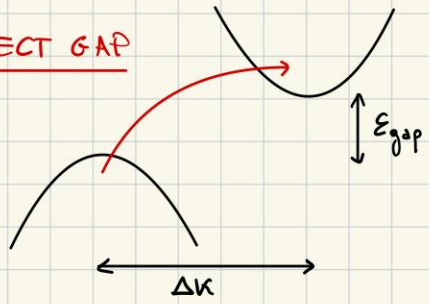


there is a non-zero prob that an e^- is thermally promoted to the conduction band $\sim e^{-E_g/K_B T}$

holes! If we apply an $\underline{E}$ field, the current density given by the e^- is equal to the current given by the holes with a charge $+e$.

In some semiconductors the top of the valence band is in a different K point from the bottom of the conduction band: (we'll only treat the previous ones)

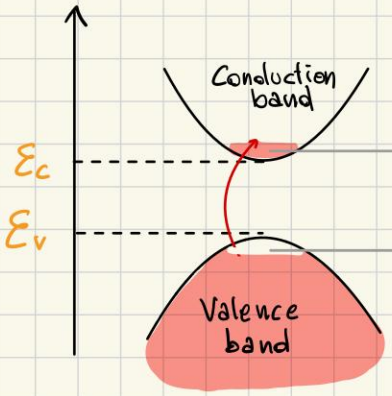
INDIRECT GAP



In this case in order to promote the e^- I have not only to pay the thermal energy but since the momentum is conserved I need a mechanism to take care of this changing of momentum ΔK. This process need to be assisted by phonons: if the e^- creates a phononous, during its promotion, the e^- can give to it this extra momentum.

let's return to the 1st case. In this situation I'll have very few e^- near the bottom of the conduction band (and very few holes near the top of the valence band) therefore is convenient to describe those e^- in the effective mass approx (near the min. the band is $\simeq$ parabolic).

(writing in the basis of the principal axis)



$$\mathcal{E}^{e}_{\underline{K}} = \mathcal{E}_c + \frac{\hbar^2}{2}\sum_{\alpha\beta}(M^{e}_{\alpha\beta})^{-1}K_\alpha K_\beta = \mathcal{E}_c + \frac{\hbar^2}{2}\sum_{\ell=1}^{3}(m^{e}_{\ell})^{-1}K_\ell^2$$

$$\mathcal{E}^{holes}_{\underline{K}} = \mathcal{E}_v - \frac{\hbar^2}{2}\sum_{\alpha\beta}(M^{h}_{\alpha\beta})^{-1}K_\alpha K_\beta = \mathcal{E}_v - \frac{\hbar^2}{2}\sum_{\ell=1}^{3}(m^{h}_{\ell})^{-1}K_\ell^2$$

The most important property of any semiconductor at temperature T is the number of electrons per unit volume in the conduction band as a function of T, and the number of holes per unit volume in the valence band as a function of T.

of electrons in the conduction band per unit volume as a function of the temperature

$$n_c(T) = \int_{\mathcal{E}_c}^{\infty} d\mathcal{E}\; g_c(\mathcal{E}) f(\mathcal{E})$$

approx. (no bands extend up to ∞) since the integral converges very fast exponentially we can extend the upper limit to ∞

$n_c(T)$: stays for negative

$g_c(\mathcal{E})$: density of states in the cond. band

$f(\mathcal{E})$: Fermi distr.

of holes in the valence band per unit volume as a function of the temperature

$$p_v(T) = \int_{-\infty}^{\mathcal{E}_v} d\mathcal{E}\; g_v(\mathcal{E})[1 - f(\mathcal{E})]$$

$p_v(T)$: stays for positive

$g_v(\mathcal{E})$: density of states in the val band

$f(\mathcal{E})$: Fermi distr.

The Fermi function is:

$$f(\mathcal{E}) = \frac{1}{e^{\beta(\mathcal{E}-\mu)}+1}$$

Usually the chemical potential is somewhere between the gap (we could see that at T=0 it is exactly in the middle of the gap). Therefore usually

$$\begin{cases} \mathcal{E}_c - \mu \gg K_B T \\ \mu - \mathcal{E}_v \gg K_B T \end{cases} \quad *$$

Then in a semiconductor electrons and holes do not obey the Fermi-statistics but the Boltzmann-statistics: i.e. they are quasi-classical objects. (their number is so small that we can neglet the degeneration of the Fermi gas)

$$n_c(T) = \int_{\mathcal{E}_c}^{\infty} d\mathcal{E}\; g_c(\mathcal{E}) f(\mathcal{E}) \simeq \int_{\mathcal{E}_c}^{\infty} d\mathcal{E}\; g_c(\mathcal{E})\, e^{-\beta(\mathcal{E}-\mu)} = e^{-\beta(\mathcal{E}_c-\mu)} \int_{\mathcal{E}_c}^{\infty} d\mathcal{E}\; g_c(\mathcal{E})\, e^{-\beta(\mathcal{E}-\mathcal{E}_c)} = N_c(T)\, e^{-\beta(\mathcal{E}_c-\mu)}$$

$$p_v(T) = \int_{-\infty}^{\mathcal{E}_v} d\mathcal{E}\; g_v(\mathcal{E})[1 - f(\mathcal{E})] \simeq \int_{-\infty}^{\mathcal{E}_v} d\mathcal{E}\; g_v(\mathcal{E})\, e^{-\beta(\mu-\mathcal{E})} = e^{-\beta(\mu-\mathcal{E}_v)} \int_{-\infty}^{\mathcal{E}_v} d\mathcal{E}\; g_v(\mathcal{E})\, e^{-\beta(\mathcal{E}_v-\mathcal{E})} = P_v(T)\, e^{-\beta(\mu-\mathcal{E}_v)}$$

The temperature dependence of $N_c(T)$ and $P_v(T)$ is *not* exponentially small because $\mathcal{E}-\mathcal{E}_c$ ($\mathcal{E}_v-\mathcal{E}$) is not a large number: they are slow-varying function of T.
Instead the T dependence of the factors $e^{-\beta(\mathcal{E}_c-\mu)}$, $e^{-\beta(\mu-\mathcal{E}_v)}$ is very strong. because of *

To calculate them we need the density of states:

$$g_{v,c}(\mathcal{E}) = 2 \int \frac{d^3k}{8\pi^3}\, \delta(\mathcal{E} - \mathcal{E}^{c,v}_k) \qquad dk = dk_1\, dk_2\, dk_3$$

Since the calculation is the same, let's do it for the conduction band:

$$g_c(\varepsilon) = \frac{1}{4\pi^3}\int dk_1\, dk_2\, dk_3\ \delta\left(\varepsilon - \varepsilon_c - \frac{\hbar^2}{2}\left(\frac{k_1^2}{m_1^e} + \frac{k_2^2}{m_2^e} + \frac{k_3^2}{m_3^e}\right)\right)$$

Changing variable : $x_i = \dfrac{\hbar k_i}{\sqrt{2 m_i^c}}$ $\quad i = 1,2,3$; $d\underline{k} = \dfrac{\sqrt{8}}{\hbar^3}\sqrt{m_1^c}\sqrt{m_2^c}\sqrt{m_3^c}\, dx_1\, dx_2\, dx_3$

$$\longrightarrow \quad g_c(\varepsilon) = \frac{(8\, m_1^c\, m_2^c\, m_3^c)^{1/2}}{4\pi^3\hbar^3}\int dx_1\, dx_2\, dx_3\ \delta(\varepsilon - \varepsilon_c - x_1^2 - x_2^2 - x_3^2) =$$

$$= \frac{(8\, m_1^c\, m_2^c\, m_3^c)^{1/2}}{4\pi^3\hbar^3}\, 4\pi \int_0^\infty dr\, r^2\, \delta(\varepsilon - \varepsilon_c - r^2) =$$

$$= \frac{(8\, m_1^c\, m_2^c\, m_3^c)^{1/2}}{\pi^2\hbar^3}\int_0^\infty dr\, r^2\, \frac{\delta(r - \sqrt{\varepsilon - \varepsilon_c})}{2\sqrt{\varepsilon - \varepsilon_c}}$$

$$\longrightarrow \quad \boxed{g_c(\varepsilon) = \begin{cases} \dfrac{(2\, m_1^c\, m_2^c\, m_3^c)^{1/2}}{\pi^2\hbar^3}\sqrt{\varepsilon - \varepsilon_c} & \text{for } \varepsilon \geq \varepsilon_c \\ 0 & \text{else where} \end{cases}}$$

$$\boxed{g_v(\varepsilon) = \begin{cases} \dfrac{(2\, m_1^v\, m_2^v\, m_3^v)^{1/2}}{\pi^2\hbar^3}\sqrt{\varepsilon_v - \varepsilon} & \text{for } \varepsilon \leq \varepsilon_v \\ 0 & \text{else where} \end{cases}}$$

Using these relations I can write: $z = \dfrac{\varepsilon - \varepsilon_c}{k_B T}$ $\qquad m_c \equiv (m_1^c m_2^c m_3^c)^{1/3}$; $m_v \equiv (m_1^v m_2^v m_3^v)^{1/3}$

$$N_c(T) = \int_{\varepsilon_c}^{\infty} d\varepsilon\, \frac{\sqrt{2}\, m_c^{3/2}}{\pi^2\hbar^3}\sqrt{\varepsilon - \varepsilon_c}\ e^{-\beta(\varepsilon - \varepsilon_c)} = \frac{\sqrt{2}\, m_c^{3/2}}{\pi^2\hbar^3}\, k_B T \int_0^{+\infty} dz\, \sqrt{z}\sqrt{k_B T}\ e^{-z}$$

$$= \frac{\sqrt{2}\, m_c^{3/2}}{\pi^2\hbar^3}(k_B T)^{3/2}\int_0^{+\infty} dz\, \sqrt{z}\, e^{-z} = \frac{\sqrt{2}\, m_c^{3/2}}{\pi^2\hbar^3}(k_B T)^{3/2}\,\frac{\sqrt{\pi}}{2}$$

Doing the same for P_v:

$$\begin{cases} N_c(T) = \dfrac{1}{4}\left(\dfrac{2\, m_c\, k_B T}{\pi\hbar^2}\right)^{3/2} \\ P_v(T) = \dfrac{1}{4}\left(\dfrac{2\, m_v\, k_B T}{\pi\hbar^2}\right)^{3/2} \end{cases}$$

(Slow varying functions of T) $\sim T^{3/2}$

However we observe that we do not know the chemical potential μ! And it is necessary to compute $n(T)$ and $p(T)$.

First of all we see that there is a relation that does not involve μ because it disappears:

$$n_c(T)\, p_v(T) = N_c\, P_v\, e^{-\beta(\varepsilon_c - \varepsilon_v)} = N_c\, P_v\, e^{-\beta E_{gap}}$$

Law of mass action

Analogy with a chemical reaction: $eh \longrightarrow e + h$: an e^- and a hole are produced by dissociation of a combined (eh) (like a chemical reaction). The ε_{gap} is the energy to pay to have such "reaction".

Most of the semiconductors can be doped i.e. replacing some atoms with other atoms with the purpose of introducing some more electrons or some more holes: extrinsic semiconductors. If the semiconductor is unpoded we are in the case of intrinsic semiconductors.

INTRINSIC CASE (UNDOPED SEMICONDUCTOR)

In this case there are no extrinsic carriers. In this case conduction band electrons can only come from occupied valence band levels (leaving holes behind them) and not from the impurities.

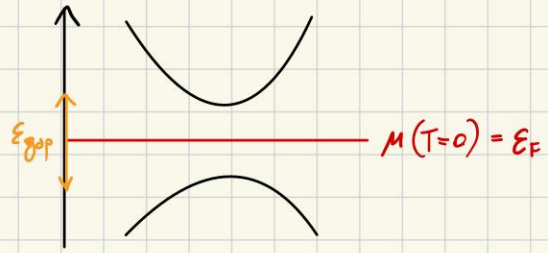
$$\longrightarrow \quad n_c(T) = p_v(T)$$

$$\longrightarrow \quad 1 = \frac{n_c(T)}{p_v(T)} = \frac{N_c}{P_v} e^{-\beta(\varepsilon_c + \varepsilon_v - 2\mu)} = \left(\frac{m_c}{m_v}\right)^{3/2} e^{-\beta(\varepsilon_c + \varepsilon_v - 2\mu)}$$

$$\longrightarrow \quad \boxed{\mu = -\frac{3}{4} K_B T \ln\left(\frac{m_c}{m_v}\right) + \frac{\varepsilon_c + \varepsilon_v}{2}} \equiv \mu_I \text{ (chemical potential in the Intrinsic case)}$$

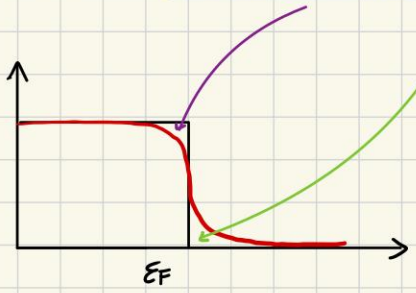
OBSERVATIONS:

- At $T = 0$ $\quad \mu = \dfrac{\varepsilon_c + \varepsilon_v}{2}$



- At $T \neq 0$ μ depends on m_c/m_v
  - $> 1 \longrightarrow \mu$ near the valence band
  - $= 1 \longrightarrow \mu$ at the center
  - $< 1 \longrightarrow \mu$ near the cond. band

The behaviour of μ has the following physical explanation: the excitations depends on Fermi function and density of states! $f(\varepsilon)$ is "democratic" in fact it's symmetric around μ, so it moves what is below ε_F, over it and whatever it takes it gives.



If the two masses are the same $\longrightarrow$ the 2 densities of states are equal μ is at the center. Instead if $m_v > m_c \longrightarrow g_v > g_c$: I'm taking more than what I'm giving so to give a little bit more I should move μ up Viceversa if $m_c > m_v \longrightarrow g_c > g_v$ I'm giving more than what I'm taking. So to take a little bit more I should move μ down.

Now combining $n_c = p_v \equiv n_i$ with the law of mass action: $n_c = p_v \equiv n_i = \sqrt{n(T)p(T)}$

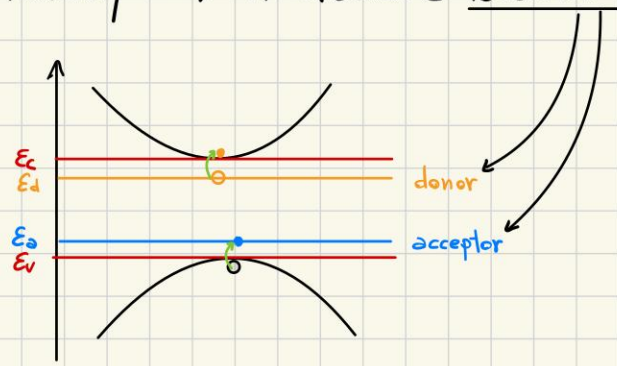
intrinsic carriers $\longrightarrow$ $\boxed{n_i \equiv \sqrt{N_c P_v}\, e^{-\beta \frac{E_{gap}}{2}}}$

EXTRINSIC CASE (DOPED SEMICONDUCTORS)

Why should I dope? Consider Si. It has 4 valence e^-; since it is even the valence band is completely filled and the conduction band empty → it is a semiconductor.
Imagine that we put Arsenic (or Borum). Arsenic has $1\,e^-$ more than Si (B one e^- left). Therefore Ar is able to put this extra e^- in the conduction band very efficiently an B is able to take $1\,e^-$ from the valence band, leaving one hole in it.

ARSENIC : donates $1\,e^-$ **DONORS**
BORUM : accepts $1\,e^-$ (donates 1 hole) **ACCEPTORS**

So we have an extrinsic method to make charge carriers. N.B. The addition of an impurity breaks the perfect periodicity → it creates a localized level. (not Bloch's levels) (impurity levels)



Because of the presence of donors or acceptors we violate the exact balance between e^- and holes that is a characteristic of Intrinsic semiconductors

$$\Delta n = n_c - p_v \neq 0 \quad \begin{cases} >0 & \text{(prevalence of donors)} \quad \text{(n-doping)} \\ <0 & \text{(prevalence of acceptors)} \quad \text{(p-doping)} \end{cases}$$

Considering also the law of action mass:

$$\begin{cases} n_c - p_v = \Delta n \\ n_c\, p_v = n_i^2 \end{cases} \longrightarrow \begin{cases} n_c = p_v + \Delta n \\ p_v^2 + \Delta n\, p_v - n_i^2 = 0 \end{cases} \overset{\star}{\longrightarrow} \begin{cases} n_c = \dfrac{\Delta n}{2} + \sqrt{\left(\dfrac{\Delta n}{2}\right)^2 + n_i^2} \\ p_v = -\dfrac{\Delta n}{2} + \sqrt{\left(\dfrac{\Delta n}{2}\right)^2 + n_i^2} \end{cases}$$

- $|\Delta n| \ll n$ $\begin{cases} p_v \simeq n_i - \dfrac{\Delta n}{2} \\ n_c \simeq n_i + \dfrac{\Delta n}{2} \end{cases}$ (low impurities limit)

- $|\Delta n| \gg n$ $\begin{cases} p_v \simeq -\dfrac{\Delta n}{2} + \dfrac{|\Delta n|}{2}\left(1 + \dfrac{2n_i^2}{\Delta n}\right) \\ n_c \simeq \dfrac{\Delta n}{2} + \dfrac{|\Delta n|}{2}\left(1 + \dfrac{2n_i^2}{\Delta n}\right) \end{cases}$

$\Delta n > 0$ $\begin{cases} p_v \simeq \dfrac{n_i^2}{\Delta n} \\ n_c = \Delta n \end{cases}$

$\Delta n < 0$ $\begin{cases} p_v = |\Delta n| \\ n_c = \dfrac{n_i^2}{|\Delta n|} \end{cases}$

We can write with this trick:

$$\begin{cases} n_c(T) = N_c(T)\, e^{-\beta(\mathcal{E}_c - \mu)}\, e^{-\beta(\mu_i - \mu_i)} = n_i(T)\, e^{-\beta(\mu_i - \mu)} \\ p_v(T) = P_v(T)\, e^{-\beta(\mu - \mathcal{E}_v)}\, e^{-\beta(\mu_i - \mu_i)} = n_i(T)\, e^{-\beta(\mu - \mu_i)} \end{cases}$$

$$\longrightarrow n_c - p_v = \Delta n = n_I \left(e^{-\beta(\mu-\mu_I)} - e^{-\beta(\mu_I-\mu)} \right) = 2 n_I \sinh\left(\beta(\mu-\mu_I)\right)$$

$$\longrightarrow \boxed{\Delta n = 2 n_I \sinh\left(\beta(\mu-\mu_I)\right)} \ *$$

- If $\Delta n > 0 \longrightarrow \mu > \mu_I$: reasonable, we are putting more e^- and then μ should be move up
- If $\Delta n < 0 \longrightarrow \mu < \mu_I$: we're adding holes and then μ should move down

DONOR'S AVERAGE # of e^-

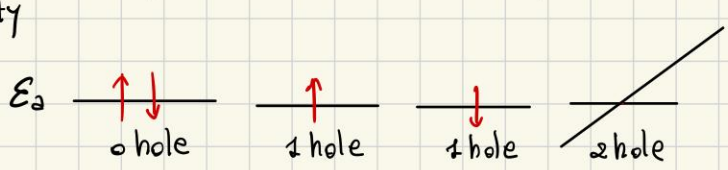
We have 4 configuration

$N_j =$ 0 , $1\uparrow$, $1\downarrow$, $2\uparrow\downarrow$

$$\langle n \rangle = \frac{\sum N_j e^{-\beta(E_j - \mu N_j)}}{\sum e^{-\beta(E_j - \mu N_j)}} \simeq \frac{2 \cdot e^{-\beta(\varepsilon_d - \mu)}}{1 + 2 e^{-\beta(\varepsilon_d - \mu)}} = \frac{1}{1 + \frac{1}{2} e^{\beta(\varepsilon_d - \mu)}} \longrightarrow \boxed{n_d = \langle n \rangle N_d}$$

ACCEPTOR'S AVERAGE # of holes

In contrast to the previous case the acceptor level can be singly or double occupied but not empty

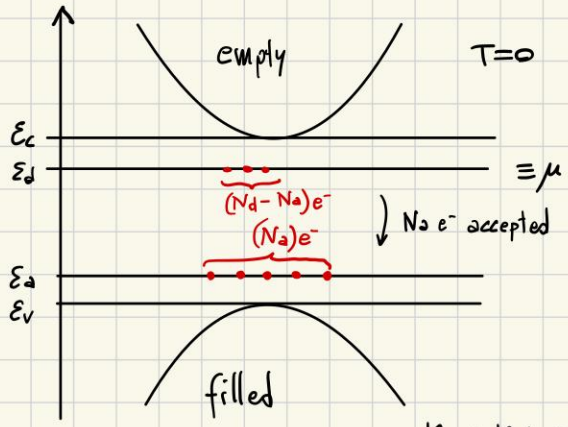


$$\langle p \rangle = \frac{2 e^{\beta\mu} + 2 e^{-\beta(\varepsilon_a - 2\mu)}}{2 e^{\beta\mu} + e^{-\beta(\varepsilon_a - 2\mu)}} = \frac{e^{\beta(\mu - \varepsilon_a)} + 1}{\frac{1}{2} e^{\beta(\mu-\varepsilon_a)} + 1} = \frac{1}{1 + \frac{1}{2} e^{\beta(\mu-\varepsilon_a)}} \longrightarrow \boxed{p_a = \langle p \rangle N_a}$$

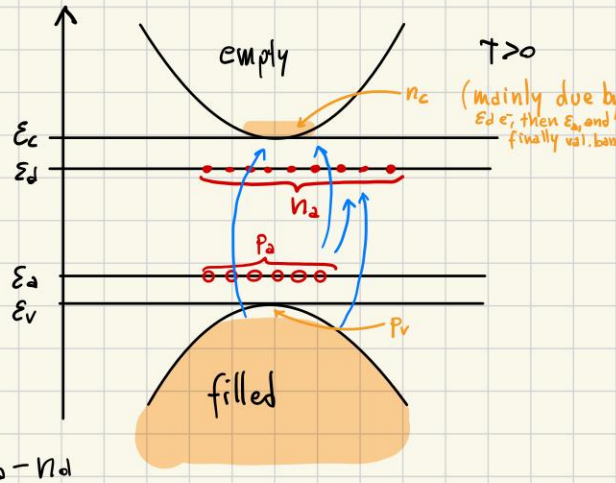
$\boxed{N_d > N_a}$

At T=0 the val. band is completely filled. ε_a is empty and ε_d has N_d e^-. To minimize energy N_a of the N_d e^- drop from ε_d to ε_a.

- VAL. BAND → FILLED ; ε_d filled with $N_d - N_a$ e^- ; cond band empty.



At T > 0 the e^- are excited and redistributed among those levels Since their # = cost, $n_c + n_d$ must exceed $N_d - N_a$ by the # of holes in the val band and acc. level).



$$n_c + n_d = N_d - N_a + p_a + p_v$$
$$\longrightarrow n_c + n_d + N_a = N_d + p_a + p_v$$
$$\longrightarrow \Delta n = n_c - p_v = N_d - N_a + p_a - n_d$$

So we have an equation for μ:

$$N_c e^{-\beta(\varepsilon_c-\mu)} + \frac{N_d}{1+\frac{1}{2}e^{\beta(\varepsilon_d-\mu)}} = N_d - N_a + \frac{N_a}{1+\frac{1}{2}e^{\beta(\mu-\varepsilon_a)}} + P_v e^{-\beta(\mu-\varepsilon_v)}$$

that we can solve numerically at computer.

Usually: $\varepsilon_d - \mu \gg k_B T$; $\mu - \varepsilon_a \gg k_B T$ (At room temperature)

$\longrightarrow$ $n_d \ll N_a$; $p_a \ll N_d$

- $n_d \ll N_a$ ↓ donors are fully ionized (they donated all e^-)
- $p_a \ll N_d$ ↓ acceptors are fully ionized

$$\longrightarrow \quad \underline{\Delta n \equiv n_c - p_v = N_d - N_a}$$

Using this result with ★ (remembering $\Delta n \gg n_I$)

$\Delta n > 0 \longrightarrow N_d > N_a$ $\quad \begin{cases} n_c \simeq N_d - N_a \\ p_v \simeq \frac{n_i^2}{N_d - N_a} \end{cases}$

$\Delta n < 0 \longrightarrow N_d < N_a$ $\quad \begin{cases} n_c \simeq \frac{n_i^2}{N_d - N_a} \\ p_v \simeq N_d - N_a \end{cases}$

Then since now we know Δn we can compute μ via ★

$$\mu = \mu_I + k_B T \sinh^{-1}\left(\frac{\Delta n}{2 n_I}\right)$$

Observation:

$$\frac{\Delta n}{2 n_I} = \sinh\left(\beta(\mu-\mu_I)\right) = \frac{1}{2}\left(e^{\beta(\mu-\mu_I)} - e^{-\beta(\mu-\mu_I)}\right)$$

$\Delta n > 0 \longrightarrow \mu > \mu_I$ $\quad \frac{\Delta n}{2 n_I} = \frac{1}{2}\left(e^{\beta(\mu-\mu_I)} - e^{-\beta(\mu-\mu_I)}\right) \longrightarrow \mu \simeq \mu_I + k_B T \ln\left(\frac{\Delta n}{n_I}\right)$

$\Delta n < 0 \longrightarrow \mu < \mu_I$ $\quad \frac{\Delta n}{2 n_I} = \frac{1}{2}\left(e^{\beta(\mu-\mu_I)} - e^{-\beta(\mu-\mu_I)}\right) \longrightarrow \mu \simeq \mu_I - k_B T \ln\left(\frac{|\Delta n|}{n_I}\right)$