

Lecture 4

Density of States and Fermi Energy Concepts

Reading:

(Cont'd) Notes and Anderson² sections 2.8-2.13

How do electrons and holes populate the bands?

Density of States Concept

In lower level courses, we state that “Quantum Mechanics” tells us that the number of available states in a cubic cm per unit of energy, the density of states, is given by:

$$g_c(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_c)}}{\pi^2 \hbar^3}, E \geq E_c$$

$$g_v(E) = \frac{m_p^* \sqrt{2m_p^*(E_v - E)}}{\pi^2 \hbar^3}, E \leq E_v$$

$$\text{unit} \equiv \left(\frac{\text{Number of States}}{\text{cm}^3} \right) / \text{eV}$$

How do electrons and holes populate the bands?

Density of States Concept

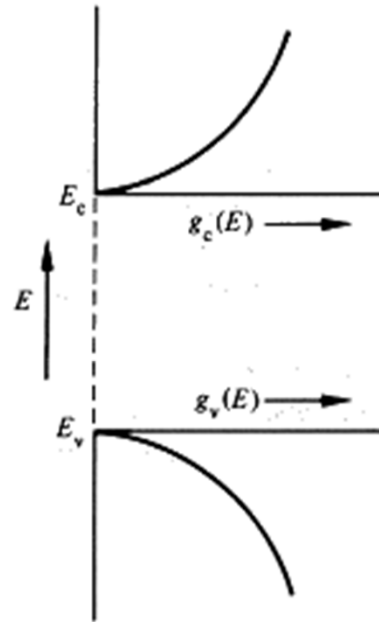


Figure 2.14 General energy dependence of $g_c(E)$ and $g_v(E)$ near the band edges. $g_c(E)$ and $g_v(E)$ are the density of states in the conduction and valence bands, respectively.

Thus, the number of states per cubic centimeter between energy E' and $E'+dE$ is

$$g_c(E')dE \text{ if } E' \geq E_c \text{ and,}$$

$$g_v(E')dE \text{ if } E' \leq E_v \text{ and,}$$

0 otherwise

But where does it come from?

How do electrons and holes populate the bands?

Where Does the Density of States Concept come from?

Approach:

1. Find the smallest volume of k -space that can hold an electron. This will turn out to be related to the largest volume of real space that can confine the electron.
2. Next assume that the average energy of the free electrons (free to move), the fermi energy E_f , corresponds to a wave number k_f . This value of k_f , defines a volume in k -space for which all the electrons must be within.
3. We then simply take the ratio of the total volume needed to account for the average energy of the system to the smallest volume able to hold an electron and that tells us the number of electrons.
4. From this we can differentiate to get the density of states distribution.

How do electrons and holes populate the bands?

Derivation of Density of States Concept

First a needed tool: Consider an electron trapped in an energy well with infinite potential barriers. Recall that the reflection coefficient for infinite potential was 1 so the electron can not penetrate the barrier.

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \Psi = E \Psi$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} - E \Psi = 0$$

$$\frac{\partial^2 \Psi}{\partial x^2} + k^2 \Psi = 0$$

General Solution : $\Psi(x) = A \sin(kx) + B \cos(kx)$

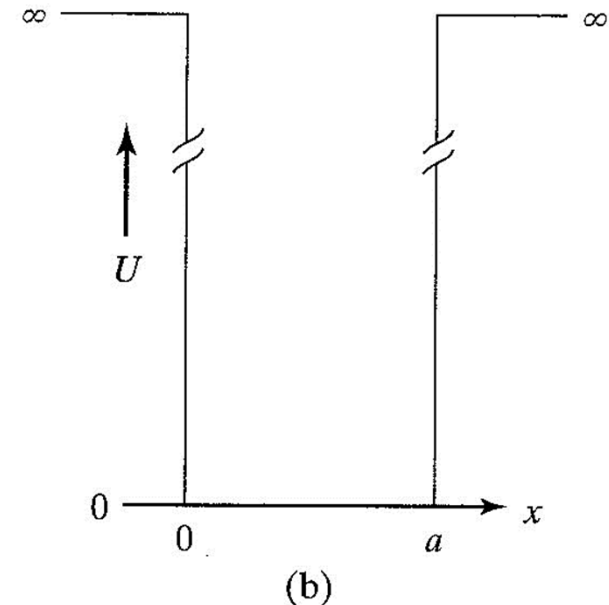
$$\text{where } k = \frac{2\pi}{\lambda} = \sqrt{\frac{2mE}{\hbar^2}} \text{ or } E = \frac{\hbar^2 k^2}{2m}$$

Boundary Conditions :

$$\Psi(0) = 0 \Rightarrow B = 0$$

$$\Psi(a) = 0 \Rightarrow A \sin(ka) = 0 \Rightarrow k = \frac{n\pi}{a} \text{ for } n = \pm 1, \pm 2, \pm 3 \dots$$

$$\Psi_n(x) = A_n \sin\left(\frac{n\pi x}{a}\right) \text{ and } E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$



After Neudeck and Pierret Figure 2.4a

How do electrons and holes populate the bands?

Derivation of Density of States Concept

What does it mean?

$$\Psi_n(x) = A_n \sin\left(\frac{n\pi x}{a}\right) \text{ and } E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

A standing wave results from the requirement that there be a node at the barrier edges (i.e. BC's: $\Psi(0)=\Psi(a)=0$). The wavelength determines the energy. Many different possible "states" can be occupied by the electron, each with different energies and wavelengths.

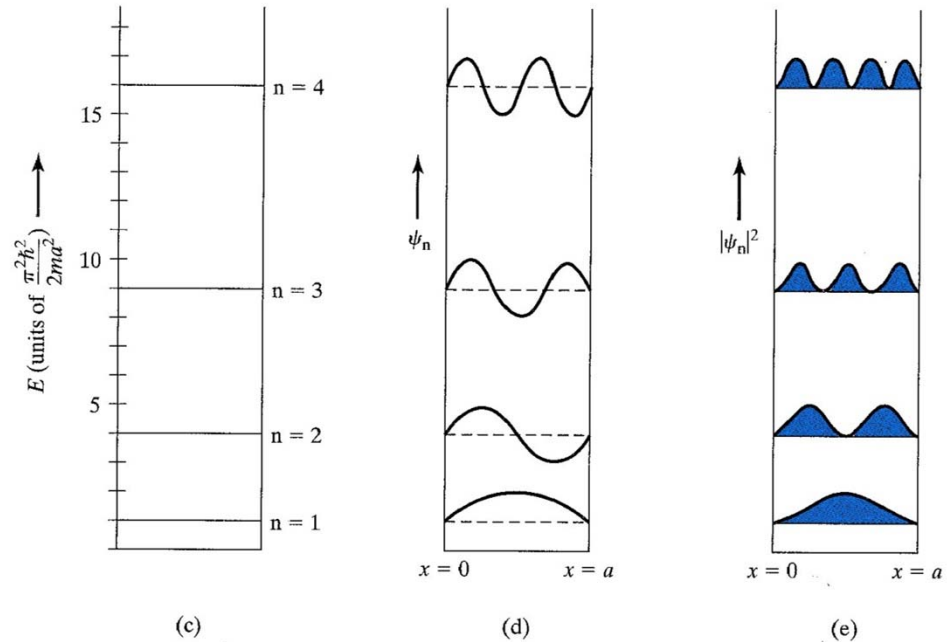


Figure 2.4 Particle in an infinitely deep one-dimensional potential well. (a) Spatial visualization of the particle confinement. (b) The assumed potential energy versus position dependence. (c) First four allowed energy levels. (d) Wavefunctions and (e) $|\psi|^2$ associated with the first four energy levels. $|\psi|^2$ is proportional to the probability of finding the particle at a given point in the potential well.

How do electrons and holes populate the bands?

Derivation of Density of States Concept

What does it mean?

$$\Psi_n(x) = A_n \sin\left(\frac{n\pi x}{a}\right) \text{ and } E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

Solution for much larger “a”. Note: offset vertically for clarity.

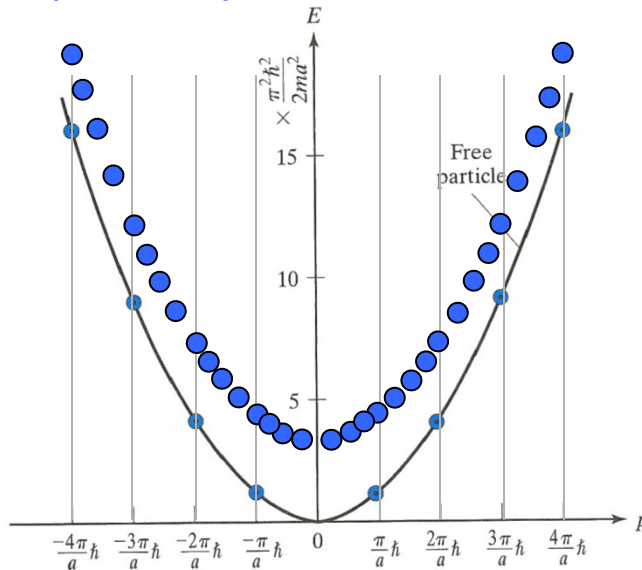


Figure 2.5 Allowed infinite-well particle energy versus counterpropagating wave momentum (discrete points) referenced against the free particle $E-\langle p \rangle$ relationship.

Recall, a free particle has $E \sim k^2$. Instead of being continuous in k^2 , E is discrete in n^2 ! I.e. the energy values (and thus, wavelengths/ k) of a confined electron are quantized (take on only certain values). Note that as the dimension of the “energy well” increases, the spacing between discrete energy levels (and discrete k values) reduces. In the infinite crystal, a continuum same as our free particle solution is obtained.

After Neudeck and Pierret Figure 2.5

How do electrons and holes populate the bands?

Derivation of Density of States Concept

We can use this idea of a set of states in a confined space (1D well region) to derive the number of states in a given volume (volume of our crystal).

Consider the surfaces of a volume of semiconductor to be infinite potential barriers (i.e. the electron can not leave the crystal). Thus, the electron is contained in a 3D box.

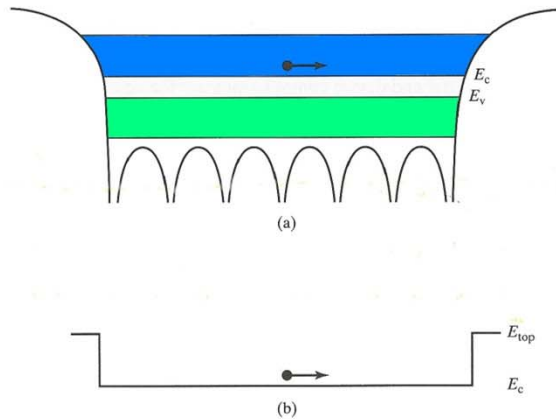


Figure 4.1 (a) Visualization of a conduction band electron moving in a crystal. (b) Idealized pseudo-potential well formed by the crystal surfaces and the band edges.

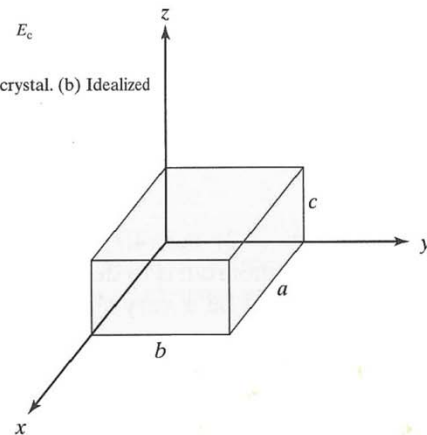


Figure 4.2 Envisioned crystal-sized box (infinitely deep three-dimensional potential well) with x , y , and z dimensions of a , b , and c , respectively.

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \Psi = E\Psi$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} - E\Psi = 0$$

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + k^2 \Psi = 0$$

$$\dots \text{for } 0 < x < a, 0 < y < b, 0 < z < c$$

$$\text{where } k = \frac{2\pi}{\lambda} = \sqrt{\frac{2mE}{\hbar^2}} \text{ or } E = \frac{\hbar^2 k^2}{2m}$$

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Using separation of variables...

$$(1) \quad \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + k^2 \Psi = 0$$

$$(2) \quad \Psi(x, y, z) = \Psi_x(x) \Psi_y(y) \Psi_z(z)$$

Inserting (2) into (1) and dividing by (2) we get...

$$\frac{1}{\Psi_x(x)} \frac{\partial^2 \Psi_x(x)}{\partial x^2} + \frac{1}{\Psi_y(y)} \frac{\partial^2 \Psi_y(y)}{\partial y^2} + \frac{1}{\Psi_z(z)} \frac{\partial^2 \Psi_z(z)}{\partial z^2} + k^2 = 0$$

Since k is a constant for a given energy, each of the three terms on the left side must individually be equal to a constant.

$$\frac{1}{\Psi_x(x)} \frac{\partial^2 \Psi_x(x)}{\partial x^2} + k_x^2 = 0, \quad \frac{1}{\Psi_y(y)} \frac{\partial^2 \Psi_y(y)}{\partial y^2} + k_y^2 = 0, \quad \frac{1}{\Psi_z(z)} \frac{\partial^2 \Psi_z(z)}{\partial z^2} + k_z^2 = 0$$

$$\text{where } k^2 = k_x^2 + k_y^2 + k_z^2$$

So this is just 3 equivalent 1D solutions which we have already done...

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Cont'd...

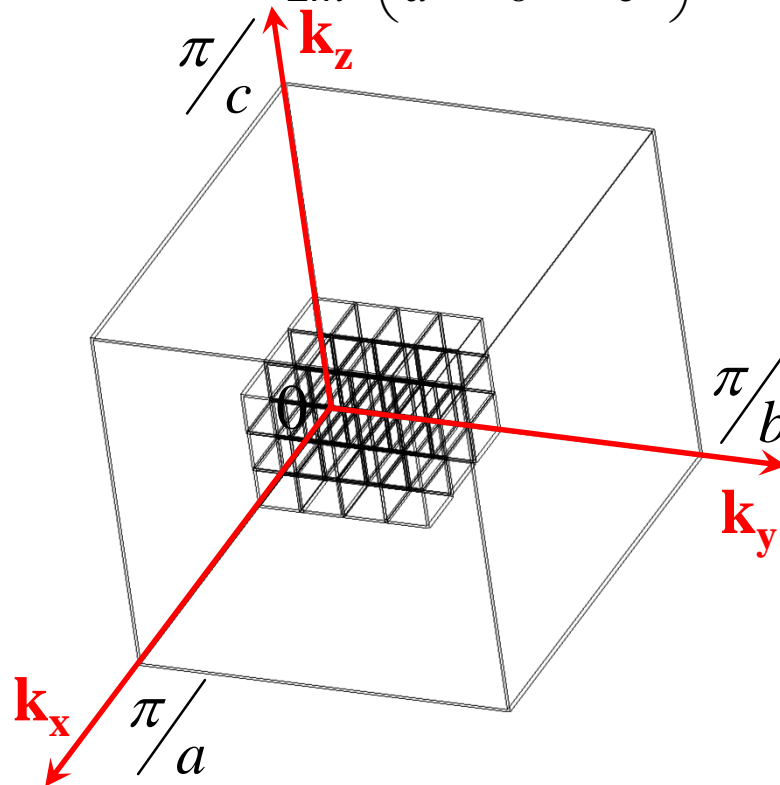
$$\Psi(x, y, z) = \Psi_x(x)\Psi_y(y)\Psi_z(z)$$

$$\Psi(x, y, z) = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

$$\text{where } k_x = \frac{n_x \pi}{a}, \quad k_y = \frac{n_y \pi}{a}, \quad k_z = \frac{n_z \pi}{a}, \quad \text{for } n = \pm 1, \pm 2, \pm 3 \dots$$

$$\text{and } E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Each solution (i.e. each combination of n_x, n_y, n_z) results in a volume of “k-space”. If we add up all possible combinations, we would have an infinite solution. Thus, we will only consider states contained in a “fermi-sphere” (see next page).



How do electrons and holes populate the bands?

Derivation of Density of States Concept

Cont'd...

$$E_f = \frac{\hbar^2 k_f^2}{2m} \Rightarrow \text{defines a momentum value for the average electron energy } E_f$$

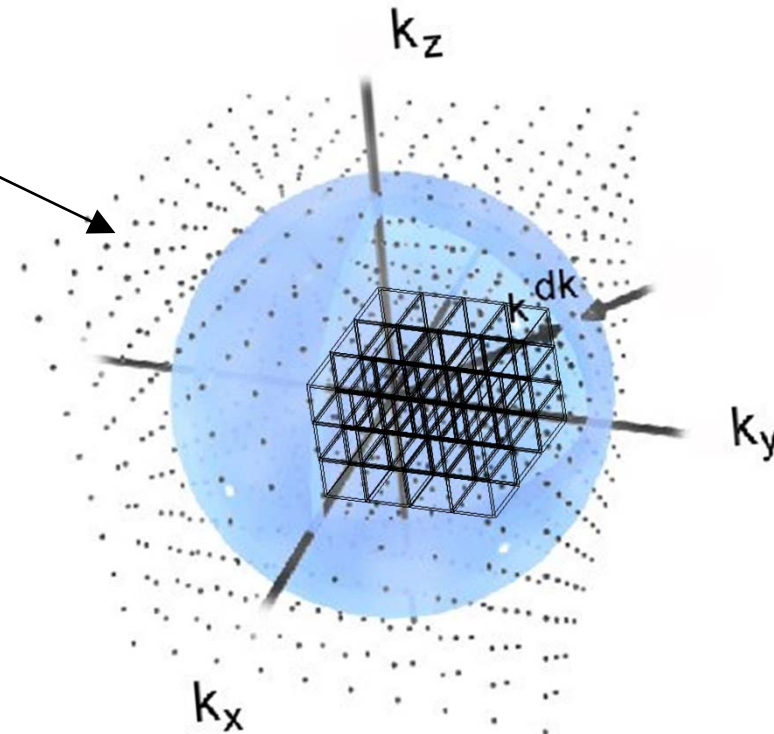
Volume of a single state “cube”:

$$V_{\text{single state}} = \left(\frac{\pi}{a}\right)\left(\frac{\pi}{b}\right)\left(\frac{\pi}{c}\right) = \left(\frac{\pi^3}{V}\right)$$

Volume of a “fermi-sphere”:

$$V_{\text{fermi-sphere}} = \left(\frac{4}{3}\pi k_f^3\right)$$

A “Fermi-Sphere” is defined by the number of states in k-space necessary to hold all the electrons needed to add up to the average energy of the crystal (known as the fermi energy).



“V” is the physical volume of the crystal where as all other volumes used here refer to volume in k-space. Note that: $V_{\text{single-state}}$ is the smallest unit in k-space. $V_{\text{single-state}}$ is required to “hold” a single electron.

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Cont'd...

k-space volume of a single state “cube”: $V_{\text{single state}} = \left(\frac{\pi}{a}\right)\left(\frac{\pi}{b}\right)\left(\frac{\pi}{c}\right) = \left(\frac{\pi^3}{V}\right)$

k-space volume of a “fermi-sphere”: $V_{\text{fermi-sphere}} = \left(\frac{4}{3}\pi k_f^3\right)$

Number of filled states in a fermi-sphere: $\equiv N = \frac{V_{\text{fermi-sphere}}}{V_{\text{single-state}}} 2x\left(\frac{1}{2}\right)x\left(\frac{1}{2}\right)x\left(\frac{1}{2}\right) = \frac{\left(\frac{4}{3}\pi k_f^3\right)}{\left(\frac{\pi^3}{V}\right)4} = \frac{V k_f^3}{3\pi^2}$

Correction for allowing 2 electrons per state (+/- spin)

Correction for redundancy in counting identical states resulting from +/- n_x , +/- n_y , +/- n_z . Specifically, $\sin(-\pi)=\sin(+\pi)$ so the state would be the same. Same as counting only the positive octant in fermi-sphere.

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Cont'd...

Number of filled states
in a fermi-sphere:

$$\equiv N = \frac{V k_f^3}{3\pi^2} \Rightarrow k_f = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

$$E_f = \frac{\hbar^2 k_f^2}{2m} = \frac{\hbar^2 \left(\frac{3\pi^2 N}{V} \right)^{2/3}}{2m} \Rightarrow E_f = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m} \text{ where } n \text{ is the electron density}$$

E_f varies in Si from 0 to ~1.1 eV as n varies from 0 to ~ $5 \times 10^{21} \text{cm}^{-3}$

Thus,
$$N = \frac{V k_f^3}{3\pi^2} = \left(\frac{V}{3\pi^2} \right) \left(\frac{2mE}{\hbar^2} \right)^{3/2}$$

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Cont'd...

$$N = \frac{V k_f^3}{3\pi^2} = \left(\frac{V}{3\pi^2} \right) \left(\frac{2mE}{\hbar^2} \right)^{3/2}$$

Finally, we can define the density of states function:

$$G(E) \equiv \# \text{ of states per energy per volume} = \left(\frac{dN}{dE} \right) / V$$

$$G(E) = \left[\frac{3}{2} \left(\frac{V}{3\pi^2} \right) \left(\frac{2mE}{\hbar^2} \right)^{1/2} \left(\frac{2m}{\hbar^2} \right) \right] / V$$

$$G(E) = \frac{m\sqrt{2m}}{\pi^2 \hbar^3} \sqrt{E}$$

Applying to the semiconductor we must recognize $m \rightarrow m^*$ and since we have only considered kinetic energy (not the potential energy) we have $E \rightarrow E - E_c$

$$G(E) = \frac{m^* \sqrt{2m^*}}{\pi^2 \hbar^3} \sqrt{E - E_c}$$

How do electrons and holes populate the bands?

Probability of Occupation (Fermi Function) Concept

Now that we know the number of available states at each energy, how do the electrons occupy these states?

We need to know how the electrons are “distributed in energy”.

Again, Quantum Mechanics tells us that the electrons follow the “Fermi-distribution function”.

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}} \quad \text{where } k \equiv \text{Boltzmann constant, } T \equiv \text{Temperature in Kelvin}$$

and $E_F \equiv$ Fermi energy (\sim average energy in the crystal)

$f(E)$ is the probability that a state at energy E is *occupied*

$1-f(E)$ is the probability that a state at energy E is *unoccupied*

How do electrons and holes populate the bands?

Probability of Occupation (Fermi Function) Concept

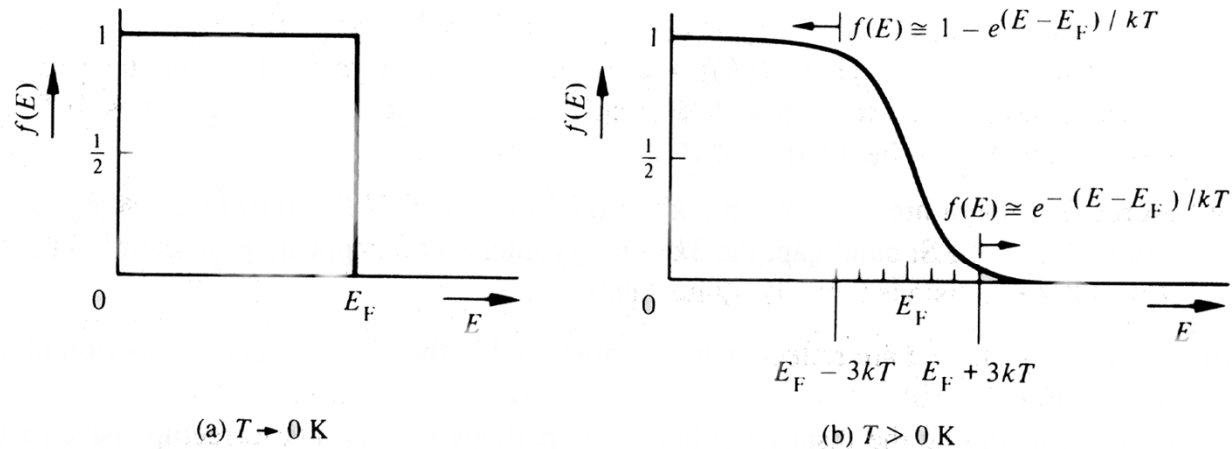


Figure 2.15 Energy dependence of the Fermi function. (a) $T \rightarrow 0 \text{ K}$; (b) generalized $T > 0 \text{ K}$ plot with the energy coordinate expressed in kT units.

At $T=0\text{K}$, occupancy is “digital”: No occupation of states above E_F and complete occupation of states below E_F

At $T>0\text{K}$, occupation probability is reduced with increasing energy.

$f(E=E_F) = 1/2$ regardless of temperature.

How do electrons and holes populate the bands?

Probability of Occupation (Fermi Function) Concept

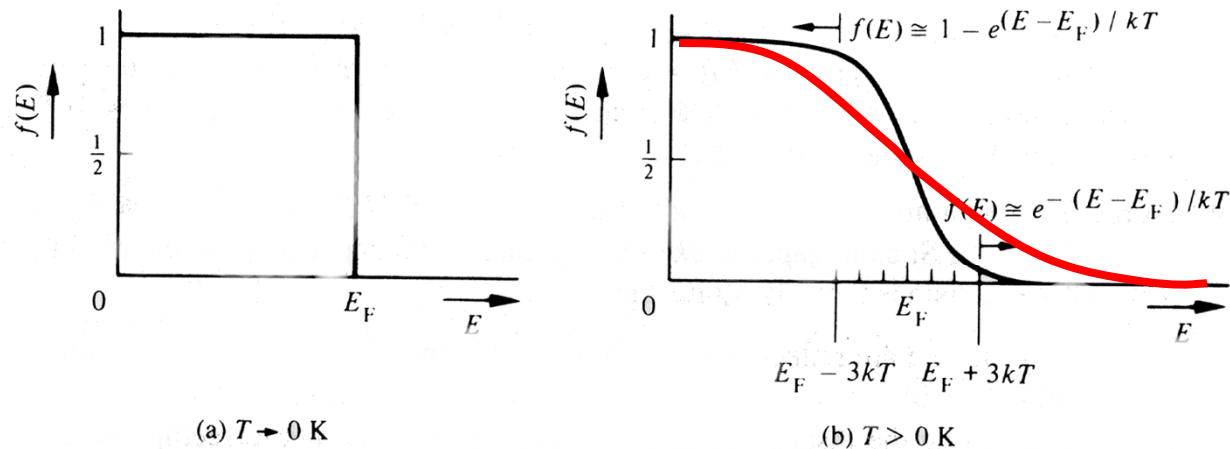


Figure 2.15 Energy dependence of the Fermi function. (a) $T \rightarrow 0 \text{ K}$; (b) generalized $T > 0 \text{ K}$ plot with the energy coordinate expressed in kT units.

At $T=0\text{K}$, occupancy is “digital”: No occupation of states above E_F and complete occupation of states below E_F

At $T>0\text{K}$, occupation probability is reduced with increasing energy.

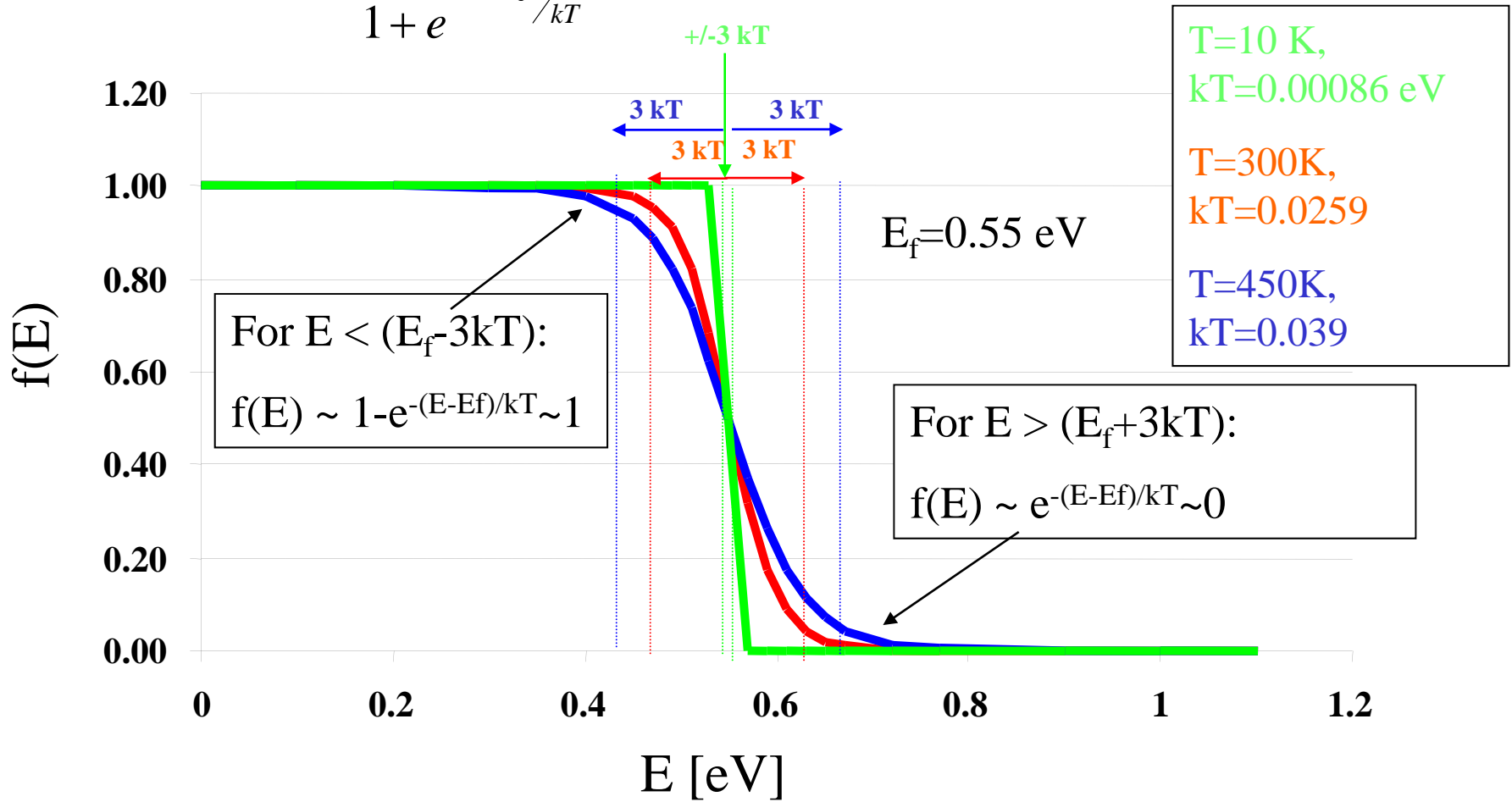
$f(E=E_F) = 1/2$ regardless of temperature.

At higher temperatures, higher energy states can be occupied, leaving more lower energy states unoccupied ($1-f(E)$).

How do electrons and holes populate the bands?

Probability of Occupation (Fermi Function) Concept

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



But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

Consider a system of N total electrons spread between S allowable states. At each energy, E_i , we have S_i available states with N_i of these S_i states filled.

We assume the electrons are indistinguishable¹.

Constraints for electrons:

- (1) Each allowed state can accommodate at most, only one electron (neglecting spin for the moment)
- (2) $N = \sum N_i = \text{constant}$; the total number of electrons is fixed
- (3) $E_{\text{total}} = \sum E_i N_i$; the total system energy is fixed

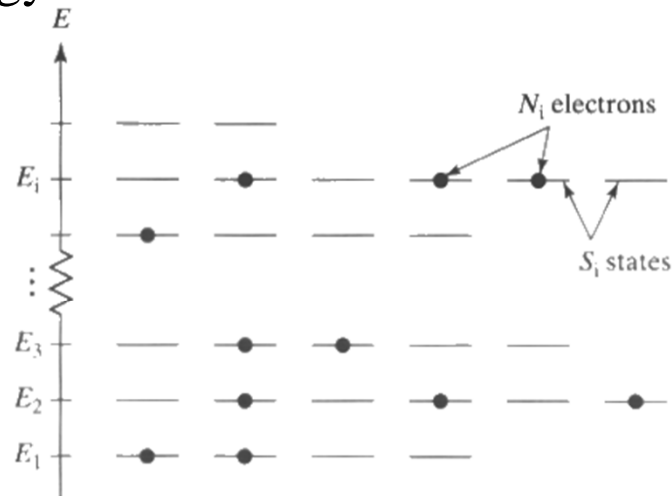


Figure 4.5 Envisioned multi-level energy system of a totally arbitrary nature which contains S_i states and N_i electrons at an energy E_i ($i = 1, 2, 3, \dots$).

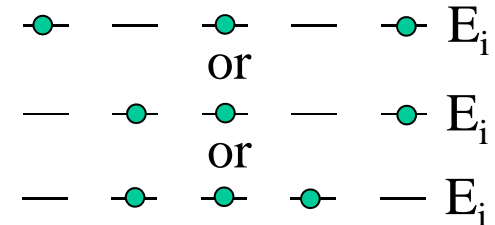
¹A simple test as to whether a particle is indistinguishable (statistically invariant) is when two particles are interchanged, did the electronic configuration change?

But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

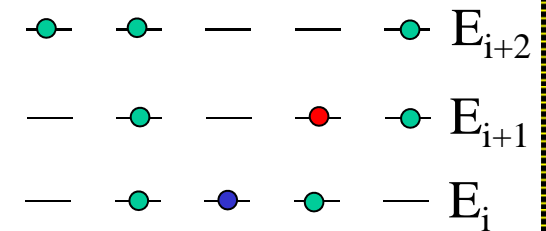
How many ways, W_i , can we arrange at each energy, E_i , N_i indistinguishable electrons into the S_i available states.

$$W_i = \frac{S_i}{(S_i - N_i)! N_i!}$$



When we consider more than one level (i.e. all i 's) the number of ways we can arrange the electrons increases as the product of the W_i 's .

$$W = \prod_i W_i = \prod_i \frac{S_i}{(S_i - N_i)! N_i!}$$



If all possible distributions are equally likely, then the probability of obtaining a specific distribution is proportional to the number of ways that distribution can be constructed (in statistics, this is the distribution with the most “complexions”). For example, interchanging the blue and red electron would result in two different ways (complexions) of obtaining the same distribution. The most probable distribution is the one that has the most variations that repeat that distribution. To find that maximum, we want to maximize W with respect to N_i 's . Thus, we will find $dW/dN_i = 0$. However, to eliminate the factorials, we will first take the natural log of the above...

$$\ln(W) = \sum \ln(S_i!) - \ln([S_i - N_i]!) - \ln(N_i!)$$

... then we will take $d(\ln[W])/dN_i=0$. Before we do that, we can use Stirling's Approximation to eliminate the factorials.

But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

Using Stirling's Approximation, $\ln(x!) \sim (x \ln(x) - x)$ so that the above becomes,

$$\ln(W) = \sum_i \ln(S_i!) - \ln([S_i - N_i]!) - \ln(N_i!)$$

⇓

$$\ln(W) = \sum_i S_i \ln(S_i) - \cancel{S_i} - (S_i - N_i) \ln([S_i - N_i]) + \cancel{(S_i - N_i)} - N_i \ln(N_i) + \cancel{N_i}$$

Collecting like terms,

$$\ln(W) = \sum_i S_i \ln(S_i) - (S_i - N_i) \ln([S_i - N_i]) - N_i \ln(N_i)$$

Now we can maximize W with respect to N_i 's. Note that since $d(\ln W) = dW/W$ when $dW=0$, $d(\ln[W])=0$.

$$\frac{d \ln(W)}{dN_i} = \sum_i \frac{\partial \ln(W)}{\partial N_i} = \sum_i [\ln([S_i - N_i]) + 1 - \ln(N_i) - 1]$$

$$d \ln(W) = \sum_i [\ln([S_i - N_i]) + \cancel{1} - \ln(N_i) - \cancel{1}] dN_i$$

To find the maximum, we set the derivative equal to 0...

Where we have used $\frac{d[x \ln(x)]}{dx} = \ln(x) + 1$

$$(4) \quad d \ln(W) = 0 = \sum_i \left[\ln \left(\frac{S_i}{N_i} - 1 \right) \right] dN_i$$

But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

From our original constraints, (2) and (3), we get...

$$\sum_i N_i = N \Rightarrow \sum_i d(N_i) = 0$$
$$\sum_i E_i N_i = E_{total} \Rightarrow \sum_i E_i d(N_i) = 0$$

Using the method of undetermined multipliers (Lagrange multiplier method) we multiply the above constraints by constants $-\alpha$ and $-\beta$ and add to equation 4 to get ...

$$\sum_i -\alpha d(N_i) = 0$$
$$\sum_i -\beta E_i d(N_i) = 0$$

⇓

$$d \ln(W) = 0 = \sum_i \left[\ln \left(\frac{S_i}{N_i} - 1 \right) - \alpha - \beta E_i \right] dN_i$$

which requires that $\ln \left(\frac{S_i}{N_i} - 1 \right) - \alpha - \beta E_i = 0$ for all i

But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

This final relationship can be solved for the ratio of filled states, N_i per states available S_i ...

$$\ln\left(\frac{S_i}{N_i} - 1\right) - \alpha - \beta E_i = 0$$

⇓

$$f(E_i) = \frac{S_i}{N_i} = \frac{1}{1 + e^{\alpha + \beta E_i}}$$

in the case of of semiconductors, we have

$$\alpha = -\frac{E_F}{kT} \quad \text{and} \quad \beta = \frac{1}{kT}$$

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

How do electrons and holes populate the bands?

Probability of Occupation

We now have the density of states describing the density of available states versus energy and the probability of a state being occupied or empty. Thus, the density of electrons (or holes) occupying the states in energy between E and $E+dE$ is:

Electrons/cm³ in the conduction band between Energy E and $E+dE$

$$g_c(E) f(E) dE \quad \text{if } E \geq E_c \quad \text{and,}$$

Holes/cm³ in the valence band between Energy E and $E+dE$

$$g_v(E) [1 - f(E)] dE \quad \text{if } E \leq E_v \quad \text{and,}$$

0 otherwise

How do electrons and holes populate the bands?

Band Occupation

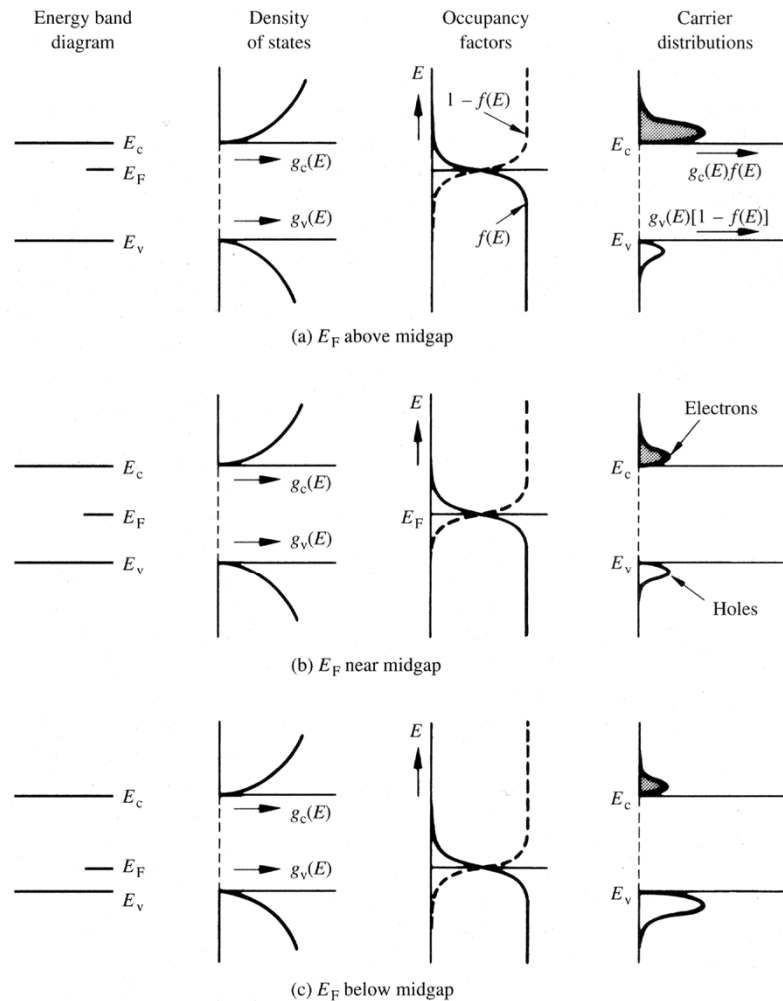
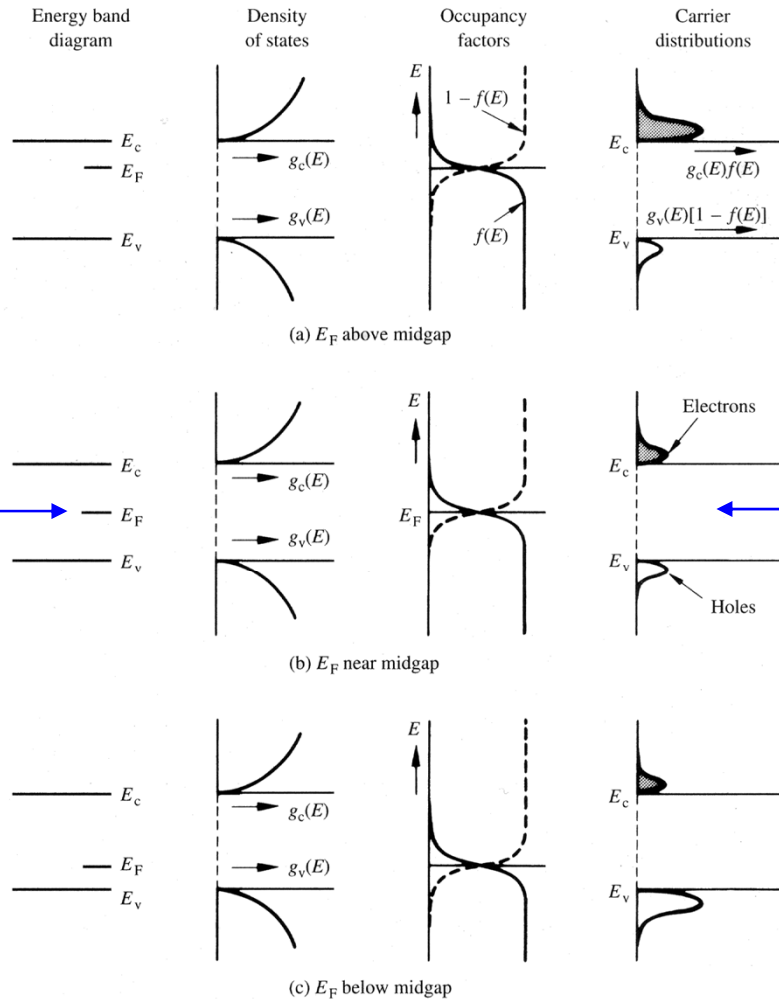


Figure 2.16 Carrier distributions (not drawn to scale) in the respective bands when the Fermi level is positioned (a) above midgap, (b) near midgap, and (c) below midgap. Also shown in each case are coordinated sketches of the energy band diagram, density of states, and the occupancy factors (the Fermi function and one minus the Fermi function).

How do electrons and holes populate the bands?

Intrinsic Energy (or Intrinsic Level)



E_f is said to equal E_i (intrinsic energy) when...



...Equal numbers of electrons and holes

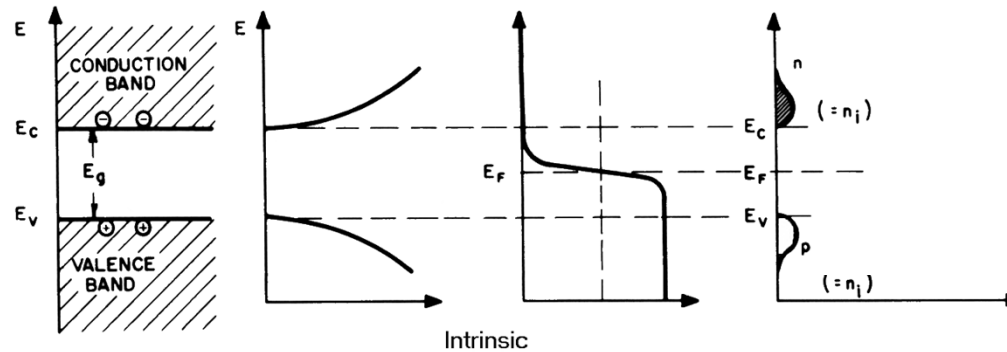


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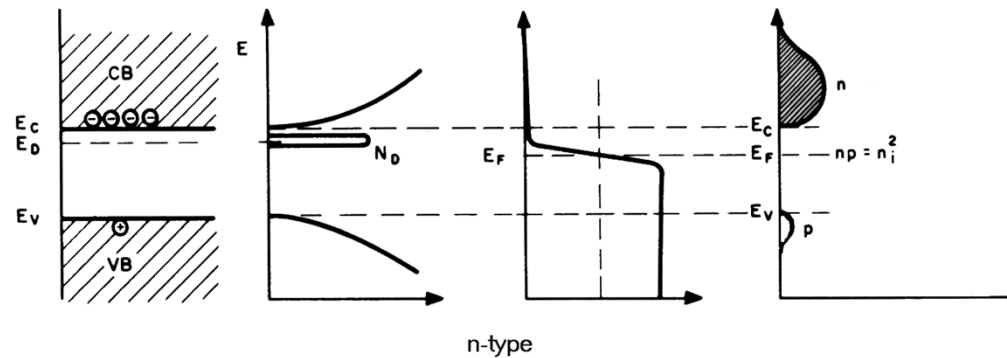
How do electrons and holes populate the bands?

Additional Dopant States

Intrinsic:
Equal number
of electrons
and holes



n-type: more
electrons than
holes



p-type: more
holes than
electrons

