## 3. Semiconductors

Silicon

The material most widely associated with photovoltaics is silicon, and its well-established properties are often the reference from which those of other PV materials are drawn. Silicon is a group-IV, tetravalent metalloid, inert, grey solid, with a high melting point (1400 ºC), a chemical analog to carbon. The four valence electrons of both Si and C make these elements compatible with tetrahedral coordination.by arrangement in the diamond structure.
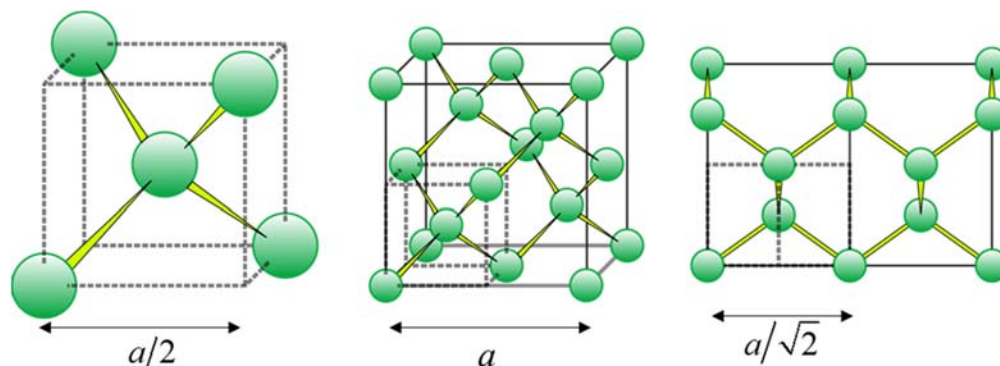

Pure Si has the diamond crystal structure of carbon, comprised of two interpenetrating face-centered cubic (fcc) lattices, with cubic lattice parameter $a = 0.54$ nm , both occupied by Si atoms, but separated by $1/4$ the cube diagonal. Tetrahedral bonds associate each atom in a sublattice to the four nearest neighbors in the other sublattice.

Tetrahedral bonding

Building from the core of a neon atom, a pair of spin-opposite electrons are first added to the 3s level, followed by two electrons in the 3p levels, which are spin aligned, according to Hund's rule.
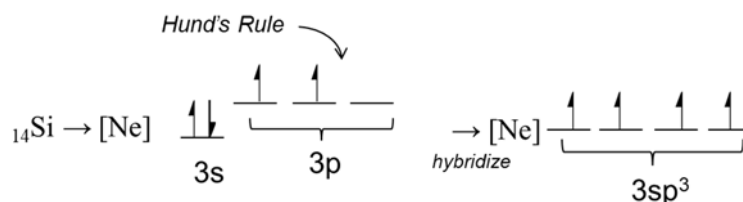
Hybridization by linear combination of the 3s/3p atomic orbitals can be used to form four molecular orbitals with minimal overlap that can be associated with a tetrahedron inscribed in a cube. Whereas the hybridized levels have higher energy for isolated atoms, they result in an overall reduction in energy in the solid by forming tetrahedral bonds.
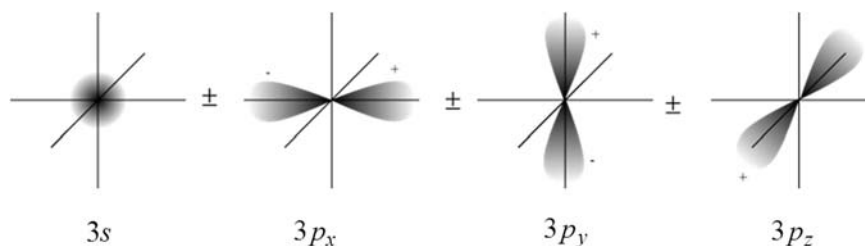

The MO wave functions are constructed from linear combinations of these four orbitals equally weighted.

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$$\psi = \frac{1}{2}\psi_s \pm \frac{1}{2}\psi_{p_x} \pm \frac{1}{2}\psi_{p_y} \pm \frac{1}{2}\psi_{p_z}$$

From the eight distinct possibilities generated from the various sign combinations, four can be selected to form a tetrahedral arrangement around any particular atom.

Origin of bandgap

Isolated molecules typically have a highest-occupied molecular orbital (HOMO) and a lower-unoccupied molecular orbital (LUMO). When a pair of such molecules interact closely, the MOs hybridized further. The energy levels repel each other, so there will be a somewhat smaller difference between the empty and filled orbitals. If we imagine repeating this process with an infinitely large number of molecules, the HOMO and LUMO will form continuous bands, called the valence band (VB) and conduction band (CB). separated by the bandgap energy E_g .
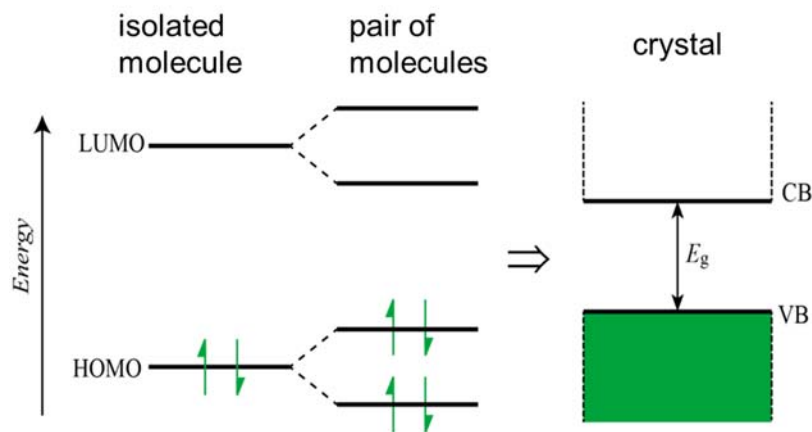
A bandgap exists when the density of states $D(E)$ in material is zero over some energy range. The bandgap is particularly important when states below the gap are primarily filled with electrons and those above the gap are primarily empty. We often categorize materials by their E_g .

insulator: $E_g \gg kT$, $E_g > 3\,\text{eV}$

semiconductor: $0.5\ \text{eV} < E_g < 3\ \text{eV}$

semi-metal: $0 < E_g < 0.5\ \text{eV}$

metal: no E_g

Bloch's theorem

Alternatively, one can construct the bands from continuous wave functions that span the entire solid, similar to the free electronic states. A useful formulation uses Bloch waves, in which the electron wave functions appear as the product of plane waves with so-called Bloch functions,.

$$\psi(\mathbf{r}) = u(\mathbf{r}) \cdot e^{2\pi i \mathbf{k} \cdot \mathbf{r}}$$

The Bloch functions have the periodicity of the crystal:

$$u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r})$$

where $\mathbf{R} = n_1 \cdot \mathbf{a}_1 + n_2 \cdot \mathbf{a}_2 + n_3 \cdot \mathbf{a}_3$ is a direct lattice vector of the crystal. Then

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$$\psi(\mathbf{r}+\mathbf{R}) = u(\mathbf{r}+\mathbf{R}) \cdot e^{2\pi i \mathbf{k}\cdot(\mathbf{r}+\mathbf{R})} = e^{2\pi i \mathbf{k}\cdot\mathbf{R}} \cdot \psi(\mathbf{r})$$

The only effect of translation by a lattice vector is a change in phase of the electron wave function.

1-D sinusoidal potential

The allowed electronic energies are the eigenvalues corresponding to solutions of the Schrodinger equation. In 1-D:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + qV(x) \right]\psi(x) = E \cdot \psi(x)$$

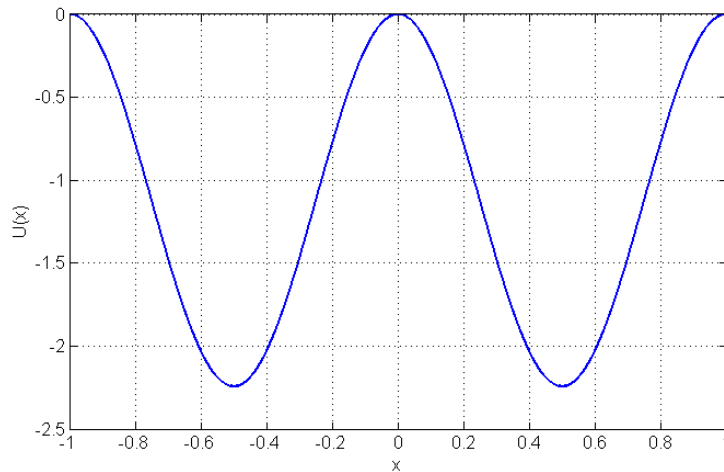The solutions can be written as:

$$\psi(x) = b(x) \cdot e^{2\pi i k x}$$

where the $b(x)$ are the Bloch functions. Their periodicity allows us to write them as Fourier series:

$$b(x) = \sum_n b_n e^{2\pi i n x/a}$$

For example, consider the potential:

$$U(x) = -\frac{1}{2}U_0 \cdot [1 + \cos(2\pi x/a)]$$

For simplicity, the average potential is zero in this case.

The computational solution of the Schrodinger equation consists of continuous bands. The dispersion relation $E(k)$ contains all of the information about which energy levels are present in the crystal. We generally translate the wavenumbers back into the 1st Brillouin zone, which extends from $-\pi/a \le k \le \pi/a$.

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Band Diagram
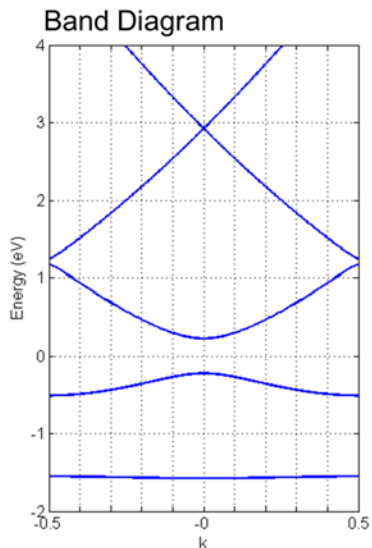
Notice that there are gaps between the bands with energies below the barrier height ($E < 0$). Above the barrier, there are no gaps between the bands.

The optoelectronic properties of semiconductors arise from more than just the distinction by bandgap. Electrical conductivity in semiconductors can be dramatically influenced by doping, temperature, and illumination. These variations are exploited to enable control of electrical conduction for numerous electronic applications.

**1-D sinusoidal potential: wave functions**
We have a continuous spectrum of energy levels in the solid. The corresponding Bloch waves are, in general, complex, but it might be helpful to plot the intensity (magnitude squared) for a few simple cases.

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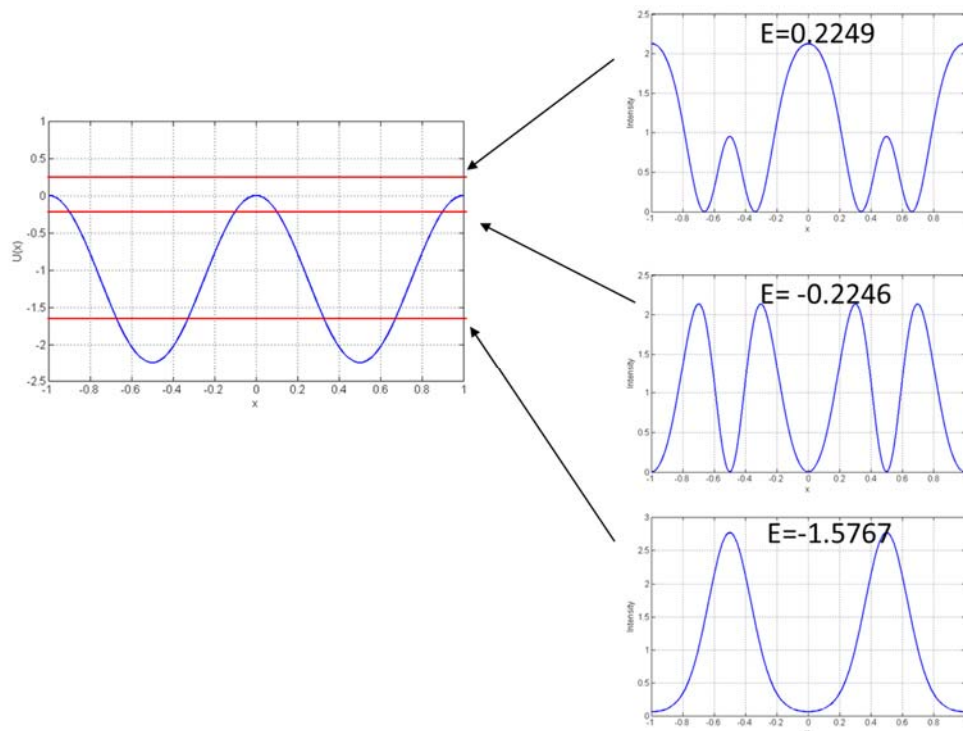
Notice that, for the bound states ($E < 0$), the wave function has its maxima centered in the well regions, whereas for continuum states ($E > 0$), the wave function can have its maxima in the barrier regions.

Band structure

Bandgap is only one parameter describing the rather complex electronic structure of semiconductors. Semiconductor bandgaps are either direct or indirect, which refers to the alignment in crystal momentum space of the VB maximum and the CB minimum. For a direct-gap semiconductor, these are aligned in wave vector; for an indirect-gap semiconductor they are not aligned. The implication is that no change in crystal momentum is required for electronic transitions between the VB and CB. Thus, the transition may represent only a change in energy of an electron. That change in energy can occur by the absorption or emission of a photon which, as a massless particle, has negligible momentum. An indirect transition, on the other hand, requires concomitant momentum change, generally by the emission or absorption of a phonon. Sophisticated theoretical methods exist to compute the electronic bandstructures of crystalline solids, but a qualitative sense of the bandgap arises from a basic quantum mechanical description.

indirect   indirect   direct
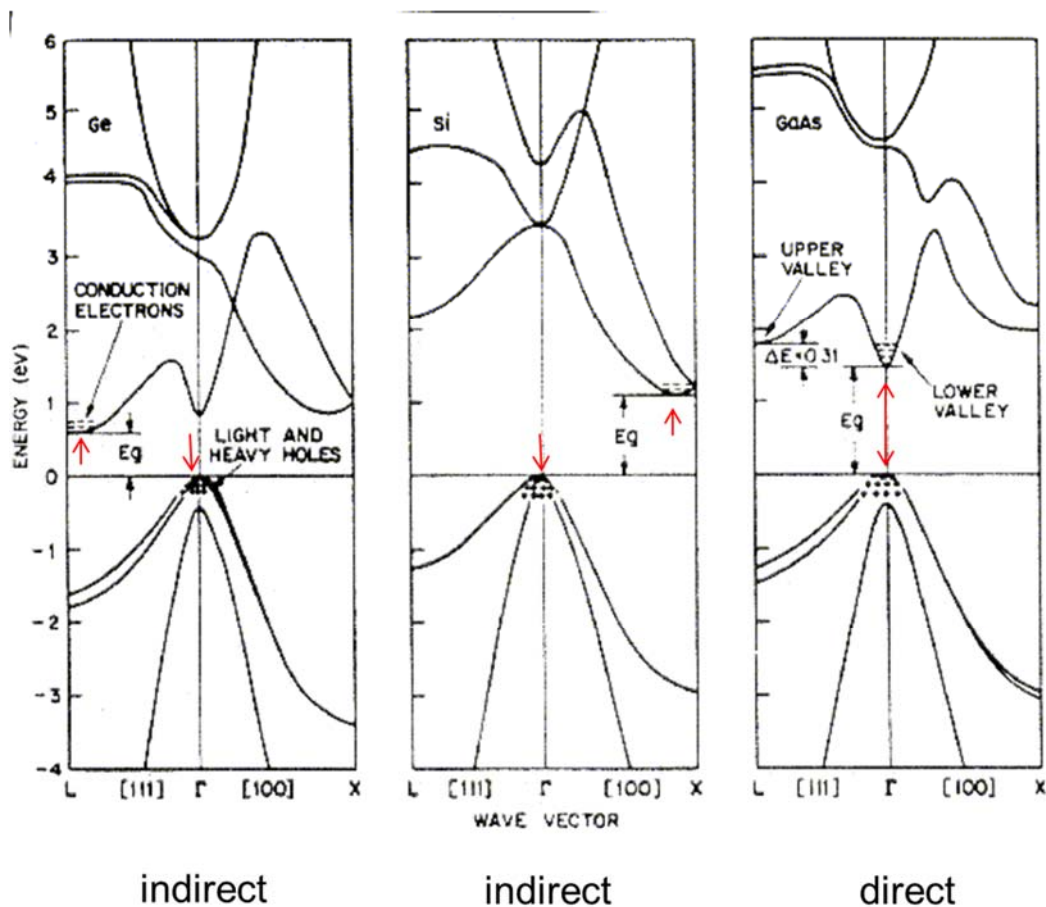
From J. I. Pankove, "Optical Processes in Semiconductors", Dover Publications, Inc., New York (1971).

Electrons and Holes

A semiconductor has a large number of primarily filled states in its VB separated by energy E_g from a large number of primarily empty states in its CB. An electron that fills a state in the CB can be considered an essentially free particle, which can carry electrical current through the crystal by virtue of its velocity and charge. Correspondingly, the absence an electron (negative charge) in the CB represents an imbalance in the net flow of charge in some direction (left). This is equivalent to the motion of a hole (positive charge) in the opposite direction (right). In the nomenclature of semiconductor, CB electrons and VB holes are collectively considered charge carriers, with equal significance and validity.

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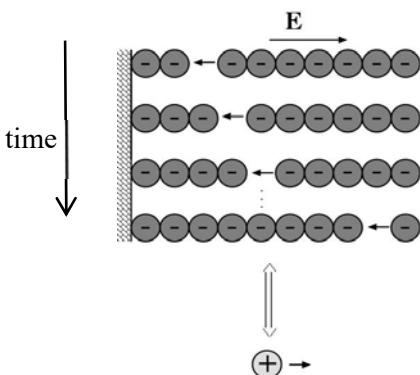
Fermi-Dirac distribution
We saw that the probability for occupation of an electron state in thermal equilibrium is given by the fermi function

$$f(E - E_F) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

The equilibrium chemical potential is referred to in electronic materials as the fermi level E_F. The occupation probability for an electron decreases from 50% as the energy of the state exceeds E_F. However, E_F often lies within the bandgap, where $D(E)$ of a pure semiconductor is zero. At absolute zero temperature (0 K), one expects the CB to be completely empty and the VB completely full. But at finite temperatures, the probability of thermally generated electrons in the CB and holes in the VB is non-zero.
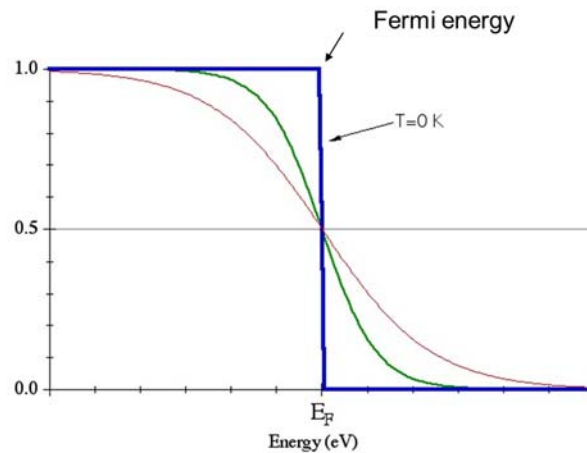
Carrier concentrations (I)
As for photons, the number of electrons per unit volume, per unit energy, are determined by the electronic density of states $D(E)$ and the Fermi function.
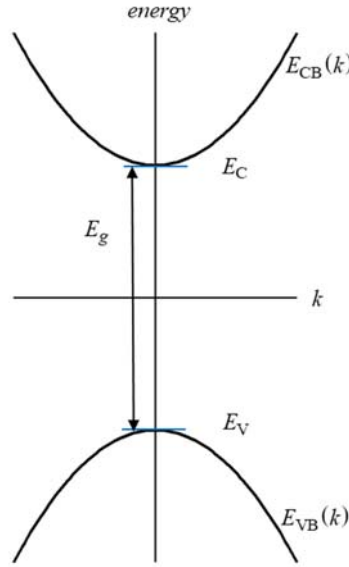
$$\frac{dn}{dE} = D(E) \cdot f(E - E_F)/V$$

Again we use the number of states in a 3-D box with linear dimension L having wavenumber in the range from 0 to k :

$$N(k) = \frac{2 \cdot \left(\frac{4}{3}\pi k^3\right)}{\left(\frac{1}{L^3}\right)} = \frac{8}{3}\pi k^3 L^3$$

Carrier concentrations (II)
Based on a qualitative understanding of the band structure, assuming the semiconductor has a direct gap at the gamma point, we can write the dispersion relations near the band edges as:

$$E_{CB}(k) \approx E_C + \frac{h^2 k^2}{2m_C} \quad \text{and} \quad E_{VB}(k) \approx E_V - \frac{h^2 k^2}{2m_V}$$

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where the denominators contain the CB and VB effective masses, which can be evaluated using:

$$\frac{1}{m_C} = \frac{1}{h^2} \frac{d^2}{dk^2} E_{CB}(k)\Big|_{k=0} \quad \text{and} \quad \frac{1}{m_V} = -\frac{1}{h^2} \frac{d^2}{dk^2} E_{VB}(k)\Big|_{k=0}$$

Solving for $k(E)$, we have:

$$k = \frac{\sqrt{2m_C}}{h} \cdot \sqrt{E - E_C} \quad \text{and} \quad k = \frac{\sqrt{2m_v}}{h} \cdot \sqrt{E_V - E}$$

Using the degeneracy $g = 2$ for spin, the number of states above the CB band edge with energy $E \geq E_C$ is given by:

$$N_C(E) = \frac{8(2m_C)^{3/2} \pi L^3}{3h^3} \cdot (E - E_C)^{3/2}$$

so, the CB DOS is found using:

$$D_C(E) = \frac{dN_C}{dE} = \frac{2(2m_C)^{3/2} \pi g L^3}{h^3} \cdot (E - E_C)^{1/2}$$

Carrier concentrations (III)

The same approach is applied to the VB to the find the number of states $E \leq E_{V0}$. Dividing by volume gives the density of states in the CB and VB are:

$$g_C(E) = \frac{D_C(E)}{L^3} = 4\pi \left(\frac{2m_C}{h^2}\right)^{3/2} \cdot (E - E_C)^{1/2}$$

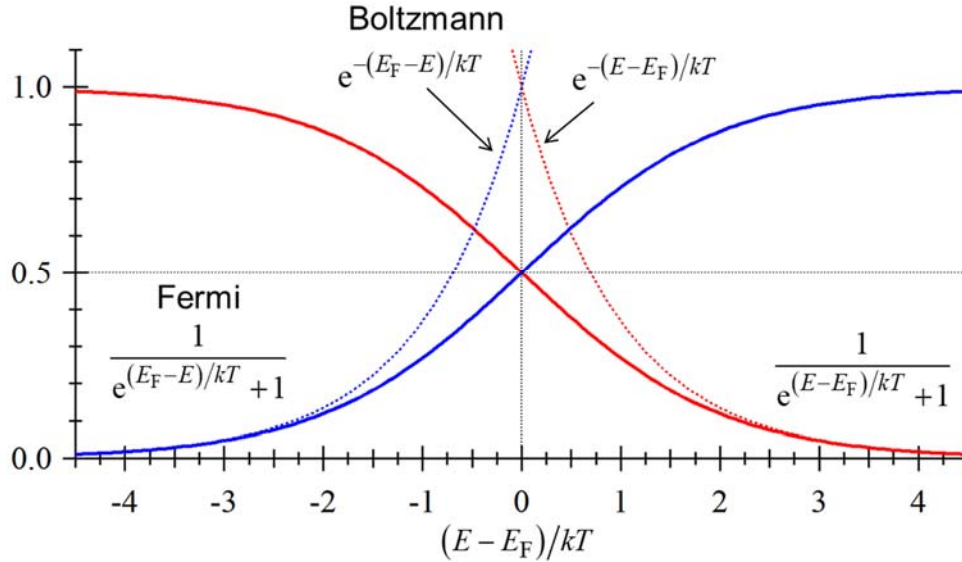$$g_V(E) = \frac{D_V(E)}{L^3} = 4\pi \left(\frac{2m_V}{h^2}\right)^{3/2} \cdot (E_V - E)^{1/2}$$

The concentrations per unit energy of electrons in the CB and holes in the VB are then :

$$\frac{dn}{dE} = D_C(E) \cdot f(E)/V = g_C(E) \cdot f(E - E_F)$$

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$$\frac{dp}{dE} = D_V(E) \cdot [1 - f(E)]/V = g_V(E) \cdot [1 - f(E - E_F)]$$

Carrier concentrations (IV)

The Fermi function reduced to the (simpler) Boltzmann function is sufficient when the occupation probability is low.

Also, notice that

$$1 - \frac{1}{e^{(E - E_F)/kT} + 1} = \frac{1}{e^{(E_F - E)/kT} + 1}$$

Carrier concentrations (V)

The density of electrons per unit energy in the CB under *non-degenerate* ($E_C - E_F \gg kT$) conditions is

$$\frac{dn}{dE} = 4\pi \left(\frac{2m_C}{h^2} \right)^{3/2} (E - E_C)^{1/2} \cdot \frac{1}{e^{(E - E_F)/kT} + 1}$$

$$\approx 4\pi \left(\frac{2m_C}{h^2} \right)^{3/2} \cdot (E - E_C)^{1/2} \cdot e^{-(E - E_F)/kT}$$

The density of holes per unit energy in the VB under non-degenerate ($E_F - E_V \gg kT$) conditions is

$$\frac{dp}{dE} = 4\pi \left(\frac{2m_V}{h^2} \right)^{3/2} (E_V - E)^{1/2} \cdot \frac{1}{e^{(E_F - E)/kT} + 1}$$

$$\approx 4\pi \left(\frac{2m_V}{h^2} \right)^{3/2} \cdot (E_V - E)^{1/2} \cdot e^{-(E_F - E)/kT}$$

Carrier concentrations (VI)

Within the parabolic-band approximation, we can plot these concentrations as functions of energy for different values of E_F . For a pure semiconductor the fermi level is usually near the center of the gap, and the material is called *intrinsic*. A shift downward of E_F increases p , but decreases n , and the material is called p-type. A shift upward of E_F increase n and decreases p ; the material is called n-type.

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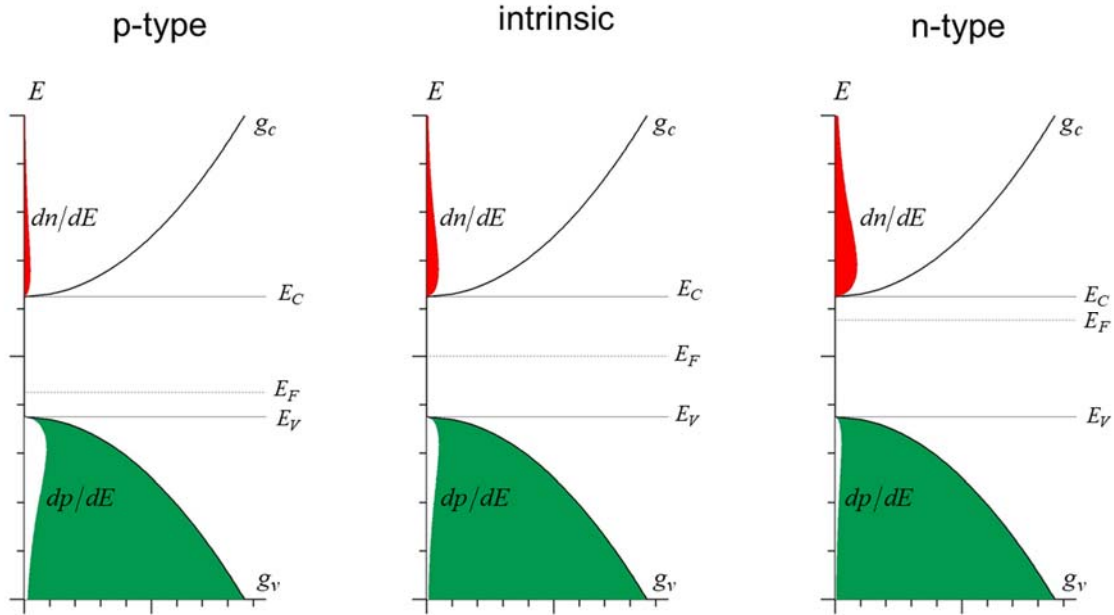
Carrier concentrations (VII)

We are often less concerned with the details of the carrier concentrations within the CB and VB than with the total concentrations within the bands, regardless of energy. In the case of the CB,

$$n = \int_{E=E_C}^{\infty} \frac{dn}{dE} \cdot dE$$

$$\approx 4\pi \left(\frac{2m_C}{h^2}\right)^{3/2} \int_{E=E_C}^{\infty} \cdot (E - E_C)^{1/2} \cdot e^{-(E-E_F)/kT} \cdot dE$$

$$n = 4\pi \left(\frac{2m_C}{h^2}\right)^{3/2} \cdot I_C$$

where

$$I_C \approx \int_{E=E_C}^{\infty} \cdot (E - E_C)^{1/2} \cdot e^{-(E-E_F)/kT} \cdot dE$$

Likewise, in the VB

$$p = \int_{E=-\infty}^{E_V} \frac{dp}{dE} \cdot dE$$

$$\approx 4\pi \left(\frac{2m_V}{h^2}\right)^{3/2} \int_{E=-\infty}^{E_V} \cdot (E_V - E)^{1/2} \cdot e^{-(E_F-E)/kT} \cdot dE$$

$$p = 4\pi \left(\frac{2m_V}{h^2}\right)^{3/2} \cdot I_V$$

where

$$I_V = \int_{E=-\infty}^{E_V} \cdot (E_V - E)^{1/2} \cdot e^{-(E_F-E)/kT} \cdot dE$$

Carrier concentrations (VIII)

We now evaluate the integral I_C. Substituting

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$$x = \left(\frac{E - E_C}{kT} \right)^{1/2}$$

then $E = E_C + kT \cdot x^2$, so $dE = 2kTx \cdot dx$. Now

$$e^{-(E-E_F)/kT} = e^{-(E_C-E_F)/kT} \cdot e^{-x^2} \quad \text{and} \quad (E - E_C)^{1/2} = (kT)^{1/2} \cdot x$$

The integral is now simply:

$$I_C = 2(kT)^{3/2} \cdot e^{-(E_C-E_F)/kT} \cdot \int_{x=0}^{\infty} x^2 \cdot e^{-x^2} \cdot dx$$

The definite integral is

$$\int_{x=0}^{\infty} x^2 \cdot e^{-x^2} \cdot dx = \frac{\sqrt{\pi}}{4}$$

giving:

$$I_C = \frac{\sqrt{\pi}}{2} (kT)^{3/2} \cdot e^{-(E_C-E_F)/kT}$$

We have:

$$n = 4\pi \left(\frac{2m_C}{h^2} \right)^{3/2} \cdot \left[\frac{\sqrt{\pi}}{2} (kT)^{3/2} \cdot e^{-(E_C-E_F)/kT} \right]$$

This allows a simple expression for the total concentration of CB electrons:

$$n = N_C \cdot e^{-(E_C-E_F)/kT}$$

using the "effective" CB density of states:

$$N_C = 2 \left(\frac{m_C kT}{2\pi\hbar^2} \right)^{3/2}$$

Carrier concentrations (IX)

We can repeat the preceding for the I_V. The result is

$$I_V = \frac{\sqrt{\pi}}{2} (kT)^{3/2} \cdot e^{-(E_F-E_V)/kT}$$

The total concentration of holes in the VB is

$$p = N_V \cdot e^{-(E_F-E_V)/kT}$$

in terms of the "effective" VB density of states:

$$N_V = 2 \left(\frac{m_V kT}{2\pi\hbar^2} \right)^{3/2}$$

It is sometimes useful to keep track of a reference "effective" DOS:

$$N_0 = 2 \left(\frac{m_0 kT}{2\pi\hbar^2} \right)^{3/2} = 2.5 \times 10^{19} \text{ cm}^{-3}$$

Then

$$N_C = \left(\frac{m_C}{m_0} \right)^{3/2} \cdot N_0 \quad \text{and} \quad N_V = \left(\frac{m_V}{m_0} \right)^{3/2} \cdot N_0$$

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Semiconductors (I)

For non-degenerate semiconductors, only need to know the position of the fermi with respect to the band edges to find the carrier concentrations. This allows us to draw a simplified energy diagram that refers only to band-edge energies, showing energy vs. position.
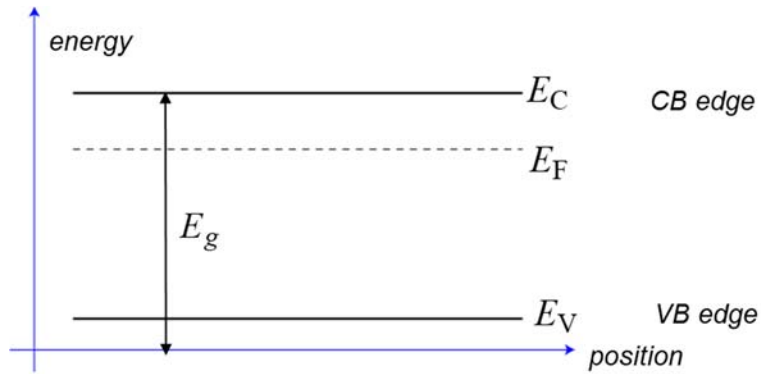
Semiconductors (II)

With these forms, it is evident that the product of n and p is a constant for a given semiconductor in equilibrium, regardless of the individual concentrations:

$$n \cdot p = N_C \cdot N_V \cdot e^{-(E_C - E_V)/kT} = N_C \cdot N_V \cdot e^{-E_g/kT} = n_i^2$$
$$\rightarrow n_i = \sqrt{N_C \cdot N_V} \cdot e^{-E_g/2kT}$$

The quantity n_i is the intrinsic carrier concentration, which is the concentration of electrons in CB and holes in VB, respectively, of a pure semiconductor in equilibrium. It leads to the alternative forms:

$$n = n_i \cdot e^{(E_F - E_i)/kT} , \quad p = n_i \cdot e^{(E_i - E_F)/kT}$$

which refer to the intrinsic energy, i.e., the Fermi level of the intrinsic (pure) semiconductor:

$$E_i = \frac{E_C + E_V}{2} - \frac{kT}{2} \cdot \ln\left(\frac{N_C}{N_V}\right) = \frac{E_C + E_V}{2} - \frac{3kT}{4} \cdot \ln\left(\frac{m_C}{m_V}\right)$$

Notice that if $m_C = m_V$, then E_i is exactly in the center of the gap. In this case, if $E_F = E_i$, then $n = p = n_i$ (i.e., the material is intrinsic).

Semiconductors (III)

It should be noted that the CB electrons are not truly free; they remain bound to the solid to maintain net charge neutrality. Somewhere above the CB edge is the vacuum level E_{vac}, above which an electron is free of the solid:
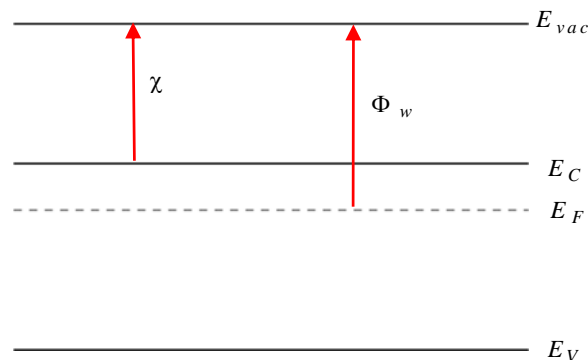
As in metals, the minimum energy to free an electron with energy E_F is the work function Φ_w. For a semiconductor, Φ_w is not a constant, but depends on the carrier concentration. A more useful, constant quantity is the energy to free an electron from the CB edge, called the electron affinity χ :

$$\chi = E_{\text{vac}} - E_C = E_{\text{vac}} - E_V + E_g$$

Using

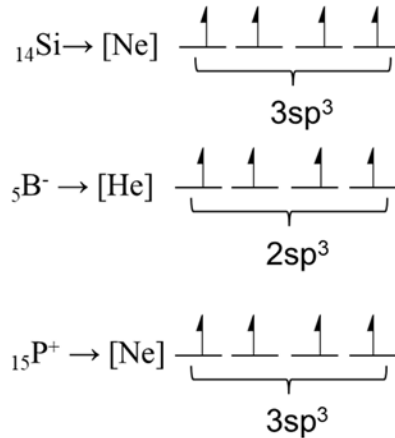$$E_C - E_F = kT \cdot \ln\left(\frac{N_C}{n}\right)$$

$$E_F - E_V = kT \cdot \ln\left(\frac{N_V}{p}\right)$$

In semiconductors, Φ_w depends on doping.

$$\Phi_w = E_{\text{vac}} - E_F = \chi + kT \cdot \ln\left(\frac{N_C}{n}\right) = \chi - kT \cdot \ln\left(\frac{N_V}{p}\right) - E_g$$

Semiconductor: Doping (I)

When substituting B/P, called electron acceptors/donors, in pure Si, the dopant atom has one missing/extra valence electron:

The dopant atom easily ionizes, by either accepting an electron (B) from the VB, or donating an electron (P) into the CB, leaving the ionized cores stationary in the lattice.

Semiconductor: Doping (II)

The Bohr model allows estimation of the ionization energy of a dopant. The effect of screening within the solid is incorporated into the Coulomb potential by substituting the permittivity ε_0 of free space with the permittivity ε for the material. The usual Bohr radius is then modified accordingly:

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_0 e^2} \rightarrow a_0^* = \frac{4\pi\varepsilon\hbar^2}{me^2}$$

where m is the effective mass of the charge carrier. Recall that the ionization energy of H is the Rydberg.

$$1 \text{ Ryd} = \frac{\hbar^2}{2m_0 \cdot a_0^2} = 13.6 \text{ eV}$$

The ionization energy of the dopant atom can then be written as:

$$V_n = \frac{\hbar^2}{2m \cdot (a_0^*)^2} = \left(\frac{m}{m_0}\right) \cdot \left(\frac{\varepsilon_0}{\varepsilon}\right)^2 \cdot (1 \text{ Ryd})$$

Semiconductor: Doping (III)

The positions of the ionized dopant levels can be added to the electron energy diagram. Electron donors levels are shown at $E_D = E_C - V_n$, slightly below the conduction band. Acceptor levels are shown at $E_A = E_V + V_p$, slightly above the valence band. We can adopt the notation shown below to indicate whether a particular level is occupied. A donor level is unoccupied when it is ionized (it has donated an electron to the CB), leaving a concentration of $N_D^{(+)}$ ionized donors. An acceptor level is occupied when it is ionized (it has accepted an electron from the VB), leaving a concentration of $N_A^{(-)}$ ionized acceptors.

ionized donor level: $E_D = E_C - V_n$

ionized acceptor level: $E_A = E_V + V_p$
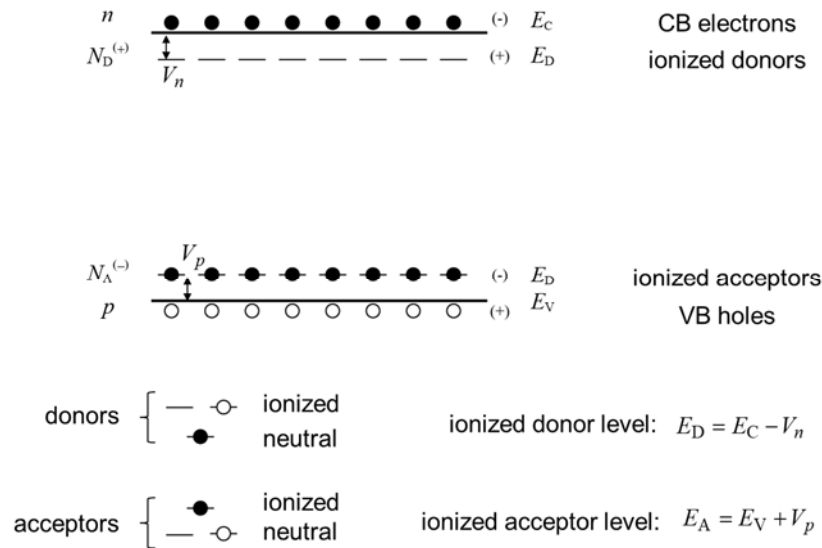
Semiconductor: Doping (IV)

Dopant atoms contribute to the electron and hole concentrations by ionization. Dopant levels indicated on the energy diagram convey the electron energies when the dopant atoms are neutral. This is the case, for example, at $T = 0$ K, when only a single dopant species is present.
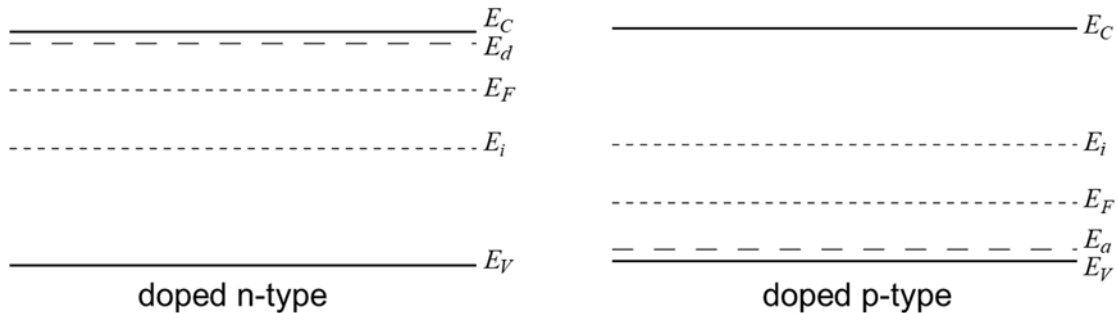
The carrier concentration in a doped semiconductor depends on various factors. With a single, shallow dopant, at 300 K, is often sufficient to start by assuming all shallow acceptors/donors are ionized, i.e., $E_D - E_F \gg kT$, $f(E_D - E_F) \approx 0$. For a material doped with N_D donors, this corresponds to $n = N_D$ and $p = n_i^2 / N_D$. The offset of the Fermi level from the CB edge is then:
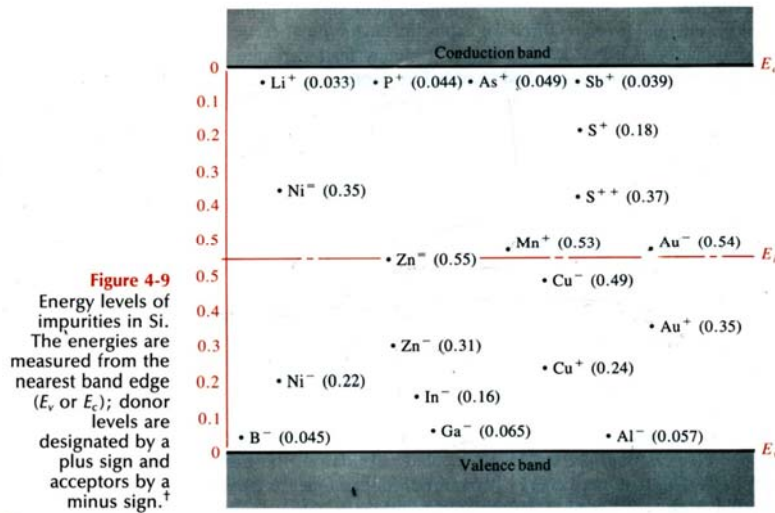
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$$E_C - E_F = kT \cdot \ln\left(\frac{N_C}{N_D}\right)$$

For an acceptor concentration of N_A, we usually start by assuming $p = N_A$ and $n = n_i^2/N_A$. The energy separation of Fermi level from the VB edge is then

$$E_F - E_V = kT \cdot \ln\left(\frac{N_V}{N_A}\right)$$

Semiconductor: Doping (V)

A diagram showing several ionization levels of impurities in Si is shown below [B. G. Streetman, Solid State Electronic Devices, 3rd Ed., Prentice Hall (1990)]. The most useful levels are doping are those close to the CB and VB edges. These are called *shallow* donors and acceptors. Those near the middle of the gap are called *deep levels* and generally act as recombination centers.

Figure 4-9 Energy levels of impurities in Si. The energies are measured from the nearest band edge (E_v or E_c); donor levels are designated by a plus sign and acceptors by a minus sign.[†]

Semiconductor: Doping (VI)

We assumed the dopant levels were fully ionized, that is the ionization energy is essentially zero. This gives $N_D = N_D^{(+)}$, so $n = N_D$. Then find E_F using

$$E_C - E_F = kT \cdot \ln\left(\frac{N_C}{n}\right)$$

It is sometime necessary to check this assumption. The separation of the donor level from E_F is given by:

$$E_D - E_F = (E_C - E_F) - (E_C - E_D) = (E_C - E_F) - V_n$$

The fraction of donor states not ionized is then

$$f(E_D - E_F) = \frac{1}{e^{(E_D - E_F)/kT} + 1}$$

The concentration of ionized donors gives a corrected estimate of n is then:

$$n = N_D^{(+)} = N_D \cdot [1 - f(E_D - E_F)]$$

We can now compute a corrected E_F

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$$E_C - E_F = kT \cdot \ln\left(\frac{N_C}{n}\right)$$

This process is iterated to convergence.

Semiconductor: Doping (VII)

Similarly, for a material doped with N_A acceptors, we can start by assuming $E_F - E_A \gg kT$, $f(E_F - E_A) \approx 1$, giving $p = N_A$. Applying

$$E_F - E_V = kT \cdot \ln\left(\frac{N_V}{p}\right)$$

Then

$$E_F - E_A = (E_F - E_V) - (E_A - E_V) = (E_F - E_V) - V_A$$

Using the revised the fraction $f(E_F - E_A)$ of acceptors that are not ionized, we obtain a corrected estimate of p:

$$p = N_A \cdot f(E_F - E_A)$$

As before, we iterate to convergence.

Semiconductor: Doping (IX)

Consider the example of Si with P at $N_D = 2 \times 10^{16}$ cm^{-3}. The ionization energy is approximately $V_n = 0.044$ eV, and the electron effective mass is $m_C / m_0 = 1.1$. Then $N_C = 2.9 \times 10^{19}$ cm^{-3}. A first estimate, assuming complete ionization ($n = N_D$), gives $E_C - E_F = 0.188$ eV. Then

$$E_D - E_F = (0.188 \text{ eV}) - (0.044 \text{ eV}) = 0.144 \text{ eV}.$$

So the ionized fraction is reduced from 100% to $f(E_D - E_F) = 99.6\%$. Now our best estimate is $n = 1.99 \times 10^{16}$ cm^{-3}. Further iteration has practically no improvement, so our initial assumption is quite valid.

Charge Density

The total charge density in a region includes not only the mobile CB electrons and VB holes, but also the ionized dopants fixed within the lattice. Assuming single ionization of donors and acceptors, the charge density becomes:

$$\rho(x) = p(x) - n(x) + N_D^{(+)}(x) - N_A^{(-)}(x)$$

We expect charge neutrality ($\rho = 0$) in a uniformly doped region, with no external influence, so:

$$n + N_a^{(-)} = p + N_d^{(+)}$$

The densities must satisfy:

$$n = n_i \cdot e^{(E_F - E_i)/kT} \qquad \text{and } p = n_i \cdot e^{(E_i - E_F)/kT}$$

The ionized dopant concentrations are

$$N_A^{(-)} = N_A \cdot [1 - f(E_F - E_A)] \text{ and } N_D^{(+)} = N_D \cdot [1 - f(E_D - E_F)]$$

To find E_F, we can apply a simple algorithm:

$$\text{If } n + N_A^{(-)} > p + N_D^{(+)}, \text{ increase } E_F$$

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If $n + N_A^{(-)} < p + N_D^{(+)}$, decrease E_F

Charge Neutrality (I)

If $N_A = 0$ and $N_D \gg n_i$, then $N_D \approx N_D^{(+)}$

$$n = N_D + p \approx N_D, \quad p \approx \frac{n_i^2}{N_D}$$

Co-doping is when both acceptors and donors are present in the same region. If $N_D - N_A = \Delta n \gg n_i$, we can still assume full ionization: $N_D^{(+)} = N_D$, $N_a^{(-)} = N_a$ However, N_A of the donated electrons serve to ionize (fill) the acceptor levels: Now

$$n \approx \Delta n, \quad p \approx \frac{n_i^2}{\Delta n} \ll \Delta n$$

This is called *compensation*. For example, assume $N_D = 8 \times 10^{16}$ cm^{-3} and $N_A = 2 \times 10^{16}$ cm^{-3}. So $n \approx N_D - N_A = 6 \times 10^{16}$ cm^{-3}.