I] Review of Quantum mechanics

① The crisis of classical mechanics
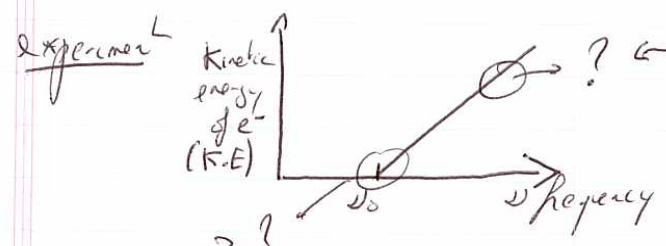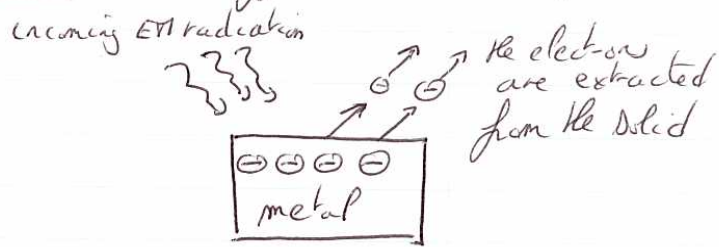
ⓐ Blackbody radiation : (1901) planck (Nobel 1918)

classical mechanics fails to explain the ~~spec~~ energy spectrum of a blackbody.

→ Electromagnetic energy could be emitted only in quantized form.

h : planck constant = $6.626\,18 \times 10^{-34}\,J.s$

$$E = h\upsilon \qquad \upsilon : \text{frequency. } (s^{-1})$$

ⓑ Photoelectric effect : hitting a solid with light

incoming EM radiation

the electron are extracted from the solid

metal

experiment

Kinetic energy of e⁻ (K.E)

υ_0

υ frequency

? ⟷ in EM theory, the energy should be proportional to the intensity of the light, it should not depend on the frequency (??)

nothing happen below a certain threshold (?)

Einstein Explanation : (1905) (Nobel 1921).

$E = h\nu$ has a physical meaning, it is the energy of a 'light quanta', particle that is called "photon" ($E = E_{ph}$)

$\Rightarrow$ photoelectric effect can then be explained using inelastic collision.
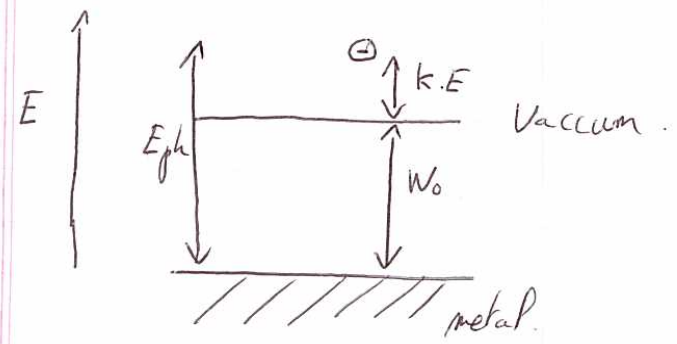
So $E_{ph} = W_0 + KE$ where W_0 is the workfunction, the energy that is required by $1 e^-$ to leave the metal.

[potential barrier]

it comes $E_{ph} = h\nu = W_0 + KE$

for $K.E = 0 \Rightarrow \underline{h\nu_0 = W_0}$

So $\boxed{KE = h(\nu - \nu_0)}$ that confirms the experimental data.

Q: Is light a wave or a particle?

A: Both (!!)

Ⓒ <u>Hydrogen atom</u> $(1e^-, 1p)$

<u>Experimental Results</u>: spectrum of EM radiation from an excited hydrogen gas is discrete (?)
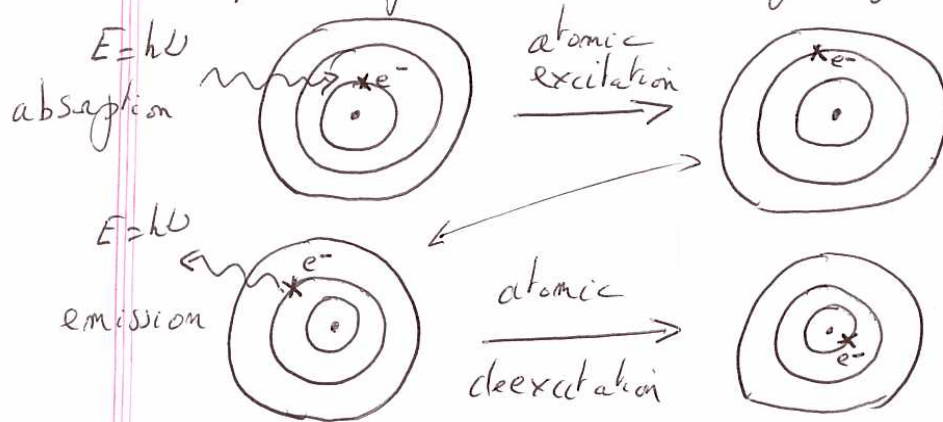
<u>Bohr explanation</u> (1913) (Nobel 1922).

starting point "Planetary model of the atom" of Rutherford

But now orbits are quantized!
(if not e^- should fall into the nuclei)

e^- can make transition between the orbits within excitation and deexcitation processes. resp. by absorption or emission of light (photon)

$E = h\nu$
absorption

atomic
excitation

$E = h\nu$
emission

atomic
deexcitation

Bohr model provides the correct electron energies.

$$\boxed{E_n \, (eV) = -\frac{Ry}{n^2}}$$

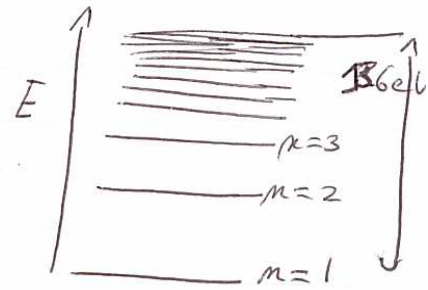$$Ry = \frac{m q^4}{(4\pi \varepsilon_0)^2 \, 2 \hbar^2}$$

$m = 9.109 \times 10^{-31} kg$

Ry is a Rydberg.

$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34} J.s$

$1 eV \longleftrightarrow 1.602 \times 10^{-19} (\equiv q) \text{ Joules}$

we get $\quad E_n(eV) = -\dfrac{13.6}{n^2}$

and a discrete spectrum.

Also for $n=1$, the Bohr radius is

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{mq^2} \simeq 0.529\text{Å} \left(1\text{Å} \equiv 10^{-10}m\right)$$

$\Rightarrow$ the Bohr model leaves many unanswered questions and it does not provide a general framework for solving problem of this type.

② __Quantum mechanics = fundamental__

ⓐ __Generalization of duality wave-particle for__
__all form of matter__

De broglie (1924) (Nobel 1929).
$\Rightarrow$ it was an assumption that was not based
on experiments

· For a given particle with momentum $\vec{p}$ and energy E
we associate a plane wave with wave vector $\vec{k}$ and
"angular" frequency $\omega(= 2\pi \nu)$
such as

$$\boxed{\vec{p} = \hbar \vec{k}} \qquad \boxed{E = \hbar \omega}$$

__Also__ $\qquad \vec{p} = m\vec{v}$ (particle with mass m and velocity v)

$\qquad \|\vec{k}\| = \dfrac{2\pi}{\lambda}$ (λ is the wavelength).

duality wave-particle $\boxed{\lambda = \dfrac{h}{p}}$

we can write this wave under "a plane wave" form

$$\boxed{\Psi(\vec{r}, t) = A \exp i(\vec{k}.\vec{r} - \omega t)}$$

③ <u>Schrödinger equation</u>. (1926) [Nobel 1933]

<u>starting point</u> : classical description of the energy E

$$E = \underset{\uparrow}{T} + \underset{\uparrow}{U} = \frac{p^2}{2m} + U$$

$\quad\quad$ K.E $\quad\quad$ potential energy.

Schrödinger converted this equation to a wave equation by defining a wave function Ψ such as:

$$\frac{p^2}{2m}\Psi + U\Psi = E\Psi$$

* if we suppose that $\Psi = A e^{i(\vec{k}\cdot\vec{n} - \omega t)}$, we can show that

$$\vec{D}\Psi = i\vec{k}\Psi \quad\quad \vec{D} = \begin{vmatrix} \partial/\partial x \\ \partial/\partial y \\ \partial/\partial z \end{vmatrix}$$

using $\underline{p = \hbar k} \implies \vec{p}\Psi = -i\hbar\vec{D}\Psi$

$\quad\quad\quad\quad$ p^2 becomes the operator $-i\hbar D$

$\quad\quad$ So $\boxed{p^2\Psi = -\hbar^2\Delta\Psi}$ $\left(\Delta \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$

* we can also show that $\dfrac{\partial\Psi}{\partial t} = -i\omega\Psi$

using $\underline{E = \hbar\omega} \implies \boxed{E\Psi = i\hbar\dfrac{\partial\Psi}{\partial t}}$

$\quad\quad$ E is the operator $i\hbar\dfrac{\partial}{\partial t}$

The Schrödinger equation finally becomes:

$$H \, \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

where H is the operator Hamiltonian.

$$H = -\frac{\hbar^2}{2m} \Delta + U(\vec{r}, t)$$

• if now we suppose that H is time independent $[U(\vec{r}, t) \equiv U(\vec{r})]$, we set $\Psi(\vec{r}, t) = \Psi(\vec{r}) e^{-i\omega t}$ and it comes the time independent Schrödinger equation

$$H \Psi(\vec{r}) = E \, \Psi(\vec{r})$$

✕ <u>Physical meaning of Ψ</u>

$$P(\vec{r}, t) = \left| \Psi(\vec{r}, t) \right|^2 d\pi \qquad$$ represent the probability density to find an "electron" in a volume $d\pi$ at time t.

<u>Remarks</u>:

(i) for time independent problem

$$\left| \Psi(\vec{r}, t) \right|^2 = \left| \Psi(\vec{r}) \right|^2 \qquad \left(Rq : |a|^2 = a \, a^* \right)$$

(ii) $\Psi(\vec{r}) = A \, e^{i\varphi}$ only $|A|^2$ (amplitude) has a physical meaning, φ (phase) does n. have one.

→ However the phase relative to the superposition of waves may

To obtain the energy spectrum of a system,
In general, one must solve the following PDE (partial differential equation) :

$$-\frac{\hbar^2}{2m}\Delta \, \Psi(\vec{r}) + U(\vec{r}) \, \Psi(\vec{r}) = E \, \Psi(\vec{r}) \quad \text{for } \vec{r} \in \Omega$$

[one needs to know $U(\vec{r})$ and the boundary condition of $\Psi(\vec{r})$ on the frontier $\partial\Omega$.]

• analytical solution exists if $U(\vec{r})$ has simple forms = (does not depend on r, depends linearly on r, r^2, $\frac{1}{r}$ ...)

• In realistic system, $U(\vec{r})$ has a very complex dependency on $\vec{r}$ ⟹ one needs to resort to numerical methods.

ⓒ Solving the Schrödinger equation using simple 1D
examples.

(No system is truly 1D, however in many of systems,
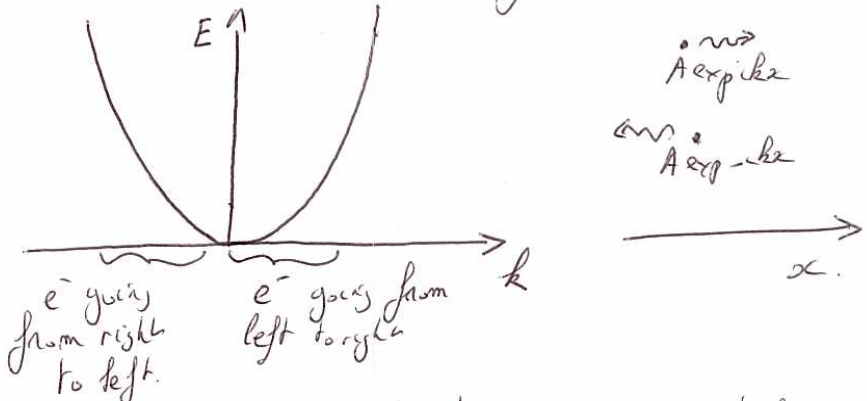1D properties dominate the behavior).

ⓘ free electron model

Here $U(\vec{r})$ does not depend on $\vec{r}$ [we set $U(\vec{r}) \equiv 0$]

$$\boxed{\Psi_{x} = A \exp ikx}$$ is solution of the schrödinger equation.

~~[×××××××××××××××××××]~~
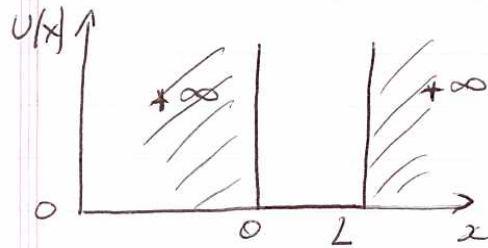
it comes $$\boxed{E = \frac{\hbar k^2}{2m}}$$ for the kinetic energy of the e^{-}.

we call this $E(k)$ relation a dispersion relation.

e^{-} going
from right
to left.

e^{-} going from
left to right.

$\dot{\sim}$ $A \exp ikx$

$\sim \dot{}$ $A \exp -ikx$

⇒ the free e^{-} model is frequently used when analyzing metals.

(ii) **e^- into a infinite quantum well.**

$$U(x)= \begin{cases} \infty & \text{for } x \leq 0 \\ 0 & \text{for } 0 < x < L \\ \infty & \text{for } x \geq L \end{cases}$$

- Boundary condition $\psi(x)=0$ for $x=0$, $x=L$.

  since the regions $x \leq 0$ and $x \geq L$ are forbidden for the e^- $[i.e.\ U(x)\psi(x)$, if $U(x) \to +\infty$, $\psi(x)=0]$

So $-\dfrac{\hbar^2}{2m} \dfrac{d^2\psi(x)}{dx^2} = E\psi(x)$ if $x \in \,]0,L[$

$$\dfrac{d^2\psi(x)}{dx^2} + k^2\psi(x)=0 \qquad \text{with} \quad k=\sqrt{\dfrac{2mE}{\hbar^2}}$$

Solutions are $\psi(x) = Ae^{ikx} + Be^{-ikx} \quad (A,B \in \mathbb{C})$

with Boundary conditions $\begin{cases} A+B=0 \Rightarrow A=-B \\ \sin kL = 0 \Rightarrow k=\dfrac{m\pi}{L} \equiv k_m \quad (m \in \mathbb{N}^*) \end{cases}$

k can take only discrete value.

$\psi_m(x) = A' \sin\left(k_m x\right)$ with orthonormalization $\displaystyle\int_0^L |\psi_m(x)|^2 = 1$
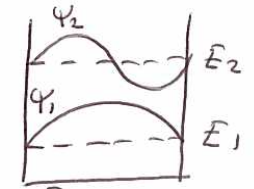
$$\Rightarrow \boxed{\psi_m(x) = \left(\dfrac{2}{L}\right)^{\frac{1}{2}} \sin\left(\dfrac{m\pi x}{L}\right)} \quad ; \quad \boxed{E_m = \dfrac{\hbar^2 k_m^2}{2m} = \dfrac{\hbar^2 m^2 \pi^2}{2mL^2}}$$

In general of the boundary conditions are equal to zero, the Schrödinger equation become a eigenvalue problems.
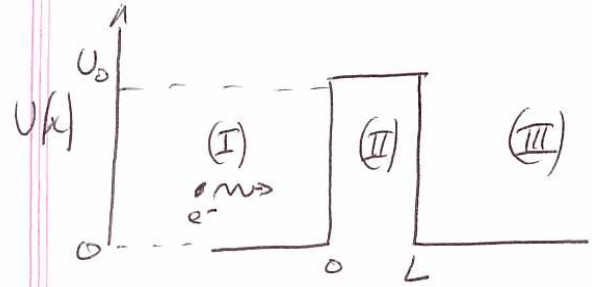
$$\boxed{H\Psi_m = E_m \Psi_m}$$

the energy spectrum is discrete

$\Rightarrow$ confinement effects in quantum mechanics

(iii). potential wall

$$U(x) = \begin{cases} 0 & \text{if } x \leq 0 \ (I) \\ U_0 & \text{if } 0 < x < L \ (II) \\ 0 & \text{if } x \geq L \ (III) \end{cases}$$

we suppose that $E < U_0 \Rightarrow$ general solution for an e^- coming from the left.

$$\psi(x) = \begin{cases} A e^{ikx} + B e^{-ikx} & (I) \quad k = \sqrt{\dfrac{2mE}{\hbar^2}} \\ C e^{Kx} + D e^{Kx} & (II) \quad K = \sqrt{\dfrac{2m(U_0 - E)}{\hbar^2}} \\ E e^{ikx} & (III) \quad k = \sqrt{\dfrac{2mE}{\hbar^2}} \end{cases}$$

propagating - traveling wave

evanescent wave.

boundary conditions at $x=0, x=L$

$$\Psi_I \big|_0 = \Psi_{II} \big|_0 \quad ; \quad \frac{d\Psi_I}{dx}\Big|_0 = \frac{d\Psi_{II}}{dx}\Big|_0$$

$$\Psi_{II} \big|_0 = \Psi_{II} \big|_L \quad ; \quad \frac{d\Psi_{II}}{dx}\Big|_L = \frac{d\Psi_{III}}{dx}\Big|_L$$
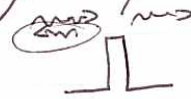
$\Rightarrow$ we get after calculations A, B, C, D, E [A is already known]

The ratio $R = \dfrac{|B|^2}{|A|^2}$ is the reflexion coefficient.

The ratio $T = \dfrac{|E|^2}{|A|^2}$ is the transmission coefficient.

In contrast to classical mechanics $T \neq 0$!
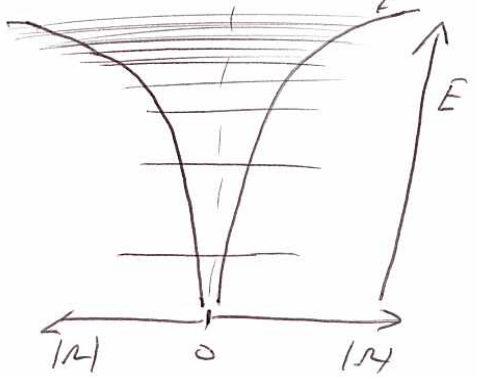
$\Rightarrow$ tunneling effect.

Also for the case $E > U_0$, we would find that $R \neq 0$ (also in contrast to classical mechanics)

* __Application:__ Schrödinger equation for Hydrogen atoms

Electrostatic potential between 1 proton and 1 electron

$$\Rightarrow \quad V(\vec{r}) = \frac{q}{4\pi\varepsilon_0 \|\vec{r}\|}$$

potential energy $\quad U(\vec{r}) = -q\, V(\vec{r})$

potential "seen" by the e^- $\;U(\vec{r})$

$$H = -\frac{\hbar^2}{2m}\Delta - \frac{q^2}{4\pi\varepsilon_0 \|r\|}$$

$H\Psi = E\Psi$ + closed boundary conditions [Ψ vanishes if $r \nearrow$]

$$\Rightarrow \quad H\Psi_m = E_m \Psi_m. \quad\Rightarrow\quad \{E_m, \Psi_m\}$$

$\Rightarrow$ hydrogen spectrum, consistent with the Bohr model.

*

d) Crystal structure

Solid material are classified by the way the atoms are arranged within the solid; 3 types of materials:
- amorphous = atoms are placed at random, no order
- poly-crystalline = order by segment, no long range order.
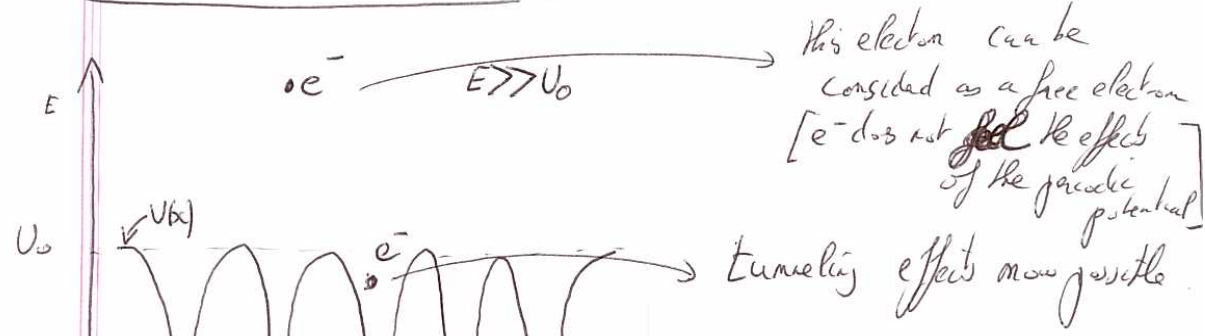- crystalline = atoms are placed in high ordered structure.

See Annex
14 of
textbook.

[We will study crystalline semiconductor where a unit cell can be repeated periodically to form the solid.

Simple example of potential in the crystal [N number of atoms]
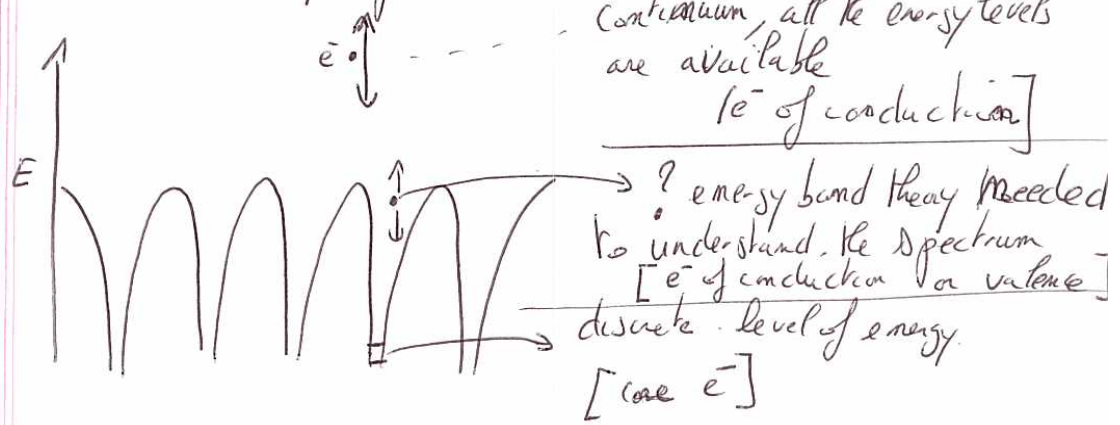
periodic potential. [chain of atoms]

nuclei

$U(x)$

how the electron behave?

e^- $\longrightarrow$ $E \gg U_0$

this electron can be considered as a free electron [e^- does not feel the effects of the periodic potential]

E

U_0 $U(x)$

e^- $\longrightarrow$ tunneling effects now possible

$E \ll U_0$

$\longrightarrow$ far inside the potential well, the e^- are confined

What is the energy spectrum ?

e^- ⌄ - - - - - - - - - continuum, all the energy levels are available

[e^- of conduction]

E

→ ? energy band theory needed to understand the spectrum

[e^- of conduction or valence]

→ discrete level of energy.

[core e^-]

Definition

valence electron = it is an e^- in an outer shell of an atom that can participate in forming chemical bonds with other atoms.

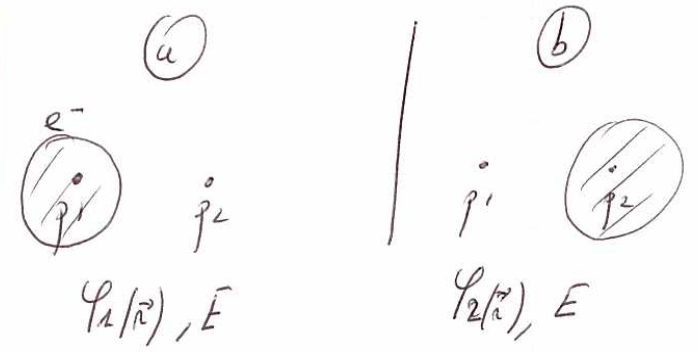core electron = e^- occupying completely filled shells under the valence shell.

conduction electron = it is an e^- that is free, ~~and has~~ a mobile charge carrier.

II | Energy band theory

(1) Intuitive approach [Look also 1.1.2 in the textbook]

H_2^+ molecule $2p, 1e^-$

2 configurations (a) and (b)

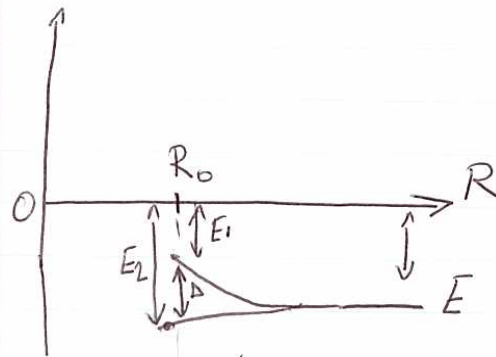

(a)
e^-

$\Psi_1(\vec{r}), E$

(b)

$\Psi_2(\vec{r}), E$

* if $d(p_1, p_2) \gg a_0$ $\Psi_1(\vec{r}), \Psi_2(\vec{r})$ are distinct states
associated to one Dame energy E.
$\Rightarrow$ the energy level is degenerate.

* if $d(p_1, p_2) \simeq a_0$, we bring them closer together,
the potential that can be seen by the e^- is given by
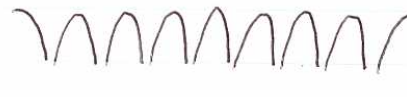

$U(r)$

tunneling effect is now possible
$\Rightarrow \Psi_1$ and Ψ_2 are coupled
$\Rightarrow$ lift the degeneracy
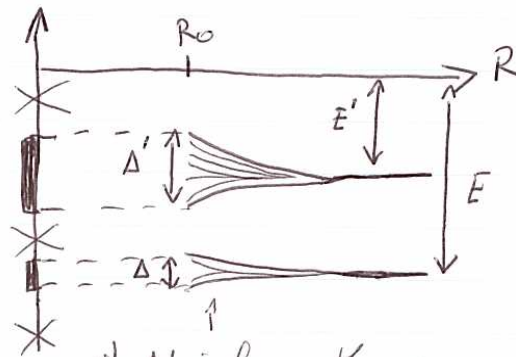$\Rightarrow$ split the energy E into E_1, E_2

R_0

O → R

E_1

E_2 Δ E

Δ depends on the strength of the coupling.

* generalization   for N number of atoms, we have now N "quantum well" [N is large]

⟹ periodic potential.

Each energy level for a given atom gives rise to N different energy levels (lift the degeneracy)

R_0 → R

Δ' E'

E

Δ

Actually, it contains $2N$ energy levels due to the spin degeneracy.

* if N is large, the energy levels are so close that they form a continuum ⟹ band.

* It also appears some forbidden band of energy between the permitted energy band.

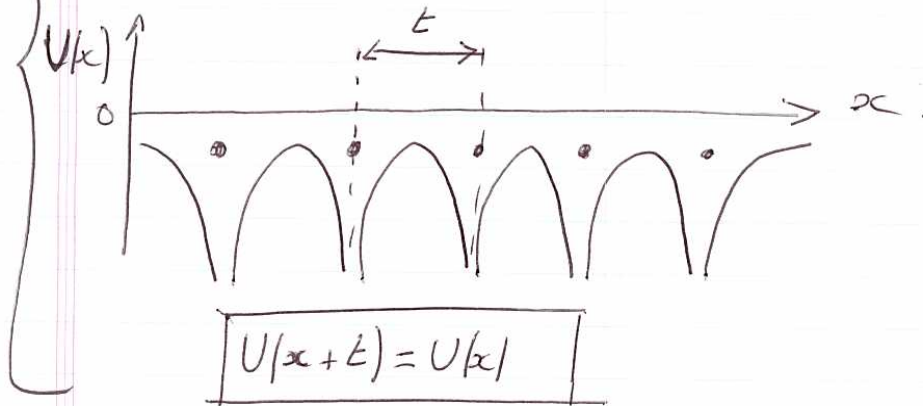* $\Delta < \Delta'$, the energy bands with smaller energy are also thinner.

$\delta\xi$ ← tunneling effect is stronger here

(2) **Analytical approach**

periodic nature of the position of the atoms in the crystal $\Rightarrow$ $U(\vec{r} + \vec{T}) = U(\vec{r})$. $\left[\begin{array}{l} U(x) \text{ accounts for} \\ \text{many body effects} \end{array}\right.$

example 1D

$$\boxed{U(x + t) = U(x)}$$

Since the potential is periodic, we can define the boundary conditions for Ψ using **the Bloch theorem**. Such as $\boxed{\Psi(x+t) = \Psi(x)\, e^{ikt}}$
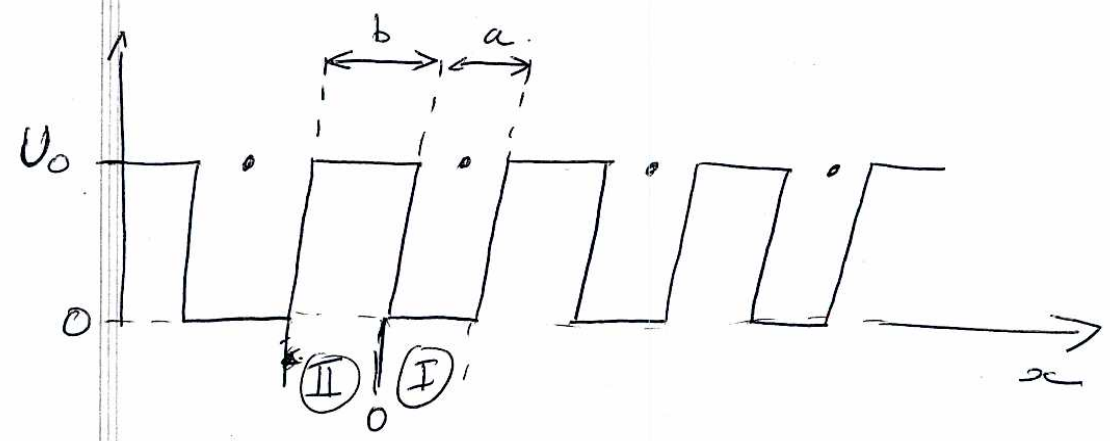
or (2nd form of the Bloch theorem)

$$\boxed{\begin{array}{l} \Psi(x) = u_k(x)\, e^{ikx} \\ u_k(x + t) = u_k(x) \end{array}}$$

ⓐ The Krönig - Penney model

1D system where $U(x)$ is replaced by a periodic sequence of rectangular potential.

$$\Psi(x) = \begin{cases} \text{Ⓘ} & A\exp(ik_1 x) + B\exp(ik_1 x) \qquad k_1 = \sqrt{\dfrac{2mE}{\hbar^2}} \\[4mm] \text{Ⓘ} & C\exp(k_2 x) + D\exp(-k_2 x) \qquad k_2 = \sqrt{\dfrac{2m(U_0 - E)}{\hbar^2}} \quad \text{if } E < U_0 \end{cases}$$

Boundary conditions =

at $x=0$ Continuity $\Psi_I(0) = \Psi_{II}(0)$.

$$\left.\frac{d\Psi_I}{dx}\right|_0 = \left.\frac{d\Psi_{II}}{dx}\right|_0$$

at $x=a$ or $x=-b$ periodicity. we introduce the vector k via Bloch theorem

$$\Psi_I(a) = e^{ik(a+b)}\Psi_{II}(-b)$$

$$\frac{d\Psi_I(a)}{d} = e^{ik(a+b)}\frac{d\Psi_{II}(-b)}{}$$

A, B, C, D

$\Rightarrow$ 4 unknowns, 4 equations, it come in the matrix form

$$\mathbb{M}x = 0 \quad \text{where} \quad x = \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix}.$$

$\det(M) = 0$ it is a necessary condition to obtain non trivial solution ; we get after calculations :

$$\left[\frac{k_2^2 - k_1^2}{2 k_2 k_1} \sinh(k_2 b) \sin(k_1 a) + \cosh(k_2 b) \cos(k_1 a) \right] = \cos(k(a+b)).$$
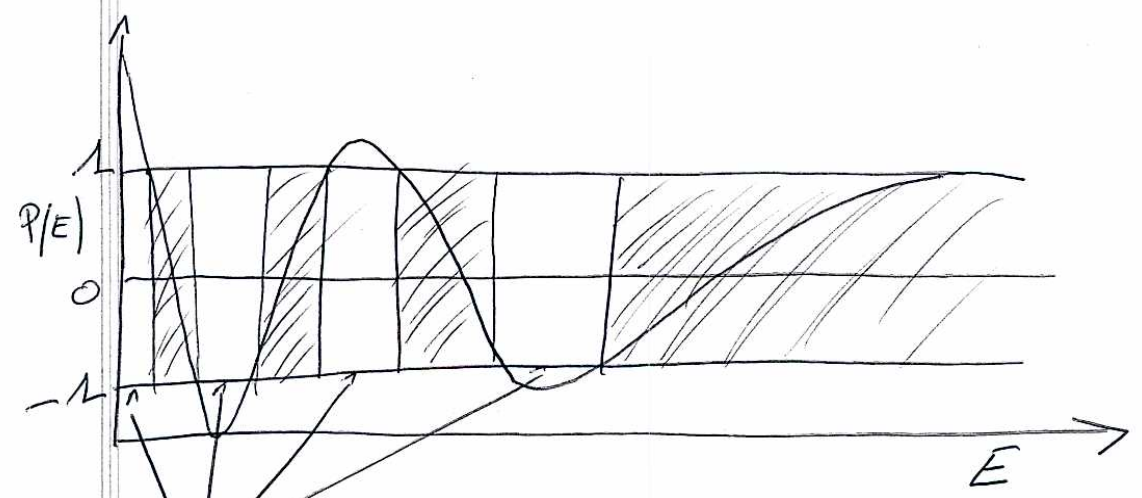
$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$

$P(E)$ since

$k_1(E) ; k_2(E).$

if $E > U_0$ in region II we rather get.

with $k_2 = \sqrt{\dfrac{2m(E-U_0)}{\hbar^2}}$ $\qquad k_2 \to i k_2$

$$\left[\frac{-k_2^2 - k_1^2}{2 k_1 k_2} \sin(k_2 b) \sin k_1 a + \cos k_2 b \cos k_1 a \right] = \cos k(a+b)$$

$\ast$ $\boxed{P(E) = \cos[k(a+b)]}$

for a specific value of k, we get the allowed value of E

$\Rightarrow$ this provides implicitly the dispersion relation $\boxed{E(k)}$

we are looking at a graphical solution.

we must have $\boxed{-1 \leq P(E) \leq 1}$

it appears region where there is no solution, we call these regions - band gaps or forbidden bands.
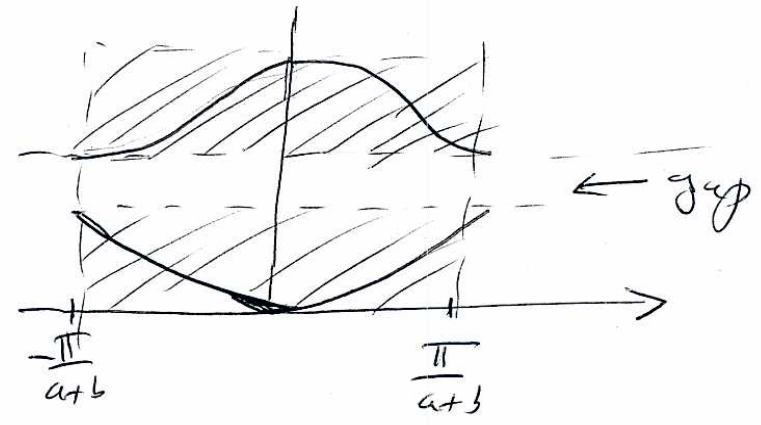
the $E(k)$ dispersion relation can be also plotted:

← free electron

permitted energy band

← gap

$-\frac{2\pi}{a+b}$ $-\frac{\pi}{a+b}$ $\frac{\pi}{a+b}$ $\frac{2\pi}{a+b}$
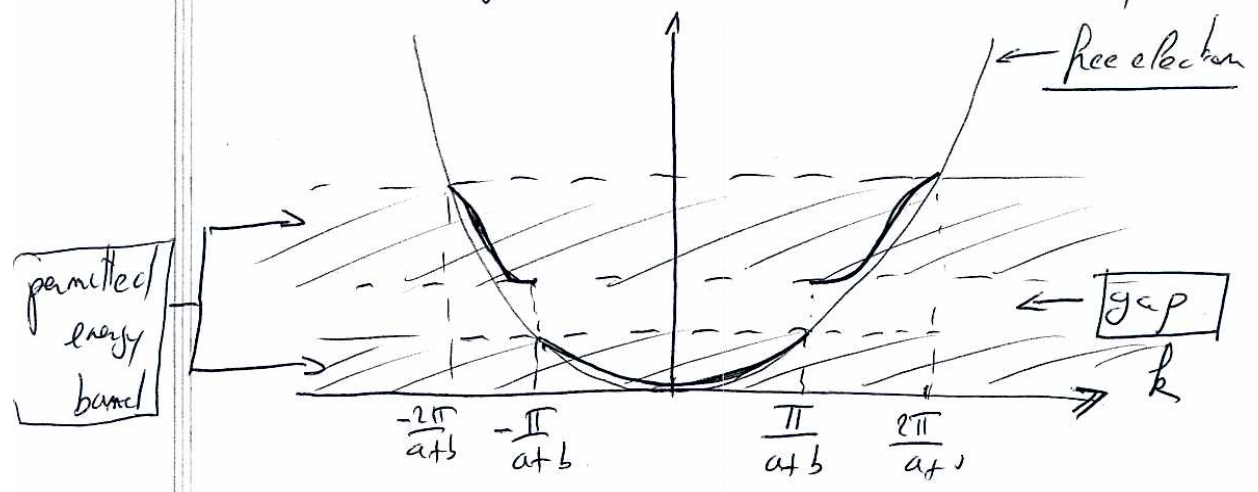
the periodicity of the solution is $\frac{2\pi}{a+b}$.

the solution can be limited in the region

$$-\frac{\pi}{a+b} \leq k \leq \frac{\pi}{a+b}$$ without loss of information.

we call this region the $\boxed{\text{first Brillouin zone.}}$

See
Figure 1.10
textbook

$\leftarrow$ gap

$$-\frac{\pi}{a+b} \qquad \frac{\pi}{a+b}$$

ⓑ General case

we need to solve

$$\boxed{-\frac{\hbar^2}{2m} \Delta \Psi + U\Psi = E\Psi} \quad \text{in } \Omega.$$

where U is an arbitrary periodic potential,
as appropriate for a periodic solid.

[Bloch theorem]: we are looking at solutions of this
form:

$$\boxed{\Psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \, u_k(\vec{r}) \quad ; \quad u_k(\vec{r}) = u_k(\vec{r}+\vec{t}).}$$

we get

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

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad}_{H_k}$$

for a given k we need to solve an eigenvalue problem and we get a set of eigenvalues $\{E_{k,m}\}$.

$$\boxed{H_k\, u_{k,m} = E_{k,m}\, u_{k,m}} \quad \circledast$$

- Numerical techniques are required here!

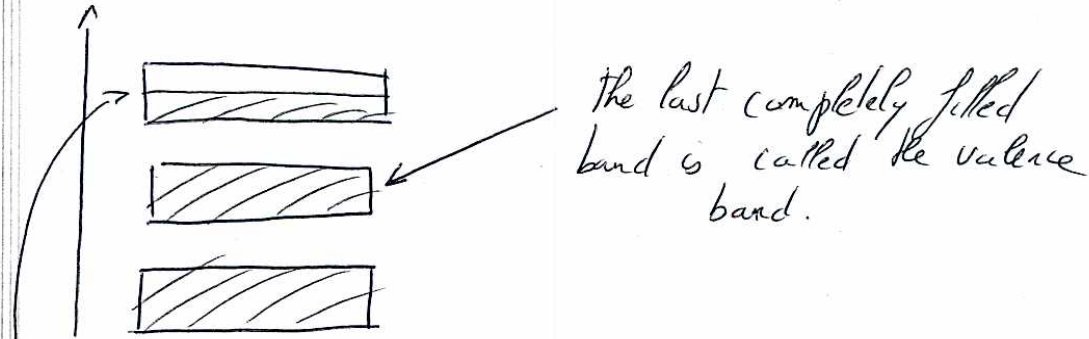- $\{E_{k,m}\}$ forms the <u>band structure</u>.

example
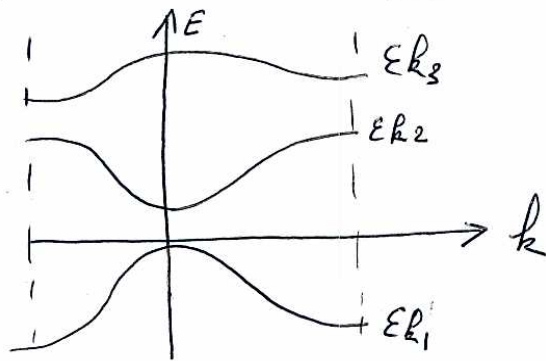
- the energy band of solid are rather complex.

(3) **Valence band and Conduction band**

e^- are filling the energy bands by increasing energy order, from the bottom to the top.

the last completely filled band is called the valence band.

the energy band directly above the valence band is called the conduction band.

Remarks

* the energy band diagram can be restricted to the valence and conduction band, since the e^- that are contained in these bands dominate the behavior of the solid.

* 2 possibilities

1) the bands are completely filled or empty [conduction band is empty]
Eg is the energy of the gap between valence and conduction band
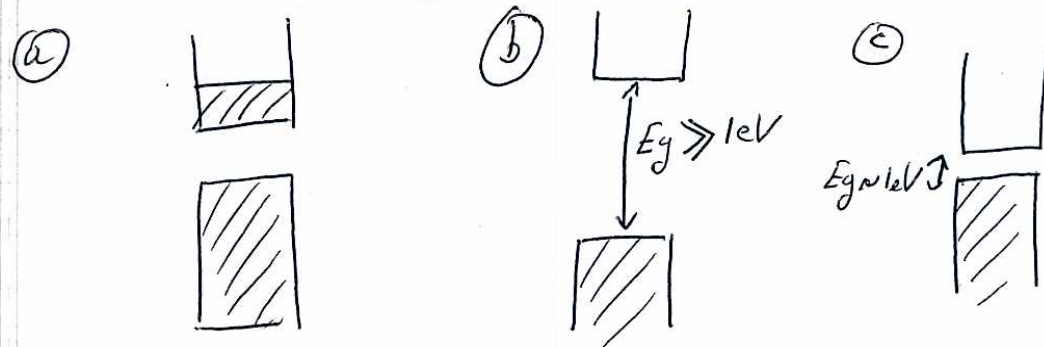
2) the conduction band is partially filled; the highest energy level is called the Fermi level

④ <u>Insulator - Metal or Semiconductor ?</u>

We consider 3 configurations

ⓐ

ⓑ $E_g \gg 1eV$

ⓒ $E_g \sim 1eV$ ↕

ⓐ There exist unfilled space in the conduction band.
At finite temperature, (thermal excitation) there exist e^- close to the fermi level, travelling in all directions and many different velocities

When an Electric field is applied, the e^- can be accelerated and it appears an electron flow.
the conduction is then possible.
These Solids are called <u>Metals</u> (good conductors)

ⓑ the energy gap is very large, the valence band is full.
and cannot carry a current since no empty state is ~~available~~ available.
These Solids are <u>Insulators</u>

ⓒ the energy gap is very small. At finite temperature (with thermal excitation) the e^- have enough energy to jump from the valence to the conduction band!

these Solids are very bad insulators and very bad conductors!
we call them Semiconductors.

(5) Band structure of Semiconductor.

For a 3D crystal, it is impossible to "represent" the bandstructure (dispersion relation $E(k)$) since $k = k_x, k_y, k$ and this involves a 4D plot.

However one can represent $E(k)$ along the main crystal directions in k-space — that allows us to analyse properties of semiconductors
[See figures]

Remark:
Semiconductor can exhibit:

— direct band gap (GaAs) = an e^- can fall or jump between the valence band and conduction band without a change in momentum.

— indirect band gap (Si, Ge) = an e^- cannot fall or jump without a change in momentum.

Figure 1: Perspective plot of the energy band structure of silicon. The figure to the left shows the Brillouin zone, and the two-dimensional section over which the energy bands are displayed. The energy bands are plotted to the right. The four surfaces lying below 0 eV are the valence bands, and the upper surface is the lowest conduction band. The maximum valence band energy occurs at $k = 0$, which on this figure is the center of the front boundary of the Brillouin-zone section. The minimum conduction-band energy occurs along the front boundary of the section, near the left and right ends. Thus, Si has an indirect-gap band structure.
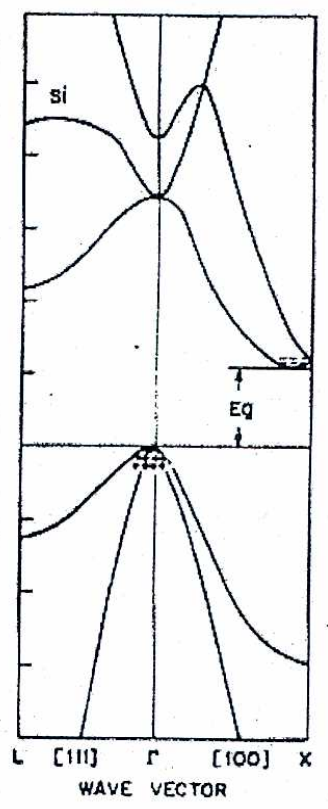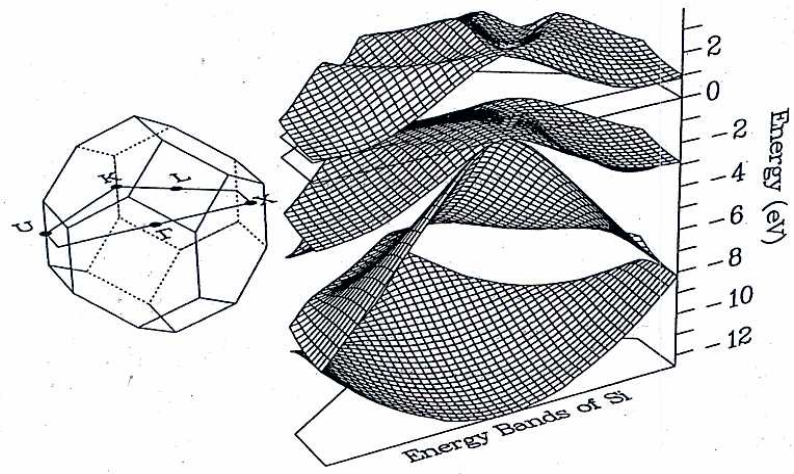
$E_g = 1.12\ eV$

Figure 2: Perspective plot of the energy band structure of gallium arsenide. The conventions of the figure are the same as those of Fig. 1. The conduction-band minimum of GaAs occurs at $k = 0$, and thus GaAs has a direct-gap band structure.
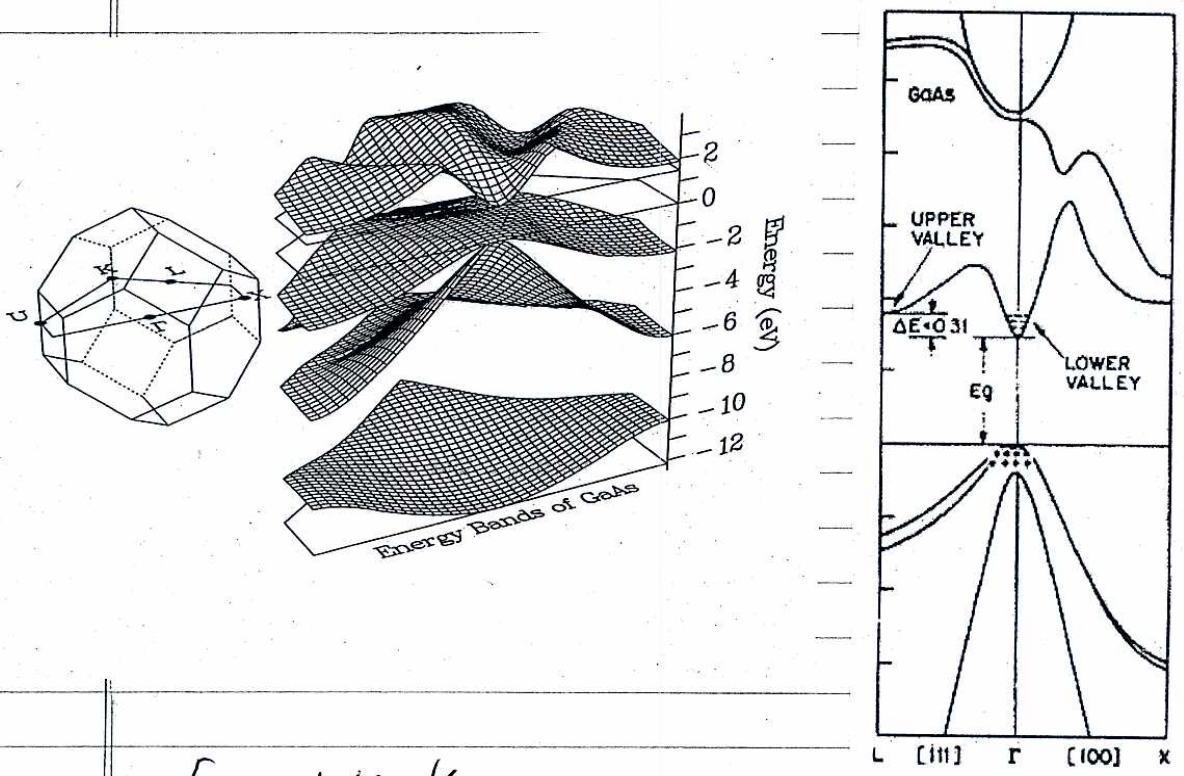
$E_g = 1.42\ eV$

⑥ Electrons and holes in Semiconductor

We know that with thermal excitation, e^- can jump from the valence band to the conduction band.

- the conduction band is then an "almost empty" band
- the valence band is an "almost full" band.

the concept of hole is introduced to keep track of the missing e^- in the valence band.

| Holes are missing electrons |

Example Si

→ [Conduction e^-
→ [hole
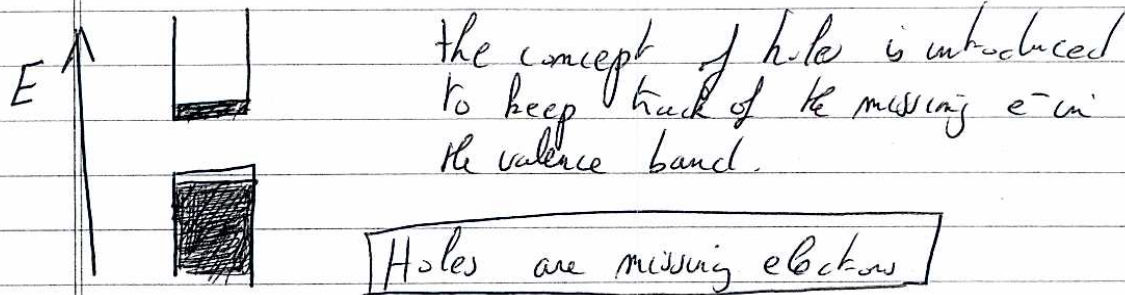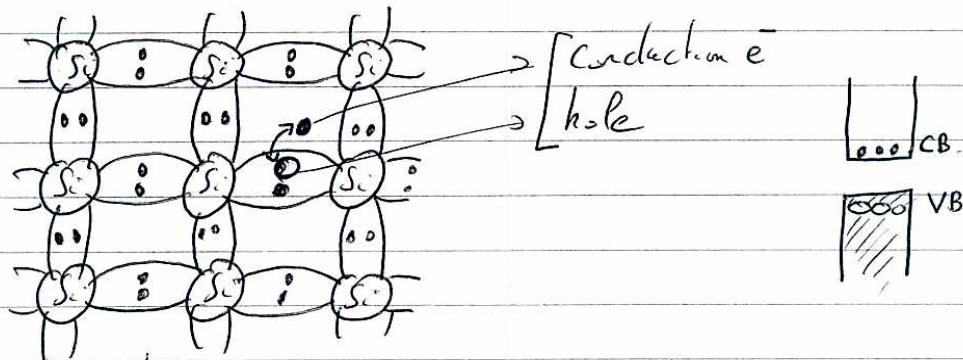
* holes behave like positively charged particle, they can move inside the valence band.

* However holes are not real particles! they rather account for the combined behavior of all the electrons.

→ this means that we have to deal with the transport of carriers in both bands

⑦ Effective mass approximation

→ For a free electron, the dispersion relation is quadratic (parabola) $E = \frac{\hbar^2 k^2}{2m}$.

→ [In a crystal, the situation is far more complex.

[However, physics of semiconductors usually deals with

electrons situated near the minimum of the conduction band,

or holes near the maximum of the valence band.

[These extrema in the dispersion relation can be
approximated by a quadratic curve (parabola)

example GaAs.

parabolic
band approximation

$\mathcal{E}_B$

VB

→ the $e^-_{(holes)}$ behave like free $e^-_{(holes)}$,
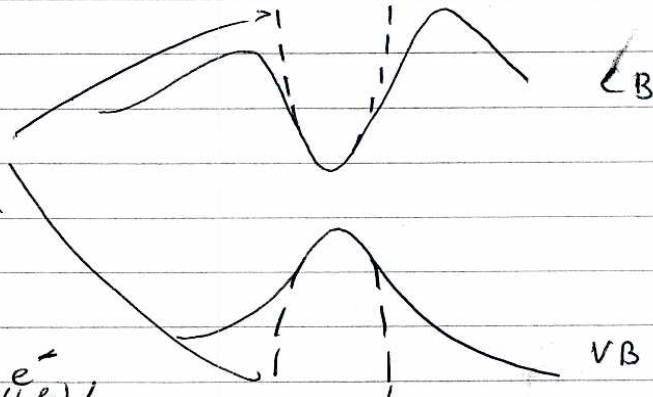
however they have now an effective mass m^* that accounts for
the crystal structure

it comes $\boxed{E = \dfrac{\hbar^2 k^2}{2m^*}}$

m^* contains all the detailed of the bandstructure around the extrema.

- in general for 3D crystal, we get an effective mass tensor

$$m^* = \begin{bmatrix} m^*_{xx} & m^*_{xy} & m^*_{xz} \\ m^*_{yx} & m^*_{yy} & m^*_{yz} \\ m^*_{zx} & m^*_{zy} & m^*_{zz} \end{bmatrix} \quad \text{with} \quad \boxed{m^*_{ij} = \dfrac{\hbar^2}{\partial^2 E / \partial k_i \partial k_j}}$$

- in particular :

For GaAs = m^* is isotropic, tensor is diagonal [all elements are equal]
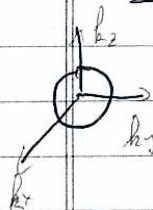
(constant energy surface are spheres)

$\dfrac{m^*}{m_0^*} = 0.067$ for e$^-$ m_0 mass of electron.

~~$\dfrac{m^*}{m_0} = 0.082$ for holes~~

For Si = tensor is diagonal, one longitudinal two transverse effective mass (m^*_ℓ, m^*_t, m^*_t).

$\boxed{\dfrac{m^*_\ell}{m_0^*} = 0.98}$, $\boxed{\dfrac{m^*_t}{m_0^*} = 0.19}$ for e$^-$

Constant energy surface are ellipsoid.

<u>6 valleys</u>
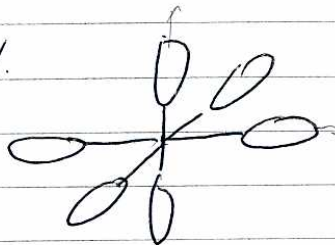
Ⅲ Semiconductors Fundamentals

1 Carrier densities

We want to know the population of e^- (resp. holes) inside the CB (resp. VB).

electron density

hole density

$$n = \int_{E_c}^{+\infty} n(E)\, dE. \qquad p = \int_{-\infty}^{E_v} p(E)\, dE$$
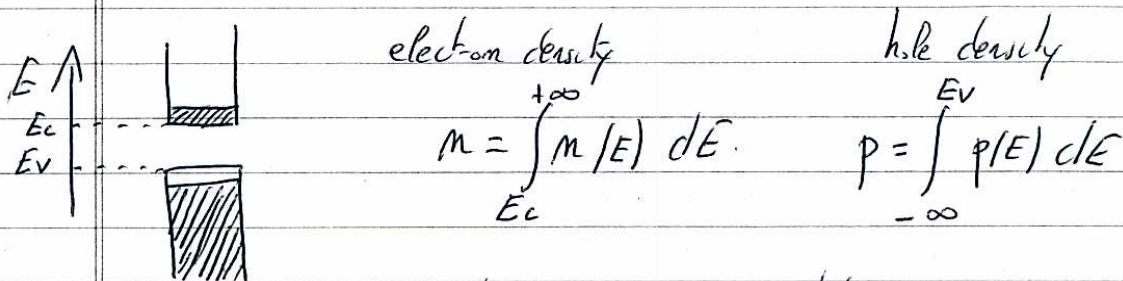
$n(E), p(E)$ density of occupied states per unit volume and energy.

One needs to answer two questions:

(a) How many states are available at each energy?
we call $g(E)\, dE$ the density of states (DOS) — number of states that are available between E and $E+dE$.

(b) What is the probability that a state is occupied by an electron?
we call $f(E)$ the distribution function for the electron.
the derivation of $f(E)$ belongs to a statistical physics course.

we will then get:

$$\begin{cases} n(E) = g_c(E) f(E) & \text{for the electrons.} \\ p(E) = g_v(E) \left[1 - f(E) \right] & \text{for the holes} \end{cases}$$

Let us answer the two question above step by step.

Ⓐ <u>Density of States</u>

According to the Bloch theorem, for periodic potential $U(\vec{r})$

$$\Rightarrow \Psi(\vec{r}) = e^{i\vec{k}\vec{r}} u_k(\vec{r}) \quad \text{with} \quad u_k(\vec{r} + \vec{L}) = u_k(\vec{r})$$

we consider a crystal with macroscopic dimension (L_x, L_y, L_z).
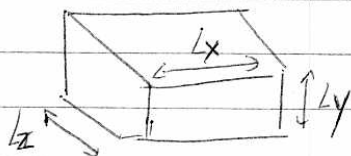
How can we choose the B.C at the edges of the macroscopic solid?

* Rather than vanishing B.C, we make use of periodic B.C [Born-Van Karman], for allowing traveling wave.

At the edges $\quad \Psi(\vec{r}+\vec{L}) = \Psi(\vec{r})$

$$\Psi(\vec{r}+\vec{L}) = \exp(i\vec{k}\vec{r}) \, \exp(\vec{k}\vec{L}) \, u\vec{k}(\vec{r}+\vec{L})$$

~~Ψ~~ $\Rightarrow \exp(i\vec{k}\cdot\vec{L}) = 1$

$\not{\equiv}$ we obtain discrete values for k.

$$\boxed{k_x = n_x \frac{2\pi}{L_x} \; ; \quad k_y = n_y \frac{2\pi}{L_y} \; ; \quad k_z = n_z \frac{2\pi}{L_z}}$$

$n_x, n_y, n_z \in \mathbb{Z}$ ($\mathbb{Z}$ direction of propagation)

in the k-space it comes:

in 3D

elementary volume
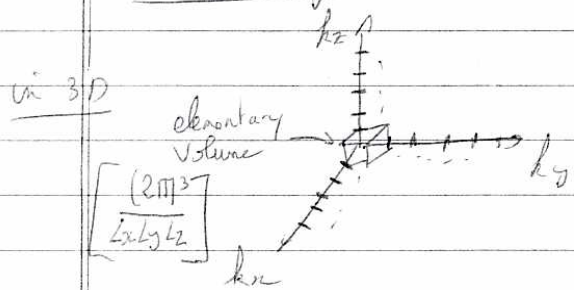
$\boxed{\dfrac{(2\pi)^3}{L_x L_y L_z}}$

the number of states that we obtain in a volume $d^3\vec{k}$

is $\quad \dfrac{d^3\vec{k}}{\left[\dfrac{(2\pi)^3}{L_x L_y L_z}\right]}$

we note $g(\vec{k}) \, d^3\vec{k}$ the DOS in the k space.

where $\boxed{g(\vec{k}) \, d^3\vec{k} = 2 \times \dfrac{V}{(2\pi)^3} \, d^3\vec{k}}$

V: volume of the crystal $\qquad \boxed{\text{spin factor}}$

for dimension $m = 1, 2, 3$, we get

$$g(\vec{k})\, d^m\vec{k}$$

in 3D $\quad d^3\vec{k} = 4\pi k^2\, dk \quad \left[\begin{array}{l}\text{elementary volume between}\\ \text{two energy spere}\end{array}\right]$

in 2D $\quad d^2\vec{k} = 2\pi k\, dk$
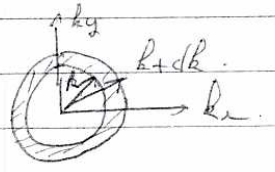
in 1D $\quad d\vec{k} = 2\, dk \quad [\,2 \text{ direction of propagation}\,]$
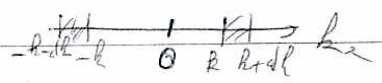
We want to know the density of state in Energy

$$g(k)\, dk = g(E)\, dE$$

one need to know the dispersion relation $E(k)$.

For Free electron or effective mass approach

we know that $\quad E(k) = \dfrac{\hbar^2 k^2}{2 m_e^*} + E_c$

it comes $\quad \boxed{dE = \dfrac{\hbar^2 k}{m_e^*}\, dk}$

So in 3D we obtain

$$\frac{2 V}{(2\pi)^3} 4\pi k^2 dk = g(E) dE.$$

$$g_c(E) = 4\pi k^2 \cdot 2 \frac{V}{(2\pi)^3} \frac{m_e^*}{\hbar^2 k} = \frac{V m_e^*}{\pi^2 \hbar^2} \sqrt{(E-E_c)} \frac{2m_e^*}{\hbar}$$

$$\boxed{g_e(E) = \frac{V}{2\pi^2 \hbar^3} (2m_e^*)^{3/2} (E-E_c)^{1/2}}$$

E_c ___

E_v ___

$g_c(E)$

$g_v(E)$

E ↑
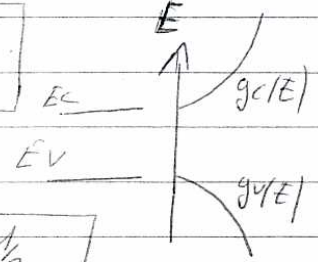
Similarly for the holes we get:

$$\boxed{g_v(E) = \frac{V}{2\pi^2 \hbar^3} (2m_h^*)^{3/2} (E_v - E)^{1/2}}$$

see Figure 1

1D, 2D, 3D cases

in general * For electron in a periodic solid, the dispersion relation and DoS do not have a single analytical form, see the example of the silicon Figure 2

however one can define an isotropic effective mass m^* in the vicinity of the minimum (resp. maximum) of the conduction band/ resp. valence band/ -

Remark: For many-valley semiconductors with anisotropic effective mass [example silicon]. For DoS calculations the effective mass is given by:

$$m^* \Rightarrow Z^{2/3} (m_x^* m_y^* m_z^*)^{1/3} \quad \text{with } Z \text{ nbe of equivalent valley}$$

silicon $\Rightarrow$ $\boxed{Z=6 \quad m^* = 6^{2/3} (m_t^2 m_l)^{1/3} = 1.08 \, m_o}$

For holes which occupy 2 bands, we call these bands light-hole (lh) and heavy-hole (hh) bands, the effective DOS mass equal [1 minima]:

$$m^* \rightarrow \left(m^{*3/2}_{hh} + m^{3/2}_{lh}\right)^{2/3}$$

for Silicon = $m^*_{lh} = 0.16\, m_0$, $m^*_{hh} = 0.53\, m_0$

$$\Rightarrow m^* = 0.59\, m_0$$

for GaAs = $m_{lh} = 0.074\, m_0$, $m_{hh} = 0.62\, m_0$

$$\Rightarrow m^* = 0.64\, m_0$$

[The effective mass for conductivity calculation is $\neq$ than the effective mass for DOS calculations.

here $$\boxed{\frac{1}{m^*} = \frac{1}{3}\left(\frac{1}{m_x} + \frac{1}{m_y} + \frac{1}{m_z}\right)}$$

K_z, K_y, K_x, k_y, k_x
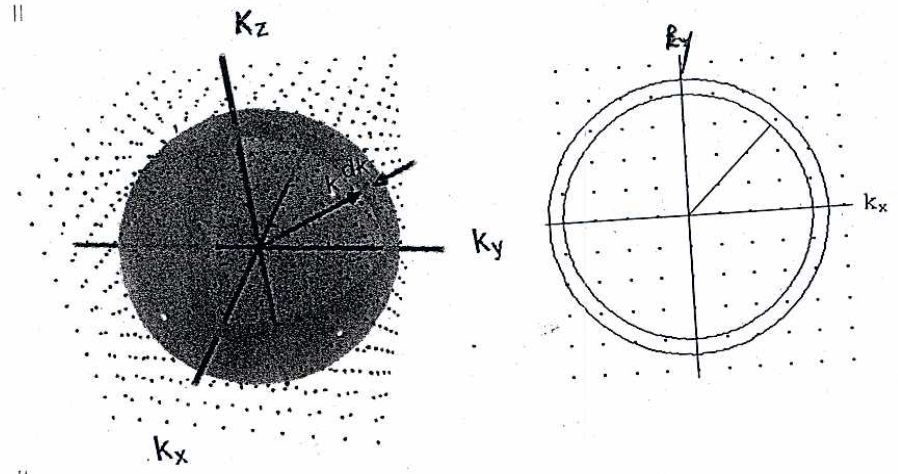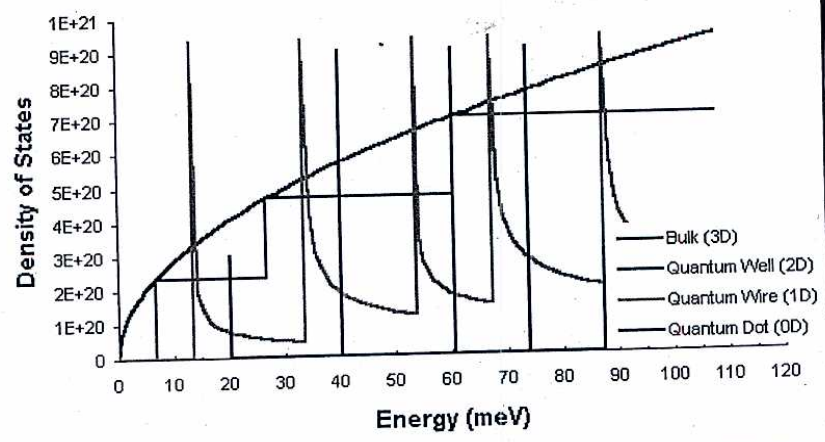
Figure 1

Figure 2
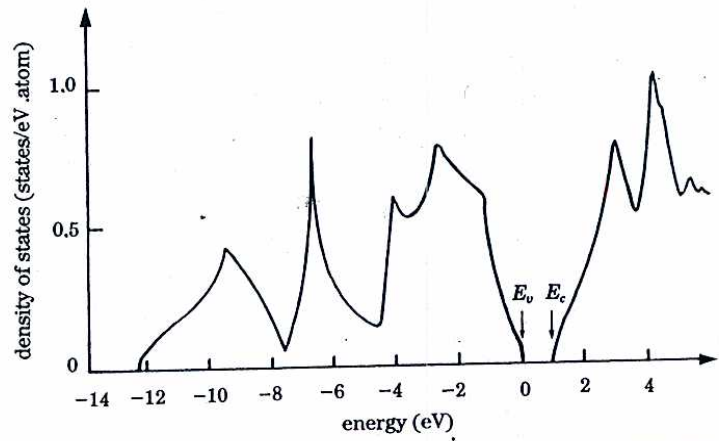
Fig. 2.5. Density of states of the valence and conduction bands of silicon, calculated by J.R. Chelikowsky and M.L. Cohen, Physical Review B **14**, 556 (1976). The energy origin is at the maximum E_v of the valence band. In the neighborhood of E_v, the maximum of the valence band, and E_c, the minimum of the conduction band, the density of states varies parabolically with energy.

ⓑ Distribution function

We know from the energy band theory and the definition of the semiconductors, that the probability for a state to be occupied by one e^- should depend on the temperature.
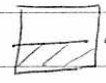
e^- obey the Fermi-Dirac statistics. [accounting for the Pauli exclusion principle].

we have :

$$f(E) = \frac{1}{1 + \exp(\beta(E - E_F))}$$

$$\beta = \frac{1}{k_B T}$$

k_B = Boltzmann cte
E_F = Fermi - level

if $T \neq 0$ $f(E_F) = \frac{1}{2}$
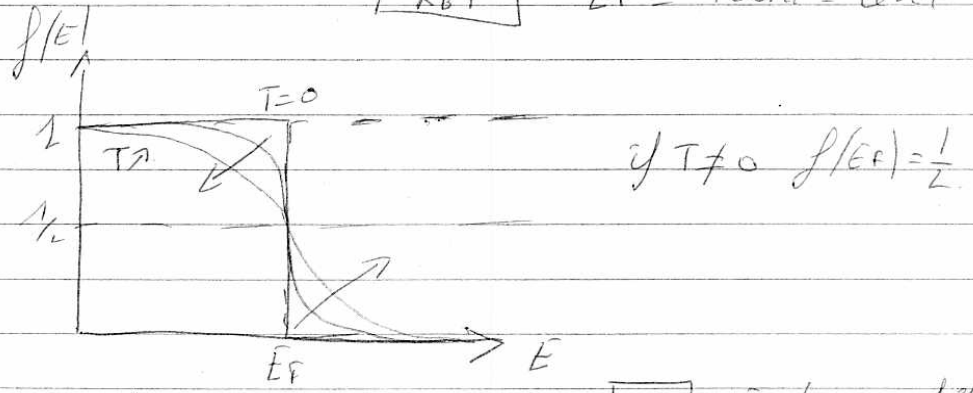
Remark

• For conductors at $T = 0$, we saw

⟵ E_F (maximum of energy for one e^-)

• For Insulators, Semiconductors, the fermi level lies between VB and CB

• For semiconductors, with increase of temperature the probability $f(E)$ to find an e^- for $E > E_F$ is different than 0.

if $(E - E_F) > 3k_BT$ ⟵

E above EF

$$f(E) \approx \exp(-\beta(E - E_F)).$$

$\Rightarrow$ Maxwell - Boltzmann distribution

usually provides the probability of occupancy of non - interacting particles at low densities. it is a classical distribution function.

$\Rightarrow$ Non - degenerate semiconductors.

if $(E - E_F) < -3k_BT$ E below EF

$$f(E) \approx 1 - \exp(-\beta(E_F - E)) \quad \text{(situation for hole)}$$

(E)   Carrier densities calculations

$$n(E) = g_C(E)\, f(E) \qquad p(E) = g_V(E)\left[1 - f(E)\right]$$
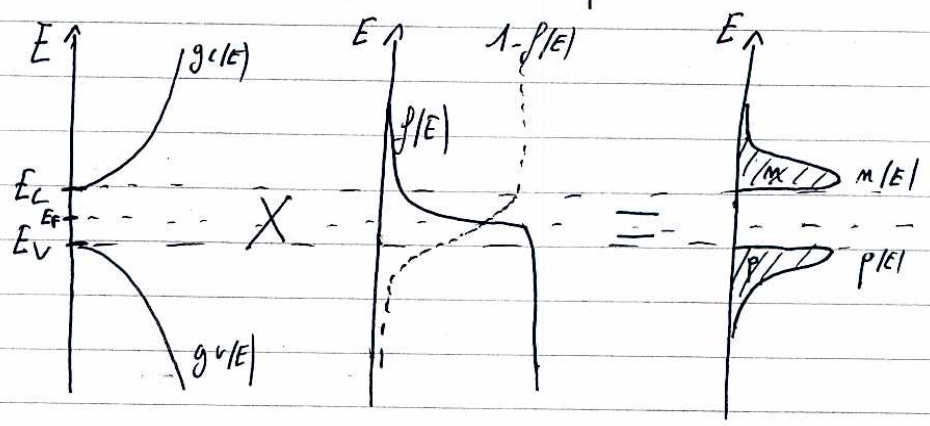
we get,

$\left[\begin{array}{l}\text{per unit of}\\\text{volume}\end{array}\right]$ $\left[n = \int_{E_c}^{+\infty} \frac{1}{2\pi^2 \hbar^3} \left(2m_e^*\right)^{\frac{3}{2}} \left(E-E_c\right)^{\frac{1}{2}} \frac{1}{1+\exp\left(\beta\left(E-\hat{E}_F\right)\right)} \, dE\right.$

$\left[p = \int_{-\infty}^{E_v} \frac{1}{2\pi^2 \hbar^3} \left(2m_h^*\right)^{\frac{3}{2}} \left(E_v-E\right)^{\frac{1}{2}} \frac{1}{1+\exp\left(\beta\left(E-E_F\right)\right)} \, dE\right.$

$*$ <u>Non - degenerate Semiconductor</u> $\qquad (E-E_F) > 3 k_B T$.

$$n_0 = \frac{1}{2\pi^2 \hbar^3} \left(2m_e^*\right)^{3/2} \int_{E_c}^{+\infty} \left(E-E_c\right)^{\frac{1}{2}} \exp\left[\left(-\beta\left(E-E_F\right)\right)\right] dE$$

$$= \frac{1}{2\pi^2 \hbar^3} \left(2m_e^*\right)^{3/2} \exp\left[-\beta\left(E_c-E_F\right)\right] \underbrace{\int_0^{+\infty} y^{\frac{1}{2}} \exp(-y) \, dy}_{\frac{\sqrt{\pi}}{2}}$$

$\Rightarrow$ $\boxed{n_0 = N_c \exp\left[-\beta\left(E_c - E_F\right)\right]}$ $\Big\}$ N_c effective DOS in the CB

$$N_c = 2 \left[\frac{2\pi m_e^* k_B T}{\hbar^2}\right]^{3/2}$$

<u>Similarly</u>
<u>for holes</u>

$$\boxed{p_0 = N_v \exp\left[\beta\left(E_v-E_F\right)\right]}$$

N_v effective density of states in VB.

$$N_v = 2 \left[\frac{2\pi m_h^* k_B T}{\hbar^2}\right]^{3/2}$$

Typical value for N_C and N_V a $T = 300 \text{ K}$.

	$N_C \ (cm^{-3})$	$N_V \ (cm^{-3})$
Si	2.8×10^{19}	1.04×10^{19}
GaAs	1.04×10^{19}	6.0×10^{18}

In general

$$n = N_C \ F_{1/2} \left[-\beta \left(E_C - E_F \right) \right]$$

$$p = N_V \ F_{1/2} \left[\beta \left(E_V - E_F \right) \right]$$

$F_{1/2}$ is the Fermi-Dirac integral.

$$F_{1/2} (\eta) = \frac{2}{\sqrt{\pi}} \int_0^{+\infty} \frac{\sqrt{\varepsilon} \ d\varepsilon}{1 + \exp(\varepsilon - \eta)}.$$

Limiting cases.

ⓐ $\eta \ll 1 \longrightarrow F_{1/2}(\eta) \approx e^\eta$ [non degenerate]

ⓑ $\eta \gg 1 \longrightarrow F_{1/2}(\eta) \approx \frac{4 \eta^{3/2}}{3 \sqrt{\pi}}$ [degenerate]

ⓒ $-4 \ll \eta \ll 4$

$$F_{1/2}(\eta) \approx \exp \left[-0.32881 + 0.74 \, 0619 \, \eta - 0.045517 \right.$$
$$\left. - 8.797 \times 10^{-4} \eta^3 + 1.5117 \times 10^{-4} \eta^4 \right.$$

(2) <u>Intrinsic Semiconductors</u>

It is a ("hypothetical") Semiconductor w/o any
impurity or defect.

the number of e^- per unit of volume in the CB, is
equal to the number of holes per unit of volume in the VB.

So $n = p = n_i$ n_i is the intrinsic carrier density

$\Rightarrow$ <u>Electrical neutrality</u>

Intrinsic Semiconductors are usually "non degenerate".

So it comes

$n_o = p_o = n_i$

For the Fermi level, we get:

$\Rightarrow E_F = E_i = \dfrac{E_c + E_v}{2} + \dfrac{k_B T}{2} \ln\left[\dfrac{N_v}{N_c}\right]$

$\Rightarrow \boxed{E_i = \dfrac{E_c + E_v}{2} + 3 \cdot \dfrac{k_B T}{4} \ln\left(\dfrac{m_h^*}{m_e^*}\right)}$

$\Rightarrow$ the intrinsic Fermi energy is usually close to the midgap energy

$*$ also $\boxed{\enclose{circle}{n_o p_o = n_i^2}}$ $\boxed{\text{mass action law}}$

$\Rightarrow n_i^2 = N_c N_v \exp[-\beta E_g]$

$\Rightarrow \boxed{n_i = \sqrt{N_c N_v} \exp\left[-\dfrac{\beta E_g}{2}\right]}$

	typically	
	E_g	$n_i (cm^{-3})$
Si	1.12	$1.45\times$
GaAs	1.424	1.79×10^{6}

The mass action law is valid for non-degenerate semicond
and under thermal equilibrium.
It is also valid for extrinsic semiconductors.

③ Extrinsic semiconductor

Semiconductor that is doped with impurities./foreign atoms.
incorporated into the crystal.
these impurities:

- can be unintentional, due to the lack of control ~~during~~
during the growth of the semiconductor
- can be added on purpose to provide free carriers
in the semiconductor.

ⓐ Donors and acceptors

Donor and acceptor impurities are commonly introduced
into semiconductor to increase electron or hole concentrations,
which modifies the electrical properties of the material.

example ‖ Si with As donor atoms (5 valence e^-).
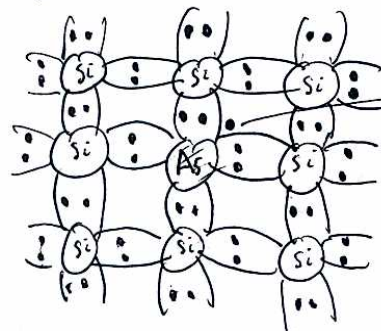
$\longrightarrow$ Conduction e^-

$As \longrightarrow As^+$ ionization.

example 2 Si with B (Boron) acceptor atoms [3 valence e⁻]
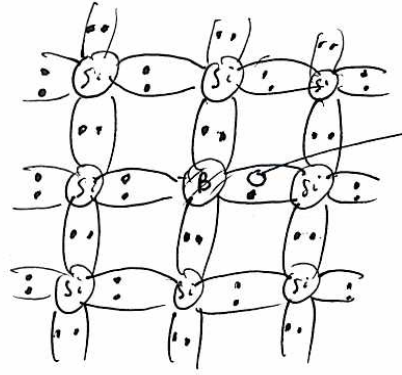
→ conduction hole

$B \to B^-$ ionization.

[acceptor since they accept an e⁻ from the valence band]

Energy band representation of extrinsic semiconductors.

- Donor / Acceptor atoms gives rise to permitted energy levels in the bandgap.

For donor, the energy level E_d is few meV below the conduction band.

For acceptor, the energy level E_a is few meV above the valence band.

At room temperature e⁻ can "jump" from the energy level E_d to the CB, [i.e. can "jump" from the VB to E_a].
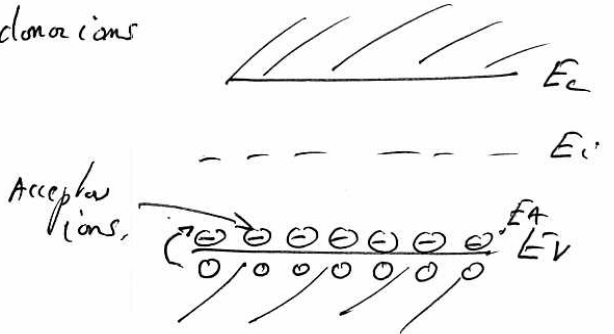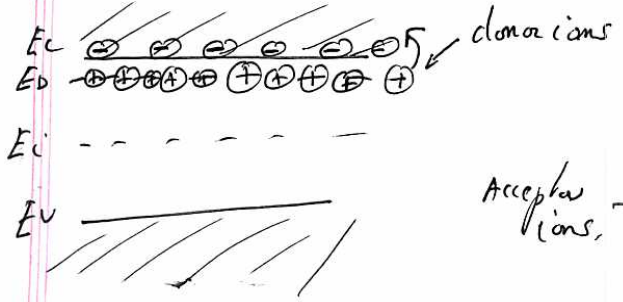
① N-type and P-type Semiconductors

[a Semicond. containing donor atoms is called N-type
["   "   "   "   acceptor atoms is called P-type.

[N-type semicond. has ~~more~~ more free e^- than hole.
[P-type "   "   "   "   "   holes than e^-

. the material is, however, charge neutral. $\boxed{n + N_A = p + N_D}$

We call N_D the donor concentration
N_A the acceptor concentration.

for non-degenerate semicond.

$$\Rightarrow \quad n = N_c \exp\left[-\beta(E_c - E_F)\right]$$

$$= N_c \exp\left[-\beta(E_c - E_i)\right] \exp\left[(E_F - E_i')\beta\right]$$

$$\boxed{n = n_i \exp\left[\beta(E_F - E_i)\right]}$$

$$\Rightarrow \quad \boxed{p = \frac{n_i^2}{n} = n_i \exp\left[-\beta(E_F - E_i)\right]}$$

[The Fermi-level adjusts itself to ensure charge neutrality
[in the semiconductor.

$\Rightarrow$

* i) N-type   charge neutrality $n \simeq N_d$ $\left(\begin{array}{c}\text{complete} \\ \text{ionization}\end{array}\right)$

$$E_F - E_i = \frac{1}{\beta} \ln\left[\frac{N_d}{n_i}\right]$$

* i) P-type $p \simeq N_a$.

$$E_F - E_i = -\frac{1}{\beta} \ln\left[\frac{N_a}{n_i}\right].$$

N-type   P-type
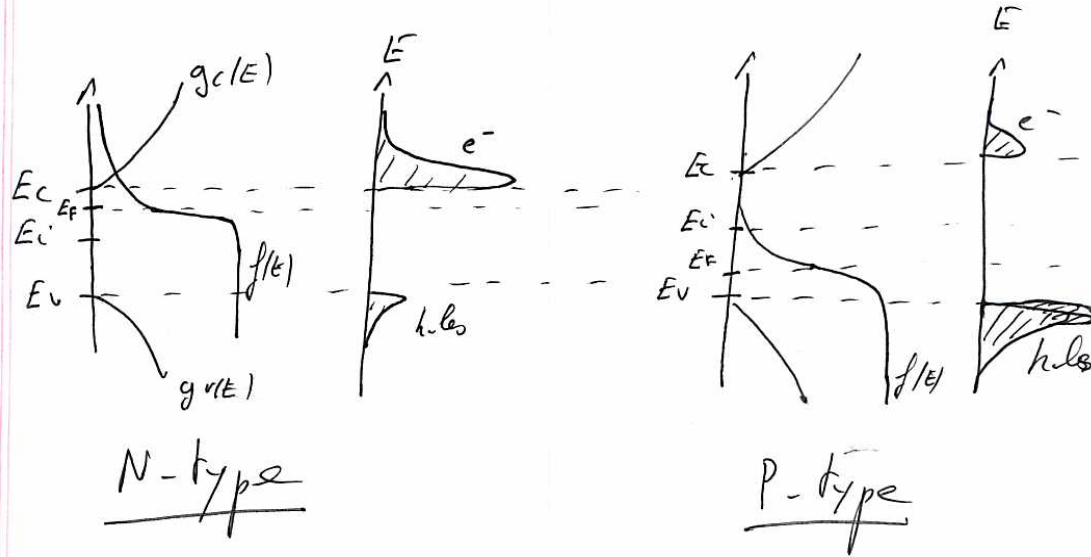
* if both Donor and acceptor impurities [compensated semiconductor]

$$\boxed{n + N_A = p + N_D} \quad \text{using} \quad \underline{np = n_i^2}.$$

we get $\Rightarrow$

$$\left[n = \frac{N_D - N_A}{2} + \sqrt{\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2} \right.$$

$$p = \frac{N_A - N_D}{2} + \sqrt{\left(\frac{N_A - N_D}{2}\right)^2 + n_i^2}$$

ⓐ Temperature Variation of n.

type N $\Rightarrow$ with N_D for donor concentration

Freeze-out
region
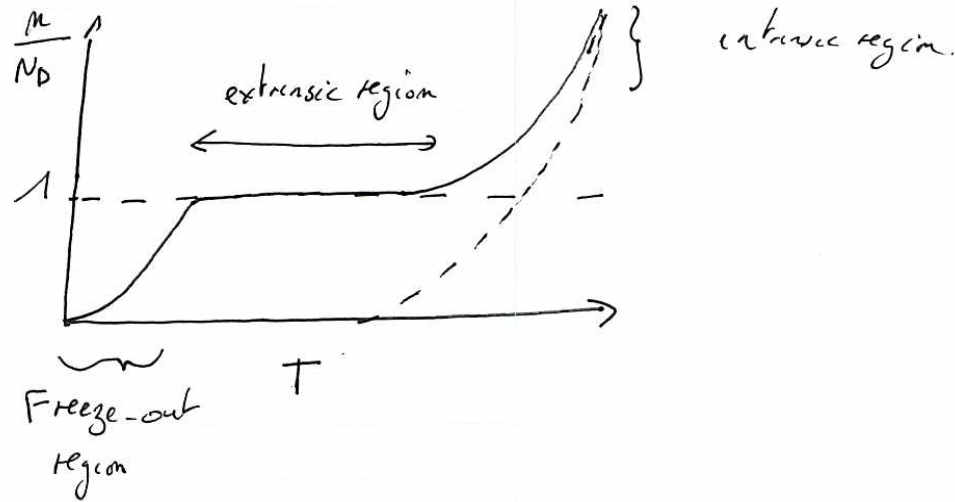
✗ at low T, the thermal energy is not enough to ionize all the donor impurities present. Some e^- are frozen at the donor energy level.

✗ if T increase, the condition of complete ionization is reached $[n = N_D]$.

✗ if T is very large, the intrinsic carrier concentration n_i, becomes comparable to the donor concentration. Beyond this point the semiconductor becomes intrinsic.

(ii) <u>Impurity bands</u>   usually doping concentration 10^{15} to 10^{18} atoms/cm³
[Number of atoms 10^{22} cm⁻³].

When doping increases, wavefunctions of the donors begin to overlap.

E ↑ $g_c(E)$

E_c

E_d - - - - - -
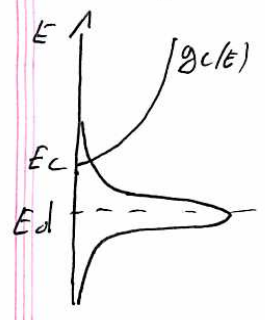
The discrete donor level ~~broadens~~ broadens into
a band which overlaps with the CB.
$\Rightarrow$ reduction of the band-gap
$\Rightarrow$ band-gap narrowing effect.

"degenerate semiconductor" or
"degenerately doped" semiconductor.

(iii) <u>Fermi levels alignment</u>

• At thermodynamic equilibrium, the Fermi-level in
a structure is unique and constant.

• The energy gap between VB and CB is also cte.

What happen if the [dopers] concentration in a semiconductor varies.

Alignment

ex

↑ Nd

M_0

X_0 X

E ↑

E_c
E_i - - - - - E_F
E_v

E_F

E_c
E_F - - - - -
E_v
E_i

Complete ~~band~~ structure
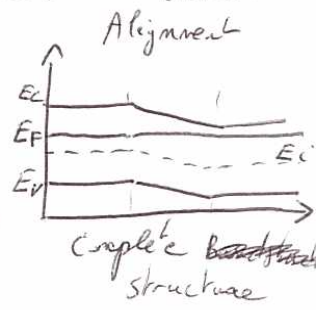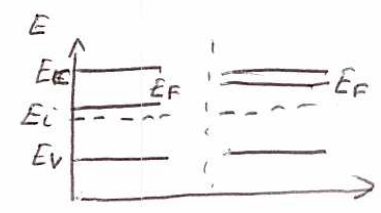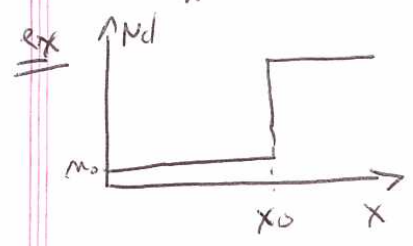
IV Theory of Electrical Conduction

1 Hierarchy of transport models

decreasing level
of Sophistication

↓

Quantum model ⟹

- e^- as a wave
- From atomistic to effective mass description of the electronic structure
- Scattering phenomena and many body effects [difficult to account for]
- necessary model to describe transport in small size semicon
  ⟹ Nanoelectronics

**Semi-Classical.
BTE (Boltzmann
Transport Equation)** ⟹

- e^- as a particle
- Quantum probabilistic Scattering rates (Fermi-Golden rule)
- Application area:
  from Microelectronics to Nanoelectron

Drift - Diffusion ⟹

- Fluid-type model for e^-
- Long device = electronics to microelectronics.

(2) Carrier Transport = basics

- Any motion of free carriers in a Semiconductor leads to a current

- Since these carriers are charge particles, this motion can be caused by an electric field. We refer to this transport mechanism as carrier drift.

- Carriers also move from region where the carrier density is high to region where it is low. We refer this phenomenon as carrier diffusion.

Total current need to account for drift and diffusion currents.

In the x direction

for e⁻ $\longrightarrow$

for holes $\longrightarrow$

$$J_n = q \, n \, \mu_n \, \mathcal{E} + q \, D_n \, \frac{dn}{dx}$$

$$J_p = q \, p \, \mu_p \, \mathcal{E} - q \, \frac{D_p \, dp}{dx}$$

Drift current
μ is the mobility

Diffusion current
D is the diffusion coefficient.

③ <u>Carrier drift</u>

ⓐ <u>Mobility</u>

★ <u>w/o Electric field</u>

$\vec{E} = 0$

- The carrier exhibits random motion (can be compared to the Brownian motion of fine particles in a liquid)

The change of directions is due to scattering

- all those small movements average out and the net displacement of the electron is zero.

★ <u>with Electric field</u>

$\vec{E} \neq 0$

- random motion still occurs but in addition, there is on average a net motion along the direction of the field

$\vec{E}$

- Due to their electric charge, e^- move on average in the opposite direction of $\vec{E}$. holes move in the same direction

CB [$e^- \longrightarrow$]

VB [$\longleftarrow h$]
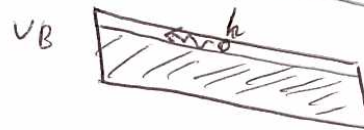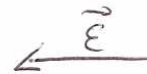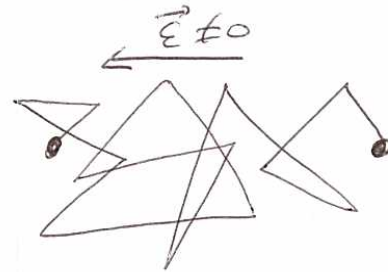
we consider the average velocity $\langle \vec{v} \rangle$ of the carriers.
Following Newton law:

$$\vec{F} = m\vec{a} = m \frac{d\langle \vec{v} \rangle}{dt}$$

$\vec{F}$ consists of the difference between the electrostatic force and
the scattering force (loss of momentum at the time of scattering)
this force is then equal to the momentum divided by the
average time between scattering events $\mathbf{Z}$:

$$\boxed{\vec{F} = q\vec{E} - \frac{m\langle \vec{v} \rangle}{Z}} \qquad q = \text{charge of the particle}$$

we get $\qquad q\vec{E} = m \frac{d\langle \vec{v} \rangle}{dt} + \frac{m\langle \vec{v} \rangle}{Z}$

under steady state current (the particle has reached a
constant average velocity)

$$q\vec{E} = \frac{m\langle \vec{v} \rangle}{Z}$$

we call μ mobility $\Rightarrow \boxed{\mu = \cancel{} = \frac{qZ}{m}}\ q>0$

μ is expected to be large. if m is small
$\qquad\qquad\qquad$ • if Z (time between scattering
$\qquad\qquad\qquad\qquad\qquad$ events) is large.

$\Big[$ For e^- $\quad \langle \vec{v}_m \rangle = -\mu_m \vec{E} \qquad \mu_n = \frac{qZ}{m_e^*}$

$\quad$ For holes $\quad \langle \vec{v}_p \rangle = \mu_p \vec{E} \qquad \mu_p = \frac{Zq}{m_h^*}$

- If effective mass of e^- /and holes is anisotropic, the effective mass is represented by a tensor (Do the mobility). Because of the symmetry of Si, one can however use a scalar expression =

$$\frac{1}{m^*} = \frac{1}{3}\left(\frac{1}{m^*_p} + \frac{2}{m^*_t}\right)$$

in Si
$$m^*_e = 0.26 m_o$$
$$m^*_h = 0.37 m_o$$

- mobility depends on ~~the interaction between~~ e^- ~~and phonons, and impurities~~ — scatterings including :

$$\frac{1}{b} = \sum_x \frac{1}{\mu_x}$$

(i) — impurity scattering = such as ionized atoms (donors and acceptors).

one can show that
$$\mu_{ii} \sim \frac{T^{3/2}}{N} \qquad N = \text{impurity concentration}$$

(ii) Lattice scattering = interactions between e^- and phonons. density of phonons increases with $T \Rightarrow$ scattering time. So mobility will decrease with T. We expect :

$$\mu_{ac} \sim T^{-3/2} \quad (\text{acoustic phonons})$$
$$\mu_{op} \sim T^{-1/2} \quad (\text{optical phonons}).$$

(iii) Surface scattering =
μ can be much lower ~~than~~ at the surface, than in the Bulk.

<u>Remark</u> · * Doping dependence · (room temperature)

$\mu \, (cm^2/V.s)$
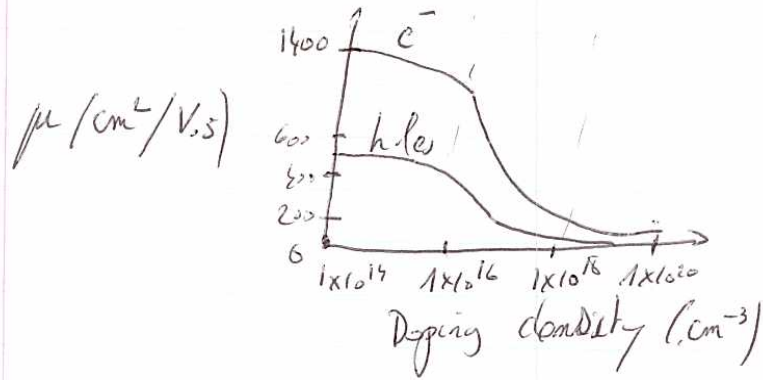
For low doping concentration, the mobility is almost cte, and is primairaily limited by phonon scattering — if the doping increases, $\mu \searrow$ due to ionized impurity scattering.

(b) <u>Drift current</u>
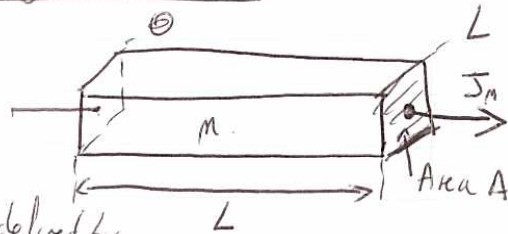
The current is defined by

$$I = \frac{Q}{t_r}$$

where Q is total charge in the semiconductor.

$Q = -qn V$ for e^- $V = LA$

$Q = qp V$ for h.b

t_r is the transit time of the particle
(time needed to go from 0 to L)

$$t_r = \frac{L}{v}$$

the current density can be written

$$\overrightarrow{J_n} = \frac{I_n}{A} = \frac{-q\,n\,\cancel{A}\,\overrightarrow{v_n}}{\cancel{A}} = -q\,n\,\overrightarrow{v_n}$$

similarly

$$\overrightarrow{J_p} = q\,p\,\overrightarrow{v_p}$$
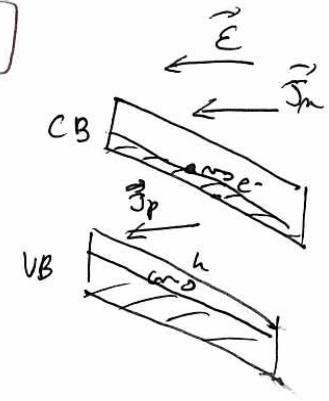
Using the relations

$$\overrightarrow{v_n} = -\mu_n\,\vec{E}$$
$$\overrightarrow{v_p} = \mu_p\,\vec{E}$$

the total current density becomes

$$\vec{J} = \overrightarrow{J_n} + \overrightarrow{J_p} = \left(q\,n\,\mu_n\,\vec{E} + q\,p\,\mu_p\,\vec{E} \right)$$

$$\vec{J} = q\left(n\,\mu_n + p\,\mu_p \right)\vec{E}$$

we set $\quad q(n\,\mu_n + p\,\mu_p) = \sigma \quad$ <u>Conductivity</u>

$$\Rightarrow \quad \vec{J} = \sigma\,\vec{E}$$

the resistivity is given by $\quad \rho = \dfrac{1}{\sigma} = \dfrac{1}{q(n\,\mu_n + q\,p\,\mu_p)}$

For N-type device $\Rightarrow \rho \simeq \dfrac{1}{q\,n\,\mu_n}$

For P-type device $\Rightarrow \rho \simeq \dfrac{1}{q\,p\,\mu_p}$

Ⓒ The Hall effect
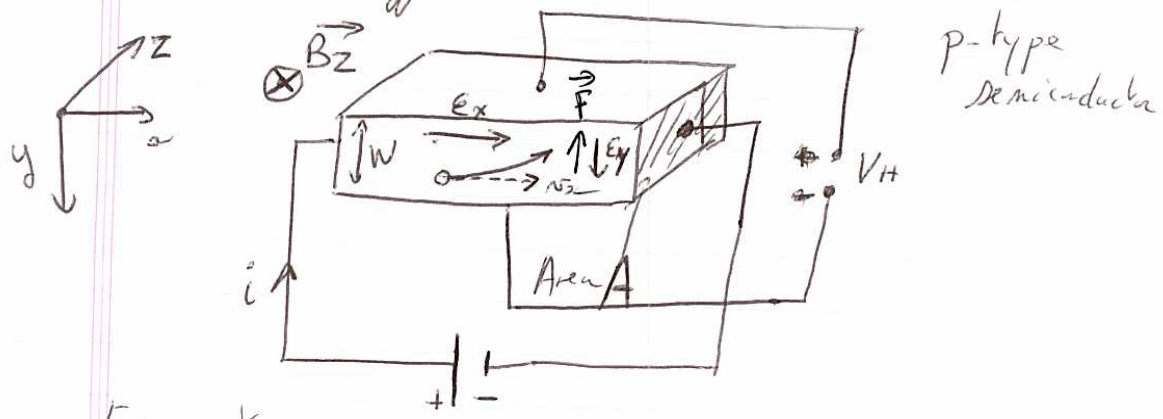
Experiment

in order to ~~measure~~ obtain the mobility of the carrier and carrier concentration.

- a magnetic field $\vec{B}$ is applied $\perp$ to the direction of the carrier flow $\Rightarrow$ a potential difference appears in the direction $\perp$ to both the current flow and $\vec{B}$. ~~(right hand rule)~~

- in the y-direction, no current can flow, it appears an Electric force which exactly counteracts the Lorentz force (obtained by right hand rule)

$\Rightarrow$ __Hall field__

it comes $\Rightarrow$ $\mathcal{E}_y = v_x B_z$

Since $\boxed{\vec{J_p} = q\,p\,\mu_p\,\vec{\mathcal{E}} = q p \vec{v_p}}$

$\Rightarrow \boxed{\mathcal{E}_y = \left[\dfrac{J_p}{qp}\right] B_z = R_H J_p B_z}$

with $R_H \equiv \dfrac{1}{qp}$ the Hall coefficient. $\boxed{\text{if } e^- \; R_H \equiv \dfrac{-1}{qn}}$

The conductivity for P-type semiconductor is

⊛ $\sigma_p = q \mu_p \cdot p$ Using Hall coefficient definition

$$\Rightarrow \quad \mu_p = R_{H,p} \sigma_p \qquad \left[\begin{array}{l} \text{or } \mu_n = -R_{H,n} \sigma_n \\ \text{for } N\text{-type device} \end{array} \right]$$

The mobility of the carriers can be obtained using a
conductivity ~~mobility~~ measurement and a Hall effect measurement.
                                                    (measure of $E_y (\equiv V_H)$ and J_p)

Once μ_p is known we get the carrier concentration using ⊛
                        or $R_H = \frac{1}{qp}$ ✓

④ Carrier diffusion

Carriers diffuse from regions where the density is high
to regions where the density is low. (carrier density gradient)

Diffusion of carriers can be obtained:
    — by varying the doping density in a semiconductor
    — by applying a thermal gradient.

∗ the flux of electrons ϕ_n (or holes ϕ_p), resulting from
the diffusion process is directly proportional to the e^-
concentration gradient dn/dx.

$$\phi_p = -D_p \frac{dp}{dx} \qquad \phi_n = -D_n \frac{dn}{dx}$$

for e^- we get $\qquad$ $J_n = -q \phi_n = q D_n \dfrac{dn}{dx}$.

for holes $\qquad\qquad$ $J_p = q \phi_p = -q D_p \dfrac{dp}{dx}$
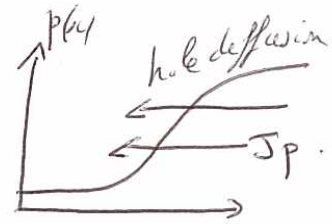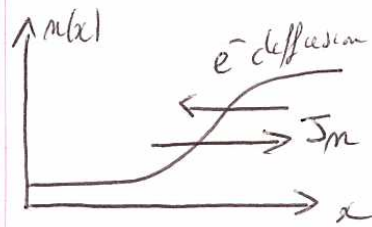
$D_n, D_p \Rightarrow$ Diffusion constants for e^- and holes /

⑤ Drift – Diffusion equation

ⓐ Total Current

Obtained by adding the current due to diffusion to the drift current, resulting in.

$$J_n = q n \mu_n \mathcal{E} + q D_n \dfrac{dn}{dx}.$$

$$J_p = q p \mu_p \mathcal{E} - q D_p \dfrac{dp}{dx}$$

$$\boxed{\begin{array}{l} \text{For in 3D} \\ \dfrac{dn}{dx} \to \nabla n \\ \vec{J_n} \to \vec{J_n} \quad \mathcal{E} \to \vec{\mathcal{E}} \end{array}}$$

The total density of the current flowing at any point in the Semiconductor is simply:

$$\vec{J} = \vec{J_n} + \vec{J_p}$$

ⓑ Einstein relationships

relation between μ and D ;

we assume =

— equilibrium conditions $\Rightarrow J_n = q_n \mu_n \mathcal{E} + q D_n \dfrac{\partial n}{\partial x} = 0$

— non - degenerate semiconductor $\Rightarrow$

$$n = N_c \exp\left[\dfrac{E_F - E_c}{k_B T}\right] \rightarrow n = n_i \exp\left[\dfrac{E_F - E_i}{k_B T}\right]$$

we get $\dfrac{\partial n}{\partial x} = \left(\dfrac{\partial E_F}{\partial x} - \dfrac{\partial E_i}{\partial x}\right) \dfrac{1}{k_B T} \cdot \underbrace{n_i \exp\left[\dfrac{E_F - E_i}{k_B T}\right]}_{n \cdot}$

$\overset{0}{\nearrow} \qquad \overset{q\mathcal{E}}{\downarrow}$

Since $\mathcal{E} = -\nabla V \overset{q\mathcal{E}}{\swarrow}$

$-q V = -q E_i$ (E potential energy)

$\mathcal{E} = \dfrac{1}{q} \nabla E_i$

$\Rightarrow \boxed{\dfrac{\partial n}{\partial x} = -\dfrac{q}{k_B T} n \mathcal{E}}$

Since (equilibrium condition) $q_n \mu_n \mathcal{E} + q D_n \left[\dfrac{-q}{k_B T}\right] n \mathcal{E} = 0$

$\Rightarrow \boxed{D_n = \dfrac{k_B T}{q} \mu_n}$ \quad also \boxed{D_p = \dfrac{k_B T}{q} \mu_p}

⑥ Transport equations

In addition to the drift diffusion equation, the transport model is also defined by

the carrier density and Poisson equations, the continuity equation

ⓐ carrier density and Poisson equations

In order to calculate J_n and J_p, one needs to know n, p and $\mathcal{E}$. $\mathcal{E}$ is obtained from the electrostatic potential V, $\mathcal{E} = -\nabla V$.

From Maxwell equation $\Longrightarrow$ Poisson equation.

$$- \Delta V_{(\vec{r})} = +q \left(- n_{(\vec{r})} + p_{(\vec{r})} + Nd_{(\vec{r})} - Na_{(\vec{r})} \right)$$

Nd, Na are known.

V depends on n and p, however n and p depends also on $V \Rightarrow$ self-consistent problem.

∗ For non-degenerate semiconductor

$$n(\vec{r}) = n_i \, \exp \left[\frac{Ef - Ei(\vec{r})}{k_b T} \right]$$

$$p(\vec{r}) = n_i \, \exp \left[\frac{-Ef + Ei(\vec{r})}{} \right.$$

Because of the electric field in the semiconductor.

$$E_i \to E_{io} - qV, \text{ potential energy due to the field}$$

E_{io} is taken as reference $\left(\begin{array}{l}\text{see alignment of} \\ \text{Fermi level case in} \\ \text{previous section}\end{array}\right)$

$$\Rightarrow \left[n(\vec{r}) = n_i \exp\left[\frac{E_F - E_{io}}{k_B T}\right] \exp\left(\frac{qV}{k_B T}\right) \right.$$

$$\left[p(\vec{r}) = n_i \exp\left[\frac{-E_F + E_{io}}{k_B T}\right] \exp\left[\frac{-qV}{k_B T}\right] \right.$$

Boltzmann relationship $\Rightarrow$ true under-
thermodynamic equilibrium conditions
$$\Rightarrow \text{no transport.}$$

$*$Under non equilibrium conditions, E_F is not unique for
e^- and holes $\Rightarrow$ due to the contacts) $\to$ $\boxed{\text{Carrier injections}}$
the expressions of n and p become very complicated.

$\left[\right.$ Boltzmann relationship are however still valid if one
introduces the notion of quasi-Fermi level $\left[\begin{array}{l} E_F \to E_{F_n}(\vec{r}) \text{ for } e^- \\ E_F \to E_{F_p}(\vec{r}) \text{ for holes}\end{array}\right.$

Quasi-Fermi levels are "imaginary reference"
$\Rightarrow$ imref (Remark spelled backwards $\to$ fermi) :-)

(b) <u>Continuity equations</u>

So far, a steady state was assumed (no time dependence for transport)

→ continuity equations describe the evolution of carrier concentration with time.

The local carrier density may vary for the following reasons:

(i) external force can be applied to a region of the semiconductor ~~carriers~~ carrier ~~injection~~ are added or removed from this region (contact)

(ii) An external source of energy can increase the hole and e^- concentration - e^- can jump from the VB to CB a free e^--hole pair is then created. (example = solar cell)

<u>generation process</u> → the <u>generation</u> rate due to this external source of energy is called <u>extrinsic</u> generation rate.

(iii) In the absence of any outside influence, free e^- and holes can be created or annihilated within a region of the semiconductor.

→ if the width of the bandgap is small enough, e^- ~~(hole)~~ can jump from CB to VB ($\overset{or}{VB}$ to CB).

→ they can also jump into a permitted energy ~~the~~ located inside the bandgap (created by impurities or defects)

if free e^- and hole are created → generation process
if free e^- and hole are lost → recombination process

The net intrinsic generation/recombination rates ~~are~~ are noted U_n for e^- and U_p for holes.

U_n and $U_p > 0$ if recombination ~~rate~~ dominates over-generation.

U_n and $U_p < 0$ if generation process dominates. over recombination.

$U_n = \left(\text{free } e^- \text{ intrinsic recombination rate} - \text{free } e^- \text{ intrinsic generation rate}\right)$

[These phenomena extrinsic and intrinsic generation/recombination
generation
process are analyzed in detail in the next section.

So finally we get:
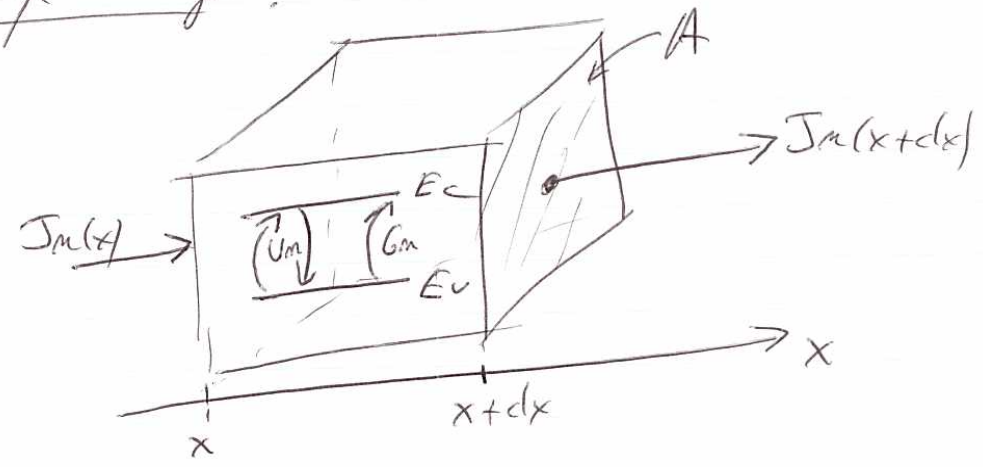
for e^- in 1D

$$A \frac{\partial n}{\partial t} dx = A \left(\frac{J_n(x)}{-q} - \frac{J_n(x+dx)}{-q} \right) + A (G_n - U_n) d$$

Variation of number of free e^- in the volume $A\,dx$ as a function of time.

number of e^- entering the volume

number of e^- flowing out of the volume.

generation / recombination processes

Using taylor expansion $\Rightarrow$
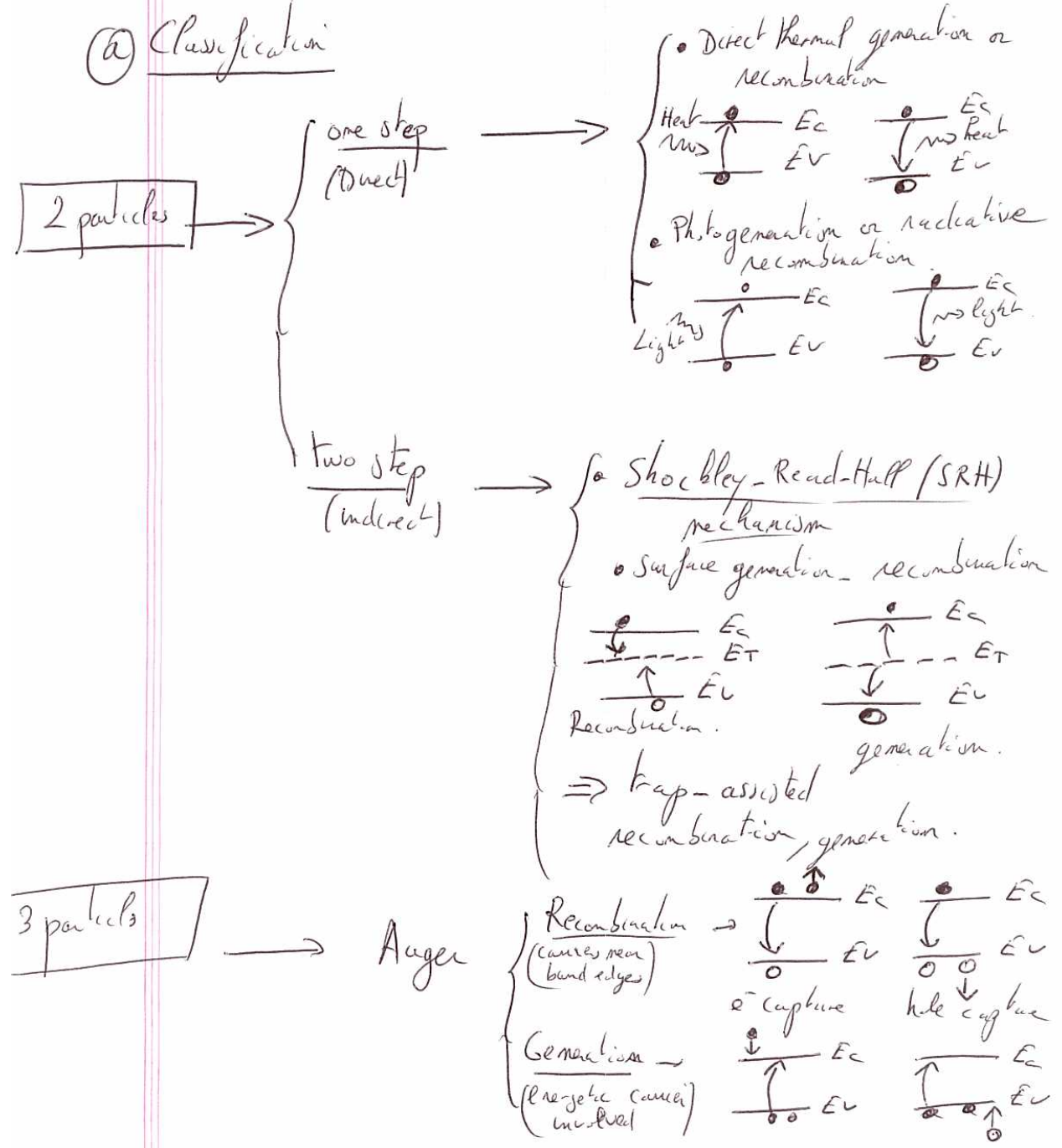
$$J_n(x + dx) = J_n(x) + \frac{d J_n(x)}{dx} dx$$

$\Rightarrow$

$$\boxed{\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_n(x)}{\partial x} + (G_n - U_n)} \quad \text{for } e^-$$

Similarly

$$\boxed{\frac{\partial p}{\partial t} = -\frac{1}{q} \frac{\partial J_p(x)}{\partial x} + (G_p - U_p)} \quad \text{for holes}$$

⑦ Carrier generation and recombination

ⓐ Classification

2 particles →

one step (Direct) →

- Direct thermal generation or recombination

- Photogeneration or radiative recombination

two step (indirect) →

- Shockley-Read-Hall (SRH) mechanism
- Surface generation - recombination

Recombination.   generation.

⇒ trap-assisted recombination, generation.

3 particles → Auger

Recombination (carriers near band edges) →

e⁻ capture   hole capture

Generation (energetic carrier involved) →

(b) band to band process

depends on the density of available e^- and holes. The generation - recombination rate is expected to be proportional to $(np - n_i^2)$ Also, in thermal equilibrium,

$U = 0$ since there is no net current.

we note that

$U = r - g$.
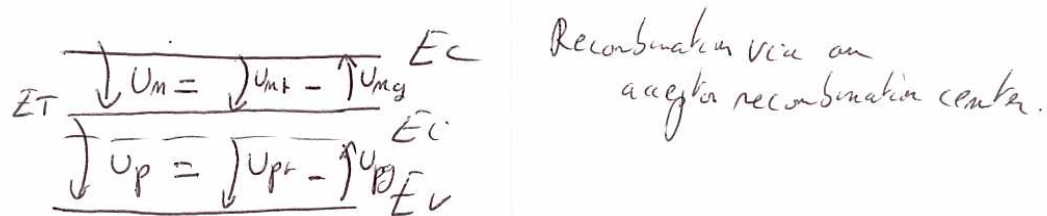
$$\boxed{\begin{array}{l} U = 0 \quad \text{if } pn = n_i^2 \text{ (equilibrium)}. \\ U > 0 \quad \text{if } pn > n_i^2 \text{ (recombination)} \\ U < 0 \quad \text{if } pn < n_i^2 \text{ (generation)}. \end{array}}$$

finally we get $\quad U = b \, (np - n_i^2)$

U acts like a "force" to bring $p \cdot n$ to its equilibrium n_i^2.

b is the bimolecular c^te

$$\begin{array}{l} b \,(GaAs) = (1.3 \pm 0.3) \times 10^{-10} \, cm^3 / s^{-1} \\ b \,(Si) = 2 \times 10^{-15} \, cm^3 / s^{-1} \end{array}$$

© Trap-assisted process (SRH mechanism)

$$U_n = U_{nr} - U_{ng}$$

Recombination via an acceptor recombination center.

$$U_n = U_{nr} - U_{ng}$$

$$\boxed{\begin{array}{l} U_{nr} = C_n \, n p_T \\ U_{ng} = e_n \, n_T \end{array}}$$

recombination rate due to the center, U_n, is proportional to density of e^- in the CB; density of empty recombination center.

$$p_T = N_T(1 - f_T).$$

where N_T is the density of recombination center.
e_n is the coefficient which represents the probability of e^- emission by the centers. and $m_T = N_T f_T$.

$$\Rightarrow \boxed{\begin{aligned} U_n &= C_n \, n \, p_T - e_n \, m_T \\ U_p &= C_p \, p \, m_T - e_p \, p_T \end{aligned}}$$

⚹ Thermal equilibrium conditions $\Rightarrow U_n = U_p = 0$

$$\begin{cases} C_n \, n \, p_T = e_n \, m_T \\ C_p \, p \, n_T = e_p \, p_T \end{cases} \Rightarrow \begin{cases} e_n = C_n \, n_1 \\ e_p = C_p \, p_1 \end{cases}$$

n_1 and p_1 are e^- and hole densities when $E_T = E_F$

$$\boxed{n_1 = n_i \exp\left[\frac{E_i - E_t}{k_B T}\right]}$$

⚹ steady state conditions $\Rightarrow U_n = U_p$

$$C_n (n \, p_T - n_1 \, m_T) = C_p (p \, m_T - p_1 \, p_T)$$

$$\Rightarrow f_T = \frac{C_n \, n + C_p \, p_1}{C_n(n + n_1) + C_p(p + p_1)} \Rightarrow U = \frac{np - n_i^2}{\dfrac{1}{C_p N_T}(n + n_1) + \dfrac{1}{C_n N_T}(p + p_1)}$$

we define carrier lifetime.

$$z_p = \frac{1}{c_p N_T} \quad ; \quad z_n = \frac{1}{c_n N_T}$$

$c_p = \sigma_p \, v_R$

$\begin{cases} \sigma_p \Rightarrow e^- \text{ capture cross section} \\ \text{(how close } e^- \text{ must be to a center to} \\ \text{be captured by it)} \\ v_R \Rightarrow \text{thermal velocity, average speed of } e^- \\ \text{due to "Brownian - like" motion.} \end{cases}$

if $\quad \sigma_n = \sigma_p = \sigma_0$

$$\Rightarrow \boxed{U = \frac{pn - n_i^2}{z_0 \left(p + n + 2 n_i \cosh\left[\dfrac{E_T - E_i}{k_B T}\right] \right)}}$$

$\star$ this expression can be further simplified for

$p \gg n$
(p-type semi)

$$\boxed{U_n = \frac{n_p - n_{p_0}}{z_n}}$$

$n_{p_0} = $ density at equilibrium

$n \gg p$
(n-type)

$$\boxed{U_p = \frac{p - p_0}{z_p}}$$

$\Rightarrow$ similar expressions obtained for surface recombination generation process

① Photogeneration.

if each photon creates
an e^--hole pair.

$$G_p, light = G_n, light = \alpha \frac{P_{opt}(x)}{E_{ph} A}$$

α is the the absorption coefficient of the material at the energy of the incoming photon. P_{opt} is the optical power.

(decrease with distance, because of the absorption of light by the semiconductor)

E_{ph} has to be larger than E_g
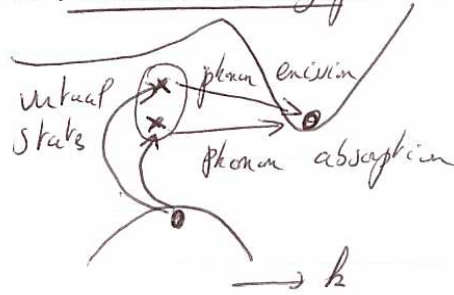$\Rightarrow$ necessary condition.

$*$ Direct band gap

$p_f = p_i$
$E_f = E_i + E_{ph}$
final initial $\searrow$ photon.

$$\alpha \sim (h\nu - E_g)^\gamma$$
$$\Rightarrow \gamma = \frac{1}{2} ; \frac{1}{3} \quad \text{for direct transitions}$$
$$= 2 \quad \text{for indirect transition (involving phonons)}$$

α Indirect band gap

virtual states, phonon emission, phonon absorption

$p_f = p_i \mp p_s$
$E_f = E_i \mp E_s$ phonon.