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EE-606: Solid State Devices
Lecture 11: Equilibrium Statistics

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Outline

1) **Law of mass-action & intrinsic concentration**
2) Statistics of donors and acceptor levels
3) Conclusion

Reference: Vol. 6, Ch. 4 (pages 110-120)

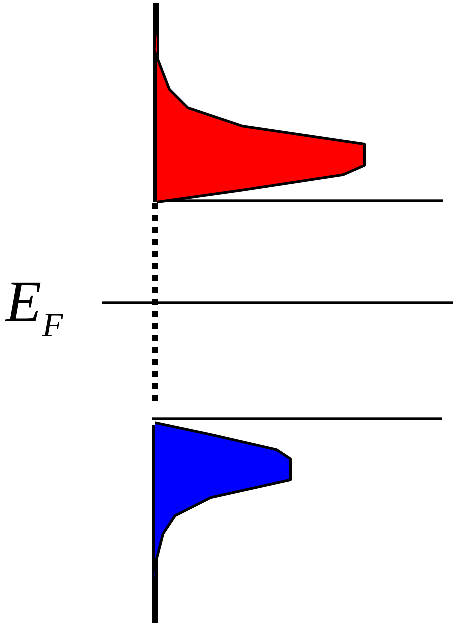
Fermi-Level for Intrinsic Semiconductors

$$n = p = n_i$$

$$n_i^2 = N_C N_V e^{-\beta E_g}$$

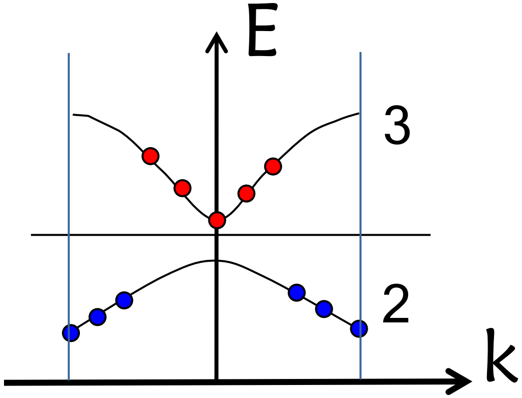
$$n_i = \sqrt{N_C N_V}\, e^{-\beta E_g/2}$$

$$E_F \equiv E_i$$



$$n = p \Rightarrow N_C e^{-\beta(E_c - E_i)} = N_V e^{+\beta(E_v - E_i)}$$

$$E_i = \frac{E_G}{2} + \frac{1}{2\beta} \ln \frac{N_V}{N_C}$$



However …

Intrinsic concentration too small ..

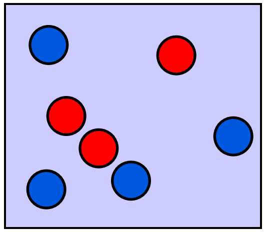
We need to do something to increase carrier concentration or conductivity of semiconductors

This is done by doping.

Looking ahead: Carrier-Density w/Doping

A bulk material must be charge neutral over all …

$$\int \left[p - n + N_D^+ - N_A^- \right] dV = 0$$



Further if the material is *spatially homogenous*

$$p - n + N_D^+ - N_A^- = 0$$

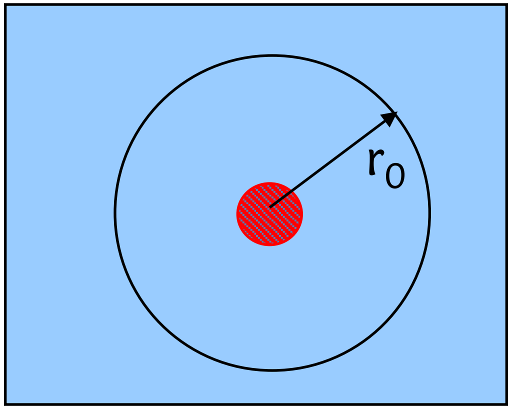
$$N_V e^{-(E_F - E_V)/k_B T} - N_C e^{-(E_C - E_F)/k_B T} + \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} - \frac{N_A}{1 + 4e^{(E_A - E_F)/k_B T}} = 0$$

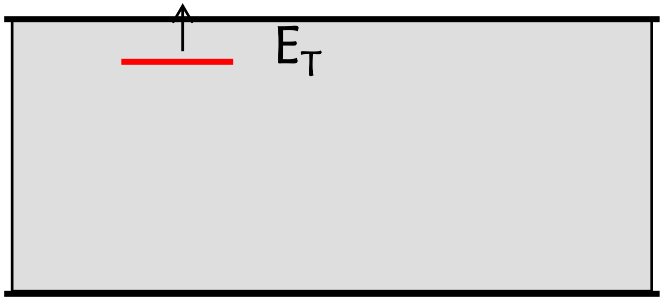
Let us see how the formula come about …

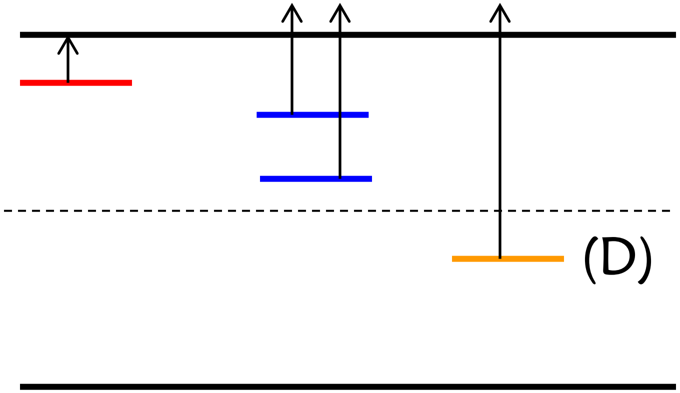
Outline

1) Law of mass-action and intrinsic concentration
2) **Statistics of donor and acceptor levels**
3) Conclusion

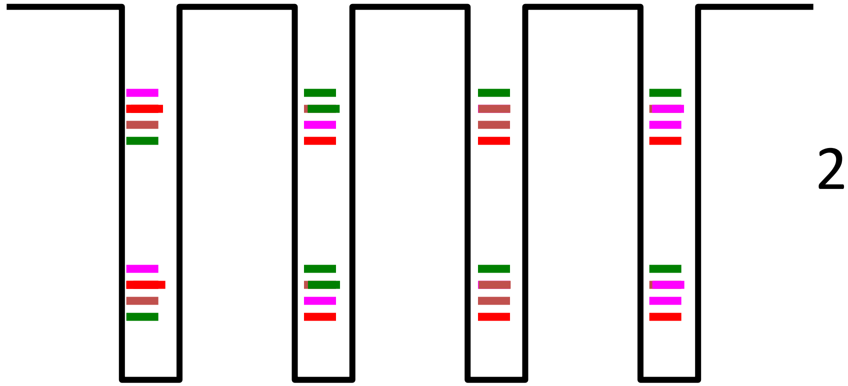
Characteristics of Donor Atoms



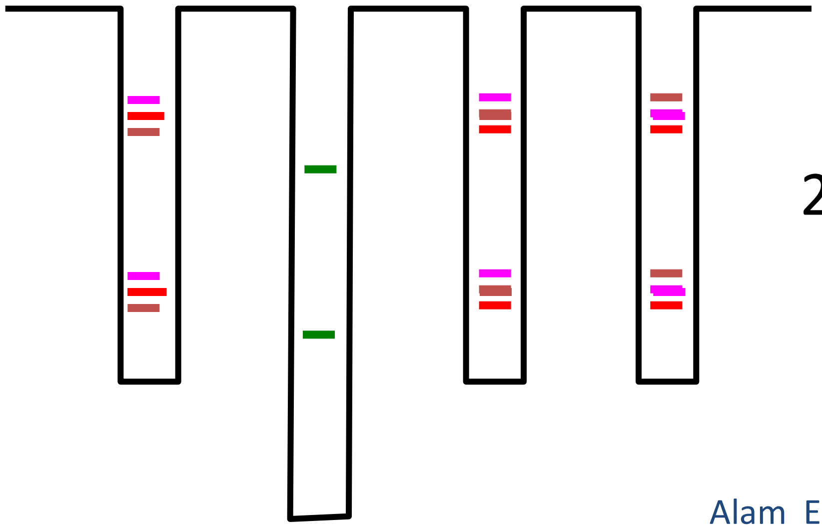




Localized vs. Delocalized States



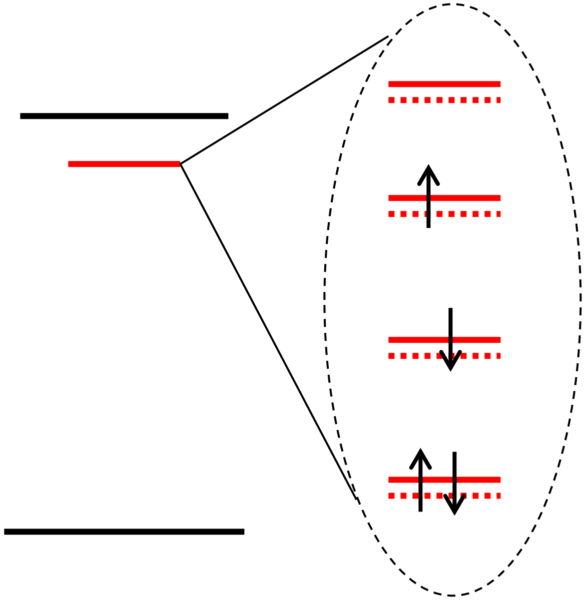
2N states/per-band (with spin)



2N-2 states/per-band (with spin)

Statistics of Donor Levels

$$P_i = \frac{e^{-(E_i - N_i E_F)/k_B T}}{\sum_i e^{-(E_i - N_i E_F)/k_B T}} \equiv \frac{e^{-(E_i - N_i E_F)/k_B T}}{Z}$$



u/d	E_i	N_i	P_i
$0/0$	0	0	$1/Z$
1/1	**x**	**x**	x

Coulomb interaction forbids this configuration

Statistics of Donor Levels

u/d	E_i	N_i	P_i
$0/0$	0	0	$1/Z$
$0/1$	1	1	$e^{-\frac{(E_i-E_F)}{k_BT}}\Big/Z$
$1/0$	1	1	$e^{-\frac{(E_i-E_F)}{k_BT}}\Big/Z$

Prob. that the donor is empty (charged)

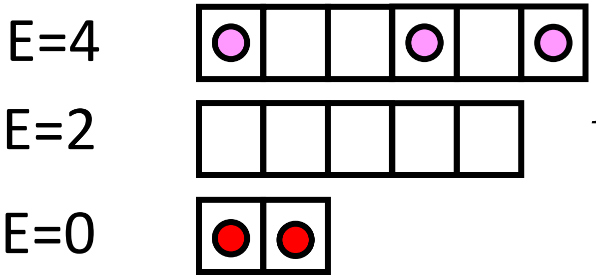
$$f_{00}=\frac{P_{00}}{P_{00}+P_{01}+P_{10}}=\frac{1/Z}{1/Z+2e^{-(E_i-E_F)/k_BT}/Z}=\frac{1}{1+2e^{(E_F-E_i)/k_BT}}$$

Prob. that the donor is filled with at least one electron (neutral)

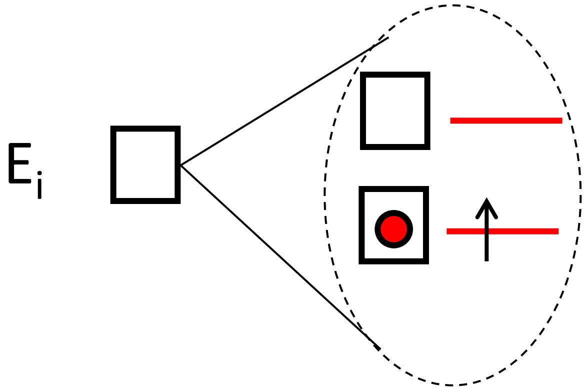
$$1-f_{00}=1-\frac{1}{1+2e^{(E_F-E_i)/k_BT}}=\frac{1}{1+\frac{1}{2}e^{(E_i-E_F)/k_BT}}$$

Note the extra factor ….

Coulomb Exclusion for Band Electrons?

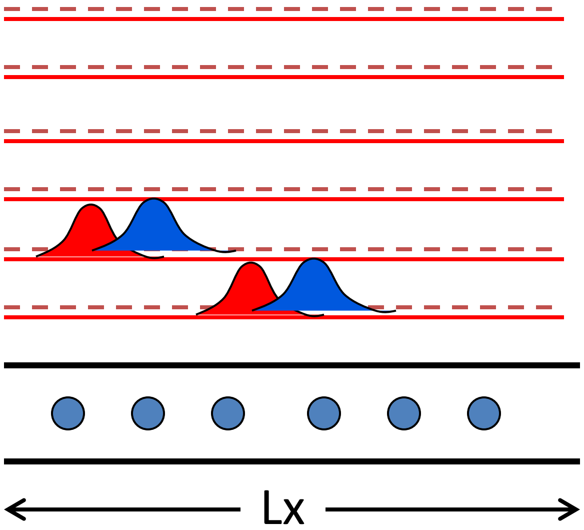


$$P_i = \frac{e^{-(E_i - N_i E_F)/k_B T}}{\sum_i e^{-(E_i - N_i E_F)/k_B T}} \equiv \frac{e^{-(E_i - N_i E_F)/k_B T}}{Z}$$



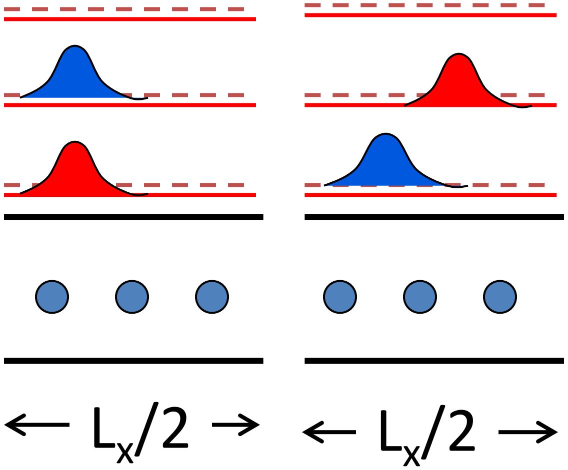
$state$	E_i	N_i	P_i
0	0	0	$1/Z$
1	1	1	$e^{-\frac{(E_i - E_F)}{k_B T}} \Big/ Z$

Localized vs. Band Electrons



E6 ← $12\pi/L_x$
E5 ← $10\pi/L_x$
E4 ← $8\pi/L_x$
E3 ← $6\pi/L_x$
E2 ← $4\pi/L_x$
E1 ← $2\pi/L_x$

Two electrons (even with opposite spin) can not be at the same position and same energy because of electrostatic repulsion

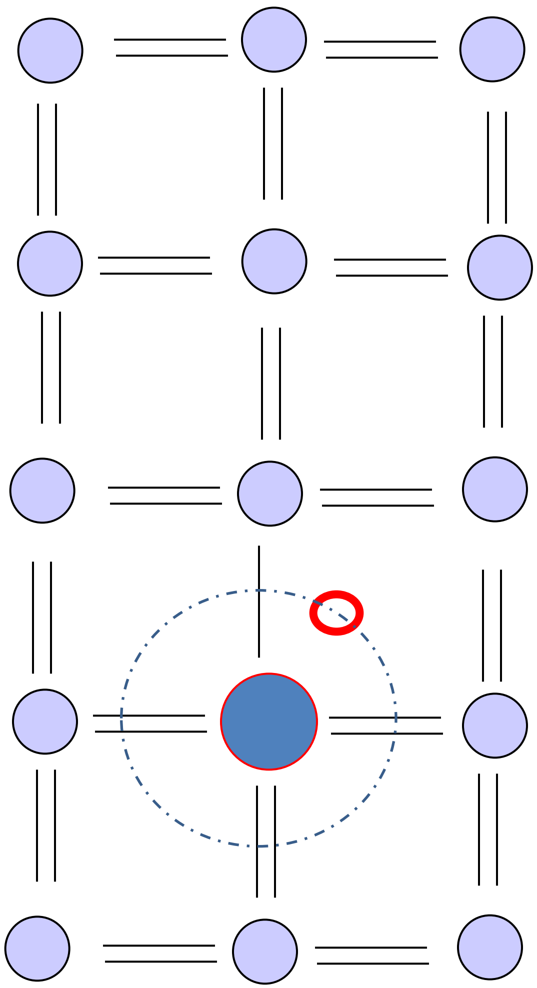


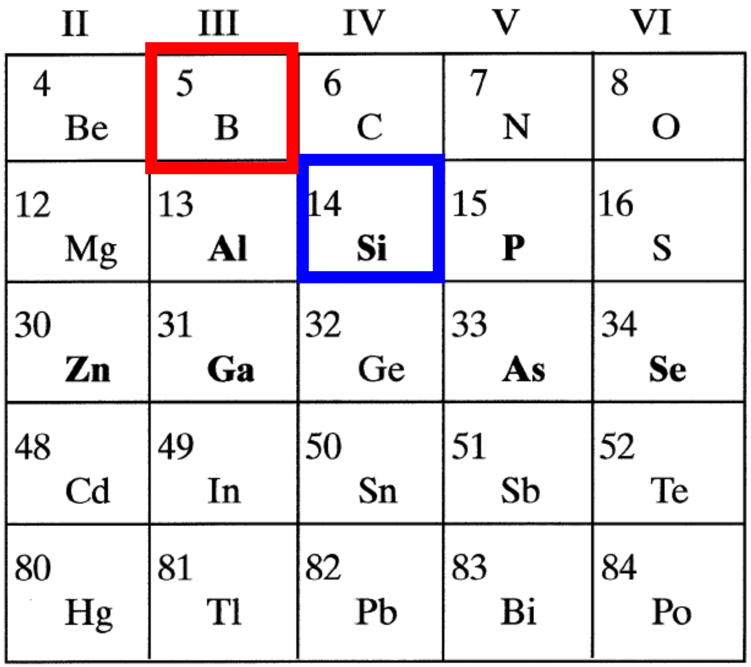
E3’ ← $6\pi/(L_x/2)$
E2’ ← $4\pi/(L_x/2)$
E1’ ← $2p/(L_x/2)$

Band electrons (with opposite spin) need not be at the same position, so they can share occupy same energy level.

When we divide space by a factor of 2, the number of states (e.g. 6 here) does not change.

Acceptor Atoms



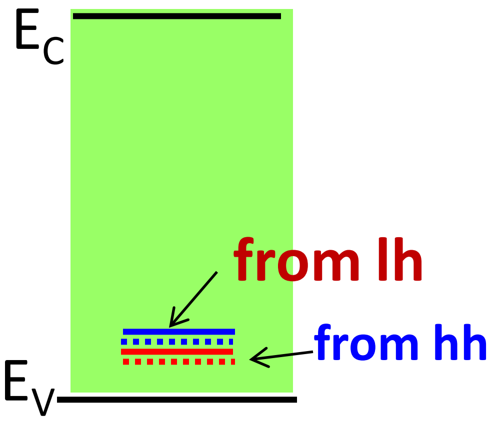


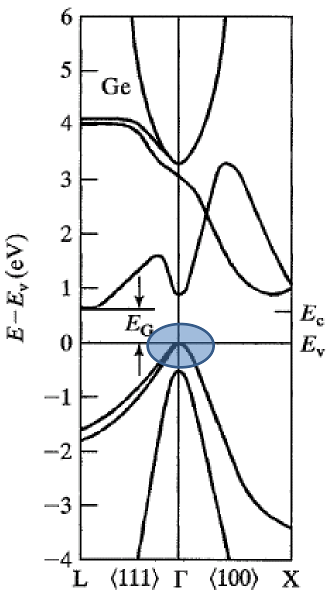
II	III	IV	V	VI
4 Be	5 B	6 C	7 N	8 O
12 Mg	13 **Al**	14 **Si**	15 **P**	16 S
30 **Zn**	31 **Ga**	32 Ge	33 **As**	34 **Se**
48 Cd	49 In	50 Sn	51 Sb	52 Te
80 Hg	81 Tl	82 Pb	83 Bi	84 Po

State [1] …. Hole present … N-1 charges

State [0] … Hole filled …. N charges

Statistics of Acceptor Levels in Si and Ge





1. Each atom contributes 2 states (up & down spin) to a band, therefore a band has 2N states.

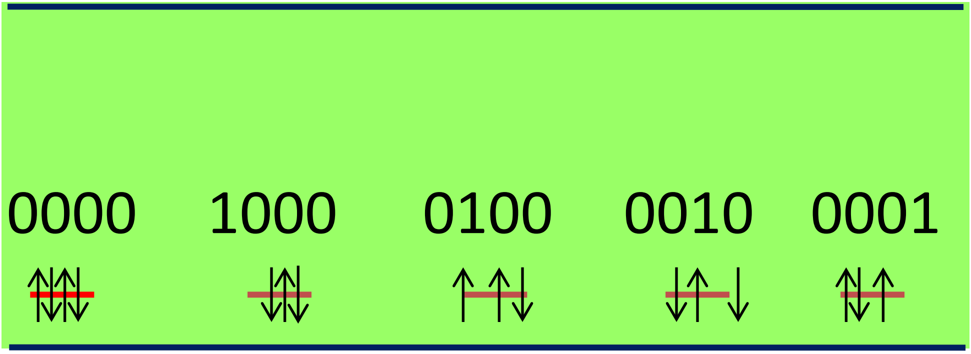
2. Every time a host atom is replaced by a impurity atom, 2 states are disappear per a band and appear as localized states (sort of).

3. Therefore an acceptor atom close to hh and lh bands removes four states from those bands.

4. Because of Coulomb interaction only 1 hole can seat in these 4 states: the states are 0000, 0001, 0010, 0100, 1000.

5. One now uses P_i to compute the occupation of acceptors.

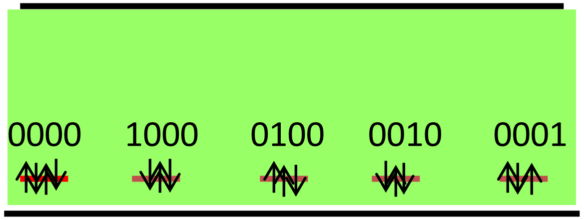
Number and Energy Considerations …



4N-4 States
In HH/LH bands

1) [0000] is the charged state as it has N electrons, but N-1 protons.
2) Single hole configuration [0001] is uncharged, as we have N-1 electrons, and N-1 protons … same is true for [0010], [0100], [1000] states.
3) Going from [0000] to [0001] states, the number of electrons goes down by 1 (N_i=-1).
4) Going from [0000] to [0001] states energy goes down by $-E_A$, because one electron is no longer occupying the high energy level at E_A.

Statistics of Acceptor Levels



$$P_{0000} = \frac{e^{-(0-0xE_F)/k_BT}}{\sum_i e^{-(E_i - N_i E_F)/k_BT}} \equiv \frac{1}{Z}$$

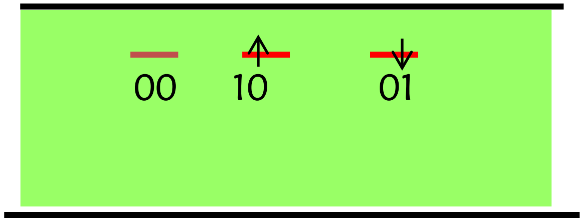
Steps 3 & 4

$$P_{0001} = P_{0010} = P_{0100} = P_{1000} = \frac{e^{-(-E_A-(-1)E_F)/k_BT}}{\sum_i e^{-(E_i - N_i E_F)/k_BT}} \equiv \frac{e^{(E_A-E_F)/k_BT}}{Z}$$

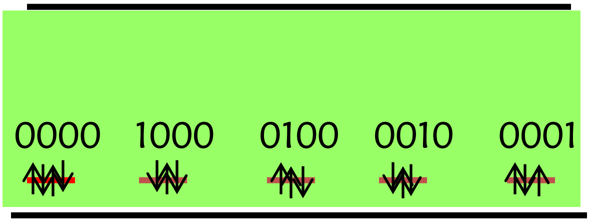
$$f_{0000} = \frac{P_{0000}}{P_{1000}+P_{0100}+P_{0010}+P_{0001}} = \frac{1}{1+4e^{(E_A-E_F)/k_BT}}$$

Filled and empty Donor/Acceptor Levels

2N-2 states



$$N_D^{empty} \equiv N_D^{+} = N_D f_{00} = N_D \frac{1}{1+2e^{(E_F-E_i)/k_BT}}$$



$$N_A^{filled} \equiv N_A^{-} = N_A \left[f_{0000} \right] = N_A \frac{1}{1+4e^{(E_A-E_F)/k_BT}}$$

4N-4 States
In HH/LH bands
(Two holes can not seat together)

Distributions are physical ….

$$f_D = \frac{N_D}{1 + g_D e^{(E_F - E_D)/k_B T}}$$

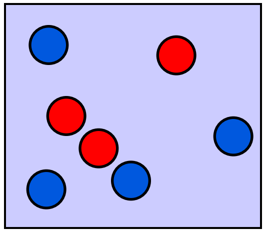
Degeneracy factor …

$$f_D = \frac{N_D}{1 + e^{\varepsilon/k_B T} e^{(E_F - E_D)/k_B T}} = \frac{N_D}{1 + e^{(E_F - E_D{}')/k_B T}}$$

Effective donor level

Summary …

A bulk material must be charge neutral over all …



$$\int \left[p - n + N_D^+ + N_A^- \right] dV = 0$$

Further if the material is *spatially homogenous*

$$p - n + N_D^+ + N_A^- = 0$$

$$N_V e^{-(E_F - E_V)/k_BT} - N_A e^{-(E_C - E_F)/k_BT} + \frac{N_D}{1 + 2e^{(E_F - E_D)/k_BT}} - \frac{N_A}{1 + 4e^{(E_A - E_F)/k_BT}} = 0$$

Conclusions

Intrinsic concentration of electrons in a semiconductor is relatively small.

The statistics of dopant levels are different because they are close to the conduction band and because they are localized. Influenced by pair-wise coulomb repulsion.

The statistics of donor and acceptor atoms are also different, because donor levels couple with single conduction band, while acceptor levels couple with two valence bands.