Qn : How many electrons (or holes) in a semiconductor material have an energy E (E to $E+dE$) at a given temperature T ?

The density of electrons with an energy E at temp T is

$$n(E,T) = g_c(E) \cdot f_{FD}(E, T; E_F)$$

The total number of electrons per unit volume with all possible energies is

$$n(T) = \int_{E_c}^{\infty} n(E,T)\, dE$$

CIRCULAR!

Fermi energy E_F is determined by $n(T)$, $p(T)$

& similarly, for holes,

$$p(T) = \int_{-\infty}^{E_v} p(E,T)\, dE$$

Note: These two numbers are equal only in intrinsic semiconductors. Because an electron moving to the conduction band will leave a hole behind in the valence band. In the case of doped or extrinsic semiconductors, they need not be the same.

Above, $n(E,T)$ is determined by Fermi Energy E_F, while $\int n(E,T)\, dE$ dictates E_F!

These two equations, then, need to be solved together SELF-CONSISTENTLY.
This means that, we cannot use any E_F to calculate $n(E,T)$. We should only use the E_F that we get by integrating $n(E,T)$.
How do we get out of this quagmire?
To calculate E_F, we need to know $n(T)$.
To calculate $n(T)$, we need to know E_F !!!

The way out of this quagmire is to introduce a simplification assumption [called non-degeneracy condition] and derive a result that is independent of E_F.
We use that to derive an expression for E_F.

The non-degeneracy assumption is

$$E_C - E_F \gg k_B T$$

$$\& \quad E_F - E_V \gg k_B T.$$

This means that E_F lies between E_C & E_V and far away from both.

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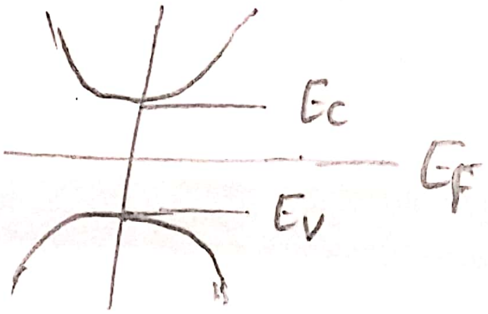

Using the above assumptions, we can write the Fermi-Dirac distribution function as

$$f_{FD}(E,T) = \frac{1}{1+\exp\left(\frac{E-E_F}{K_BT}\right)} \approx \exp\left(\frac{-(E-E_F)}{K_BT}\right)$$

because $E-E_F \gg K_BT$ whenever E lies in the conduction band or valence band energy range, according to our non-degeneracy assumption. $\exp\left(\frac{E-E_F}{K_BT}\right) \gg 1$ & the 1 in the denominator can be ignored.

Using this, we can calculate the electron density in a given energy range E to $E+dE$.

$$n(E) = \underbrace{\frac{4\pi(2m_n^*)^{3/2}}{h^3}\sqrt{E-E_c}}_{g_c(E)} \cdot \underbrace{\exp\left(\frac{-(E-E_F)}{K_BT}\right)}_{\approx f_{FD}(E)}$$

and similarly,

$$p(E) = \frac{4\pi(2m_p^*)^{3/2}}{h^3}\sqrt{E_v-E} \cdot \exp\left(\frac{-(E_F-E)}{K_BT}\right)$$

Then the total number of $\bar{e}$'s per unit volume is $\int n(E)\,dE$, which is,

$$n_0 = 2\left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2} \exp\left(\frac{-(E_c - E_F)}{k_B T}\right)$$

or $$\boxed{n_0 = N_c(T)\cdot \exp\left(\frac{-(E_c - E_F)}{k_B T}\right)}$$

$N_c(T)$ = effective density of states function for conduction band.

It can also be written as

$$N_c(T) = 2.5\left(\frac{m_n^*}{m}\right)^{3/2} \times \left(\frac{T}{300\,K}\right)^{3/2} \times 10^{19}/cm^3$$

$$P_V(T) = 2.5\left(\frac{m_p^*}{m}\right)^{3/2} \times \left(\frac{T}{300\,K}\right)^{3/2} \times 10^{19}/cm^3$$

kelvin. Not Boltzmann const.

$$\boxed{P_0 = P_V(T)\exp\left(-\frac{(E_F - E_V)}{k_B T}\right)}$$

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Multiplying the expression for n_0 & p_0,

we get

$$\boxed{n_0 p_0 = N_c(T) P_v(T) . \exp\left(\frac{-E_g}{K_B T}\right)}$$

⇓

"Law of mass action" for Semi-conductors

This equation does not have E_F in it!

We can use this to calculate E_F.

Intrinsic case:

In the intrinsic case, the number of e⁻s equals number of holes. ∴ $n_0 = p_0 := n_i$.

$$n_i^2 = \left[N_c(T) . P_v(T)\right] \exp\left(\frac{-E_g}{K_B T}\right)$$

or

$$\boxed{n_i(T) = \left[N_c(T) P_v(T)\right]^{1/2} \exp\left(\frac{-E_g}{2 K_B T}\right)}$$

Note that the intrinsic carrier concentration is a very strong function of temperature!

Accepted values of n_i for

Silicon	—	$1.5 \times 10^{10} / cm^3$
GaAs	—	$1.8 \times 10^{6} / cm^3$
Ge	—	$2.4 \times 10^{13} / cm^3$

In the intrinsic case, since $n_0 = p_0$, we have

$$N_c \exp\left(\frac{-(E_c - E_{Fi})}{k_B T}\right) = P_v \cdot \exp\left(\frac{-(E_{Fi} - E_v)}{k_B T}\right)$$

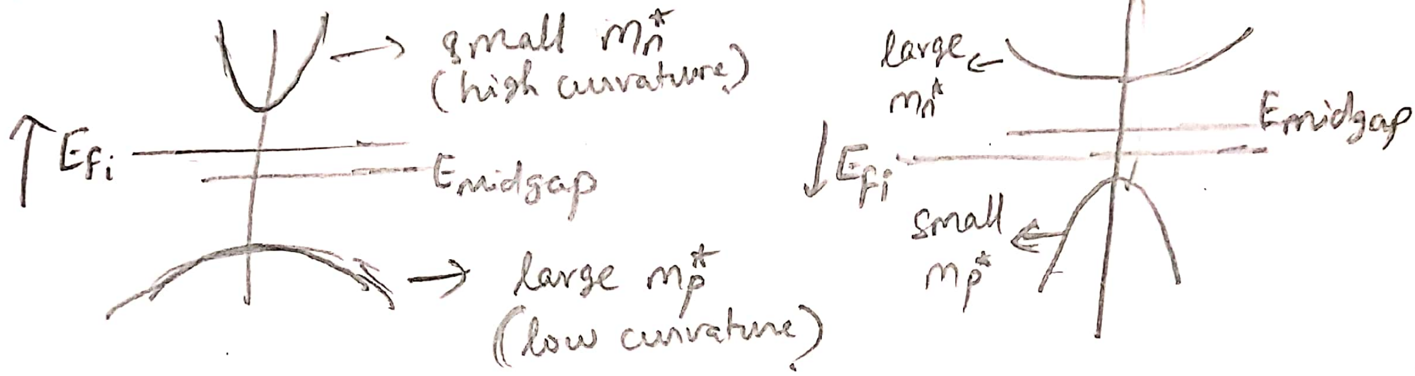
from which we can calculate E_{Fi}, the Fermi energy for intrinsic semiconductors, as a function of temperature.

$$\boxed{\begin{aligned} E_{Fi} &= \frac{1}{2}(E_c + E_v) + \frac{1}{2} k_B T \ln\left(\frac{P_v}{N_c}\right) \\ &= \frac{1}{2}(E_c + E_v) + \frac{3}{4} k_B T \ln\left(\frac{m_p^*}{m_n^*}\right) \end{aligned}}$$

Since $\frac{1}{2}(E_c + E_v) = E_{midgap}$,

$$E_{Fi} - E_{midgap} = \frac{3}{4} k_B T \ln\left(\frac{m_p^*}{m_n^*}\right)$$

The above equation says that, if the effective mass of holes is larger than that of electrons, then E_f moves towards E_c & if it is smaller, E_f moves towards E_V.



Graphical representation of electron concentration in valence & conduction band:

We wrote down the electron concentration within a given energy range E & $E+dE$ as

$$n(E)\,dE = g_c(E)\, f_{FD}(E)\, dE$$

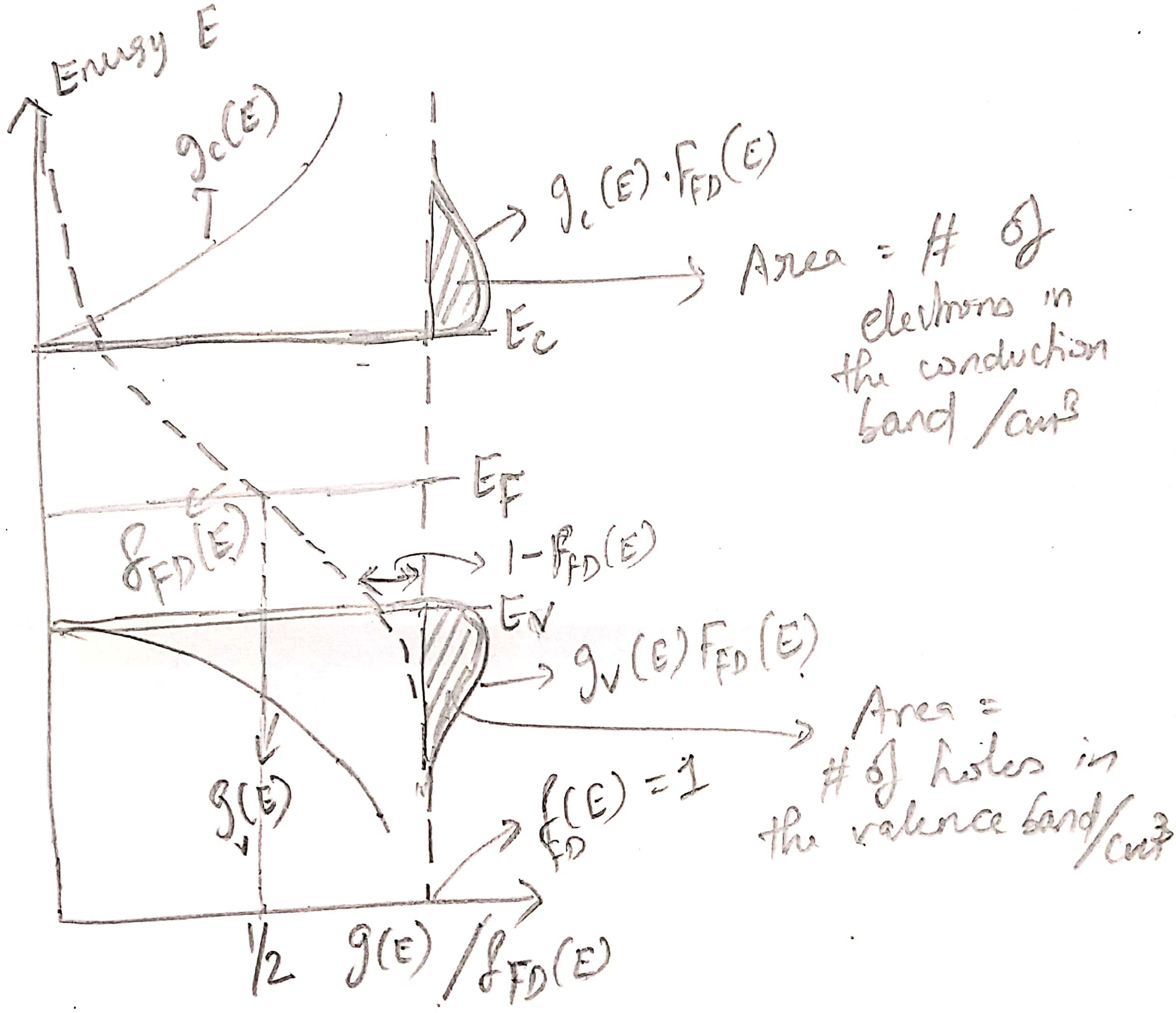
& for holes, $p(E)\,dE = g_V(E)\left(1 - f_{FD}(E)\right) dE.$

We also know that

$$g_{c/V}(E) \sim \sqrt{E} \quad \&$$

$$f_{FD}(E) \sim e^{-E/k_BT}.$$

Multiplying these two functions give us $n(E)$. Graphically, it can be shown as follows:



In this picture, we have assumed that $m_p^* = m_n^*$ so the density of states $g_c(E)$ & $g_v(E)$ are symmetrical & so, the Fermi energy E_F lies midway between E_C & E_V.

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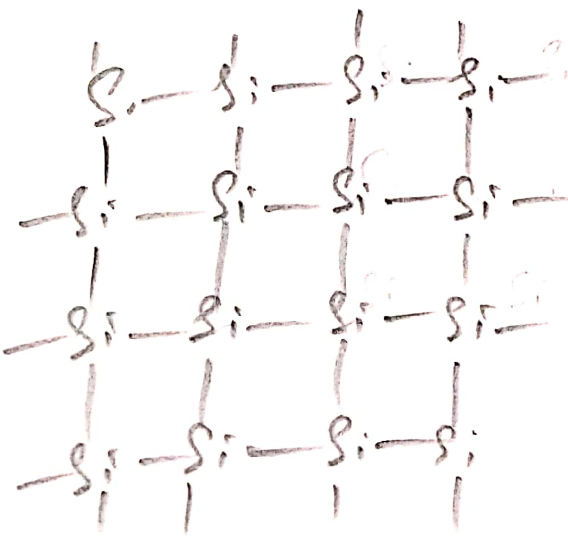
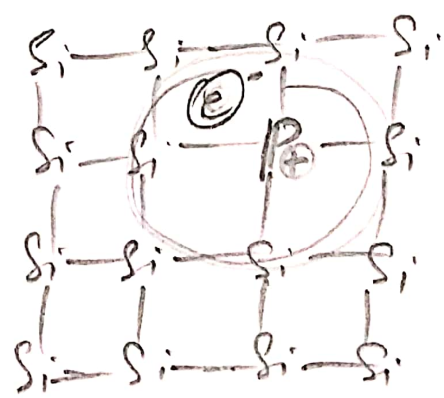
Extrinsic Case :

Earlier, we have treated the case where $n_0 = p_0$, ie, the number of electrons equals number of holes. This is the case in intrinsic semiconductors, which are so pure that there are no extra e^-s or holes introduced by impurities. But modern applications, such as pn diodes, require that the semiconductors have more e^-s than holes or vice versa. This is done by introducing other atomic elements in the semiconductor – DOPING.

Silicon, which can form four covalent bonds with its neighbors, can be drawn as follows:

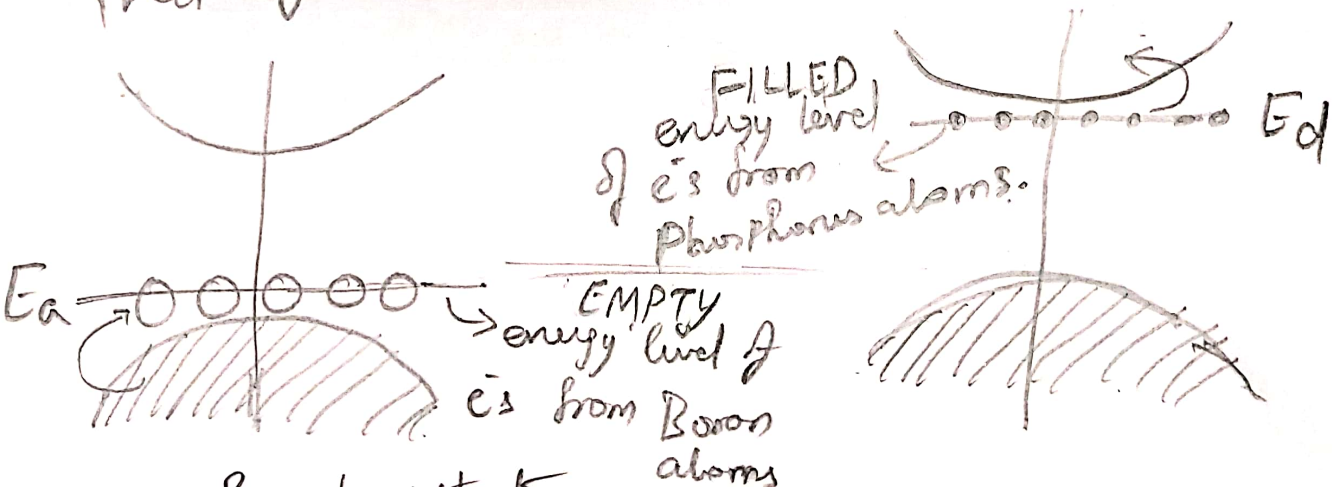


When pentavalent phosphorus atom is added,



P donates an extra electron to the material.

Similarly, when a trivalent material such as Boron, is added, it captures an electron and forms four bonds, instead of the three that it is capable of. Since this electron is bound to the Boron atom bond, its energy would be closer to the valence band. Contrast this with the electron donated by the P atom. It is relatively free to move around, like conduction electrons, & hence its energy will be closer to that of the conduction band electrons.



Si band structure

Because the energy difference between the valence band maximum & the acceptor levels are small, electrons from the

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even at very low temperatures, ... creating vacancies in the valence band: holes. This creates holes without the concomittant creation of electrons in the conduction band, unlike intrinsic semiconductors.

Similarly, the electrons in the donor levels E_d can jump to the conduction band providing electrons which can conduct electricity.

The former case, when Si is doped with B, is an example of a <u>P-TYPE</u> material & the latter, when Si is doped with P, is an example of <u>N-TYPE</u> material.