

# The physical meaning of Fermi-Dirac statistics

Costas J. Papachristou<sup>1</sup>

Hellenic Naval Academy

In this article we use material from this author's textbook "*Introduction to Electromagnetic Theory and the Physics of Conducting Solids*" (Springer, 2020).<sup>2</sup>

## 1. Occupation density and density of states

We consider a quantum system consisting of a large number of identical particles. We assume that the energy of each particle may take on certain values  $E_1, E_2, E_3, \dots$ , characteristic for this system. We say that each particle may *occupy* one of the available energy levels  $E_1, E_2, E_3, \dots$ , of the system. We also assume that the system occupies *unit volume*. Hence, all physical quantities concerning this system will be specified *per unit volume*. At some instant the particles are distributed to the various energy levels so that  $n_i$  particles (per unit volume) occupy the level  $E_i$  (which means that each of these  $n_i$  particles has energy  $E_i$ ), as seen in Fig. 1.

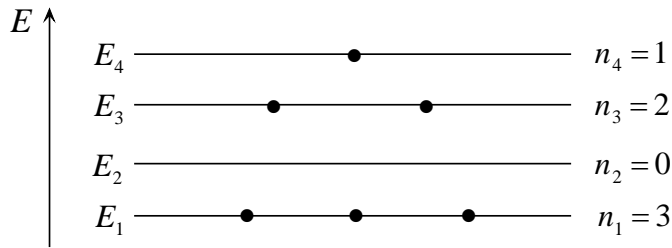


Fig. 1

The total number of particles in the system is equal to

$$n = \sum_i n_i \quad (1)$$

while the total energy of the system is<sup>3</sup>

$$U = \sum_i n_i E_i \quad (2)$$

The ordered set  $(n_1, n_2, n_3, \dots) \equiv (n_i)$  constitutes a *partition* and defines a *microstate* of the system, compatible with the macroscopic state determined by the number  $n$  of particles, the total energy  $U$ , etc. By the expression (2) we implicitly assume that the particles do not interact (or, at least, do not interact too strongly) with one another, so that we may define an average energy separately for each particle. This is approximately true for the molecules of ideal gases, as well as for the free electrons in metals.

If the system is *isolated* (i.e., does not exchange matter or energy with its surroundings) the  $n$  and  $U$  are constant. However, Eqs. (1) and (2) do not determine the

<sup>1</sup> Email: [cjpapachristou@gmail.com](mailto:cjpapachristou@gmail.com)

<sup>2</sup> Manuscript: <https://arxiv.org/abs/1711.09969>

<sup>3</sup> We assume that the values  $E_i$  of the energy are characteristic of the specific *kind* of system and do *not* depend on the total number of particles (thus are independent of the volume of the system).

partition ( $n_i$ ) uniquely, given that different partitions ( $n_i$ ), ( $n_i'$ ), ( $n_i''$ ), etc, may correspond to the same values of  $n$  and  $U$ . Now, for given  $n$  and  $U$  there is a *most probable* partition (microstate). When the system is in that state of maximum probability we say that it is in *statistical equilibrium* (in thermodynamics the term *thermal equilibrium* is used). When an isolated system reaches a state of statistical equilibrium it tends to remain in that state – unless, of course, it is disturbed by some external action. Furthermore, in a state of equilibrium the system has a well-defined, constant temperature  $T$ . As a rule, *we will always assume that the systems we consider are in statistical equilibrium.*

Assume now that the particles in the system have energies that vary *continuously* from  $E_1$  to  $E_2$  ( $E_1 \leq E \leq E_2$ ) instead of taking on discrete values  $E_1, E_2, E_3, \dots$ . This is the case for the free electrons in a metal – their energies varying continuously within the limits of the conduction band – as well as for the molecules of an ideal gas that occupies a large volume. In this case there is an infinite number of energy levels varying between the limit values  $E_1$  and  $E_2$ . The distribution of the particles of the system among these levels is now described with the aid of a function  $n(E)$ , to be called the *occupation density*, defined as follows:

*The product  $n(E)dE$  represents the number of particles, per unit volume, whose energies have values between  $E$  and  $E+dE$ .*

One may say that the occupation density  $n(E)$  expresses the *distribution of energy* in the system. More accurately, for a given value  $E$  of the energy, the corresponding value  $n(E)$  describes the “tendency” of the particles in the system to occupy energy levels in the vicinity of  $E$ : a larger  $n(E)$  means a larger number of particles in the energy region between  $E$  and  $E+dE$ .

The total number  $n$  of particles in the system, per unit volume, is equal to

$$n = \int_{E_1}^{E_2} n(E) dE \quad (3)$$

In the case of metals,  $n$  represents the concentration of free electrons (number of free electrons per unit volume); that is, the *electronic density* of the metal.

The quantum state of a particle in the system is described with the aid of a set of quantum numbers, characteristic of the particular kind of system. In general, to every value  $E$  of the energy (that is, to every energy level) there correspond many different quantum states. Some of them will be occupied by particles while others will be vacant. In a manner similar to the definition of the occupation density  $n(E)$ , we define the *density of states*  $N(E)$  as follows:

*The product  $N(E)dE$  represents the number of states, per unit volume of the system, whose energies have values between  $E$  and  $E+dE$ .*

Like the occupation density, the density of states is only defined if the energies of the particles vary in a continuous manner. It is also obvious that we cannot expect to find any particles in an energy region where there are no allowable quantum states. Therefore,  $n(E)=0$  when  $N(E)=0$ . The converse is *not* true, given that there may exist allowable energy regions where all states are vacant (this is, e.g., the case with the upper part of the conduction band of a metal).

## 2. The ideal gas

An important problem in statistical physics is the distribution of energy in an *ideal monatomic gas*. Since every gas molecule consists of a single atom, its energy is purely *translational kinetic* (there is no intermolecular potential energy, nor is there the rotational or the vibrational kinetic energy typical of a composite molecule). The molecular energy levels are thus given by the relation  $E_i = \frac{1}{2} m v_i^2$ , where  $m$  is the mass of a molecule and where  $v_i$  are the possible values of the velocity of the molecules. For given physical conditions, each level  $E_i$  is occupied by all molecules having a common speed  $v_i$ .

The gas is a quantum system confined within the limited space of its container. According to quantum mechanics, the energy of the molecules is quantized and therefore the  $v_i$  and  $E_i$  take on discrete values, as suggested by the use of the index  $i$ . But, when the volume  $V$  occupied by the gas is large, we can approximately assume that the molecular kinetic energy  $E = \frac{1}{2} m v^2$  is not quantized but varies in a *continuous* fashion. The energy distribution in the system, therefore, involves the concepts of occupation density and density of states, defined in the previous section. As can be shown [1,2], the density of states is given by the expression<sup>4</sup>

$$N(E) = \frac{2\pi}{h^3} (2m)^{3/2} E^{1/2} \quad (4)$$

Regarding the occupation density  $n(E)$ , we recall that it is defined by demanding that the product  $n(E)dE$  represents the number of molecules, per unit volume, having energies between  $E$  and  $E+dE$ . As is found [1,2], when the gas is in statistical equilibrium,

$$n(E) = \frac{2\pi n}{(\pi kT)^{3/2}} E^{1/2} e^{-E/kT} \quad (5)$$

where  $n$  is the concentration of the molecules (number of molecules per unit volume) and  $T$  is the absolute temperature. Note that *there is no limit to the number of molecules that can occupy a given quantum state*. In other words, the molecules of the ideal gas do not obey the *Pauli exclusion principle*.

The *average (kinetic) energy* of the molecules at temperature  $T$  is given by [1,2]

$$\langle U \rangle = \frac{3}{2} kT \quad (6)$$

The constant  $k$  appearing in Eqs. (3.5) and (3.6) is called the *Boltzmann constant* and is equal to

$$k = 8.62 \times 10^{-5} \text{ eV / K} = 1.38 \times 10^{-23} \text{ J / K} \quad (7)$$

---

<sup>4</sup> Since the energy  $E$  is purely kinetic, we have that  $E \geq 0$ ; thus the presence of  $E$  inside a square root is acceptable.

If  $N$  is the total number of molecules in the gas, the total energy of the system is equal to  $N\langle U \rangle$ . Thus, if  $V$  is the volume occupied by the gas, the *total energy per unit volume* of the system is

$$U = \frac{N}{V}\langle U \rangle = n\langle U \rangle = \frac{3}{2}nkT \quad (8)$$

Notice that, according to (6),

*the absolute temperature  $T$  of an ideal gas is a measure of the average kinetic energy of the molecules in a state of statistical equilibrium.*

In particular, *the kinetic energy of the molecules vanishes at absolute zero ( $T=0$ )*. As we will see in Sec. 4, an analogous statement is *not* valid for the free electrons in a metal, despite the superficial similarities of the latter system with the molecules of an ideal gas.

### 3. Bosons and fermions

The *Maxwell-Boltzmann theory* for an ideal gas, outlined in the previous section, is essentially a *classical* theory. Although we regarded the gas molecules as quantum particles (for example, we assumed that they occupy quantum states) the underlying analysis in essence treats the molecules as classical particles since it does not take into account one of the most important principles of quantum theory; namely, the *uncertainty principle*. [Don't be deceived by the presence of the quantum constant  $h$  in Eq. (4); the basic result (5) for the occupation density may be derived by entirely classical methods, without recourse to quantum mechanics.] Such an omission of quantum principles is not allowable in the case of electrons, given their exceedingly microscopic nature in comparison to gas molecules. The treatment of such profoundly quantum problems is the subject of quantum statistics.

In quantum statistics, *identical* particles that *interact* with one another are considered *indistinguishable*. By "identical particles" we mean particles that may replace one another without any observable effects in the macroscopic state of the system. (For example, the free electrons in a metal are identical particles since it doesn't matter *which* individual electrons occupy an energy level; it only matters *how many* electrons occupy that level.) In classical mechanics, where the notion of the trajectory of a particle is physically meaningful, it is possible to distinguish identical particles that interact by simply following the path of each particle in the course of an experiment. We say that classical particles are *distinguishable*. This is the view adopted by the Maxwell-Boltzmann theory for the molecules of ideal gases.

Things are not that simple, however, for systems of extremely microscopic particles such as, e.g., the electrons in a metal, given that the uncertainty principle does not allow a precise knowledge of the trajectories of such purely quantum particles (in quantum theory the notion of the trajectory is meaningless). Therefore, when *identical* quantum particles interact with one another, it is impossible to distinguish one from another during an experiment. We say that interacting identical particles are *indistinguishable*. (Identical particles that do *not* interact are considered distinguishable.)

Thus, quantum statistics is the enhancement of the corresponding classical theory by taking into account the implications of the uncertainty principle. According to the quantum theory, there are two kinds of fundamental particles in Nature, which follow

separate statistical laws of distribution of energy when they are grouped to form systems of identical and indistinguishable particles:

- the particles that obey the Pauli exclusion principle are called *fermions* and they follow the *Fermi-Dirac distribution law*;
- the particles that do *not* obey the Pauli exclusion principle are called *bosons* and they follow the *Bose-Einstein distribution law*

(see discussion in Appendix A). As has been observed,

*particles having half-integer spins (e.g., electrons) are fermions, while particles with integral spins (e.g., photons) are bosons.*

Accordingly,

*two or more identical fermions may not occupy the same quantum state in a system, whereas an arbitrary number of identical bosons may occupy the same quantum state.*

Given that even the molecules of ideal gases are quantum systems consisting of various kinds of fermions (electrons, protons, neutrons, not to mention quarks!) we may wonder whether the Maxwell-Boltzmann distribution law has any use after all. Well, what keeps the classical theory in the game is the fact that, *for systems in which the uncertainty principle can be ignored*, both Fermi-Dirac and Bose-Einstein statistics reduce to Maxwell-Boltzmann statistics. Such a semi-classical system is an ideal gas of low density (i.e., having a small concentration of molecules) at a high temperature. In this case quantum effects are not significant and the use of classical statistical methods leads to correct physical predictions.

#### 4. Fermi-Dirac distribution law for a metal

Fermi-Dirac statistics applies to systems of identical and indistinguishable particles that obey the Pauli exclusion principle; that is, to systems of *fermions*. The free electrons in a metal are an important example of such a system. Although the energies of the electrons are quantized, we may approximately regard these energies as varying continuously within the limits of the conduction band. This approximation is valid when the volume of space within which the motion of the electrons takes place is relatively large (a similar condition is valid for the molecules of an ideal gas).

The mobile electrons in a metal are called *free* because of their ability to move in between the positive ions without being subject to forces of appreciable strength (except, of course, when the electrons accidentally collide with the ions). In general, a free particle has constant potential energy that may arbitrarily be assigned zero value. The energy  $E$  of a free electron is thus *purely kinetic*, which means that  $E \geq 0$ . We will therefore assume that the energy of a free electron in the metal may take on all values from 0 up to  $+\infty$ . (The upper limit is, of course, purely theoretical since the energy of an electron in the interior of a metal may not exceed the *work function* of that metal, equal to the minimum energy required in order that the electron may “escape” from the crystal.)

Let  $N(E)$  be the density of states in the conduction band of the metal. We recall that this function is defined so that the product  $N(E)dE$  is equal to the number of

quantum states (per unit volume) with energies between  $E$  and  $E+dE$  (equivalently, equal to the number of states belonging to all energy levels between  $E$  and  $E+dE$  in the conduction band). As can be shown [1-5] the function  $N(E)$  is given by the expression

$$N(E) = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} \equiv \gamma E^{1/2} \quad (9)$$

where  $m$  is the mass of the electron. By comparing (9) with (4) we observe that the density of states for the electrons in a metal is twice that for the molecules of an ideal gas. This is due to the two possible orientations of the electron spin, that is, the two possible values of the quantum number  $m_s$  ( $=\pm 1/2$ ). This consideration does not appear in the Maxwell-Boltzmann distribution since the classical theory does not take into account purely quantum concepts such as that of the spin of a particle.

To find the distribution of energy for the free electrons in a metal we must determine the occupation density  $n(E)$ . As we know, this function is defined so that the product  $n(E)dE$  represents the number of free electrons (per unit volume of the metal) with energies between  $E$  and  $E+dE$  (equivalently, the number of electrons occupying the energy levels between  $E$  and  $E+dE$  in the conduction band). Because of the Pauli exclusion principle, the number of electrons in this elementary energy interval cannot exceed the number of available quantum states in that interval:

$$n(E)dE \leq N(E)dE \quad \Rightarrow \quad 0 \leq \frac{n(E)}{N(E)} \leq 1$$

We observe that the quotient  $n(E)/N(E)$  satisfies the necessary conditions in order to represent probability (see Appendix B). We thus define the *probability function*  $f(E)$ :

$$f(E) = \frac{n(E)}{N(E)} \quad \Leftrightarrow \quad n(E) = f(E)N(E) \quad (10)$$

The function  $f(E)$  represents the *fraction of states of energy  $E$  that are occupied by electrons*, or, equivalently, the *occupation probability* for any state of energy  $E$ .

The analytical expression for  $f(E)$  is given by the *Fermi-Dirac distribution function*

$$\boxed{f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}} \quad (11)$$

where  $T$  is the absolute temperature,  $k$  is the Boltzmann constant (7), and  $E_F$  is a parameter called the *Fermi energy* (or *Fermi level*, on an energy-level diagram) for the considered metal. We note that, although the present discussion concerns free electrons in metals, the expression (11) is generally valid for *all* systems of fermions.

By combining (10), (11) and (9) we can now write an expression for the occupation density  $n(E)$ , which quantity determines the distribution of energy for the free electrons in the metal:

$$n(E) = f(E)N(E) = \frac{\gamma E^{1/2}}{1 + e^{(E-E_F)/kT}} \quad (12)$$

The physical significance of the Fermi energy  $E_F$  can be deduced from (11) after making the following mathematical observations:

- For  $T \rightarrow 0$ ,  $\lim_{T \rightarrow 0^+} \left[ e^{(E-E_F)/kT} \right] = \begin{cases} \infty, & E > E_F \\ 0, & E < E_F \end{cases}$
- For  $T > 0$ ,  $e^{(E-E_F)/kT} = 1$  when  $E = E_F$

Therefore,

$$\text{for } T = 0 \Rightarrow f(E) = \begin{cases} 0, & E > E_F \\ 1, & E < E_F \end{cases} \quad (13)$$

while

$$\text{for } T > 0 \Rightarrow f(E_F) = \frac{1}{2} \quad (14)$$

These are physically interpreted as follows:

1. For  $T=0$ , *all* states with energies  $E < E_F$  (i.e., all states up to the Fermi level) are *occupied* by electrons, while *all* states with  $E > E_F$  are *empty*.
2. For  $T > 0$ , *half* the states with energy  $E = E_F$  are occupied. That is, the occupation probability of any state on the Fermi level is equal to 50%.

We notice that the function  $f(E)$  is non-continuous for  $E = E_F$  when  $T = 0$ . Hence, the occupation probability on the Fermi level is indeterminate for  $T = 0$ . Figure 2 shows the graph of  $f(E)$  for  $T = 0$  and  $T > 0$ . A diagram of this form applies, in general, to *any* system of fermions (not just to free electrons in metals).

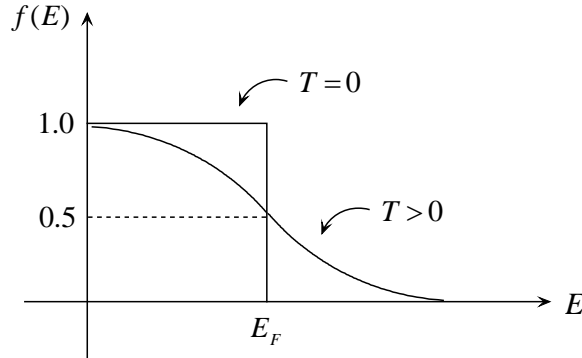


Fig. 2

As we saw, the Fermi energy  $E_F$  places an upper limit to the energies of the free electrons in a metal at  $T=0$ . Since the energy of a free electron is purely kinetic, we can write:

$$E_F = (E_{kinetic})_{max} \quad \text{for } T=0 \quad (15)$$

That is,

*the Fermi energy of a metal represents the maximum kinetic energy of the free electrons at absolute zero ( $T = 0$ ).*

Therefore, at  $T=0$ , all quantum states in the conduction band ranging from the lowest energy level  $E=0$  up to the Fermi level  $E=E_F$  are occupied by the free electrons, while all states above  $E_F$  are empty. The diagram in Fig. 3 shows the conduction band of the metal for  $T=0$ .

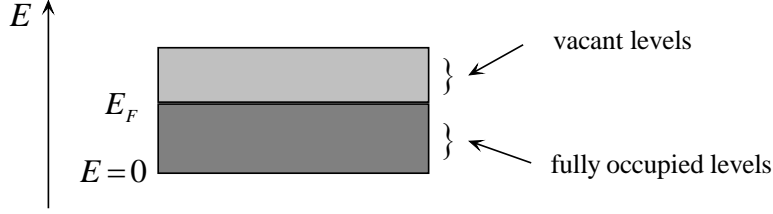


Fig. 3

We notice a fundamental difference of the Fermi-Dirac theory for electrons from the classical theory for ideal gases. According to the latter theory, all gas molecules must have zero (kinetic) energy at absolute zero. On the other hand, at  $T=0$  the free electrons in a metal have (kinetic) energies ranging from zero up to the Fermi energy. This occurs because the electrons, being fermions, obey the Pauli exclusion principle which does not allow all of them to occupy the lowest energy level  $E=0$ , given that this level does not possess a sufficient number of quantum states to accommodate all electrons. At temperatures  $T > 0$ , however, by receiving thermal energy, some free electrons acquire (kinetic) energies greater than  $E_F$ . These electrons then occupy energy levels above the Fermi level within the conduction band. As we saw, on the Fermi level itself *half* the available quantum states are occupied for  $T > 0$ .

We now describe a method for determining the Fermi energy  $E_F$  of the system of mobile electrons in a metal. Let  $n$  be the *electronic density* of the metal (number of free electrons per unit volume) and let  $n(E)$  be the occupation density of the Fermi-Dirac distribution. These two quantities are related by Eq. (3):

$$n = \int_{E_1}^{E_2} n(E) dE = \int_0^{\infty} n(E) dE \quad (16)$$

where here we have put  $E_1=0$  and  $E_2=+\infty$  (a purely theoretical limit, of course!). Using the expression (12) for  $n(E)$ , we have:

$$n = \int_0^{\infty} \frac{\gamma E^{1/2}}{1 + e^{(E-E_F)/kT}} dE \quad (17)$$

If we could compute the integral in (17) analytically, the only thing to do would be to solve the result for  $E_F$  and thus express the Fermi energy as a function of  $n$  and  $T$ . Since, however, handling the above integral is not an easy task, we will restrict ourselves to something much easier; namely, we will evaluate  $E_F$  for the special case where  $T=0$ . From (10), (9) and (13) we have that, at this temperature,

$$n(E) = f(E)N(E) = \begin{cases} 0, & E > E_F \\ \gamma E^{1/2}, & 0 \leq E < E_F \end{cases} \quad (18)$$



Substituting (18) into (16), we find

$$n = \int_0^{E_F} n(E) dE + \int_{E_F}^{\infty} n(E) dE = \int_0^{E_F} \gamma E^{1/2} dE + 0 \Rightarrow$$

$$n = \frac{2}{3} \gamma E_F^{3/2} \quad (19)$$

so that

$$E_F = \left( \frac{3n}{2\gamma} \right)^{2/3} \quad (20)$$

We observe that the Fermi energy of the metal at  $T=0$  depends only on the concentration  $n$  of free electrons and is independent of the dimensions of the crystal (i.e., of the total number of ions). As can be proven (see [4], Sec. 9-3) the value of  $E_F$  that we have found does not change much at higher temperatures. Thus, although derived for  $T=0$ , relation (20) will be assumed valid for all  $T$ . Typical values of  $E_F$  for metals range from about  $3\text{ eV}$  to  $12\text{ eV}$ .

### 5. Fermi-Dirac distribution for an intrinsic semiconductor

In an *intrinsic* semiconductor [3-5] (i.e., one without impurities) the electronic system of interest consists of the valence electrons of the atoms; specifically, the electrons that participate in covalent bonds as well as those that are free. In terms of energy, the aforementioned two groups of electrons belong to the *valence band* and the *conduction band*, respectively. The distribution of electrons within the allowable energy states is determined by the occupation density  $n(E)$ , which is related to the density of states  $N(E)$  and the probability function  $f(E)$  by

$$n(E) = f(E) N(E) \quad (21)$$

As we know, the product  $n(E)dE$  represents the number of electrons, per unit volume of the material, with energies between  $E$  and  $E+dE$ .

The form of the function  $N(E)$ , analogous to the expression (9) for metals, depends on the energy region within which this function is defined [3-5] (see Fig. 4):

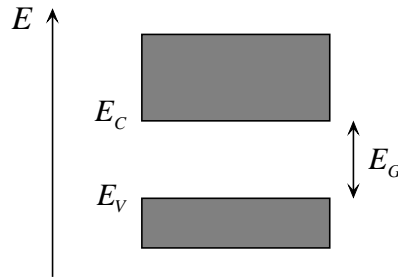


Fig. 4

a. In the *conduction band*,

$$N(E) = \gamma (E - E_C)^{1/2}, \quad E \geq E_C \quad (22)$$

b. In the *valence band*,

$$N(E) = \gamma(E_V - E)^{1/2}, \quad E \leq E_V \quad (23)$$

c. In the *forbidden band* of a pure semiconductor there are no allowable quantum states; therefore,

$$N(E) = 0, \quad E_V < E < E_C \quad (24)$$

The probability function for the electrons is given by the Fermi-Dirac formula:

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}} \quad (25)$$

where  $E$  admits values in the above-mentioned three energy regions. We would now like to find the probability function  $f_p(E)$  for the *holes* in the valence band of a semiconductor. We think as follows: A quantum state at an energy level  $E$  in the valence band is either occupied by an electron or “occupied” by a hole. If  $f(E)$  and  $f_p(E)$  are the corresponding occupation probabilities, then

$$f(E) + f_p(E) = 1 \quad \Leftrightarrow \quad f_p(E) = 1 - f(E) \quad (26)$$

Substituting the expression (25) for  $f(E)$ , we find that

$$f_p(E) = \frac{e^{(E-E_F)/kT}}{1 + e^{(E-E_F)/kT}} \quad (27)$$

Physically, the function  $f_p(E)$  represents the fraction of states of energy  $E$  that are *not* occupied by electrons, or, equivalently, the probability of non-occupation of a state of energy  $E$ .

## 6. Fermi energy in semiconductors

The Fermi energy of an *intrinsic* semiconductor [3-5] is given by Eq. (28), where the energy levels  $E_V$  and  $E_C$  were introduced in the previous section (see Fig. 5):

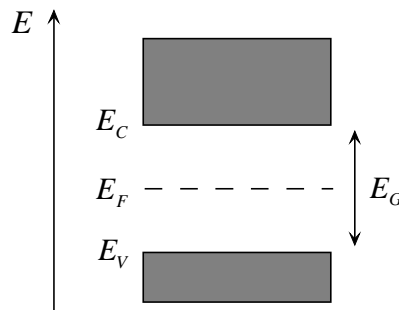


Fig. 5

$$E_F = \frac{E_V + E_C}{2} \quad (28)$$

We write:

$$E_F = \frac{E_V + (E_V + E_G)}{2} = E_V + \frac{E_G}{2} \quad (29)$$

This means that

*the Fermi level of an intrinsic semiconductor is located at the center of the forbidden band.*

Furthermore,  $E_F$  is *independent of temperature*, as well as independent of the dimensions of the crystal (that is, of the number of atoms in the lattice).

How should we interpret the presence of  $E_F$  inside the forbidden band of a pure semiconductor? Must we conclude that there *is*, after all, some allowable energy level in an energy region that we normally consider inaccessible to the electrons? No! Generally speaking, the Fermi energy  $E_F$  is only a parameter of the Fermi-Dirac distribution law and *does not necessarily represent an allowable energy level for the electrons*. That is, the Fermi level may or may not contain allowable quantum states. In metals,  $E_F$  is an allowable energy level since it is located inside the conduction band. This is not the case for intrinsic semiconductors, where the Fermi level is located inside the forbidden band.

We note that the presence of the Fermi level  $E_F$  inside the forbidden band is consistent with the general physical interpretation of the Fermi energy given in Sec. 4. Let us explain why:

(a) For  $T > 0$  we know that  $f(E_F) = 1/2$ . That is, half the states of the Fermi level are occupied by electrons. In our case, however, the level  $E_F$  is located inside the forbidden band; hence it may not possess allowable quantum states. Thus on the Fermi level we have the following situation:

$$\frac{1}{2} \times 0 \text{ states} \Rightarrow 0 \text{ electrons}$$

which is reasonable, given that no energy level inside the forbidden band of an *intrinsic* semiconductor may contain electrons.

(b) For  $T=0$ , all *allowable* energy levels below  $E_F$  are completely filled while all *allowable* levels above  $E_F$  are empty. But, allowable levels immediately below and above  $E_F$  exist in the valence and the conduction band, respectively. Hence, all levels in the valence band are fully occupied by the atomic valence electrons, while no energy level within the conduction band contains electrons. Physically this means that, for  $T=0$ , all covalent bonds are intact and there are no free electrons in the crystal.

The fact that the level  $E_F$  is at the center of the forbidden band reflects a symmetry between electrons and holes in an intrinsic semiconductor, their concentrations  $n$  and  $p$  being equal to each other and equal to the intrinsic concentration  $n_i$ :

$$n = p = n_i \quad (\text{pure semiconductor}) \quad (30)$$

In a sense, the Fermi level “keeps equal distances” from the energy bands occupied by free electrons and holes, the two charge carriers being equally important in an intrinsic semiconductor.

The Fermi level of a pure semiconductor will be affected if we dope the crystal with impurities. The doping will spoil the electron-hole balance expressed by Eq. (30). In an  $n$ -type semiconductor the majority carriers are the electrons in the conduction band, while in a  $p$ -type semiconductor the majority carriers are the holes in the valence band. The Fermi level will then shift *toward the band occupied by the majority carriers* in each case. Thus, in an  $n$ -type semiconductor the Fermi level moves closer to the conduction band, while in a  $p$ -type semiconductor it moves closer to the valence band, as shown in Fig. 6.

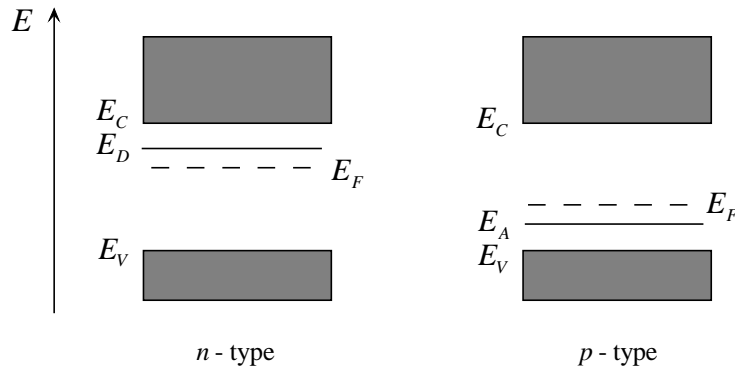


Fig. 6

In contrast to an intrinsic semiconductor, where  $E_F$  is independent of temperature (the Fermi level always lies at the center of the forbidden band), in doped semiconductors  $E_F$  changes with temperature. Specifically, as  $T$  increases,  $E_F$  moves *toward the center of the forbidden band*. This happens because, by the increase of temperature more and more covalent bonds are “broken” in the crystal, which results in an increase of concentration of intrinsic carriers (both electrons and holes) relative to the carriers contributed by the impurity atoms. The concentrations of electrons and holes thus progressively become equal and the semiconductor tends to return to its intrinsic state, with a simultaneous shift of the Fermi level toward the middle of the energy gap. Conversely, as  $T \rightarrow 0$ , the Fermi level  $E_F$  passes *above* the donor level  $E_D$  for  $n$ -type doping, or *below* the acceptor level  $E_A$  for  $p$ -type doping.

The value of  $E_F$  also depends on the concentration of impurity atoms. Adding more donor (acceptor) atoms in an  $n$ -type ( $p$ -type) semiconductor results in a further shift of the Fermi level toward the conduction (valence) band. In cases of extremely high doping, i.e., for  $N_D > 10^{19}$  donor atoms/cm<sup>3</sup> or  $N_A > 10^{19}$  acceptor atoms/cm<sup>3</sup>, the Fermi level may even move into the conduction band or the valence band, respectively!

### Appendix A. Symmetry properties of boson and fermion wavefunctions

As mentioned in Sec. 3, in quantum statistics particles are regarded as *identical* and *indistinguishable*. Regarding the latter property, we note that in quantum mechanics the finite size and the spreading of wave packets that describe individual particles make it impossible to distinguish between identical particles that interact with each other to an appreciable extent, in which case their wave packets overlap significantly. Hence, interacting identical particles are treated as indistinguishable.

Consider a pair of identical particles – call them 1 and 2 – and denote by  $\Psi(1,2)$  the wavefunction of this system, where the notation indicates that particle 1 occupies the ‘first’ quantum state while particle 2 occupies the ‘second’ state, each state being characterized by a certain set of quantum numbers. Now, a physical quantity such as the probability density is determined by the real combination  $\Psi^*\Psi=|\Psi|^2$ . Since the particles are identical, the *physical* state of the system should not be altered by interchanging the particles. Thus we require that  $|\Psi(1,2)|^2 = |\Psi(2,1)|^2 \Rightarrow \Psi(1,2)=\lambda\Psi(2,1)$ , where  $\lambda$  is (generally) complex and  $|\lambda|=1$ .

Since  $\lambda$  is a property of the wavefunction, independent of the identity of the particles occupying the given states, we could equally well write  $\Psi(2,1)=\lambda\Psi(1,2)$ . Therefore,

$$\Psi(1,2) = \lambda\Psi(2,1) = \lambda[\lambda\Psi(1,2)] = \lambda^2\Psi(1,2) \Rightarrow \lambda^2 = 1$$

so that  $\lambda=\pm 1$ . This means that  $\Psi(1,2)=\pm\Psi(2,1)$ . Two situations are possible regarding the symmetry property of the wavefunction and the corresponding identity of the quantum particles:

$$\Psi(1,2) = \Psi(2,1) \Leftrightarrow \text{even (symmetric) wavefunction} \Leftrightarrow \text{bosons};$$

$$\Psi(1,2) = -\Psi(2,1) \Leftrightarrow \text{odd (antisymmetric) wavefunction} \Leftrightarrow \text{fermions}$$

Consider now two identical particles 1 and 2, as well as two one-particle states  $\psi_a$  and  $\psi_b$  available for these particles. If the particles are distinguishable then it makes sense to tell with certainty which particle is in state  $\psi_a$  and which is in state  $\psi_b$ . According to quantum mechanics the wave function of the system will be either

$$\Psi(1,2) = \psi_a(1)\psi_b(2)$$

or

$$\Psi(1,2) = \psi_a(2)\psi_b(1)$$

(provided that the particles do not interact too strongly). But, if the particles are *indistinguishable*, we cannot say which particle is in which state. The wavefunction must therefore reflect this indeterminacy by allowing for all possible situations. For *identical bosons* the (normalized) wavefunction of the system is the *symmetric* combination

$$\Psi(1,2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] = \Psi(2,1) \quad (\text{A.1})$$

while for *identical fermions* the wavefunction of the system is the *antisymmetric* combination

$$\Psi(1,2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] = -\Psi(2,1) \quad (\text{A.2})$$

Note in particular that *two identical fermions cannot occupy the same quantum state*, which statement constitutes the *Pauli exclusion principle*. Indeed, if  $\psi_a=\psi_b$  then the fermion wavefunction (A.2) is equal to  $\Psi(1,2)=0 \Rightarrow |\Psi(1,2)|^2=0$ , so that the probability density for this configuration is zero. The boson wavefunction (A.1), on the other hand, is nonzero for  $\psi_a=\psi_b$ , which reflects the fact that an *arbitrary* number of identical bosons can occupy the same quantum state [2].

## Appendix B. Occupation probability for fermion states

In Sec. 4 we took it for granted that the fraction of states of energy  $E$  that are occupied by electrons equals the occupation probability for any state of energy  $E$ . We will now verify the validity of this statement.

As can be shown (see, e.g., [1]) the number of ways of distributing  $n$  identical fermions in  $N$  quantum states of energy  $E$  ( $n \leq N$ ) is given by

$$Q_{n,N} = \frac{N!}{n!(N-n)!}$$

(Remember that, by the Pauli exclusion principle, *each state can accommodate at most one particle.*) In particular, for  $n=1$  and  $n=N$  we have  $Q_{1,N}=N$  and  $Q_{N,N}=1$ , respectively.

We want to find the probability that any given state of energy  $E$  will be occupied by a particle. The number of distributions in which this state is occupied equals the number of ways the remaining  $(n-1)$  particles can be distributed in the remaining  $(N-1)$  states. That is,

$$Q_{n-1,N-1} = \frac{(N-1)!}{(n-1)![(N-1)-(n-1)]!} = \frac{(N-1)!}{(n-1)!(N-n)!}$$

The occupation probability  $P$  for that state is then

$$P = \frac{\text{number of distributions with given state occupied}}{\text{total number of distributions}} \Rightarrow$$

$$P = \frac{Q_{n-1,N-1}}{Q_{n,N}} = \frac{n!}{(n-1)!} \frac{(N-1)!}{N!} = n \cdot \frac{1}{N} \Rightarrow$$

$$P = \frac{n}{N} = \text{fraction of states of energy } E \text{ that are occupied}$$

In particular, for  $n=1$  and  $n=N$  we have  $P=1/N$  and  $P=1$ , respectively.

## References

1. M. Alonso, E. J. Finn, *Fundamental University Physics*, Volume III, *Quantum and Statistical Physics* (Addison-Wesley, 1968).
2. S. Lokanathan, R. S. Gambhir, *Statistical and Thermal Physics: An Introduction* (Prentice-Hall of India, 1991).
3. J. Millman, C. C. Halkias, *Integrated Electronics* (McGraw-Hill, 1972).
4. A. J. Dekker, *Solid State Physics* (Macmillan, 1981).
5. R. Turton, *The Physics of Solids* (Oxford, 2000).