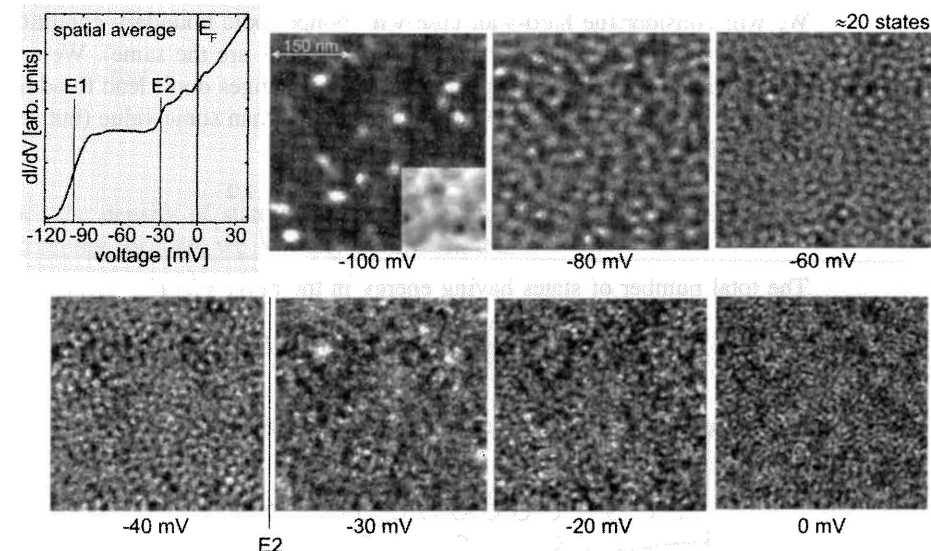


related material for semiconductor materials is presented. Then, in Chapter 9, we revisit quantum well, quantum wire, and quantum dot structures, and discuss implementations using semiconductor materials. Important applications of semiconducting quantum dots are described, especially relating to their optical properties.

Chapter 10 describes the movement of charge over nanoscopic (and sometimes larger) length scales. Of course, the flow of electrical current in wires and in macroscopic circuits is well known, and the concept of resistance is integral to any discussion of current flow. Modeling a material as having a certain resistivity is a standard technique in electrical technology, with the classical concept of resistivity being related to electron collisions with the material lattice, or with impurities.[†] The length an electron travels between collisions depends on the material and on the temperature, but it is generally on the order of tens of nanometers, or more. However, when device length scales on the order of a few nanometers are of interest, such that, on average, few or no collisions will take place, obviously a collision-based model will not suffice. This is the regime of what is called *ballistic transport*, and in Chapter 10, the general concepts of ballistic transport are described. In this chapter as well, transport in carbon nanotubes and nanowires is discussed, as is the transport of spin.

PARTICLE STATISTICS AND DENSITY OF STATES



The local density of states of Fe-covered InAs, obtained by STM. Voltage values are the various bias voltages used. (Courtesy of Prof. Dr. Roland Wiesendanger, Executive Director of the Institute of Applied Physics (IAP) and Interdisciplinary Nanoscience Center Hamburg (INCH).)

In this chapter, the concepts of density of states and particle statistics are introduced. In short, density of states relates to how many electronic states are available in a certain structure at a certain energy, and particle statistics give the probability that a certain energy state will be occupied. Recall that in previous quantum well problems, the *allowed* energy states were obtained (e.g., (4.53)), but there was no way to say which states would actually be “filled” by electrons, except if we had a certain number of electrons in the ground state. With the concepts developed in this chapter, we can examine how many allowed states are near an energy of interest, and the probability that those states will actually be filled with electrons.

[†]However, recall that in the quantum model described in Chapter 5, collisions are actually necessary to frustrate Bloch oscillations and allow current to flow.

Therefore, density of states and particle statistics concepts are indispensable in the study of bulk materials, and, as previously discussed, have utility when considering relatively small material samples as well.

8.1 DENSITY OF STATES

Considering again the case of an electron in a three-dimensional bounded region of space (Section 4.3.2), we often find it useful to know how many quantum states lie within a particular energy range, say, between E and $E - \Delta E$. From the equation for energy, (4.54), the number of states below a certain energy E_n is equal to the number of states inside a sphere of radius

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2} = \sqrt{\frac{E_n}{E_1}}, \quad (8.1)$$

as shown in Fig. 8.1.

We will consider the hard-wall case with nonperiodic boundary conditions ($\alpha = 1/2$ in (4.60); the results using periodic boundary conditions are the same). We only count the first octant of the aforementioned sphere, since sign changes don't lead to additional states. Then, the total number of states N_T having energy less than some value (but with $E \gg E_1$) is approximately the volume of the octant,

$$N_T = \frac{1}{8} \frac{4}{3} \pi n^3 = \frac{\pi}{6} \left(\frac{E}{E_1} \right)^{3/2}. \quad (8.2)$$

The total number of states having energy in the range $(E, E - \Delta E)$ is

$$\Delta N_T = \frac{\pi}{6E_1^{3/2}} \left((E)^{3/2} - (E - \Delta E)^{3/2} \right) \quad (8.3)$$

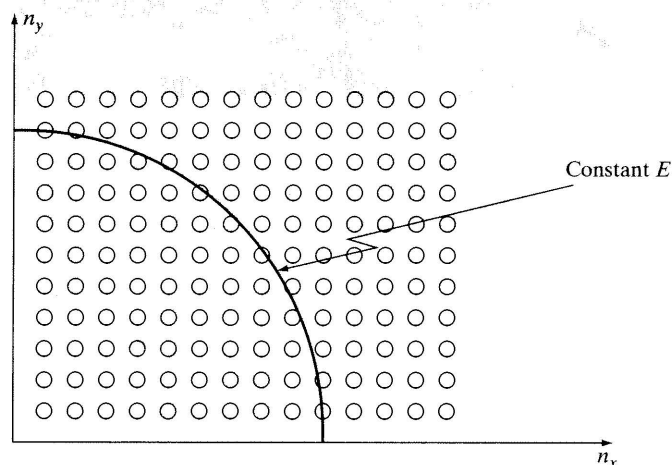


Figure 8.1 Electronic states in the n_y - n_x plane. The states below a certain energy E_n lie inside a circle of radius E_n/E_1 .

$$\begin{aligned} &= \frac{\pi}{6E_1^{3/2}} \left((E)^{3/2} - E^{3/2} \left(1 - \frac{\Delta E}{E} \right)^{3/2} \right) \\ &\simeq \frac{\pi E^{3/2}}{6E_1^{3/2}} \left(1 - \left(1 - \frac{3}{2} \frac{\Delta E}{E} \right) \right) \\ &= \frac{\pi E^{1/2}}{4E_1^{3/2}} (\Delta E), \end{aligned}$$

where we used $(1 - x)^p \simeq 1 - px$ for $x \ll 1$.

The *density of states* (DOS), $N(E)$, is defined as the number of states per unit volume per unit energy around an energy E . The total number of states in a unit volume in an energy interval dE around an energy E is (replacing ΔN_T , ΔE with dN_T , dE , respectively)

$$dN_T = N(E) dE = \frac{\pi E^{1/2}}{4E_1^{3/2}} dE, \quad (8.4)$$

so that

$$N(E) = \frac{\pi E^{1/2}}{4E_1^{3/2}} = \frac{2^{3/2} m_e^{*3/2} E^{1/2}}{4\hbar^3 \pi^2}$$

(since the density of states is per unit volume, we set $L^3 = 1$ in the expression for E_1). Accounting for spin, we multiply by 2, such that

$$N(E) = \frac{2^{1/2} m_e^{*3/2} E^{1/2}}{\hbar^3 \pi^2}, \quad (8.5)$$

and if the electron has potential energy V_0 , the density of states becomes

$$N(E) = \frac{2^{1/2} m_e^{*3/2} (E - V_0)^{1/2}}{\hbar^3 \pi^2}, \quad (8.6)$$

where $E > V_0$. The density of states is shown in Fig. 8.2.

Note that (8.6) was derived assuming the energy relationship (4.54), which holds for an electron in an ideal quantum well. More generally, the parabolic E - k relationship usually holds for electrons in real materials near the bandedges, which are generally the most important energies. However, energy relationships different from (4.54) will result in different density of states. For example, electrons at energies removed from the bandedges generally do not have a parabolic E - k relationship. Phonons also have a different density of states, since their energy equation is different from (4.54).

To gain an appreciation of (8.6), assuming $m_e^* = m_e$ we have

$$N(E) = 1.06 \times 10^{56} (E_{\text{Joules}} - V_0)^{1/2} \quad \text{J}^{-1} \text{m}^{-3}, \quad (8.7)$$

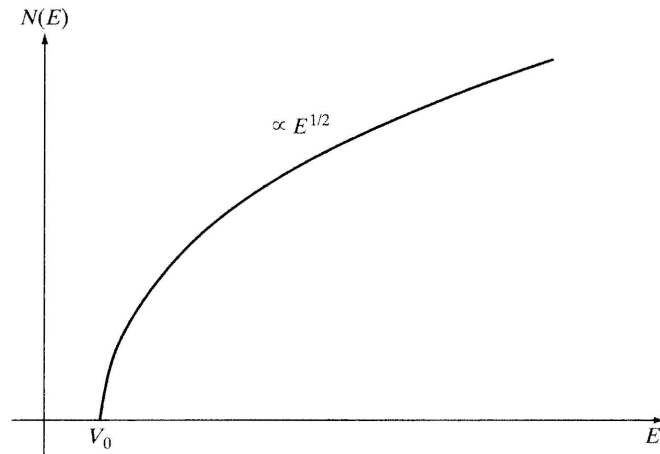


Figure 8.2 Density of states for a three-dimensional system.

where E_{Joules} indicates that the energy is in units of joules. Often the DOS is expressed in units of $\text{eV}^{-1}\text{cm}^{-3}$, where $E_{\text{Joules}} = E_{\text{eV}} \times e$. Therefore,

$$\begin{aligned} N(E) &= 1.06 \times 10^{56} (E_{\text{Joules}} - V_0)^{1/2} \frac{1}{\text{J}} \frac{1}{\text{m}^3} \times \frac{\text{J}}{\frac{1}{e} \text{eV}} \frac{\text{m}^3}{(100 \text{ cm})^3} & (8.8) \\ &= 1.7 \times 10^{31} (E_{\text{Joules}} - V_0)^{1/2} \quad \text{eV}^{-1}\text{cm}^{-3} \\ &= 6.8 \times 10^{21} (E_{\text{eV}} - V_{0,\text{eV}})^{1/2} \quad \text{eV}^{-1}\text{cm}^{-3}. \end{aligned}$$

For example, if $E = 0.1 \text{ eV}$ and $V_0 = 0$, then $N(E) = 2.15 \times 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$.

Thinking physically, if there are enough electrons to fill the various states (or, at least fill the states of interest), then the density of states $N(E)$ is the density of electrons having energy E . Furthermore, often one is interested in the *local density of states* (LDOS), which is the density of states as a function of position in a material. This can be obtained from STM images by measuring the differential conductance dI/dV , since the tunneling current is proportional to the local electron density. Such an image is shown on page 261.

8.1.1 Density of States in Lower Dimensions

In discussing electron transport in nanosystems we will often need the density of states in sub-three-dimensional systems. In one dimension, such as for a quantum wire, the density of states is defined as the number of available states per unit length per unit energy around an energy E . To be specific, for an electron confined to a line segment of length L , from (4.35),

$$E_n = \frac{\hbar^2 \pi^2}{2m_e^* L^2} n^2, \quad (8.9)$$

and the total number of states below a certain energy is equal to the number of states inside an interval of length

$$N_T = n = \left(\frac{E}{E_1} \right)^{1/2}. \quad (8.10)$$

The total number of states having energy in the range $(E, E - \Delta E)$ is

$$\begin{aligned} \Delta N_T &= \frac{1}{E_1^{1/2}} (E^{1/2} - (E - \Delta E)^{1/2}) = \frac{1}{E_1^{1/2}} \left(E^{1/2} - E^{1/2} \left(1 - \frac{\Delta E}{E} \right)^{1/2} \right) \\ &\simeq \frac{1}{E_1^{1/2}} \left(E^{1/2} - E^{1/2} \left(1 - \frac{\Delta E}{2E} \right) \right) = \frac{1}{E_1^{1/2} E^{1/2}} \left(\frac{\Delta E}{2} \right). \end{aligned} \quad (8.11)$$

The total number of states in a unit length in an energy interval dE around an energy E is (again, replacing ΔN_T , ΔE with dN_T , dE , respectively),

$$dN_T = N(E) dE = \frac{1}{2} \frac{1}{E_1^{1/2} E^{1/2}} dE, \quad (8.12)$$

so that

$$N(E) = \frac{1}{2} \frac{1}{E_1^{1/2} E^{1/2}} = \frac{\sqrt{2m_e^*}}{2\hbar\pi} E^{-1/2}. \quad (8.13)$$

(Since the density of states is per unit length, we set $L = 1$.) Accounting for spin, we multiply by 2 to obtain

$$N(E) = \frac{\sqrt{2m_e^*}}{\pi\hbar} E^{-1/2}, \quad (8.14)$$

and if the electron has potential energy V_0 , we have

$$N(E) = \frac{\sqrt{2m_e^*}}{\pi\hbar} (E - V_0)^{-1/2}, \quad (8.15)$$

where $E > V_0$. The density of states for an electron confined to a one-dimensional line segment is shown in Fig. 8.3.

Using similar ideas, we find that the density of states for an electron confined to a two-dimensional region of space (such as a quantum well) is

$$N(E) = \frac{m_e^*}{\pi\hbar^2}, \quad (8.16)$$

for $E > V_0$, which is shown in Fig. 8.4. For example, if an electron is confined to two dimensions, with $m_e^* = m_e$,

$$N(E) = \frac{m_e}{\pi\hbar^2} = 2.6 \times 10^{37} \text{ J}^{-1}\text{m}^{-2} = 4.17 \times 10^{14} \text{ eV}^{-1}\text{cm}^{-2}. \quad (8.17)$$

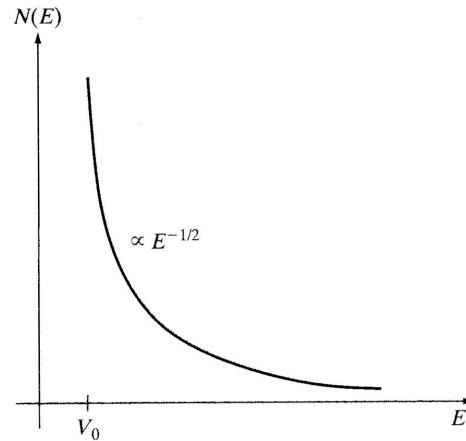


Figure 8.3 Density of states for a one-dimensional system.

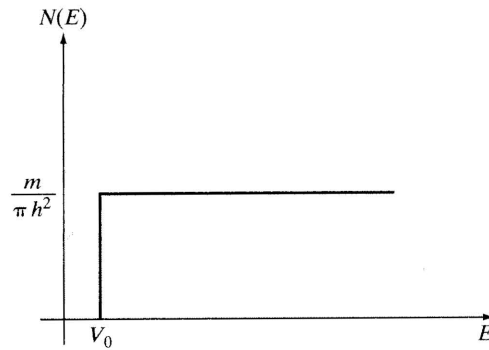


Figure 8.4 Density of states for a two-dimensional system.

The previous derivations made use of the fact that, because the structure was large in three, two, or one dimension, the energy states E_n formed a quasi continuum. That is, we start with the discrete states E_n , but then assume that the energy levels are closely spaced in obtaining the density of states. However, in a zero-dimensional system (such as a quantum dot), the states are truly discrete (i.e., they don't form a quasi continuum). So in this case, the density of states is merely a delta function,

$$N(E) = 2 \sum_n \delta(E - E_n), \quad (8.18)$$

where the factor of two accounts for spin. In real quantum dots, the infinitely narrow delta functions are broadened by electron collisions in the material comprising the dot.

All physically realizable structures are actually three dimensional, and so it may seem strange to consider low-dimensional systems. However, as discussed previously, three-dimensional structures that can appropriately confine electrons can implement an effectively

two-, one-, and even zero-dimensional system. The density of states in quantum structures will be further discussed in Chapter 9.

8.1.2 Density of States in a Semiconductor

We found previously that the three-dimensional density of states for electrons in a constant potential V_0 (i.e., in an empty box) is (8.6),

$$N(E) = \frac{2^{1/2} m_e^{*3/2} (E - V_0)^{1/2}}{\hbar^3 \pi^2}, \quad (8.19)$$

where $E > V_0$. In a crystalline solid, this expression also holds because the effective mass can account for the crystal structure, and the potential can account for energy bandedges. For example, the three-dimensional density of states in a semiconductor is given by

$$N_c(E) = \frac{2^{1/2} m_c^{*3/2} (E - E_c)^{1/2}}{\hbar^3 \pi^2}, \quad (8.20)$$

$$N_v(E) = \frac{2^{1/2} m_v^{*3/2} (E_v - E)^{1/2}}{\hbar^3 \pi^2}, \quad (8.21)$$

where the subscript indicates either the conduction or valence band, $m_{c,v}^*$ is the effective mass appropriate to the band,[†] $E > E_c$ for N_c , and $E < E_v$ for N_v . For semiconductors where the effective mass differs along different directions, the most appropriate effective mass to use is $m^* = (m_1^* m_2^* m_3^*)^{1/3}$, where m_i^* is the effective mass in the i th direction. For silicon the effective mass varies in two directions, resulting in the longitudinal and transverse effective mass, m_l^* and m_t^* , respectively. Therefore, in the conduction band of silicon, accounting for the six equivalent conduction band valleys, we find that an appropriate density of states is

$$N_c(E) = 6 \frac{2^{1/2} m_c^{*3/2} (E - E_c)^{1/2}}{\hbar^3 \pi^2}, \quad (8.22)$$

where

$$m_c^* = (m_l^* m_t^{*2})^{1/3}. \quad (8.23)$$

8.2 CLASSICAL AND QUANTUM STATISTICS

In earlier chapters, we have found solutions to Schrödinger's equation for free electrons, and for electrons confined to certain regions of space. These solutions represented *possible*

[†]Note that the density of states is higher for larger effective mass values. Thus, the heavy holes tend to denominate the properties of the valence band, although both heavy and light holes are important.

states of the corresponding quantum system. In the previous section, we obtained the density of states, which describes the number of these states in the vicinity of a certain energy. What remains to be found is the number of occupied states, i.e., which states, and how many states, are actually filled.[†] For this we need to know the probability of a state being occupied at an energy E . This probability is given by the distribution $f(E)$, and next we consider several common distributions.

1. Classical or Boltzmann Distribution

This distribution applies when particles are distinguishable from each other (such as classical particles), with no other constraints on their behavior. The Boltzmann distribution arises from classical statistical mechanics, and is given by

$$f^B(E) = f^B(E, \mu, T) = e^{-\frac{E-\mu}{k_B T}}. \quad (8.24)$$

The quantity μ is the chemical potential, usually simply replaced by the Fermi energy E_F , and k_B is Boltzmann's constant ($k_B = 1.38 \times 10^{-23}$ J/K).

2. Fermi–Dirac Distribution

The Fermi–Dirac distribution applies when the particles in question are indistinguishable, and when only one particle can occupy a particular state (e.g., electrons). Therefore, the Fermi–Dirac distribution applies to quantum particles that obey the exclusion principle, and is given by

$$f(E) = f(E, \mu, T) = \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1}, \quad (8.25)$$

where again we usually make the replacement $\mu = E_F$. When $E - E_F \gg k_B T$ (known as the *Boltzmann approximation*; $k_B T \simeq 0.025$ eV at room temperature), the first term in the denominator is large compared to the second term, and the Fermi–Dirac distribution becomes the classical Boltzmann distribution (8.24). In the limit $T = 0$, the Fermi–Dirac distribution becomes a step function,

$$f(E, E_F, T = 0) = \begin{cases} 0, & E > E_F, \\ 1, & E < E_F, \end{cases} \quad (8.26)$$

as shown in Fig. 8.5. Thus, at $T = 0$ K, all states below E_F are completely filled and all states above E_F are empty. Although the step function is not well defined at $E = E_F$, since for all $T > 0$ the Fermi–Dirac distribution crosses through the point $f(E) = 1/2$ when $E = E_F$, then $f(E = E_F, E_F, 0)$ can be defined to be $1/2$. The Fermi–Dirac distribution for $T \gg 0$ is also shown in Fig. 8.5, where it can be seen that only states within a few $k_B T$ of the Fermi energy are likely to be excited. In many materials (especially metals) at even quite high temperatures, $k_B T$ is very small

[†]As previously remarked, by a “filled state” we mean that an electron is in that state, i.e., that an electron is represented by the corresponding state function. For a one-electron system, one state would be filled; the electron is in a certain state. For N electrons, N states would be filled.

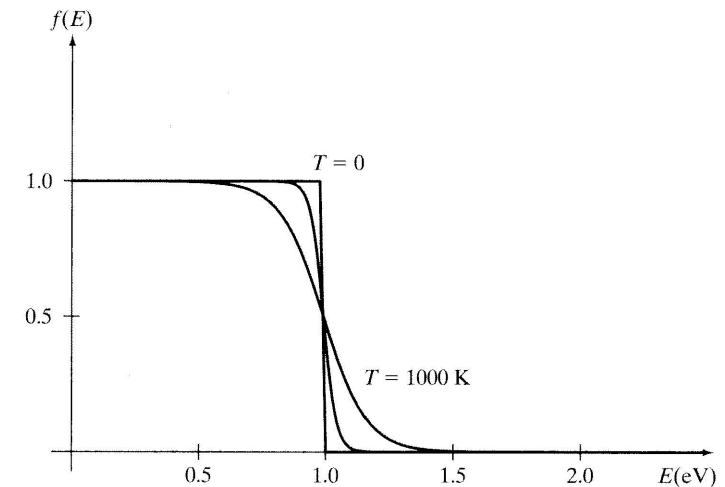


Figure 8.5 Fermi–Dirac distribution for $E_F = 1$ eV at $T = 0, 300,$ and $1,000$ K.

compared to the Fermi energy, and, thus, electrons at the Fermi energy are of principal importance. In fact, to use the Fermi sea notion described in Section 4.4, since $k_B T$ is often small compared to E_F , the excited states above E_F are said to be merely “ripples on the Fermi sea.”

3. Bose–Einstein Distribution

The Bose–Einstein distribution applies when the particles are indistinguishable, but can occupy the same available states. That is, it applies to quantum particles that do not obey the exclusion principle—for example, photons and phonons. The Bose–Einstein distribution is

$$f^{BE}(E) = f^{BE}(E, \mu, T) = \frac{1}{e^{\frac{E-\mu}{k_B T}} - 1}. \quad (8.27)$$

We can see that at large values of energy, all three distributions are equal. This is because of the de Broglie wavelength (2.15)—as energy increases, the de Broglie wavelength decreases, and for very high energies, the de Broglie wavelength is vanishingly small, such that the particle becomes like a classical particle. Since we are interested in electrons, we will be concerned primarily with the Fermi–Dirac distribution.

Using the Fermi–Dirac distribution, we find that since the probability of a level being occupied by an electron is $f(E)$, then the probability of a level not being occupied by an electron (i.e., being occupied by a hole), is

$$1 - f(E) = \frac{1}{e^{\frac{E_F - E}{k_B T}} + 1}, \quad (8.28)$$

since[†]

$$\frac{1}{e^{\frac{E-E_F}{k_B T}} + 1} + \frac{1}{e^{\frac{E_F-E}{k_B T}} + 1} = 1. \quad (8.30)$$

8.2.1 Carrier Concentration in Materials

With the concept of the density of states and of the Fermi–Dirac distribution, we can now find the total number of filled electronic states per unit volume, and also obtain a useful formula for the Fermi level. In general, we can determine the electron concentration n (m^{-3}) by multiplying the electronic density of states, $N(E)$, and the probability that a state is occupied, $f(E)$, and integrating over energy,

$$n = \int N(E) f(E, E_F, T) dE. \quad (8.31)$$

The limits of integration would depend on the specific circumstances, such as the energy range of interest, etc. The number of filled states per unit volume at $T = 0$ is

$$N_f = \int_0^\infty N(E) f(E, E_F, T = 0) dE \quad (8.32)$$

$$= \int_0^{E_F} N(E) dE. \quad (8.33)$$

For the electron confined to a three-dimensional space, using (8.6) we have[‡]

$$N_f = \int_0^{E_F} \frac{2^{1/2} m_e^{*3/2} E^{1/2}}{\hbar^3 \pi^2} dE = \frac{2^{1/2} m_e^{*3/2}}{\hbar^3 \pi^2} \frac{2}{3} E_F^{3/2}, \quad (8.34)$$

which must equal the total number of electrons per unit volume, N . Then, if we know the total number of electrons in a system, we can find the Fermi level as

$$E_F = \left(3N \frac{\hbar^3 \pi^2}{(2m_e^*)^{3/2}} \right)^{2/3} \quad (8.35)$$

[†]To see this, let $u = e^{\frac{E-E_F}{k_B T}}$, such that $1/u = e^{\frac{E_F-E}{k_B T}}$. Then,

$$\begin{aligned} \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1} + \frac{1}{e^{\frac{E_F-E}{k_B T}} + 1} &= \frac{1}{u+1} + \frac{1}{\frac{1}{u}+1} \\ &= \frac{1}{u+1} + \frac{u}{1+u} = 1. \end{aligned} \quad (8.29)$$

[‡]Integrating over the specified limits and using (8.6) implies that this calculation is valid for an electron gas model. This is applicable to most metals, and serves as an approximation for semiconductors that are doped at a sufficiently high level (so that we can consider the material to be a particle gas of the dopant carriers). An analogous calculation for semiconductors not in the highly doped limit is given in the next section.

$$= \left(\frac{\hbar^2}{2m_e^*} \right) (3N\pi^2)^{2/3}. \quad (8.36)$$

In a typical metal, E_F is in the range of a few eV. For example, assuming one electron per 0.1 nm^3 (10^{22} electrons/ cm^3), which is a typical order of magnitude for many materials, we have

$$E_F = 1.67 \text{ eV}. \quad (8.37)$$

In two dimensions, using (8.14) we have

$$N = N_f = \int_0^{E_F} N(E) dE = \int_0^{E_F} \frac{m_e^*}{\pi \hbar^2} dE = \frac{m_e^*}{\pi \hbar^2} E_F, \quad (8.38)$$

leading to

$$E_F^{(2d)} = \frac{\pi \hbar^2}{m_e^*} N. \quad (8.39)$$

In one dimension,

$$E_F^{(1d)} = \left(\frac{\hbar^2}{2m_e^*} \right) \left(\frac{\pi N}{2} \right)^2. \quad (8.40)$$

Later we will need a few other useful quantities related to the Fermi level. The *Fermi wavevector* is the wavevector at the Fermi energy. If the energy–wavevector relationship is[†]

$$E = \frac{\hbar^2 k^2}{2m_e^*}, \quad (8.41)$$

then the Fermi wavevector is

$$k_F = \frac{(2m_e^* E_F)^{1/2}}{\hbar} \quad (8.42)$$

$$= (3N\pi^2)^{1/3} \quad \text{in three dimensions,} \quad (8.43)$$

$$= (2\pi N)^{1/2} \quad \text{in two dimensions,} \quad (8.44)$$

$$= \frac{\pi N}{2} \quad \text{in one dimension.} \quad (8.45)$$

Of course, N is the appropriate number density (m^{-3} , m^{-2} , m^{-1} in three dimensions, two dimensions, and one dimension, respectively). The relationship between Fermi energy and Fermi wavevector is depicted in Fig. 8.6.

[†]This quadratic dependence between E and k occurs for free electrons (Section 4.1), spatially confined electrons in otherwise empty space (Section 4.3), and for electrons in crystalline materials near energy bandedges (Section 5.4.4). Recall that for semiconductors, the bandedges are the most important sections of the energy band.

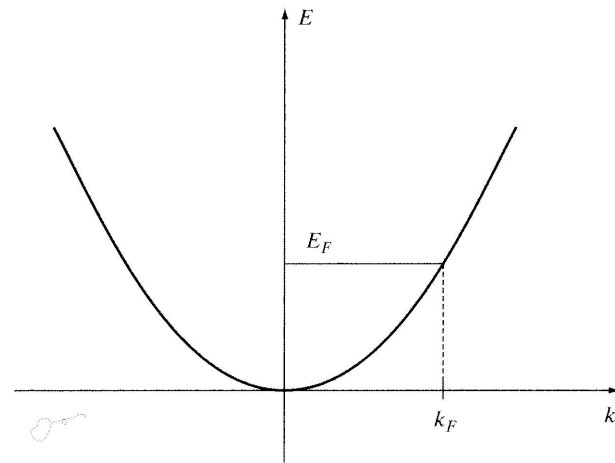


Figure 8.6 Energy versus wavevector showing the Fermi level and Fermi wavevector.

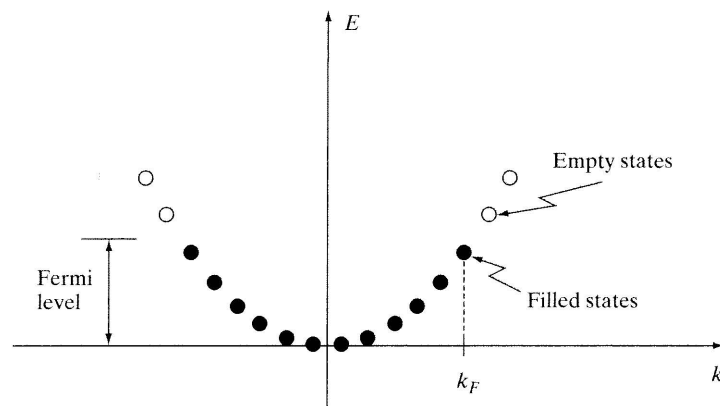


Figure 8.7 Energy versus wavenumber for discrete energy levels. Filled circles denote filled states, and empty circles denote empty states. Only values of energy and wavenumber represented by circles are allowed.

We are usually interested in confined regions of space, leading to discrete states, such as considered in Section 4.3. In this case, the wavenumber k will be discrete along some (perhaps multiple) coordinate(s), and the energy-wavevector diagram will look like Fig. 8.7. In this figure, note that the Fermi level is shown halfway between the highest filled state and the next higher empty state. This may occur, or it may lie at the level of the highest filled state, depending on the number of electrons, per the definition of chemical potential given in Section 4.4. This is discussed in Section 8.2.3, where the Fermi level is considered to be the energy state that has a probability of $\frac{1}{2}$ of being occupied by an electron at $T = 0$ K.

If we consider confinement in two dimensions, say, along the x - and y -coordinates, then we can view the occupation of states as being those states within the Fermi circle, as

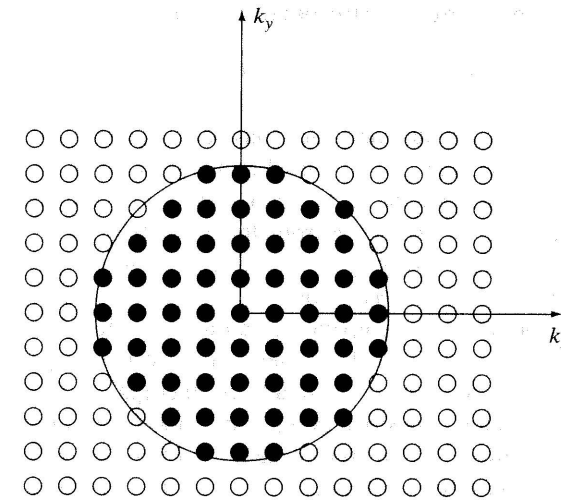


Figure 8.8 Electronic states in the k_x - k_y plane. The states within the Fermi circle shown are occupied.

shown in Fig. 8.8. For confinement in three dimensions, we obtain a Fermi sphere, rather than a Fermi circle.

The Fermi wavelength is

$$\lambda_F = \frac{2\pi}{k_F}, \quad (8.46)$$

and the *Fermi velocity* is, from the momentum-wavevector relationship (2.15) ($m_e^*v = p = \hbar k$),

$$v_F = \frac{\hbar k_F}{m_e^*}. \quad (8.47)$$

Note that the relationship between the Fermi wavelength, Fermi wavenumber, and Fermi velocity are completely general, unlike the parabolic relationship between Fermi energy and Fermi wavenumber (8.41).

Table 8.1 shows the Fermi energy, velocity, and wavelength for a few common elements in three dimensions. More values are provided in Table II in Appendix B.

TABLE 8.1 FERMI ENERGY, FERMI VELOCITY, AND FERMI WAVELENGTH FOR SEVERAL COMMON ELEMENTS.

Element	E_F (eV)	v_F ($\times 10^6$ m/s)	λ_F (nm)
Li	4.74	1.29	0.56
Na	3.24	1.07	0.68
K	2.12	0.86	0.85
Cu	7.00	1.57	0.46
Ag	5.49	1.39	0.52

8.2.2 The Importance of the Fermi Electrons

Before leaving this section, it is worthwhile to examine some ideas related to the Fermi level. For example, it is a fact that many electrons contribute to conduction in metals, and yet we have said previously that only electrons having energy near the Fermi level contribute to conduction (i.e., that electrons near the Fermi level are the “important” electrons). However, there is no contradiction; there are many electrons that have energy near to the Fermi level, and these are the many electrons that contribute to conduction. Considering copper, for example, we find that using $E_F = 7.0$ eV, (8.34) leads to the density of electrons as $N(E_F) = 1.8 \times 10^{22} \text{ cm}^{-3}$. Thus, there are a large number of states around the Fermi level.

In addition, at room temperature (around 293 K), $k_B T = 0.025$ eV. This energy is very small compared with the Fermi level in most metals, as shown in Table 8.1. That is, since Boltzmann’s constant is so small, the thermal energy gained by electrons, even at quite high temperatures, is small compared to the Fermi energy. Therefore, in conductors, electrons in the absence of an applied field can often be considered to have energy E_F (i.e., thermal energy can often be ignored). For example, consider again copper, where $E_F = 7$ eV. Let’s assume that in order for thermal effects to be important, we need $k_B T = 3.5$ eV, which is one-half the Fermi energy. The corresponding temperature is $T \sim 40,600$ K, and even at this temperature $k_B T$ is only one-half of the Fermi level! Therefore, filled states deep within the Fermi sphere will not play much role in electronic interactions, and we are most interested in electrons and states near the Fermi surface.

However, in semiconductors, thermal energy can liberate a large number of electrons, especially from donors or acceptors (creating free electrons and holes), changing significantly the material’s electronic properties. In this case, electron energies are typically above the Fermi level, as described in Section 5.4.

Aside from thermal effects, it turns out that even in the event of other energy inputs, in metals the electron’s energy is still approximately the Fermi energy. For example, consider what happens to the electron’s energy if we apply an electric field. The resulting drift velocity (the velocity of the net current) is very low, typically on the order of mm/s (see Section 10.1), which is many orders of magnitude smaller than the Fermi velocity. Even assuming that we apply a large field of 100 V/m to copper, and that the field accelerates an electron over the mean free path of 40 nm, the energy gained from the field is

$$\begin{aligned} E &= Fd = e(100)(40 \times 10^{-9}) = 6.4 \times 10^{-25} \text{ J} \\ &= 4 \times 10^{-6} \text{ eV,} \end{aligned} \quad (8.48)$$

which is miniscule compared to the Fermi energy. So again, electrons in metals act approximately as if they have energy E_F . This is true even at very high temperatures, even near the melting temperature of a metal.

8.2.3 Equilibrium Carrier Concentration and the Fermi Level in Semiconductors

In semiconductors, in particular, we are often interested in determining the carrier concentration available for electrical conduction. We can determine the carrier concentration in

the conduction band by multiplying the electron density of states in the conduction band, $N_e(E)$, and the probability that a state is occupied, $f(E, E_F, T)$, and summing over all energies in the band,

$$n = \int_{E_c}^{\infty} N_e(E) f(E, E_F, T) dE, \quad (8.49)$$

where $f(E, E_F, T)$ is the Fermi–Dirac function. This leads to

$$\begin{aligned} n &= \int_{E_c}^{\infty} \left(\frac{\sqrt{2} m_e^{*3/2} (E - E_c)^{1/2}}{\pi^2 \hbar^3} \right) \left(\frac{1}{e^{\frac{E - E_F}{k_B T}} + 1} \right) dE \\ &= \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} \int_{E_c}^{\infty} \left(\frac{(E - E_c)^{1/2}}{e^{\frac{E - E_F}{k_B T}} + 1} \right) dE. \end{aligned} \quad (8.50)$$

If $(E - E_F) / (k_B T) \gg 1$ (i.e., the Boltzmann approximation), then

$$n = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} \frac{e^{\frac{E_F}{k_B T}}}{e^{\frac{E - E_c}{k_B T}}} \int_{E_c}^{\infty} (E - E_c)^{1/2} e^{-\frac{E - E_c}{k_B T}} dE. \quad (8.51)$$

With

$$\begin{aligned} \int_{E_c}^{\infty} \left((E - E_c)^{1/2} e^{-\frac{E - E_c}{k_B T}} \right) dE &= e^{-\frac{E_c}{k_B T}} \int_{E_c}^{\infty} (E - E_c)^{1/2} e^{-\frac{E - E_c}{k_B T}} dE \\ &= e^{-\frac{E_c}{k_B T}} (k_B T)^{1/2} (k_B T) \int_0^{\infty} u^{1/2} e^{-u} du \\ &= e^{-\frac{E_c}{k_B T}} (k_B T)^{3/2} \frac{1}{2} \sqrt{\pi}, \end{aligned} \quad (8.52)$$

using the change of variables $u = (E - E_c) / (k_B T)$, $du = dE / (k_B T)$, and

$$\int_0^{\infty} u^{1/2} e^{-u} du = \frac{1}{2} \sqrt{\pi}, \quad (8.53)$$

then

$$n = 2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{\frac{E_F - E_c}{k_B T}} = N_c e^{-\frac{(E_c - E_F)}{k_B T}}. \quad (8.54)$$

N_c is known as the *effective density of states at the conduction band edge*. For example, for silicon, $N_c \simeq 2.8 \times 10^{19} \text{ cm}^{-3}$ at room temperature.

Taking the natural logarithm of the previous equation, we have an expression for the Fermi level,

$$E_F = E_c + k_B T \ln \frac{n}{N_c}. \quad (8.55)$$

A similar calculation for the holes leads to

$$p = 2 \left(\frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{3/2} e^{\frac{E_v - E_F}{k_B T}} = N_v e^{-\frac{(E_F - E_v)}{k_B T}}, \quad (8.56)$$

where N_v is called the *effective density of states at the valence band edge*.

In summary, we have

$$n = N_c e^{-\frac{(E_c - E_F)}{k_B T}}, \quad (8.57)$$

$$p = N_v e^{-\frac{(E_F - E_v)}{k_B T}}. \quad (8.58)$$

Note that we haven't indicated whether (8.57) and (8.58) refer to intrinsic or extrinsic semiconductors. In fact, they typically apply to both in thermal equilibrium (assuming the Boltzmann approximation is valid), where the presence or absence of dopant atoms is reflected in the position of the Fermi level. For intrinsic semiconductors, the condition $n_i = p_i$ leads to

$$2 \left(\frac{m_e^* k_B T}{2\pi\hbar^2} \right)^{3/2} e^{\frac{E_F - E_c}{k_B T}} = 2 \left(\frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{3/2} e^{\frac{E_v - E_F}{k_B T}} \quad (8.59)$$

$$\Rightarrow E_{F_i} = \frac{E_c + E_v}{2} + \frac{3k_B T}{4} \ln \frac{m_h^*}{m_e^*}.$$

Therefore, the intrinsic Fermi level is near the middle of the bandgap. (If the effective electron and hole masses are equal, the intrinsic Fermi level is precisely in the middle of the bandgap.)[†] The top of the valence band is usually set to $E = 0$, and in this case, $E_{F_i} = E_g/2$. Furthermore, for intrinsic semiconductors, obviously $n_i p_i = n_i^2$, so that

$$n_i = \sqrt{N_c N_v} e^{-\frac{E_g}{2k_B T}}. \quad (8.60)$$

From (8.60) we see that carrier concentration increases exponentially as bandgap decreases. For silicon at room temperature, $n_i \simeq 1.5 \times 10^{10} \text{ cm}^{-3}$.

For extrinsic n-type semiconductors, if we assume that the dopant concentration N_d is much higher than the intrinsic carrier concentration n_i (typical doping levels in conventional devices are on the order of 10^{15} atoms/cm³ or more), and that all dopant atoms are ionized (the usual situation), then for an n-type material,

$$n \simeq N_d. \quad (8.61)$$

[†]It is convenient to view the Fermi level as the energy state that has a probability of $\frac{1}{2}$ of being occupied by an electron. Since at $T = 0 \text{ K}$ all states below E_v are filled, and all states above E_c are empty, then the equal probability point lies in the middle of the bandgap, even though no allowed states are located in the gap. This is consistent with the definition of the chemical potential in Section 4.4.

Substituting this into (8.57), we have

$$E_F = E_c - k_B T \ln \left(\frac{N_c}{N_d} \right). \quad (8.62)$$

Of course, with this Fermi level, (8.57) yields $n = N_d$.

Note that if the doping level is very high such that $N_d \simeq N_c$, then E_F approaches E_c and the semiconductor is said to be *degenerate*. However, in this case, the Boltzmann approximation breaks down, and a more careful analysis must be used.

In a similar manner, for a p-type semiconductor with an acceptor doping density $N_a \gg p_i$,

$$E_F = E_v + k_B T \ln \left(\frac{N_v}{N_a} \right),$$

which approaches the value $E_F = E_v$ for $N_a \simeq N_v$ (e.g., $N_v \simeq 10^{19} \text{ cm}^{-3}$ for silicon at room temperature).

Since the product

$$np = N_c N_v e^{-\frac{E_g}{k_B T}} = n_i^2 \quad (8.63)$$

is independent of the Fermi level, it should hold for doped (extrinsic) semiconductors as well; (8.63) is known as the *mass-action law*. It holds in the extrinsic case since an increase in one carrier type (electrons or holes) tends to diminish, through recombination, the other carrier type.

8.3 MAIN POINTS

In this chapter, we have considered the idea of particle statistics and the density of states, and implications to the Fermi level and carrier concentrations. In particular, after studying this chapter you should understand

- the concept of density of states in various spatial dimensions, and the significance of the density of states;
- how the density of states can be measured;
- quantum and classical statistics for collections of large numbers of particles, including the Boltzmann, Fermi–Dirac, and Bose–Einstein distributions;
- the role of density of states and quantum statistics in determining the Fermi level;
- applications of density of states and quantum statistics to determine carrier concentration in materials, including in doped semiconductors.

8.4 PROBLEMS

1. Energy levels for a particle in a three-dimensional cubic space of side L with hard walls (boundary conditions (4.50)) were found to be (4.54)

$$E_n = \frac{\hbar^2 \pi^2}{2m_e^* L^2} (n_x^2 + n_y^2 + n_z^2), \quad (8.64)$$

$n_{x,y,z} = 1, 2, 3, \dots$, which leads to the density of states (8.6). Using periodic boundary conditions (4.55), we found energy levels to be (4.59)

$$E_n = \frac{2\hbar^2\pi^2}{m_e^*L^2} (n_x^2 + n_y^2 + n_z^2), \quad (8.65)$$

$n_{x,y,z} = 0, \pm 1, \pm 2, \dots$. Following a derivation similar to the one shown for (8.6), show that the same density of states arises from (8.65).

- Derive (8.16), the density of states in two dimensions.
- The density of states in a one-dimensional system is given by (8.15),

$$N(E) = \frac{\sqrt{2m_e^*}}{\pi\hbar} E^{-1/2}, \quad (8.66)$$

assuming zero potential energy.

- Use this formula to show that the Fermi energy in terms of the total number of filled states at $T = 0$ K, N_f , is (8.40),

$$E_F = \frac{\hbar^2}{2m_e^*} \left(\frac{\pi N_f}{2} \right)^2. \quad (8.67)$$

- If there are N electrons in a one-dimensional box of length L , show that the energy level of the highest energy electron is E_F , given by (8.67). Use the fact that the energy levels in a one-dimensional box are (4.35),

$$E_n = \frac{\hbar^2}{2m_e^*} \left(\frac{n\pi}{L} \right)^2, \quad n = 1, 2, 3, \dots \quad (8.68)$$

- Assume that the density of states in a one-dimensional system is given by

$$N(E) = \frac{\sqrt{2m}}{\pi\hbar} E^{-1/3} \quad (8.69)$$

at zero potential energy.

- Use this formula to obtain the Fermi energy.
 - What is the relationship between the de Broglie wavelength and the Fermi wavelength?
- The electron carrier concentration in the conduction band can be determined by multiplying the electron density of states in the conduction band, $N_e(E)$, and the probability that a state is occupied, $f(E, E_F, T)$, and then summing over all energies to yield (8.54) on page 275. Perform the analogous calculations for determining the hole carrier concentration in the valence band, leading to (8.56).
 - The Fermi wavelength in three-dimensional copper is $\lambda_F = 0.46$ nm. Determine the Fermi wavelength in two-dimensional copper.
 - Determine the Fermi wavelength of electrons in three-dimensional aluminum and zinc.
 - What is the electron concentration in an n-type semiconductor at room temperature if the material is doped with 10^{14} cm $^{-3}$ donor atoms? How would one determine the hole concentration?

- The concept of the Fermi energy can be used to give some confidence of electron-electron screening in conductors (i.e., the ability to ignore interactions among electrons), previously described in Sections 3.5 and 4.2. To see this, approximate the electron's kinetic energy by the Fermi energy. Then, for an electron density N m $^{-3}$, assuming that the average distance between electrons is $N^{-1/3}$, show that the ratio of Coulomb potential energy to kinetic energy goes to zero as N goes to infinity, showing that the electrons essentially screen themselves.
- Constructive and destructive interference of electromagnetic waves (light, radio-frequency signals, etc.) is one of the most commonly exploited phenomena in classical high-frequency devices. For example, resonance effects result from wave interference, and are used to form filters, impedance transformers, absorbers, antennas, etc. In contrast to these electromagnetic (i.e., photon) devices, which obey Bose-Einstein statistics, electron waves are fermions, and obey Fermi-Dirac statistics and the exclusion principle. Describe how it is possible for a large collection of bosons to form a sharp interference pattern, yet this will not be observed by a large collection of electrons in a solid. Does this make sense considering Fig. 2.6 on page 29, where sharp electron interference was, in fact, observed?