Number of electrons (& holes) in intrinsic semiconductors

Need n_i to determine conductivity σ etc. $(n_i = p_i)$

Since there are typically 10^{28} atoms m^{-3} in silicon, for example, we cannot study the individual motion of each electron. However, current, charge, etc. involve net motion of large numbers of carriers, so can use statistical method to find the electrical properties. So we find the average behaviour of electrons rather than detailed dynamics.

For example, we define a *distribution function* (**Fermi-Dirac function**)

P(E)= gives the *probability* that an electron has an energy E (at some temperature T).
e.g. If $P(E_1) = 0.2$, 20% of electrons have $E = E_1$

The statistics that govern detailed form of P(E) depends on
1) type of particle
2) how they interact (e.g. molecules in gas – no interaction = subject to Boltzmann statistics)

For solids: 1) electrons
2) obey Pauli exclusion principle

Fermi-Dirac (F.D.) statistics govern the behaviour of such interacting electrons. The F.D. distribution function, P(E) is then of the form

E_F = fermi energy or level

$$P(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

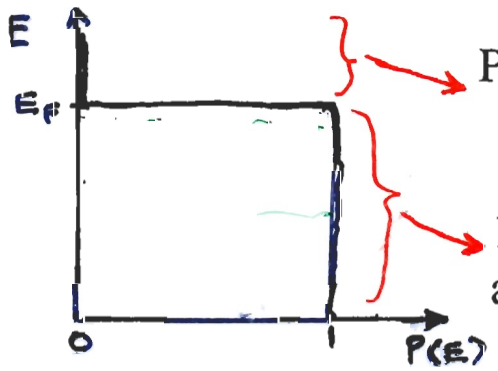
P(E) is probability that an electron has energy E, and varies from 0 to1. k = Boltzmann constant = 1.38 x 10^{-23} JK^{-1}, T = temperature in kelvin and E is electron energy.

At T=0K,
For $E>E_F$,

$$P(E) = \frac{1}{1 + \exp(\infty)} = 0$$

For $E<E_F$,

$$P(E) = \frac{1}{1 + \exp(-\infty)} = 1$$



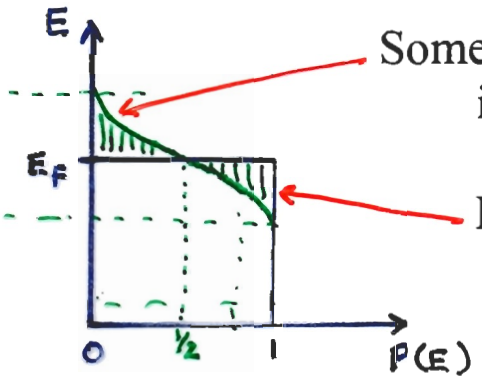
Probability that electrons occupy levels for $E>E_F = 0$ all levels empty

100% probability that levels $E<E_F$ are occupied all levels full

All levels above E_F - empty
All levels below E_F - full

No electron can have $E>E_F$ at T= 0K
So E_F is the maximum energy of electron at 0K

At T>0K, some electrons near E_F can acquire enough thermal energy and have $E>E_F$. Those at levels << E_F cannot move – no empty levels available. Then

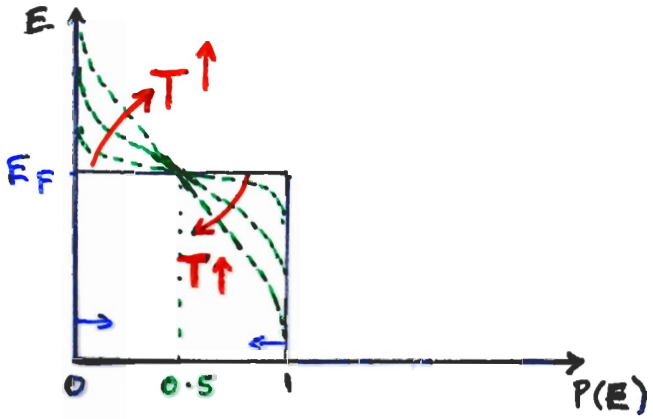


Some finite possibility that electron energy is at level $>E_F$

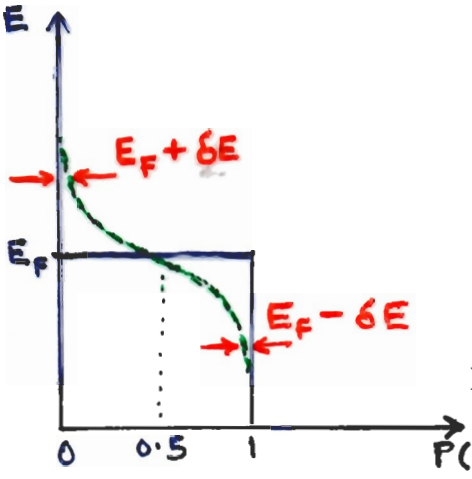
Probability that levels $<E_F$ are all full no longer 100%

The actual shape of P(E) depends on equation (1).

From eqn. (1) as T ↑, probability that electron can have $E>E_F$ increases, so



P(E) is symmetrical about E_F

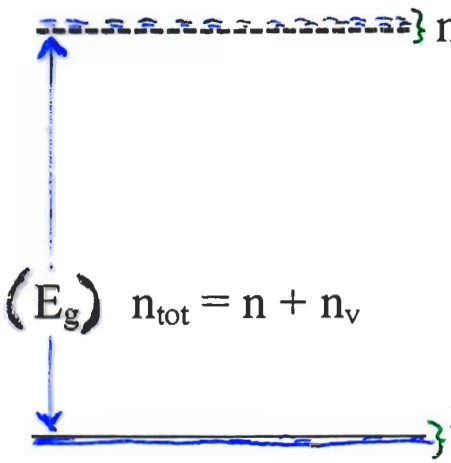


$$P(E_F+\delta E) = 1 - P(E_F-\delta E)$$

Probability that e^- is at $(E_F+\delta E)$ = probability that e^- is not at $(E_F-\delta E)$

Apply to semiconductor

Band structure



Simplify by assuming Eg>> width of bands, such that all energies within a band are effectively the same. (10^{-22} eV spacing can be ignored)

The probability that an electron can acquire sufficient energy to be in C.B. is:

probability that it has energy $E_v+E_g = P(E_v+E_g)$

$$P(E_v + E_g) = \frac{1}{1+\exp\left(\frac{E_v + E_g - E_F}{kT}\right)}$$

If we assume n m^{-3} electrons in C.B. at temperature T then,.
n = total no. of electrons x probability of electrons being in C.B.
$n=n_{tot}$ x $P(E_v+E_g)$

$$n = \frac{n_{tot}}{1+\exp\left(\frac{E_v + E_g - E_F}{kT}\right)}$$

Similarly, if there are n_v m^{-3} electrons in V.B, the probability of occupancy of V.B. is:

$$P(E_v) = \frac{1}{1+\exp\left(\frac{E_v - E_F}{kT}\right)}$$

and therefore

$$n_v = \frac{n_{tot}}{1+\exp\left(\frac{E_v - E_F}{kT}\right)}$$

Since $n_{tot} = n + n_v$,

From eqns. (1) and (2)

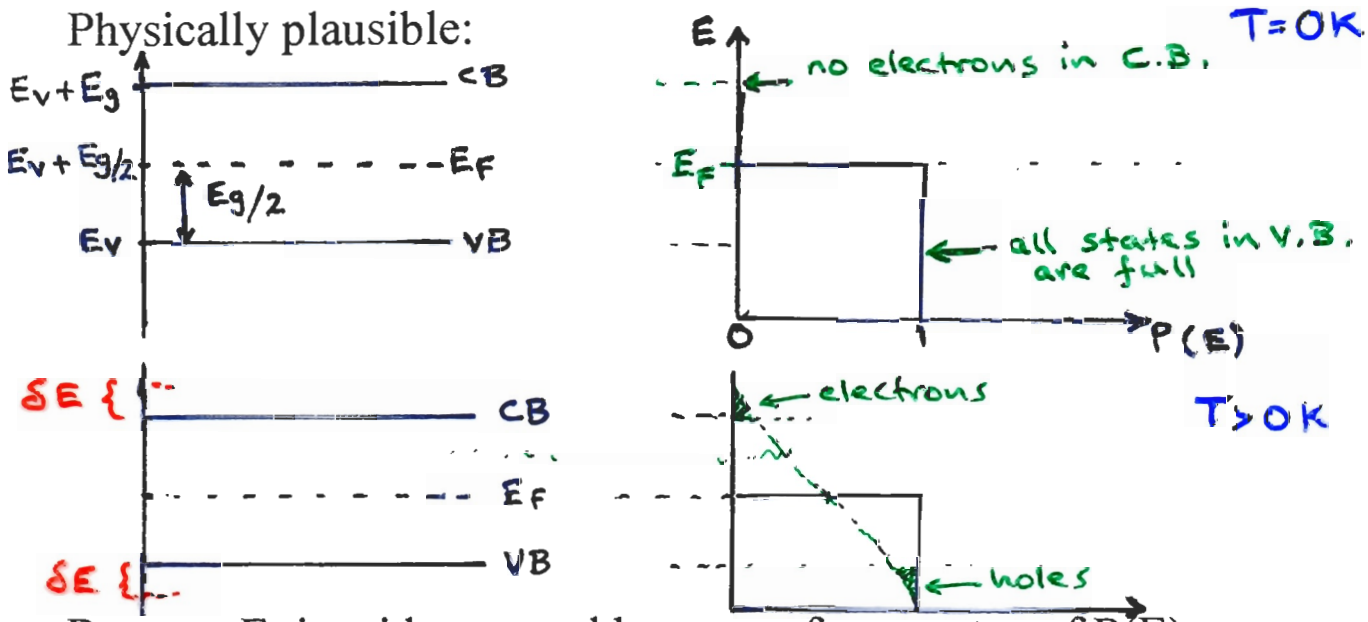
$$n_{tot} = \frac{n_{tot}}{1+\exp\left(\frac{E_v + E_g - E_F}{kT}\right)} + \frac{n_{tot}}{1+\exp\left(\frac{E_v - E_F}{kT}\right)}$$

rearrange this equation and we get:

$E_F = E_V + E_g/2$

So in **intrinsic** semiconductor E_F is **midway** between V.B. and C.B

Physically plausible:



Because E_F is mid-gap, and because of symmetry of P(E) about E_F, probability that electron is δE above bottom of C.B. = probability that electron **does not** occupy level δE below top of V.B.

This ensures that **n=p=n_i**

From eqn. (1)

$$n_i = \frac{n_{tot}}{1 + \exp\left(\frac{E_v + E_g - E_F}{kT}\right)}$$

Since $E_F = E_V + E_g/2$,

$$n_i = \frac{n_{tot}}{1+\exp\left(\frac{E_v + E_g - E_v - E_g/2}{kT}\right)} = \frac{n_{tot}}{1+\exp\left(\frac{E_g}{2kT}\right)}$$

For a certain material, E_g is fixed, $n_i \alpha \exp(-1/T)$,
i.e. as T ↑, n_i increases exponentially

Also as materials change, E_g changes and at fixed T,
as E_g ↑, n_i decreases exponentially, i.e. $n_i \alpha \exp(-E_g)$

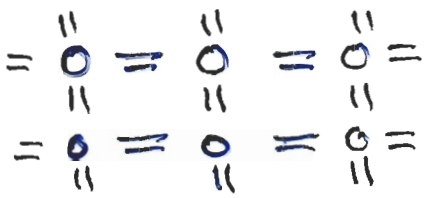
Doped semiconductors

Intrinsic semiconductors rarely used so use extrinsic (doped) semiconductor since

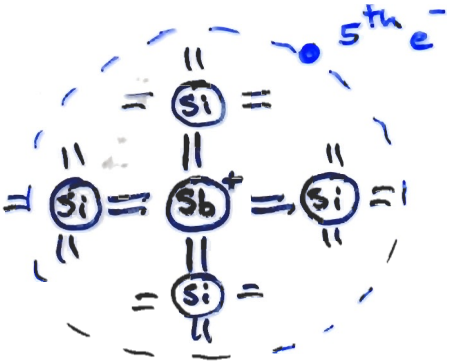
1) $\sigma \neq f(T)$
2) can choose σ by varying doping

n-type

Intrinsic (parent) material is Si, Ge. Have 4 electrons and 4 vacancies in the outer shell. Covalently bonded in diamond type structure.



n-type donors, phosphorus (P), arsenic (As), antimony (Sb), all have 5 electrons and 3 vacancies in outer shell. Dopant atoms substitute at Si site.



Only 4 electrons taken up as covalent bonds. 'Extra electron loosely bound to parent donor at 0K.

- behaves like hydrogen (Bohr) atom except:

i) $m \rightarrow m_e^*$

ii) $\varepsilon_o \rightarrow \varepsilon = \varepsilon_o \varepsilon_r$ since atom is in a dielectric e.g. Si

For hydrogen,

$$E_i = \frac{me^4}{8\varepsilon_o^2 h^2 n^2} = 13.6eV$$ for n=1 (ignore –ive sign)

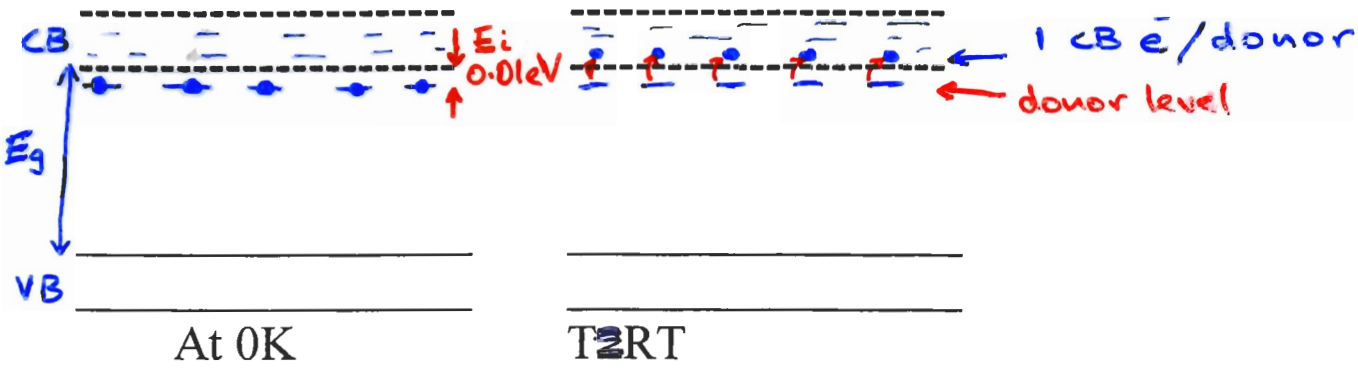
For donor atom,

$$E_i = \frac{13.6m_e^*}{\varepsilon_r^2 m}$$ Since for Si $\varepsilon_r \sim 16$, $m_e^*/m = 0.6$,

$E_i = 0.03$eV – experimentally we observe $E_i \approx 0.01$eV 10 meV

At most temperatures, $kT > E_i$; (kT @ RT ~0.026 eV)
So at RT all donors are ionised (free). Each donor contributes 1 electron to C.B.
$n = N_d$ the donor density.
(note -no extra holes produced in V.B.!)

free electrons



$\sigma = f(N_d) \neq f(T)$ provided all N_d's are ionised, e.g. at RT

Also small levels of dopant increase σ a lot.
e.g. intrinsic Si, $n_i = n = p = 10^{16}\ m^{-3}$ at RT

$$N_d = \frac{10^{28}}{10^6} = 10^{22}\, m^{-3} = n$$

Doped 1 part in 10^6 with phosphorus, then for 10^{28} atoms per m^3,

Then,

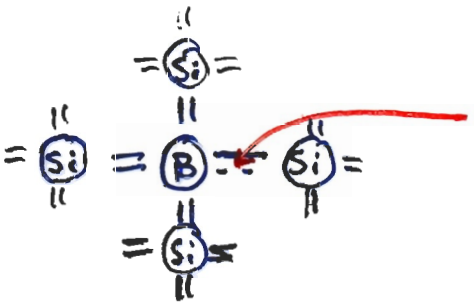
$$\frac{\sigma_n}{\sigma_i} \approx \frac{n}{n_i} = \frac{10^{22}}{10^{16}} = 10^6$$

* Also, $\mathbf{np = n_i^2}$ (very important & true for all doping conditions)

$$p = \frac{n_i^2}{n} = \frac{(10^{16})^2}{10^{22}} = 10^{10} << p_i (= 10^{16})$$

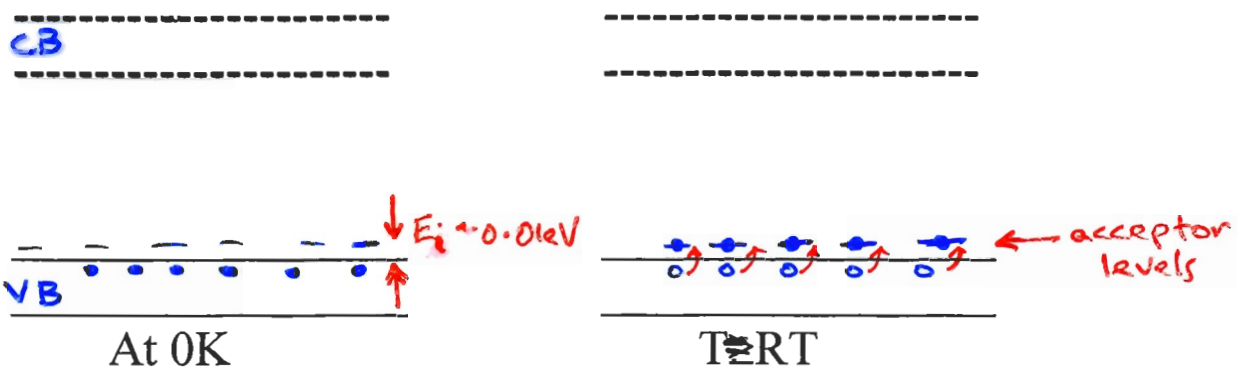
We can therefore ignore n_i and p in n-doped material,
e.g. $\sigma = n_e\mu_e + \cancel{p_e\mu_h}$
ignore

p-type:
dopants are called acceptors – 3 electrons and 5 vacancies in the outer shell, e.g. boron (B), Al, Ga….Substitutional doping in Si,



vacancy – loosely bound to parent – at RT, nearby bound e^- can move into vacancy and create a hole
(∴ movement of hole)

energy needed again ~0.01eV
every Boron atom produces 1 hole, i.e. N_a (acceptor density) = p (free holes)



Each acceptor creates 1 empty level

holes created in V.B.
if $E>E_i$, e- moves into acceptor levels – 1 hole/acceptor

Again, no extra electrons created in C.B.

$p = N_a >> p_i$

$n << n_i$ (since $np = n_i^2$)

$\sigma_p >> \sigma_i$