Modern Theory of Solids

Course code: 053311 PHY 3101
Course title: Electrical Engineering Materials
Bachelor of Science in Electrical and Electronic Engineering
Jashore University of Science and Technology

Content

Band theory of solids, Band theory from molecular orbital, Bloch theorem, Kronig-Penny model, effective mass, density-of-states. Carrier statistics: Maxwell-Boltzmann and Fermi-Dirac distributions, Fermi energy. Modern theory of metals: Determination of Fermi energy and average energy of electrons, classical and quantum mechanical calculation of specific heat.

References

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CHAPTER

4

Modern Theory of Solids

One of the great successes of modern physics has been the application of quantum mechanics or the Schrödinger equation to the behavior of molecules and solids. For example, quantum mechanics explains the nature of the bond between atoms, and its consequences. How can carbon bond with four other carbon atoms? What determines the direction and strength of a bond? An intuitively obvious outcome from quantum mechanics is that the energy of the electron is still quantized in the molecule. In addition, the application of quantum mechanics to many atoms, as in a solid, leads to energy bands within which the electron energy levels are almost continuous. The electron energy falls within possible values in a band of energies. It is nearly impossible to comprehend the principles of operation of modern solid-state electronic devices without a good grasp of the band theory of solids. Since we are dealing with a large number of electrons in the solid, we must consider a statistical way of describing their behavior, just as we use the Maxwell distribution of velocities to explain the behavior of gas atoms. An equally important question, therefore, is "What is the probability that an electron is in a state with energy E within an energy band?"

4.1 HYDROGEN MOLECULE: MOLECULAR ORBITAL THEORY OF BONDING

Consider what happens when two hydrogen atoms approach each other to form the hydrogen molecule. This is the H–H (or H_2) system. Let us examine the energy levels of the H–H system as a function of the interatomic distance R. When the atoms are infinitely separated, each atom has its own set of energy levels, labeled $1s$, $2s$, $2p$, etc. The electron energy in each atom is -13.6 eV with respect to the "free" state (electron infinitely separated from the parent nucleus). The energy of the two isolated hydrogen atoms is twice -13.6 eV.

As the atoms approach closer, the electrons interact both with each other and with the other nuclei. To obtain the wavefunctions and the new energy of the electrons, we need to find the new potential energy function *PE* for the electrons in this new environment and then solve the Schrödinger equation with this new *PE* function. The new energy is actually *lower* than twice −13.6 eV, which means that the H_2 formation is energetically favorable.

The bond formation between two H atoms can be easily explained by describing the behavior of the electron within the molecule. We use a **molecular orbital** ψ, which depends on the interaction of individual atomic wavefunctions and is regarded as an electron wavefunction within the molecule.

In the H_2 molecule, we cannot have two sets of identical atomic ψ_{1s} orbitals, for two reasons. First, this would violate the Pauli exclusion principle, which requires that, in a given system of electrons (those within the H_2 molecule), we cannot have two sets of identical quantum numbers. When the atoms were separated, we did not have this problem, because we had two isolated systems.

Second, as the two atoms approach each other, as shown in Figure 4.1, the atomic ψ_{1s} wavefunctions overlap. This overlap produces two new wavefunctions with different energies and hence different quantum numbers. When the two atomic wavefunctions interfere, they can overlap either in phase (both positive or both negative)

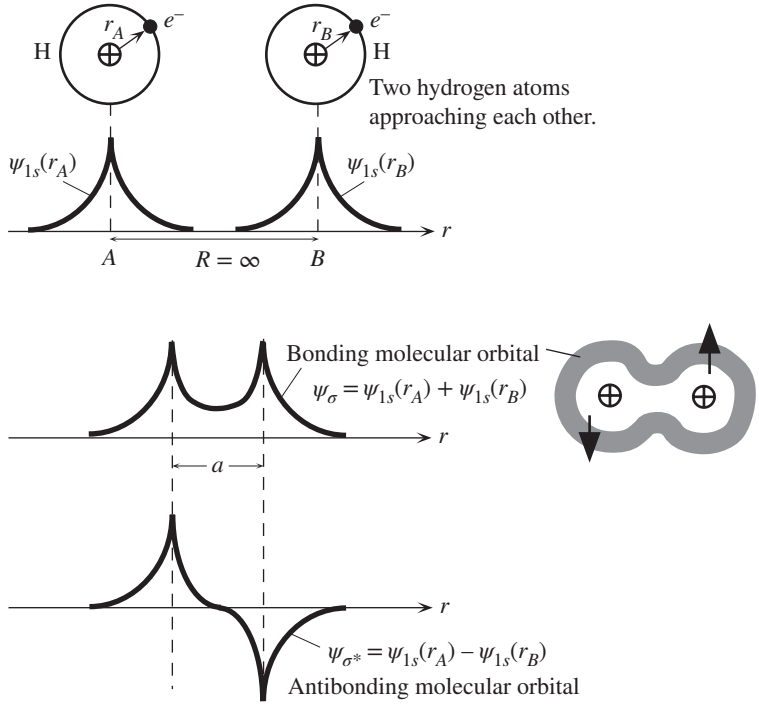


Figure 4.1 Formation of molecular orbitals, bonding, and antibonding (ψ_σ and ψ_{σ^*}) when two H atoms approach each other.

The two electrons pair their spins and occupy the bonding orbital ψ_σ.

or out of phase (one positive and the other negative), as a result of which two molecular orbitals are formed. These are conventionally labeled ψ_σ and ψ_{σ^*} as illustrated in Figure 4.1. Thus, two of the molecular orbitals in the H–H system are

$$\psi_\sigma = \psi_{1s}(r_A) + \psi_{1s}(r_B) \quad [4.1]$$

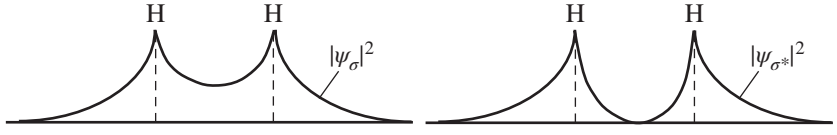
$$\psi_{\sigma^*} = \psi_{1s}(r_A) - \psi_{1s}(r_B) \quad [4.2]$$

where the two hydrogen atoms are labeled A and B, and r_A and r_B are the respective distances of the electrons from their parent nucleus. In generating two separate molecular orbitals ψ_σ and ψ_{σ^*} from a linear combination of two identical atomic orbitals ψ_{1s}, we have used the **linear combination of atomic orbitals (LCAO)** method.

The first molecular orbital ψ_σ is *symmetric* and has considerable magnitude between the nuclei, whereas the second ψ_{σ^*}, is *antisymmetric* and has a node between the nuclei. The resulting electron probability distributions $|\psi_\sigma|^2$ and $|\psi_{\sigma^*}|^2$ are shown in Figure 4.2.

In an analogy to hydrogenic wavefunctions, since ψ_{σ^*} has a node, we would expect it to have a higher energy than the ψ_σ orbital and therefore a different energy quantum number, which means that the Pauli exclusion principle is no longer violated. We can also expect that because $|\psi_\sigma|^2$ has an appreciable electron concentration between the two nuclei, the electrostatic PE, and hence the total energy for the wavefunction ψ_σ, will be lower than that for ψ_{σ^*}, as well as those for the individual atomic wavefunctions.

Of course, the true wavefunctions of the electrons in the H_2 system must be determined by solving the Schrödinger equation, but an intelligent guess is that these must look like ψ_σ and ψ_{σ^*}. We can therefore use ψ_σ and ψ_{σ^*} in the Schrödinger equation, with the correct form of the PE term V, to evaluate the energies E_σ and E_{σ^*} of ψ_σ and ψ_{σ^*}, respectively, as a function of R. The PE function V in the H–H system has positive PE contributions arising from electron–electron repulsions and proton–proton

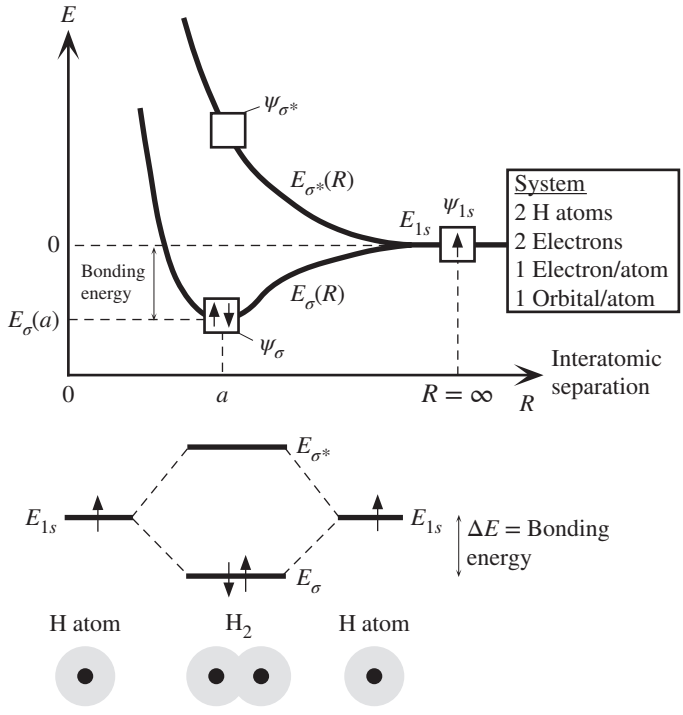


(a) Electron probability distributions for bonding and antibonding orbitals, ψ_σ and ψ_{σ^*}.



(b) Lines representing contours of constant probability (darker lines represent greater relative probability).

Figure 4.2



(a) Energy of ψ_σ and ψ_{σ^*} vs. the interatomic separation *R*.

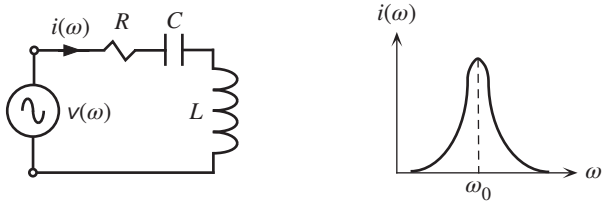
(b) Schematic diagram showing the changes in the electron energy as two isolated H atoms, far left and far right, come together to form a hydrogen molecule.

Figure 4.3 Electron energy in the system comprising two hydrogen atoms.

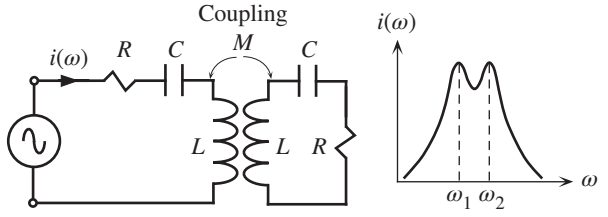
repulsions, but negative *PE* contributions arising from the attractions of the two electrons to the two protons.

The two energies, E_σ and E_{σ^*}, are widely different, with E_σ below E_{1s} and E_{σ^*} above E_{1s}, as shown schematically in Figure 4.3a. As R decreases and the two H atoms get closer, the energy of the ψ_σ orbital state passes through a minimum at $R = a$. Each orbital state can hold two electrons with spins paired, and within the two hydrogen atoms, we have two electrons. If these enter the ψ_σ orbital and pair their spins, then this new configuration is energetically more favorable than two isolated H atoms. It corresponds to the hydrogen molecule H_2. The energy difference between that of the two isolated H atoms and the E_σ minimum energy at $R = a$ is the bonding energy, as illustrated in Figure 4.3a. When the two electrons in the H_2 molecule occupy the ψ_σ orbital, their probability distribution (and hence, the negative charge distribution) is such that the negative *PE*, arising from the attractions of these two electrons to the two protons, is stronger in magnitude than the positive *PE*, arising from electron–electron repulsions and proton–proton repulsions and the kinetic energy of the two electrons. Therefore, the H_2 molecule is energetically stable.

The wavefunction ψ_σ corresponding to the lowest electron energy is called the **bonding orbital,** and ψ_{σ^*} is the **antibonding orbital.** When two atoms are brought together, the two identical atomic wavefunctions combine in two ways to generate two different molecular orbitals, each with a different energy. Effectively, then, an



(a) There is one resonant frequency, ω_0, in an isolated *RLC* circuit.



(b) There are two resonant frequencies in two coupled *RLC* circuits: one below and the other above ω_0.

Figure 4.4

atomic energy level, such as E_{1s}, splits into two, E_σ and E_{σ^*}. The splitting is due to the interaction (or overlap) between the atomic orbitals. Figure 4.3b schematically illustrates the changes in the electron energy levels as two isolated H atoms are brought together to form the H_2 molecule.

The splitting of a one-atom energy level when a molecule is formed is analogous to the splitting of the resonant frequency in an *RLC* circuit when two such circuits are brought together and coupled. Consider the *RLC* circuit shown in Figure 4.4a. The circuit is excited by an ac voltage source. The current peaks at the resonant frequency ω_0, as indicated in Figure 4.4a. When two such identical *RLC* circuits are coupled together and driven by an ac voltage source, the current develops two peaks, at frequencies ω_1 and ω_2, below and above ω_0, as illustrated in Figure 4.4b. The two peaks at ω_1 and ω_2 are due to the mutual inductance that couples the two circuits, allowing them to interact. From this analogy, we can intuitively accept the energy splitting observed in Figure 4.3a.

Consider what happens when two He atoms come together. Recall that the 1*s* orbital has paired electrons and is full. The 1*s* atomic energy level will again split into two levels, E_σ and E_{σ^*}, associated with the molecular orbitals ψ_σ and ψ_{σ^*}, as illustrated in Figure 4.5. However, in the He–He system, there are four electrons, so two occupy the ψ_σ orbital state and two go to the ψ_{σ^*} orbital state. Consequently, the system energy is not lowered by bringing the two He atoms closer. Furthermore, quantum mechanical calculations show that the antibonding energy level E_{σ^*} shifts higher than the bonding level E_σ shifts lower. By the same token, although we could put an additional electron at E_{σ^*} in H_2 to make H_2^-, we could not make H_2^{2-} by placing two electrons at E_{σ^*}.

From the He–He example, we can conclude that, as a general rule, the overlap of full atomic orbital states does not lead to bonding. In fact, full orbitals repel each other, because any overlap results in an increase in the system energy. To form a

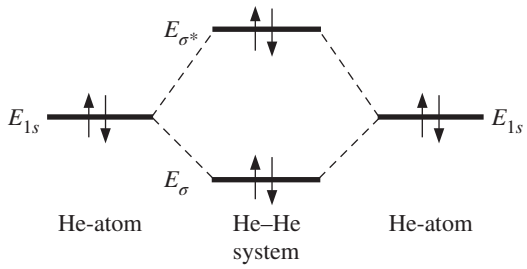


Figure 4.5 Two He atoms have four electrons. When He atoms come together, two of the electrons enter the E_σ level and two the E_{σ^*} level, so the overall energy is greater than two isolated He atoms.

bond between two atoms, we essentially need an overlap of half-occupied orbitals, as in the H_2 molecule.

EXAMPLE 4.1 **HYDROGEN HALIDE MOLECULE (HF)** We already know that H has a half-occupied $1s$ orbital, which can take part in bonding. Since the F atom has the electronic structure $1s^2 2s^2 p^5$, two of the p orbitals are full and one p orbital, p_x, is half full. This means that only the p_x orbital can participate in bonding. Figure 4.6 shows the electron orbitals in both H and F. When the H atom and the F atom approach each other to form an HF molecule, the ψ_{1s} orbital of H overlaps the p_x orbital of F. There are two possibilities for the overlap. First, ψ_{1s} and p_x can overlap in phase (both positive or both negative), to give a ψ_σ orbital that does not have a node between H and F, as shown in Figure 4.6. Second, they can overlap out of phase (one positive and the other negative), so that the overlap orbital ψ_{σ^*} has a node (similar to ψ_{σ^*} in Figure 4.1). We know from hydrogen atomic wavefunctions in Chapter 3 that orbitals with more nodes have higher energies. The molecular orbital ψ_σ therefore corresponds to a bonding orbital with a lower energy than the ψ_{σ^*} orbital. The two electrons, one from ψ_{1s} and the other from p_x, enter the ψ_σ orbital with spins paired, thereby forming a bond between H and F.

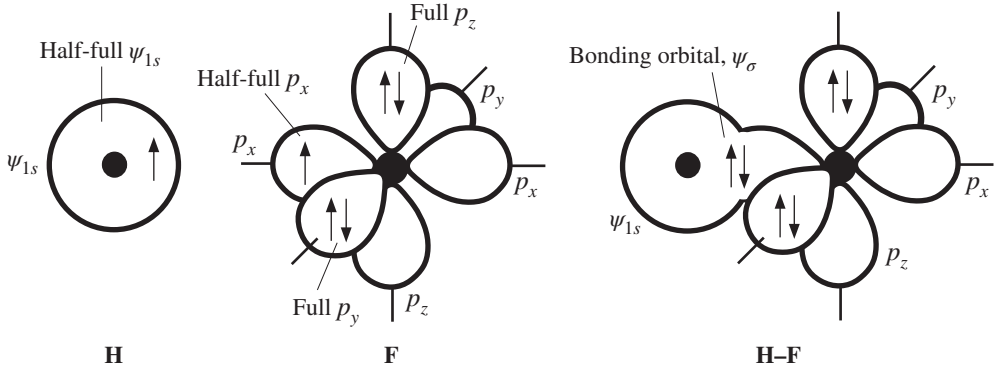


Figure 4.6 H has one half-empty ψ_{1s} orbital.
F has one half-empty p_x orbital but full p_y and p_z orbitals. The overlap between ψ_{1s} and p_x produces a bonding orbital and an antibonding orbital. The two electrons fill the bonding orbital and thereby form a covalent bond between H and F.

4.2 BAND THEORY OF SOLIDS

4.2.1 ENERGY BAND FORMATION

When we bring three hydrogen atoms (labeled A, B, and C) together, we generate three separate molecular orbital states, ψ_a, ψ_b, and ψ_c, from three ψ_{1s} atomic states. Again, this occurs in three different ways, as illustrated in Figure 4.7a. As in the case of the H_2 molecule, each molecular orbital must be either *symmetric* or *antisymmetric* with respect to center atom B. The reason is that the molecule A–B–C in which A, B, and C are identical atoms, is symmetric with respect to B. Thus, each wavefunction must be either symmetric or antisymmetric, that it must have even or odd parity.[1] The orbitals that satisfy even and odd requirements are

$$\psi_a = \psi_{1s}(A) + \psi_{1s}(B) + \psi_{1s}(C) \quad \text{[4.3a]}$$

$$\psi_b = \psi_{1s}(A) - \psi_{1s}(C) \quad \text{[4.3b]}$$

$$\psi_c = \psi_{1s}(A) - \psi_{1s}(B) + \psi_{1s}(C) \quad \text{[4.3c]}$$

where $\psi_{1s}(A)$, $\psi_{1s}(B)$, and $\psi_{1s}(C)$ are the $1s$ atomic wavefunctions centered around the atoms A, B, and C, respectively, as shown in Figure 4.7a. For example, the wavefunction $\psi_{1s}(A)$ represents $\psi_{1s}(r_A)$, which is centered around A and has the form $\exp(-r_A/a_o)$, where r_A is the distance from the nucleus of A, and a_o is the Bohr radius. Notice that $\psi_{1s}(B)$ is missing in Equation 4.3b, so ψ_b is antisymmetric.

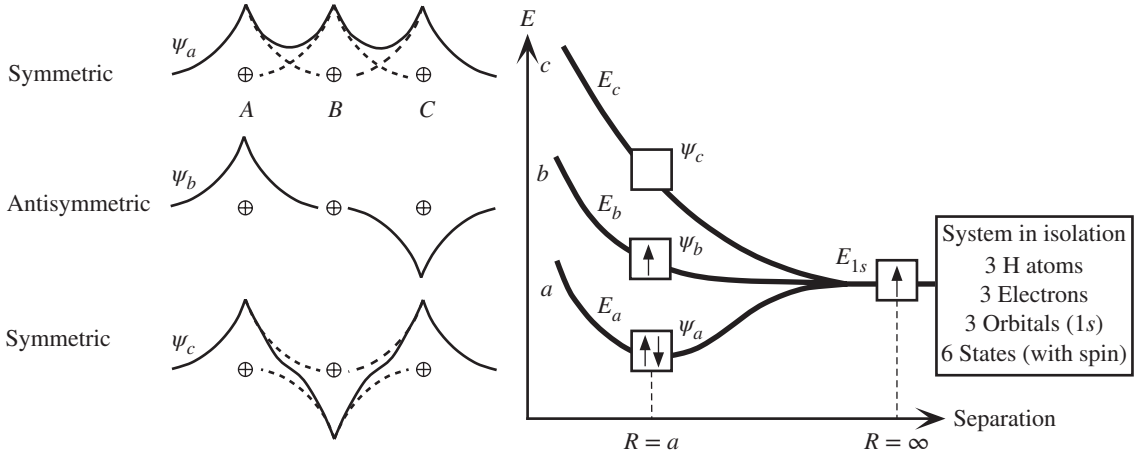
The energies E_a, E_b, and E_c of ψ_a, ψ_b, and ψ_c can be calculated from the Schrödinger equation by using the *PE* function of this system (the *PE* also includes proton–proton repulsions). It is clear that since ψ_a, ψ_b, and ψ_c are different, their energies E_a, E_b, and E_c are also different. Consequently, the $1s$ energy level splits into three separate levels, corresponding to the energies of ψ_a, ψ_b, and ψ_c, as depicted by Figure 4.7b. By analogy with the electron wavefunctions in the hydrogen atom, we can argue that if the molecular wavefunction has more nodes, its energy is higher. Thus, ψ_a has the lowest energy E_a, ψ_b has the next higher energy E_b, and ψ_c has the highest energy E_c, as shown in Figure 4.7b. There are three electrons in the three-hydrogen system. The first two pair their spins and enter orbital ψ_a at energy E_a, and the third enters orbital ψ_b at energy E_b. Comparing Figures 4.7 and 4.3, we notice that although H_2 and H_3 both have two electrons in the lowest energy level, H_3 also has an extra electron at the higher energy level (E_b), which tends to increase the net energy of the atom. Thus, the H_3 molecule is much less stable than the H_2 molecule.[2]

Now consider the formation of a solid. Take N Li (lithium) atoms from infinity and bring them together to form the Li metal. Lithium has the electronic configuration $1s^2 2s^1$, which is somewhat like the hydrogen atom, since the K shell is closed and the third electron is alone in the $2s$ orbital.

Based on our previous discussions, we assume that the atomic energy levels will split into N separate energy levels. Since the $1s$ subshell is full and is close to the

[1] We saw in Chapter 3 that the wavefunctions of an electron in a 1D PE well were either symmetric or antisymmetric. Whenever the potential energy V in the Schrödinger equation has a point of symmetry, the wavefunctions are symmetric or antisymmetric with respect to this point.

[2] See G. Pimentel and R. Spratley, *Understanding Chemistry,* San Francisco: Holden-Day, Inc., 1972, pp. 682–687 for an excellent discussion.



(a) Three molecular orbitals from three ψ_{1s} atomic orbitals overlapping in three different ways.

(b) The energies of the three molecular orbitals, labeled *a*, *b*, and *c*, in a system with three H atoms.

Figure 4.7

nucleus, it will not be affected much by the interatomic interactions; consequently, the energy of this state will experience only negligible splitting, if any. Since the 1*s* electrons will stay close to their parent nuclei, we will not consider them during formation of the solid.

In the system of N isolated Li atoms, we have N electrons in N ψ_{2s} orbitals at the energy E_{2s}, as illustrated in Figure 4.8 (at infinite interatomic separation). Let us assume that N is large (typically, $\sim 10^{23}$). As N atoms are brought together to form the solid, the energy level at E_{2s} splits into N finely separated energy levels. The maximum width of the energy splitting depends on the closest interatomic distance a in the solid, as apparent in Figure 4.3a. The atoms separated by a distance greater than $R = a$ give rise to a lesser amount of energy splitting. The interatomic interactions between N ψ_{2s} orbitals thus spread the N energy levels between the bottom and top levels, E_B and E_T, respectively, which are determined by the closest interatomic distance a. Put differently, E_B and E_T are determined by the distance between nearest neighbors. It is obvious that with N very large, the energy separation between two consecutive energy levels is very small; indeed, it is almost infinitesimal and not as exaggerated as in Figure 4.8.

Remember that each energy level E_i in the Li metal of Figure 4.8 is the energy of an electron wavefunction $\psi_{\text{solid}}(i)$ in the solid, where $\psi_{\text{solid}}(i)$ is one particular combination of the N atomic wavefunctions ψ_{2s}. There are N different ways to combine N atomic wavefunctions ψ_{2s}, since each can be added in phase or out of phase, as is apparent in Equations 4.3a to c (see also Figure 4.7a and b). For example, when all N ψ_{2s} are summed in phase, the resulting wavefunction $\psi_{\text{solid}}(1)$ is like ψ_a in Equation 4.3a, and it has the lowest energy. On the other hand, when N ψ_{2s} are summed with alternating phases, $+ - + \ldots$, the resulting wavefunction $\psi_{\text{solid}}(N)$ is like ψ_c,

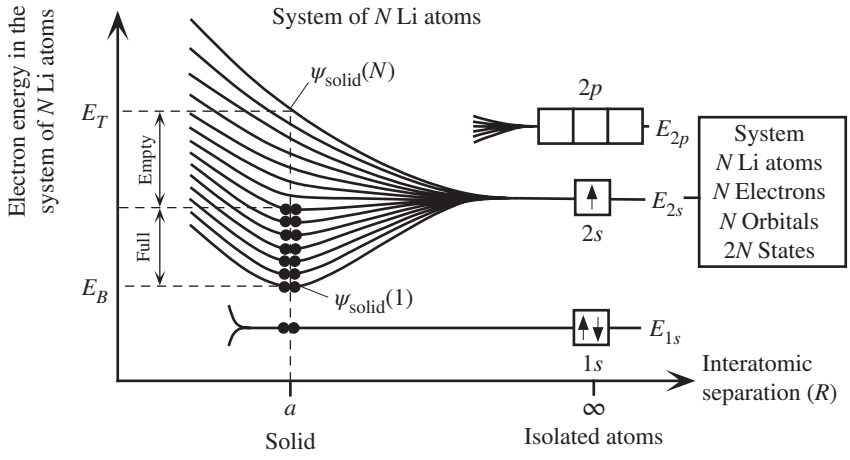


Figure 4.8 The formation of a 2*s* energy band from the 2*s* orbitals when *N* Li atoms come together to form the Li solid.

There are *N* 2*s* electrons, but 2*N* states in the band. The 2*s* band is therefore only half full. The atomic 1*s* orbital is close to the Li nucleus and remains undisturbed in the solid. Thus, each Li atom has a closed *K* shell (full 1*s* orbital).

and it has the highest energy. Other combinations of ψ_{2s} give rise to different energy values between E_B and E_T.

The single 2*s* energy level E_{2s} therefore splits into N ($\sim 10^{23}$) finely separated energy levels, forming an **energy band,** as illustrated in Figure 4.8. Consequently, there are N separate energy levels, each of which can take two electrons with opposite spins. The N electrons fill all the levels up to and including the level at $N/2$. Therefore, the band is half full. We do not mean literally that the band is full to the half-energy point. The levels are not spread equally over the band from E_B to E_T, which means that the band cannot be full to the half-energy point. Half filled simply means half the states in the band are filled from the bottom up.

We have generated a half-filled band from a half-filled isolated 2*s* energy level. The energy band resulting from the splitting of the atomic 2*s* energy level is loosely termed the **2*s* band.** By the same token, the atomic 1*s* levels are full, so any 1*s* band that forms from these 1*s* states will also be full. We can get an idea of the separation of energy levels in the 2*s* band by noting that the maximum separation, $E_T - E_B$, between the top and bottom of the band is on the order of 10 eV, but there are some 10^{23} atoms, giving rise to 10^{23} energy levels between E_B and E_T. Thus, the energy levels are finely separated, forming, for all practical purposes, a continuum of energy levels.

The 2*p* energy level, as well as the higher levels at 3*s* and so on, also split into finely separated energy levels, as shown in Figure 4.9. In fact, some of these energy levels overlap the 2*s* band; hence, they provide further energy levels and "extend" the 2*s* band into higher energy levels, as indicated in Figure 4.10, which shows how energy bands in metals are often represented. The vertical axis is the electron energy. The top of the 2*s* band, which is half full, overlaps the bottom of the 2*p* band, which itself is overlapped near the top by the 3*s* band. We therefore have a band of energies

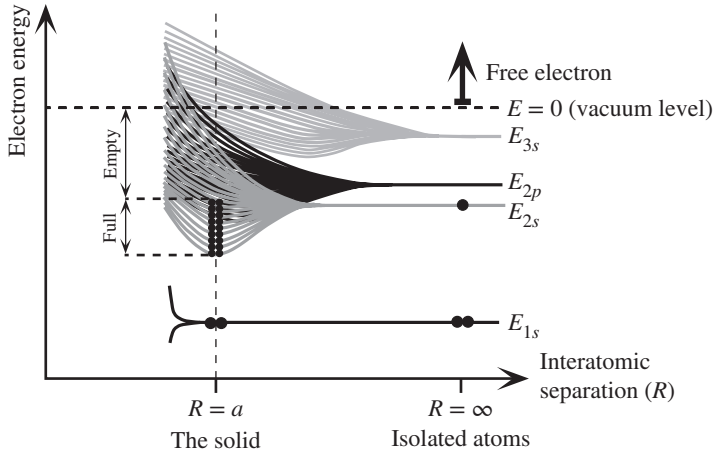


Figure 4.9 As Li atoms are brought together from infinity, the atomic orbitals overlap and give rise to bands (Schematic only.)

Outer orbitals overlap first. The 3*s* orbitals give rise to the 3*s* band, 2*p* orbitals to the 2*p* band, and so on. The various bands overlap to produce a single band in which the energy is nearly continuous.

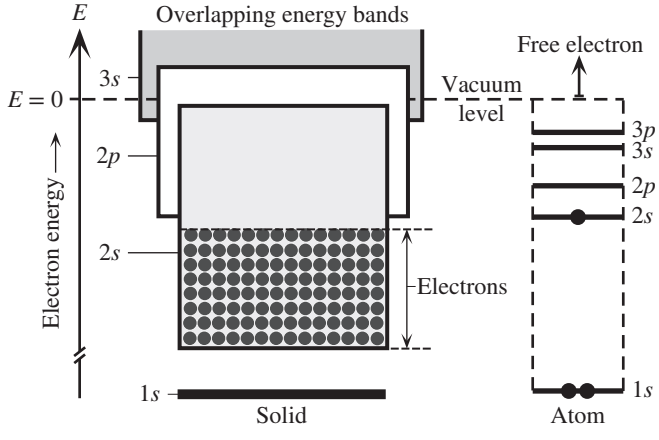


Figure 4.10 In a metal, the various energy bands overlap to give a single energy band that is only partially full of electrons.

There are states with energies up to the vacuum level, where the electron is free.

that stretches from the bottom of the 2*s* band all the way to the vacuum level, as depicted in Figure 4.11. The reader may wonder what happened to the 3*d*, 4*s*, etc., bands. The energies of these bands (including the top portion of the 3*s* band) are normally above the vacuum level. However, this does not mean that an electron within the bulk of the crystal cannot be given an energy higher than the vacuum level, as discussed later in this section.

At a temperature of absolute zero, or nearly so, the thermal energy is insufficient to excite the electrons to higher energy levels, so all the electrons pair their spins and fill each energy level from E_B up to an energy level E_{FO} that we call the Fermi level at 0 K, as shown in Figure 4.11. The energy value for the Fermi level depends on where we take the reference energy. For example, if we take the vacuum level as the zero reference, then for the Li metal, E_{FO} is at –2.5 eV. The Fermi level is normally measured with respect to the bottom of the band, in which case, it is simply termed the Fermi energy and denoted E_{FO}. For the Li metal, E_{FO} is 4.7 eV, which is with respect to the bottom of the band. The Fermi level has considerable significance, as we will discover later in this chapter.

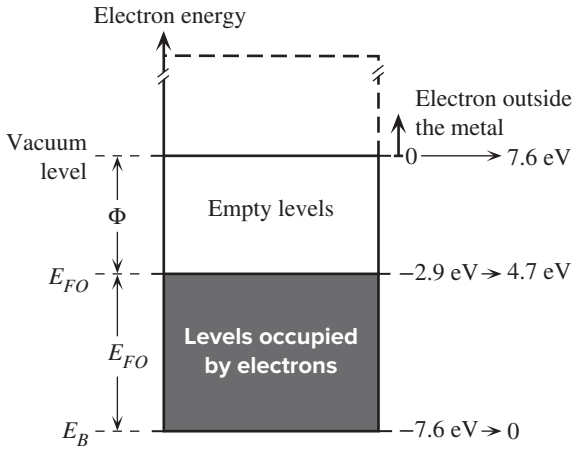


Figure 4.11 Typical electron energy band diagram for a metal.

All the valence electrons are in an energy band, which they only partially fill. The top of the band is the vacuum level, where the electron is free from the solid ($PE = 0$).

Table 4.1 Fermi energy and work function of selected metals (polycrystalline)

	Metal							
	Ag	**Al**	**Au**	**Cs**	**Cu**	**Li**	**Mg**	**Na**
Φ (eV)	4.26	4.28	5.1	2.14	4.65	2.9	3.66	2.75
E_{FO} (eV)	5.5	11.7	5.5	1.58	7.0	4.7	7.1	3.2

At absolute zero, all the energy levels up to the Fermi level are full. The energy required to excite an electron from the Fermi level to the vacuum level, that is, to liberate the electron from the metal, is called the **work function** Φ of the metal. As the temperature increases, some of the electrons get excited to higher energy levels. To determine the probability of finding an electron at an energy level E, we must consider what is called "particle statistics," a topic that is key to understanding the behavior of electronic devices. Clearly, the probability of finding an electron at 0 K at some energy $E < E_{FO}$ is unity, and at $E > E_{FO}$, the probability is zero. Table 4.1 summarizes the Fermi energy and work function of a few selected metals.

The electrons in the energy band of a metal are loosely bound valence electrons which become free in the crystal and thereby form a kind of **electron gas.**[3] It is this electron gas that holds the metal ions together in the crystal structure and constitutes the metallic bond. This intuitive interpretation is shown in Figure 4.9. When solid Li is formed from N atoms, the N electrons fill all the lower energy levels up to $N/2$. The energy of the system of N Li atoms, according to Figure 4.9, is therefore much less than that of N isolated Li atoms by virtue of the N electrons taking up lower energy levels. It must be emphasized that the electrons within a band do not belong to any specific atom but to the whole solid. We cannot identify a given

[3] The energy band in a metal is only partially full, and the electrons in the band are those valence electrons donated by each metal atom. Some authors therefore call this band a valence band. But, these valence electrons are those very electrons that contribute to electrical conduction, so the band is called a conduction band. One convenient view is to simply consider the band as a partially filled conduction band.

electron in the band with a certain Li atom. All the 2*s* electrons essentially form an electron gas and have energies that fall within the energy band. These electrons are constantly moving around in the metal which in terms of quantum mechanics means that their wavefunctions must be of the traveling wave type and not the type that localizes the electron around a given atom (*e.g.*, ψ_{n,ℓ,m_ℓ} in the hydrogen atom). We can represent each electron with a wavevector k so that its momentum p is $\hbar k$.

The energy band diagram in Figure 4.11 is widely used in explaining the electrical properties of metals. However, it gives the impression that any electron inside the metal that has an energy $E_{FO} + \Phi$ can escape the metal; that is, an electron cannot have an energy more than $E_{FO} + \Phi$ inside the metal. This is not true. An electron inside the bulk of the metal crystal is far away from the surface, and even if we impart an energy greater than $E_{FO} + \Phi$, it is unlikely to find the surface of the metal and escape. An electron inside the metal that has an energy $E_{FO} + \Phi$ or more, can only escape the metal into vacuum if it happens to be moving towards the surface, and reaches the surface before it is scattered away. A better representation of the energy band of a metal is to indicate the vacuum level on the surface only and allow the band of energies inside the metal to extend to higher energies as in Figure 4.12. If you examine Figure 4.9 for $R = a$, and ignore the vacuum level line, it is quite apparent that the energy levels extend to higher and higher levels; these are the energies that would be available to an electron inside the bulk of the crystal away from the surface.

When a photon of energy $hf > \Phi$ is incident on a metal crystal, it can be absorbed by an electron at or near E_F, which will be excited to a higher energy. If the electron is moving towards the crystal surface, and it is not scattered by other electrons, thermal vibrations of the crystal, impurities or defects, before it reaches the surface it can be emitted out from the metal into vacuum. This light induced electron emission process is called **photoemission.** The electron labeled 1 in Figure 4.12 is able to reach the surface but electron 2 cannot because it is traveling in the wrong direction, away from the surface. Electron 2 loses its excess energy (energy above E_{FO}) through interactions with other electrons, collisions with vibrating metal ions, impurities and crystal defects, and eventually returns back to E_{FO}.

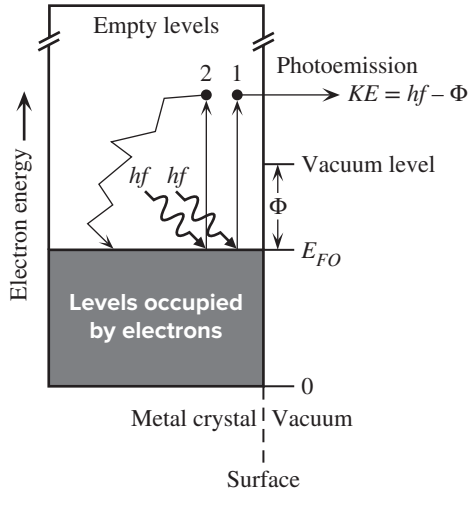


Figure 4.12 An electron inside the metal is allowed to have energies more than $E_{FO} + \Phi$. Suppose that we illuminate the metal with photons and the photon energy $hf > \Phi$. When an electron at E_{FO} absorbs a photon, it is excited to a higher energy level above $E_{FO} + \Phi$. Electron 1 is traveling towards and 2 away from the surface. Electron 1 is able to reach the surface without being scattered and has sufficient energy to escape the metal into vacuum. Electron 2 however is scattered by other electrons, lattice vibrations, impurities, and crystal defects; loses its excess energy and returns back to E_{FO}.

4.2.2 PROPERTIES OF ELECTRONS IN A BAND

Since the electrons inside the metal crystal are considered to be "free," their energy is *KE*. These electrons occupy all the energy levels up to E_{FO} as shown in the band diagram of Figure 4.13a. The energy E of an electron in a metal increases with its momentum p as $p^2/2m_e$. Figure 4.13b shows the energy versus momentum behavior of the electrons in a hypothetical one-dimensional (1D) crystal. The energy increases with momentum whether the electron is moving toward the left or right. Electrons take on all available momentum values until their energy reaches E_{FO}. For every electron that is moving right (such as *a*), there is another (such as *b*) with the same energy but moving left with the same magnitude of momentum. Thus, the average momentum is zero and there is no net current.

Consider what happens when an electric field E_x is applied in the $-x$ direction. The electron *a* at the Fermi level and moving along in the $+x$ direction experiences a force eE_x along the same direction. It therefore accelerates and gains momentum and hence has energy as shown in Figure 4.13c. (The actual energy gained from the field is very small compared with E_{FO}, so Figure 4.13c is highly exaggerated.) The electron *a* at E_{FO} can move to higher energy levels because these adjacent higher levels are empty. The momentum state vacated by *a* is filled by the electron immediately below which now gains energy and moves up, and so on. An electron that is moving in the $-x$ direction, however, is decelerated (its momentum decreases) and hence loses energy as indicated by *b* moving to *b′* in Figure 4.13c. The electrons that are moving in the $+x$ direction gain energy, and those that are moving in the $-x$ direction, lose energy. The whole electron momentum distribution therefore shifts in the $+x$ direction as in Figure 4.13c. Eventually the electron *a*, now at *a′*, is scattered by a lattice vibration. Typically lattice vibrations have small energies but substantial momentum. The scattered electron must find an *unoccupied* momentum state with roughly the same energy, and it must change its momentum substantially. The

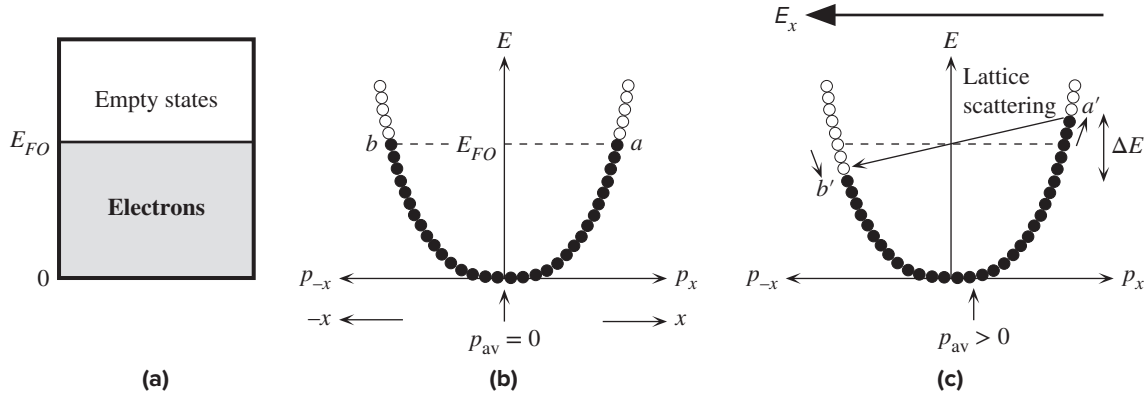


Figure 4.13 (a) Energy band diagram of a metal. (b) In the absence of a field, there are as many electrons moving right as there are moving left. The motions of two electrons at each energy cancel each other as for *a* and *b*. (c) In the presence of a field in the $-x$ direction, the electron *a* accelerates and gains energy to *a′* where it is scattered to an empty state near E_{FO} but moving in the $-x$ direction. The average of all momenta values is along the $+x$ direction and results in a net electric current.

electron at a' is therefore scattered to an empty state around E_{FO} but with a momentum in the opposite direction. Its momentum is *flipped* as shown in Figure 4.13c. The average momentum of the electrons is no longer zero but finite in the $+x$ direction. Consequently there is a current flow in the $-x$ direction, along the field, as determined by this average momentum p_{av}. Notice that a moves up to a' and b falls down to b'. Under steady-state conduction, lattice scattering simply replenishes the electrons at b' from a'. Notice that for energies below b', for every electron moving right there is another moving left with the same momentum magnitude that cancels it. Thus, electrons below the b' energy level do *not* contribute to conduction and are excluded from further consideration. Notice that electrons above the b' level are only moving right and their momenta are not canceled. Thus, the conductivity is determined by the electrons in the energy range ΔE from b' to a' about the Fermi level as shown in Figure 4.13c. Further, as the energy change from a to a' is orders of magnitude smaller than E_{FO}, we can summarize that conduction occurs by the drift of electrons at the Fermi level.[4] (If we were to calculate ΔE for a typical metal for typical currents, it would be $\sim 10^{-6}$ eV whereas E_{FO} is 1–10 eV. The shift in the distribution in Figure 4.13c is very small indeed; a' and b', for all practical purposes, are at the Fermi level.)

Conduction can be explained very simply and intuitively in terms of a band diagram as shown in Figure 4.14. Notice that the application of the electric field bends the energy band, because the electrostatic PE of the electron is $-eV(x)$ where $V(x)$ is the voltage at position x. However, $V(x)$ changes linearly from 0 to V, by virtue of $dV/dx = -E_x$. Since $E = -eV(x)$ adds to the energy of the electron, the energy band must bend to account for the additional electrostatic energy. Since only the electrons near E_{FO} contribute to electrical conduction, we can represent this by drifting the electrons at E_{FO} down the potential hill. Although these electrons possess a very high mean velocity ($\sim 10^6$ ms^{-1}), as determined by the Fermi energy, they drift very slowly (10^{-2}–10^{-1} ms^{-1}) with a velocity that is drift mobility $\times$ field.

When a metal is illuminated, provided the wavelength of the radiation is correct, it will cause the emission of electrons from the metal as in the photoelectric effect. Since Φ is the "minimum energy" required to excite an electron into the vacuum level (out from the metal), the longest wavelength radiation required is $hc/\lambda = \Phi$.

The addition of heat to a metal can excite some of the electrons in the band to higher energy levels. Thus heat can also be absorbed by the conduction electrons of a metal. We also know that the addition of heat increases the amplitude of atomic vibrations. We can therefore guess that the heat capacity of a metal has two terms which are due to energy absorption by the lattice vibrations and energy absorption by conduction electrons. It turns out that at room temperature the energy absorption by lattice vibrations dominates the heat capacity whereas at the lowest temperatures (typically a few Kelvins) the electronic contribution is important.

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[4] In some books (including the first edition of this textbook) it is stated that the electrons at E_{FO} can gain energy from the field and contribute to conduction but not those deep in the band (below b'). This is a simplified statement of the fact that at a level below E_{FO} there is one electron moving along in the $+x$ direction and gaining energy and another one at the same energy but moving along in the $-x$ direction and losing energy so that an average electron at this level does not gain energy.

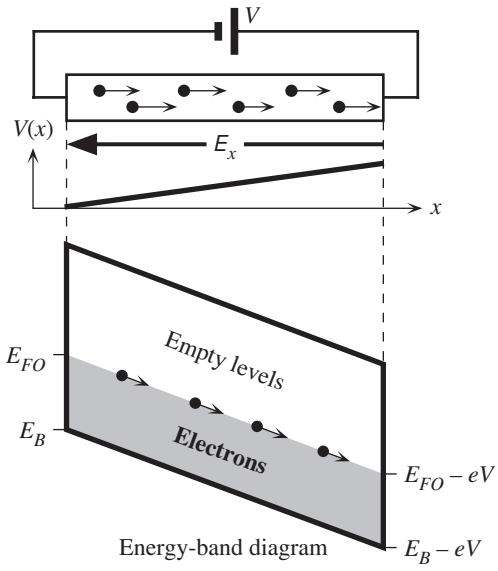


Figure 4.14 Conduction in a metal is due to the drift of electrons around the Fermi level. When a voltage is applied, the energy band is bent to be lower at the positive terminal so that the electron's potential energy decreases as it moves toward the positive terminal.

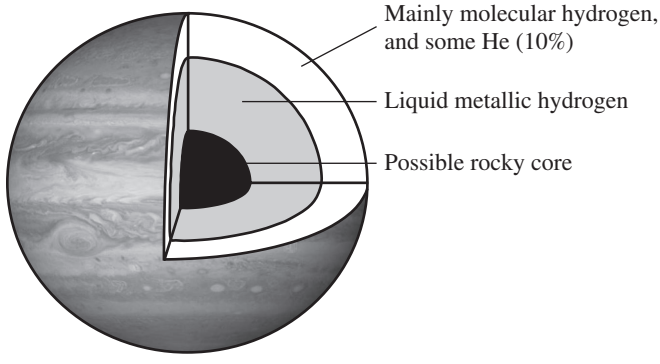


Figure 4.15 The interior of Jupiter is believed to contain liquid hydrogen, which is metallic.

EXAMPLE 4.2

METALLIC LIQUID HYDROGEN IN JUPITER AND ITS MAGNETIC FIELD The surface of Jupiter, as visualized schematically in Figure 4.15, mainly consists of a mixture of molecular hydrogen and He gases. Deep in the planet, however, the pressure is so tremendous that the hydrogen molecular bond breaks, leaving a dense ocean of hydrogen atoms. Hydrogen has only one electron in the 1*s* energy level. When atoms are densely packed, the 1*s* energy level forms an energy band, which is then only half filled. This is just like the Li metal, which means we can treat liquid hydrogen as a liquid metal, with electrical properties reminiscent of liquid mercury. Liquid hydrogen can sustain electric currents, which in turn can give rise to the magnetic fields on Jupiter. The origin of the electric currents are not known with certainty. We do know, however, that the core of the planet is hot and emanates heat, which causes convection currents. Temperature differences can readily give rise to electric currents, by virtue of thermoelectric effects, as discussed in Section 4.8.2.

EXAMPLE 4.3 **WHAT MAKES A METAL?** The Be atom has an electronic structure of $1s^2 2s^2$. Although the Be atom has a full $2s$ energy level, solid Be is a metal. Why?

SOLUTION

We will neglect the K shell ($1s$ state), which is full and very close to the nucleus, and consider only the higher energy states. In the solid, the $2s$ energy level splits into N levels, forming a $2s$ band. With $2N$ electrons, each level is occupied by spin-paired electrons. The $2s$ band is therefore full. However, the empty $2p$ band, from the empty $2p$ energy levels, overlaps the $2s$ band, thereby providing empty energy levels to these $2N$ electrons. Thus, the conduction electrons are in an energy band that is only partially filled; they can gain energy from the field to contribute to electrical conduction. Solid Be is therefore a metal.

EXAMPLE 4.4 **FERMI SPEED OF CONDUCTION ELECTRONS IN A METAL** In copper, the Fermi energy of conduction electrons is 7.0 eV. What is the speed of the conduction electrons around this energy?

SOLUTION

Since the conduction electrons are not bound to any one atom, their PE must be zero within the solid (but large outside), so all their energy is kinetic. For conduction electrons around the Fermi energy E_{FO} with a speed v_F, we have

$$\frac{1}{2}mv_F^2 = E_{FO}$$

so that

$$v_F = \sqrt{\frac{2E_{FO}}{m_e}} = \sqrt{\frac{2(1.6 \times 10^{-19}\ \text{J/eV})(7.0\ \text{eV})}{(9.1 \times 10^{-31}\ \text{kg})}} = 1.6 \times 10^6\ \text{m s}^{-1}$$

Although the Fermi energy depends on the properties of the energy band, to a good approximation it is only weakly temperature dependent, so v_F will be relatively temperature insensitive, as we will show later in Section 4.7.

4.3 SEMICONDUCTORS

The Si atom has 14 electrons, which distribute themselves in the various atomic energy levels as shown in Figure 4.16. The inner shells ($n = 1$ and $n = 2$) are full and therefore "closed." Since these shells are near the nucleus, when Si atoms come together to form the solid, they are not much affected and they stay around the parent Si atoms. They can therefore be excluded from further discussion. The $3s$ and $3p$ subshells are farther away from the nucleus. When two Si atoms approach, these electrons strongly interact with each other. Therefore, in studying the formation of bands in the Si solid, we will only consider the $3s$ and $3p$ levels.

The first task is to examine why Si actually bonds with four neighbors, since the $3s$ orbital is full and there are only two electrons in the $3p$ orbitals. The full $3s$ orbital should not overlap a neighbor and become involved in bonding. Since only two $3p$ orbitals are half full, bonds should be formed with two neighboring Si atoms.

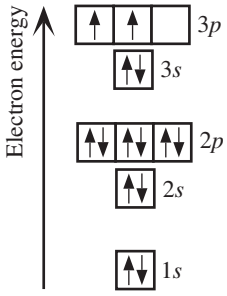


Figure 4.16 The electronic structure of Si.

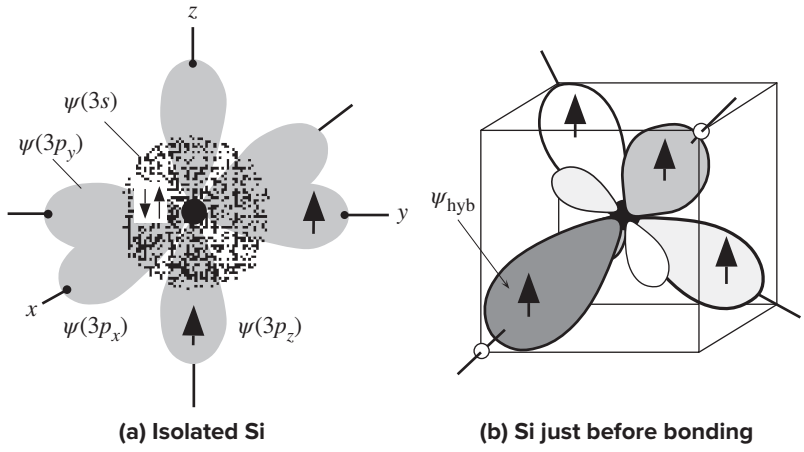


Figure 4.17 (a) Si is in Group IV in the Periodic Table. An isolated Si atom has two electrons in the 3*s* and two electrons in the 3*p* orbitals. (b) When Si is about to bond, the one 3*s* orbital and the three 3*p* orbitals become perturbed and mixed to form four hybridized orbitals, ψ_{hyb}, called sp^3 orbitals, which are directed toward the corners of a tetrahedron. The ψ_{hyb} orbital has a large major lobe and a small back lobe. Each ψ_{hyb} orbital takes one of the four valence electrons.

In reality, the 3*s* and 3*p* energy levels are quite close, and when five Si atoms approach each other, the interaction results in the four orbitals $\psi(3s)$, $\psi(3p_x)$, $\psi(3p_y)$, and $\psi(3p_z)$ mixing together to form four new **hybrid orbitals,** which are directed in tetrahedral directions; that is, each one is aimed as far away from the others as possible as illustrated in Figure 4.17. We call this process sp^3 **hybridization,** since one *s* orbital and three *p* orbitals are mixed. (The superscript 3 on *p* has nothing to do with the number of electrons; it refers to the number of *p* orbitals used in the hybridization.)

The four sp^3 hybrid orbitals, ψ_{hyb}, each have one electron, so they are half occupied. This means that four Si atoms can have their orbitals ψ_{hyb} overlap to form bonds with one Si atom, which is what actually happens; thus, one Si atom bonds with four other Si atoms in tetrahedral directions.

In the same way, one Si atom bonds with four H atoms to form the important gas SiH_4, known as silane, which is widely used in the semiconductor technology to fabricate Si devices. In SiH_4, four hybridized orbitals of the Si atom overlap with the 1*s* orbitals of four H atoms. In exactly the same way, one carbon atom bonds with four hydrogen atoms to form methane, CH_4.

There are two ways in which the hybrid orbital ψ_{hyb} can overlap with that of the neighboring Si atom to form two molecular orbitals. They can add in phase (both positive or both negative) or out of phase (one positive and the other negative) to produce a bonding or an antibonding molecular orbital ψ_B and ψ_A, respectively, with energies E_B and E_A as shown in Figure 4.18a to c. Each Si–Si bond thus corresponds to two paired electrons in a bonding molecular orbital ψ_B. In the solid, there are $N(\sim 5 \times 10^{22}\ \text{cm}^{-3})$ Si atoms, and there are nearly as many such ψ_B bonds. The interactions between the ψ_B orbitals (*i.e.*, the Si–Si bonds) lead to the splitting of the E_B energy level to *N* levels, thereby forming an energy band labeled the **valence band** (VB) by

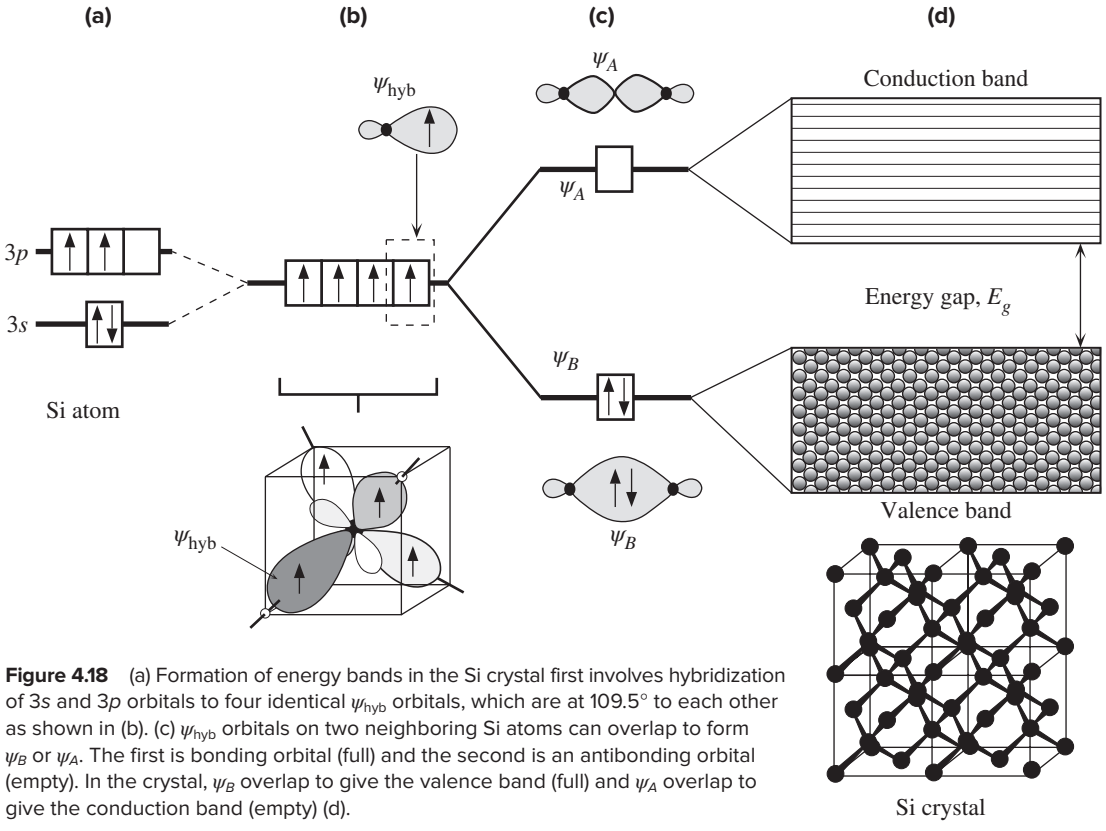


Figure 4.18 (a) Formation of energy bands in the Si crystal first involves hybridization of 3*s* and 3*p* orbitals to four identical ψ_{hyb} orbitals, which are at 109.5° to each other as shown in (b). (c) ψ_{hyb} orbitals on two neighboring Si atoms can overlap to form ψ_B or ψ_A. The first is bonding orbital (full) and the second is an antibonding orbital (empty). In the crystal, ψ_B overlap to give the valence band (full) and ψ_A overlap to give the conduction band (empty) (d).

virtue of the valence electrons it contains. Since the energy level E_B is full, so is the valence band. Figure 4.18c and d illustrate the formation of the VB from E_B.

In the solid, the interactions between the N number of ψ_A orbitals result in the splitting of the energy level E_A to N levels and the formation of an energy band that is completely empty and separated from the full valence band by a definite energy gap E_g. In this energy region, there are no states; therefore, the electron cannot have energy with a value within E_g. The energy band formed from $N\psi_A$ orbitals is a **conduction band** (CB), as also indicated in Figure 4.18c and d.

The electronic states in the VB (and also in the CB) extend throughout the whole solid, because they result from $N\psi_B$ orbitals interfering and overlapping each other. As before $N\psi_B$, orbitals can overlap in N different ways to produce N distinct wavefunctions ψ_{vb} that extend throughout the solid. We cannot relate a particular electron to a particular bond or site because the wavefunctions ψ_{vb} corresponding to the VB energies are not concentrated at a single location. The electrical properties of solids are based on the fact that in solids, such as semiconductors and insulators, there are certain bands of allowed energies for the electrons, and these bands are separated by energy gaps, that is, bandgaps. The valence and conduction bands for the ideal Si crystal shown in Figure 4.18d are separated by an **energy gap,** or a **bandgap,** E_g, in which there are no allowed electron energy levels.

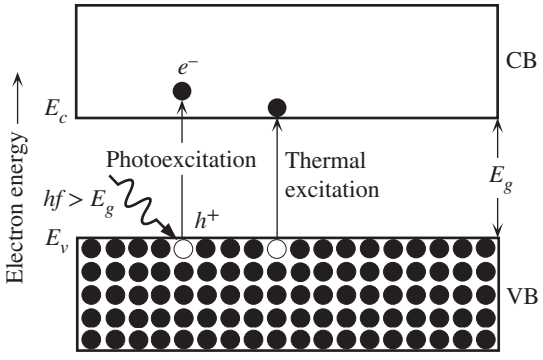


Figure 4.19 A simplified energy band diagram of a semiconductor. CB is the conduction band and VB is the valence band. At 0 K, the VB is full of electrons and the CB is empty. If a photon of energy $hf > E_g$ is incident on the semiconductor, it can be absorbed by an electron in the VB, which becomes photoexcited into the CB. Some electrons in the VB can be excited into the CB by thermal excitation, that is, occasional rupturing of Si-Si bonds by energetic lattice vibrations. Thermal generation creates electron and hole pairs.

We can generalize the energy band diagram of a semiconductor as shown in Figure 4.19. At absolute zero of temperature the VB will be full of electrons and the CB will be empty. The conductivity of this ideal semiconductor would be zero as there are no free carriers to drift. It is possible to excite an electron from the VB to the CB if a photon of energy hf equal or greater than the bandgap is incident on this semiconductor. The photon can be absorbed by an electron in the VB, which becomes **photoexcited** into the CB[5]. An electron in the CB is essentially in an empty band. We can consider this electron in the CB as a free carrier with a certain effective mass m_e^*. If there is an electric field E_x along x then this photoexcited electron will be acted on by a force, $F = -eE_x$, and it will try to move in the $-x$ direction. For it to do so, there must be empty higher energy levels, so that as the electron accelerates and gains energy, it moves up in the band. When an electron collides with a lattice vibration, it loses the energy acquired from the field and drops down within the CB. Again, it should be emphasized that states in an energy band are extended; that is, the electron is not localized to any one atom.

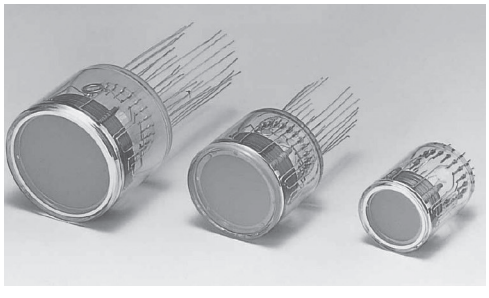
Note also that the photogeneration of an electron from the VB to the CB leaves behind a VB state with a missing electron. This unoccupied electron state has an apparent positive charge, because this crystal region was neutral prior to the removal of the electron. The VB state with the missing electron is called a **hole** and is denoted h^+. The hole can "move" in the direction of the field by exchanging places with a neighboring valence electron hence it contributes to conduction, as will be discussed in Chapter 5.

At temperatures above absolute zero, the atoms in a solid vibrate due to their thermal energy. Some of the atoms can acquire a sufficiently high energy from thermal fluctuations to strain and rupture their bonds. Physically, there is a possibility that the atomic vibration will impart sufficient energy to the electron for it to surmount the bonding energy and leave the bond. The electron must then enter a higher energy state. In the case of Si, this means entering a state in the CB, as shown in Figure 4.19. The excitation of electrons from the VB to the CB by lattice vibrations is called **thermal generation,** and results in the generation of electrons in the

[5] In pure intuitive terms, the incident photon has sufficient energy to be able to rupture a Si–Si bond and release a free electron. An electron is free only in the CB, so this process implies the photoexcitation of an electron from the VB to the CB.

CB and holes in the VB as shown in Figure 4.19. The electrons in the CB and holes in the VB can contribute to conduction, and semiconductors above absolute zero of temperature have a finite conductivity.

EXAMPLE 4.5 **ELECTRON AFFINITY AND PHOTOMULTIPLIER TUBES** Photomultiplier tubes are used in various high gain photodetection applications that involve detecting low light intensities. A simplified structure of a photomultiplier tube is shown in Figure 4.20. The tube is evacuated and has a photocathode for receiving photons as signal. An incoming photon causes photoemission of an electron from the photocathode material. The photocathode can be metal, in which case the photoemission will be as in Figure 4.12. Usually, the photocathode is a semiconductor, or a metal that has its surface coated with a semiconductor. The photoemission in this case is shown in Figure 4.21a. The vacuum level is at an energy χ above the conduction band edge E_c. The energy χ needed to remove an electron from E_c to the vacuum is called the **electron affinity** of the semiconductor. Thus, only those photons with an energy $hf > E_g + \chi$ can cause photoemission, because the electron has to be excited from the valence band (VB) to energies in the CB that are above χ as shown in Figure 4.21a. The photoemitted electron is then accelerated by a positive voltage applied to an electrode called a dynode as in Figure 4.20. When the accelerated projectile electron strikes the dynode material, it causes the emission of electrons from the dynode surface. Electron bombardment induced electron emission from a material is called **secondary electron emission.** When the accelerated electron strikes the dynode D_1 it can release several electrons. All these electrons, the original and the secondary electrons, are then accelerated by the more positive voltage applied to the dynode D_2. On impact with D_2, further electrons are released by secondary emission. The secondary emission process continues at each dynode stage until the final electrode, called the anode, is reached whereupon all the electrons are collected which results in a signal. Typical applications for photomultiplier tubes are in X-ray and nuclear medical instruments (X-ray CT scanner, positron CT scanner, gamma camera, etc.), radiation measuring instruments (*e.g.*, radon counter), X-ray diffractometers and radiation measurement in high energy physics research.



Photomultiplier tubes.
Courtesy of Hamamatsu.

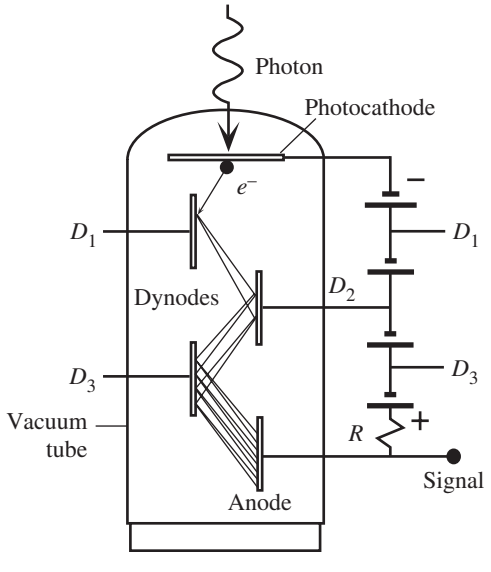


Figure 4.20 The photomultiplier tube.

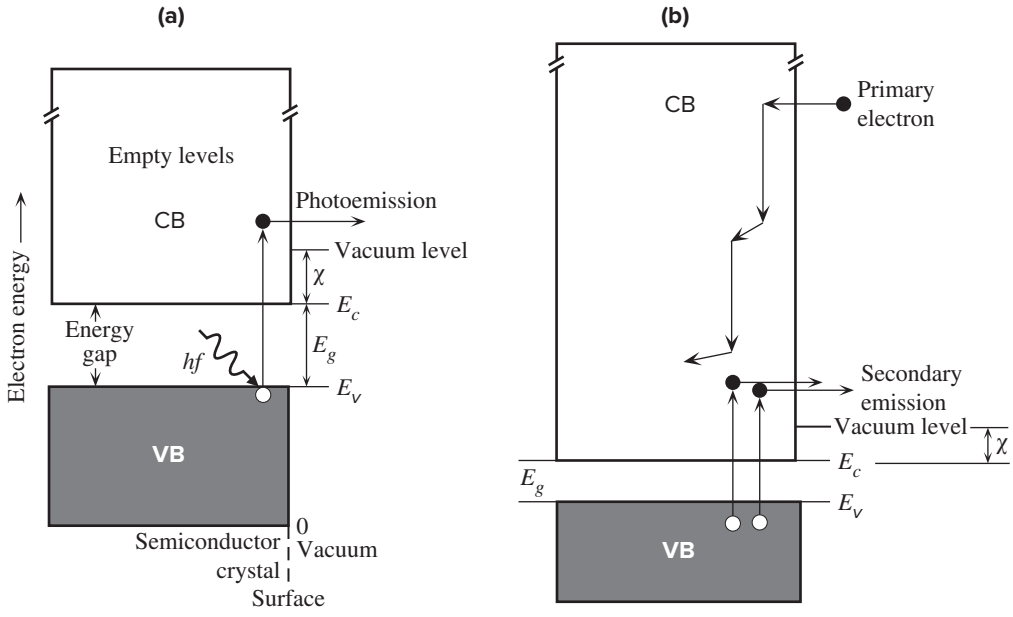


Figure 4.21 (a) Photoemission process in a semiconductor is different than in a metal and excites an electron from the VB to the CB. If this electron has a kinetic energy greater than the electron affinity and if it can reach the surface before being scattered, it can be emitted. (b) A primary projectile electron with sufficient energy knocks out an electron from the VB into the CB. The electron in the CB is a secondary electron that can escape the semiconductor if it can reach the surface. There may be several secondary electrons generated. Further, the primary electron can also be emitted back to vacuum.

When a sufficiently energetic electron impinges on a dynode material it knocks out an electron from the dynode. Usually, the dynode is a semiconducting material so that the incident energetic primary electron enters the CB and interacts with the valence electrons. This interaction results in an electron that is knocked out from the VB into the high energy levels in the CB, above $E_c + \chi$; and if it is close to the surface, it can escape as shown in Figure 4.21b. Notice that the primary electron generates an electron and hole pair (EHP) as the electron is excited from the VB to the CB. A sufficiently energetic primary electron can release several secondary electrons, and it may itself escape the semiconductor, for example, if it is scattered towards the surface. The **secondary electron yield** δ is defined as

Secondary electron yield

$$\delta = \frac{\text{Number of secondary electrons emitted}}{\text{Number of incident primary electrons}}$$

Given that the electron multiplication at each dynode is δ, the overall gain after N dynodes is δ^N. The dynode material in modern photomultipliers have δ values around 5 – 10; and with several dynodes, the electron multiplication can easily reach $\sim 10^6$. Typical dynode materials are compounds such as BeO, GaP, MgO, Cs_3Sb.

EXAMPLE 4.6

CUTOFF WAVELENGTH OF A Si PHOTODETECTOR What wavelengths of light can be absorbed by a Si photodetector given $E_g = 1.1$ eV? Can such a photodetector be used in fiber-optic communications at light wavelengths of 1.31 μm and 1.55 μm?

SOLUTION

The energy bandgap E_g of Si is 1.1 eV. A photon must have at least this much energy to excite an electron from the VB to the CB, where the electron can drift. Excitation corresponds to the breaking of a Si–Si bond. A photon of less energy does not get absorbed, because its energy will put the electron in the bandgap where there are no states. Thus, $hc/\lambda > E_g$ gives

$$\lambda < \frac{hc}{E_g} = \frac{(6.6 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{(1.1\ \text{eV})(1.6 \times 10^{-19}\ \text{J/eV})}$$
$$= 1.13 \times 10^{-6}\ \text{m} \qquad \text{or} \qquad 1.1\ \mu\text{m}$$

Since optical communications networks use wavelengths of 1.3 and 1.55 μm, these light waves will not be absorbed by Si and thus cannot be detected by a Si photodetector.

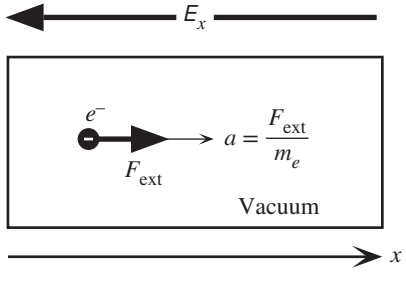
4.4 ELECTRON EFFECTIVE MASS

When an electric field E_x is applied to a metal, an electron near the Fermi level can gain energy from the field and move to higher energy levels, as shown in Figure 4.13. The external force $F_{\text{ext}} = eE_x$ is in the x direction, and it drives the electron along x. The acceleration of the electron is still given by $a = F_{\text{ext}}/m_e$, where m_e is the mass of the electron in vacuum.

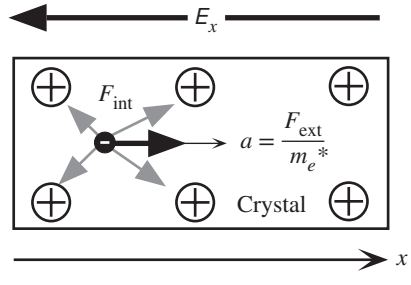
The law $F_{\text{ext}} = m_e a$ cannot strictly be valid for the electron inside a solid, because the electron interacts with the host ions and experiences internal forces F_{int} as it moves around, as depicted in Figure 4.22. The electron therefore has a *PE* that varies with distance. Recall that we interpret mass as inertial resistance against acceleration per unit applied force. When an external force F_{ext} is applied to an electron in the vacuum level, as in Figure 4.22a, the electron will accelerate by an amount

$$a_{\text{vac}} = \frac{F_{\text{ext}}}{m_e} \qquad [4.4]$$

as determined by its mass m_e in vacuum.



(a) An external force F_{ext} applied to an electron in a vacuum results in an acceleration $a_{\text{vac}} = F_{\text{ext}}/m_e$.



(b) An external force F_{ext} applied to an electron in a crystal results in an acceleration $a_{\text{cryst}} = F_{\text{ext}}/m_e^*$.

Figure 4.22

When the same force F_{ext} is applied to the electron inside a crystal, the acceleration of the electron will be different, because it will also experience internal forces, as shown in Figure 4.22b. Its acceleration in the crystal will be

$$a_{cryst} = \frac{F_{ext} + F_{int}}{m_e} \quad [4.5]$$

where F_{int} is the sum of all the internal forces acting on the electron, which is quite different than Equation 4.4. To the outside agent applying the force F_{ext}, the electron will appear to be exhibiting a different inertial mass, since its acceleration will be different. It would be most useful for the external agent if the effect of the internal forces in F_{int} could be accounted for in a simple way, and if the acceleration could be calculated from the external force F_{ext} alone, through something like Equation 4.4. This is indeed possible.

In a crystalline solid, the atoms are arranged periodically, and the variation of F_{int}, and hence the PE, or $V(x)$, of the electron with distance along x, is also periodic. In principle, then, the effect on the electron motion can be predicted and accounted for. When we solve the Schrödinger equation with the periodic PE, or $V(x)$, we essentially obtain the effect of these internal forces on the electron motion. It has been found that when the electron is in a band that is not full, we can still use Equation 4.4, but instead of the mass in vacuum m_e, we must use the effective mass m_e^* of the electron in that particular crystal. The **effective mass** is a quantum mechanical quantity that behaves in the same way as the inertial mass in classical mechanics. The acceleration of the electron in the crystal is then simply

$$a_{cryst} = \frac{F_{ext}}{m_e^*} \quad [4.6]$$

The effects of all internal forces are incorporated into m_e^*. It should be emphasized that m_e^* is obtained theoretically from the solution of the Schrödinger equation for the electron in a particular crystal, a task that is by no means trivial. However, the effective mass can be readily measured. For some of the familiar metals, m_e^* is very close to m_e. For example, in silver, $m_e^* = m_e$ for all practical purposes, whereas in lithium $m_e^* = 2.2m_e$, as shown in Table 4.2. On the other hand, m_e^* for many metals and semiconductors is appreciably different than the electron mass in vacuum and can even be negative. (m_e^* depends on the properties of the band that contains the electron as discussed in Section 5.13.)

Table 4.2 Effective mass m_e^* of electrons in some metals

Metal	Ag	Au	Bi	Cu	Fe	K	Li	Mg	Na	Zn
$\frac{m_e^*}{m_e}$	1.0	1.1	0.008	1.3	12	1.2	2.2	1.3	1.2	0.85

Note: Table compiled from multiple sources; values are typical.

4.5 DENSITY OF STATES IN AN ENERGY BAND

Although we know there are many energy levels (perhaps $\sim 10^{23}$) in a given band, we have not yet considered how many states (or electron wavefunctions) there are per unit energy per unit volume in that band. Consider the following *intuitive* argument. The crystal will have N atoms and there will be N electron wavefunctions ψ_1, ψ_2, . . . , ψ_N that represent the electron within the whole crystal. These wavefunctions are constructed from N different combinations of atomic wavefunctions, ψ_A, ψ_B, ψ_C, . . . as schematically illustrated in Figure 4.23a,[6] starting with

$$\psi_1 = \psi_A + \psi_B + \psi_C + \psi_D + \cdots$$

all the way to alternating signs

$$\psi_N = \psi_A - \psi_B + \psi_C - \psi_D + \cdots$$

and there are $N(\sim 10^{23})$ combinations. The lowest-energy wavefunction will be ψ_1 constructed by adding all atomic wavefunctions (all in phase), and the highest-energy wavefunction will be ψ_N from alternating the signs of the atomic wavefunctions, which will have the highest number of nodes. Between these two extremes, especially around $N/2$, there will be many combinations that will have comparable energies and fall near the middle of the band. (By analogy, if we arrange $N = 10$ coins by heads and tails, there will be many combinations of coins in which there are 5 heads and 5 tails, and only one combination in which there are 10 heads or 10 tails.) We therefore expect the number of energy levels, each corresponding to an electron wavefunction in the crystal, in the central regions of the band to be very large as depicted in Figure 4.23b and c.

Figure 4.23c illustrates schematically how the energy and volume density of electronic states change across an energy band. We define the **density of states** $g(E)$ such that $g(E)\,dE$ is the number of states (*i.e.*, wavefunctions) in the energy interval E to $(E + dE)$ per unit volume of the sample. Thus, the number of states per unit volume up to some energy E' is

$$S_v(E') = \int_0^{E'} g(E)\,dE \qquad [4.7]$$

which is called the total number of states per unit volume with energies less than E'. This is denoted $S_v(E')$.

To determine the density of states function $g(E)$, we must first determine the number of states with energies less than E' in a given band. This is tantamount to calculating $S_v(E')$ in Equation 4.7. Instead, we will improvise and use the energy levels for an electron in a 3D potential well. Recall that the energy of an electron in a cubic PE well of size L is given by

$$E = \frac{h^2}{8m_e L^2}(n_1^2 + n_2^2 + n_3^2) \qquad [4.8]$$

[6] This intuitive argument, as schematically depicted in Figure 4.23a, is obviously highly simplified because the solid is three-dimensional (3D) and we should combine the atomic wavefunctions not on a linear chain but on a 3D lattice. In the 3D case there are large numbers of wavefunctions with energies that fall in the central regions of the band.

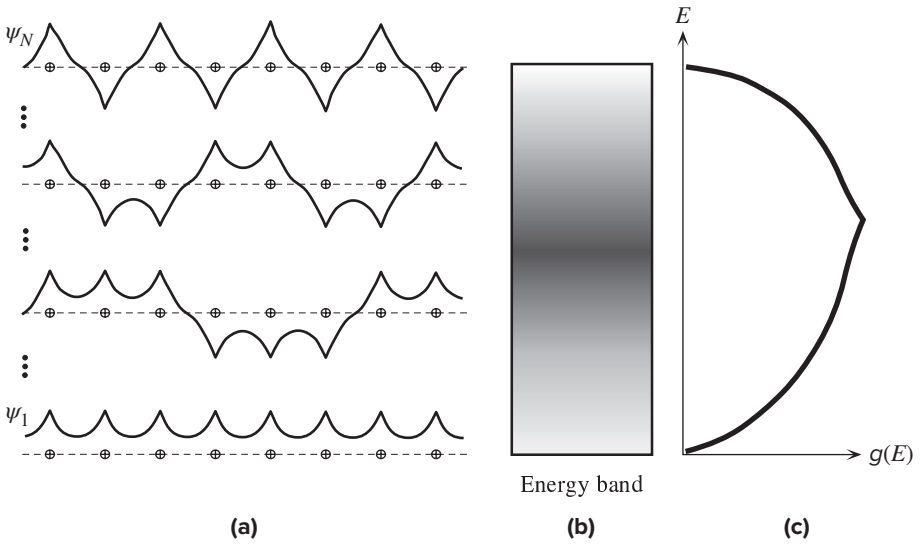


Figure 4.23 (a) In the solid there are N atoms and N extended electron wavefunctions from ψ_1 all the way to ψ_N. There are many wavefunctions, states, that have energies that fall in the central regions of the energy band. Note that although only eight atoms are shown, these are eight sequential atoms among N atoms, and N is very large. Overall, the wavefunctions for N atoms must be symmetric or antisymmetric. (b) The distribution of states in the energy band; darker regions have a higher number of states. (c) Schematic representation of the density of states $g(E)$ versus energy E.

where n_1, n_2, and n_3 are integers 1, 2, 3, ... The spatial dimension L of the well now refers to the size of the entire solid, as the electron is confined to be somewhere inside that solid. Thus, L is very large compared to atomic dimensions, which means that the separation between the energy levels is very small. We will use Equation 4.8 to describe the energies of **free electrons** inside the solid (as in a metal).

Each combination of n_1, n_2, and n_3 is one electron orbital state. For example, $\psi_{n_1,n_2,n_3} = \psi_{1,1,2}$ is one possible orbital state. Suppose that in Equation 4.8 E is given as E'. We need to determine how many combinations of n_1, n_2, n_3 (*i.e.*, how many ψ) have energies less than E', as given by Equation 4.8. Assume that $(n_1^2 + n_2^2 + n_3^2) = n'^2$. The object is to enumerate all possible choices of integers for n_1, n_2, and n_3 that satisfy $n_1^2 + n_2^2 + n_3^2 \leq n'^2$.

The two-dimensional 2D case is easy to solve. Consider $n_1^2 + n_2^2 \leq n'^2$ and the 2D ***n*-space** where the axes are n_1 and n_2, as shown in Figure 4.24. The 2D space is divided by lines drawn at $n_1 = 1, 2, 3, \ldots$ and $n_2 = 1, 2, 3, \ldots$ into infinitely many boxes (squares), each of which has a unit area and represents a possible state ψ_{n_1,n_2}. For example, the state $n_1 = 1$, $n_2 = 3$ is shaded, as is that for $n_1 = 2$, $n_2 = 2$.

Clearly, the area contained by n_1, n_2 and the circle defined by $n'^2 = n_1^2 + n_2^2$ (just like $r^2 = x^2 + y^2$) is the number of states that satisfy $n_1^2 + n_2^2 \leq n'^2$. This area is $\frac{1}{4}(\pi n'^2)$.

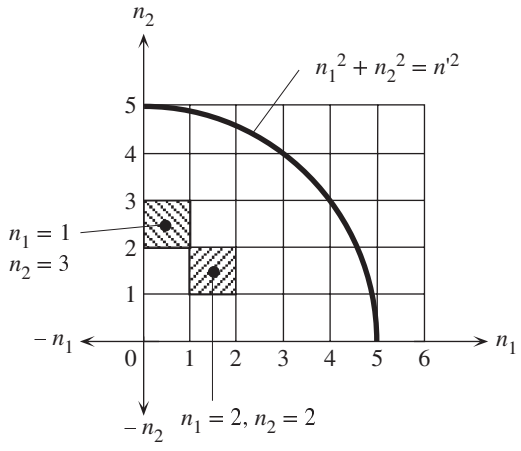


Figure 4.24 Each state, or electron wavefunction in the crystal, can be represented by a box at n_1, n_2.

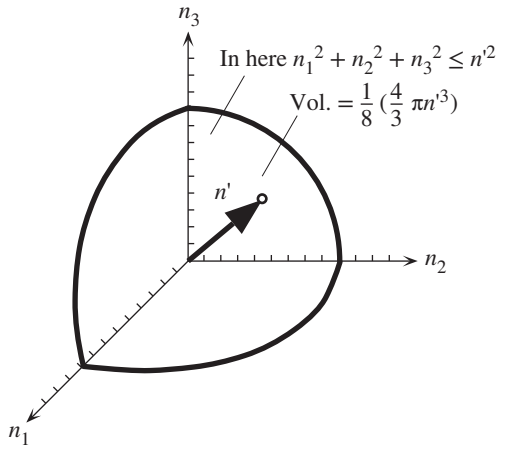


Figure 4.25 In three dimensions, the volume defined by a sphere of radius n' and the positive axes n_1, n_2, and n_3, contains all the possible combinations of positive n_1, n_2, and n_3 values that satisfy $n_1^2 + n_2^2 + n_3^2 \leq n'^2$.

In the 3D case, $n_1^2 + n_2^2 + n_3^2 \leq n'^2$ is required, as indicated in Figure 4.25. This is the volume contained by the positive n_1, n_2, and n_3 axes and the surface of a sphere of radius n'. Each state has a unit volume, and within the sphere, $n_1^2 + n_2^2 + n_3^2 \leq n'^2$ is satisfied. Therefore, the number of orbital states $S_{\text{orb}}(n')$ within this volume is given by

$$S_{\text{orb}}(n') = \frac{1}{8}\left(\frac{4}{3}\pi n'^3\right) = \frac{1}{6}\pi n'^3$$

Each orbital state can take two electrons with opposite spins, which means that the number of states, including spin, is given by

$$S(n') = 2S_{\text{orb}}(n') = \frac{1}{3}\pi n'^3$$

We need this expression in terms of energy. Substituting $n'^2 = 8m_e L^2 E'/h^2$ from Equation 4.8 in $S(n')$, we get

$$S(E') = \frac{\pi L^3 (8m_e E')^{3/2}}{3h^3}$$

Since L^3 is the physical volume of the solid, the number of states per unit volume $S_v(E')$ with energies $E \leq E'$ is

$$S_v(E') = \frac{\pi(8m_e E')^{3/2}}{3h^3} \qquad [4.9]$$

Furthermore, from Equation 4.7, $dS_v/dE = g(E)$. By differentiating Equation 4.9 with respect to energy, we get

Density of states

$$g(E) = (8\pi 2^{1/2})\left(\frac{m_e}{h^2}\right)^{3/2} E^{1/2} \qquad [4.10]$$

Equation 4.10 shows that the density of states $g(E)$ increases with energy as $E^{1/2}$ from the bottom of the band. As we approach the top of the band, according to our understanding in Figure 4.23c, $g(E)$ should decrease with energy as $(E_{top} - E)^{1/2}$, where E_{top} is the top of the band, so that as $E \rightarrow E_{top}$, $g(E) \rightarrow 0$. The electron mass m_e in Equation 4.10 should be the *effective mass* m_e^* as in Equation 4.6. Further, Equation 4.10 strictly applies only to *free electrons* in a crystal. However, we will frequently use it to approximate the true $g(E)$ versus E behavior near the band edges for both metals and semiconductors.

Having found the distribution of the electron energy states, Equation 4.10, we now wish to determine the number of states that actually contain electrons; that is, the probability of finding an electron at an energy level E. This is given by the Fermi–Dirac statistics.

As an example, one convenient way of calculating the population of a city is to find the density of houses in that city (*i.e.*, the number of houses per unit area), multiply that by the probability of finding a human in a house, and finally, integrate the result over the area of the city. The problem is working out the chances of actually finding someone at home, using a mathematical formula. For those who like analogies, if $g(A)$ is the density of houses and $f(A)$ is the probability that a house is occupied, then the population of the city is

$$n = \int_{\text{City}} f(A)g(A)\, dA$$

where the integration is done over the entire area of the city. This equation can be used to find the number of electrons per unit volume within a band. If E is the electron energy and $f(E)$ is the probability that a state with energy E is occupied, then

$$n = \int_{\text{Band}} f(E)g(E)\, dE$$

where the integration is done over all the energies of the band.

EXAMPLE 4.7

X-RAY EMISSION AND THE DENSITY OF STATES IN A METAL Consider what happens when a metal such as Al is bombarded with high-energy electrons. The inner atomic energy levels are not disturbed in the solid, so these inner levels remain as distinct single levels, each one localized to the parent atom. When an energetic electron hits an electron in one of the inner atomic energy levels, it knocks out this electron from the metal leaving behind a vacancy in the inner core as depicted in Figure 4.26a. An electron in the energy band of the solid can then fall down to occupy this empty state and emit a photon in the process. The energy difference between the energies in the band and the inner atomic level is in the X-ray range, so the emitted photon is an X-ray photon. Since electrons occupy the band from the bottom E_B to the Fermi level E_F, the emitted X-ray photons have a range of energies corresponding to transitions from E_B and E_F to the inner atomic level as shown in Figure 4.26b. These energies are in the soft X-ray spectrum. We assumed that the levels above E_F are almost empty, though, undoubtedly, there is no sharp transition from full to empty levels at E_F. Further, since the

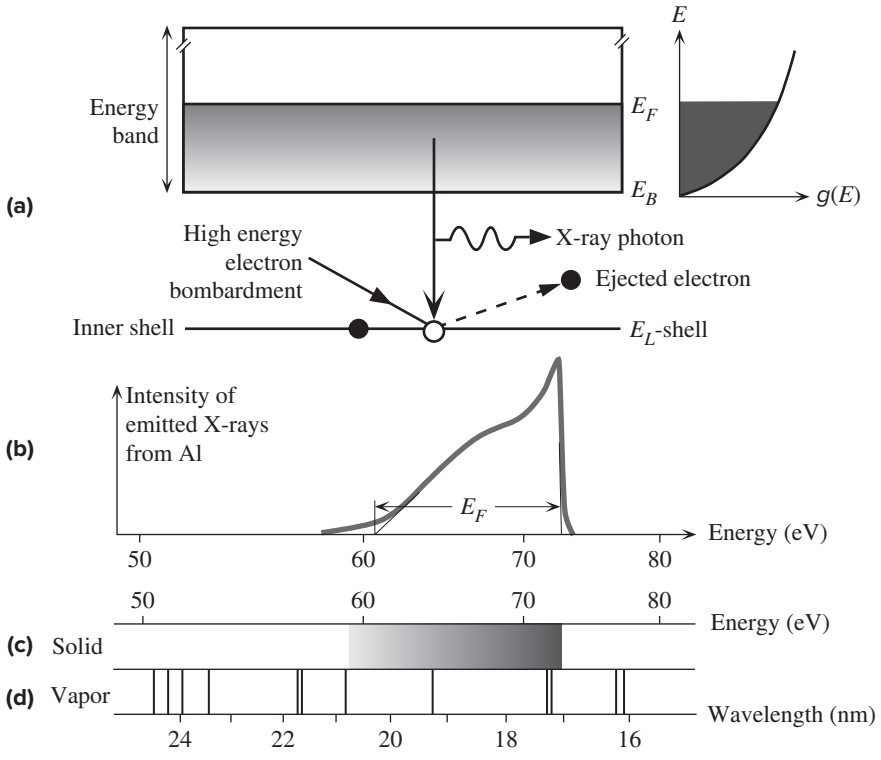


Figure 4.26 (a) High-energy electron bombardment knocks out an electron from the closed inner *L* shell leaving an empty state. An electron from the energy band of the metal drops into the *L* shell to fill the vacancy and emits a soft X-ray photon in the process. (b) The spectrum (intensity versus photon energy) of soft X-ray emission from a metal involves a range of energies corresponding to transitions from the bottom of the band and from the Fermi level to the *L* shell. The intensity increases with energy until around E_F where it drops sharply. (c) and (d) contrast the emission spectra from a solid and vapor (isolated gas atoms).

Source: Kinner, H.W.B., *Reports on Progress in Physics,* 5, 257, 1938 and Crisp, R.S. and Williams S.E., *Philosophical Magazine,* 5, 1205, 1960.

density of states increases from E_B toward E_F, there are more and more electrons that can fall down to the inner atomic level as we move from E_B toward E_F. Therefore, the intensity of the emitted X-ray radiation increases with photon energy until the energy reaches the Fermi level beyond which there are only a small number of electrons available for the transit. Figure 4.26c and d contrasts the emission spectra from an aluminum crystal (solid) and its vapor. The line spectra from a vapor become an emission band in the spectrum of the solid. The emitted radiation from the solid that involves the transitions of the conduction band electrons to core levels is called **soft X-ray emission spectrum.**

The X-ray intensity emitted from Al in Figure 4.26b starts to rise at around 61 eV and then sharply falls around 73 eV. Thus the energy range is 12 eV, which represents approximately the Fermi energy with respect to the bottom of the band, that is, $E_F \approx 73 - 61 = 12$ eV with respect to E_B.

EXAMPLE 4.8

DENSITY OF STATES IN A BAND Given that the width of an energy band is typically ~10 eV, calculate the following, in per cm^3 and per eV units:

a. The density of states at the center of the band.

b. The number of states per unit volume within a small energy range kT about the center.

c. The density of states at kT above the bottom of the band.

d. The number of states per unit volume within a small energy range of kT to $2kT$ from the bottom of the band.

SOLUTION

The density of states, or the number of states per unit energy range per unit volume $g(E)$, is given by

$$g(E) = (8\pi 2^{1/2})\left(\frac{m_e}{h^2}\right)^{3/2} E^{1/2}$$

which gives the number of states per cubic meter per Joule of energy. Substituting $E = 5$ eV, we have

$$g_{\text{center}} = (8\pi 2^{1/2})\left[\frac{9.1 \times 10^{-31}}{(6.626 \times 10^{-34})^2}\right]^{3/2} (5 \times 1.6 \times 10^{-19})^{1/2} = 9.50 \times 10^{46}\ \text{m}^{-3}\ \text{J}^{-1}$$

Converting to cm^{-3} and eV^{-1}, we get

$$\begin{aligned} g_{\text{center}} &= (9.50 \times 10^{46}\ \text{m}^{-3}\ \text{J}^{-1})(10^{-6}\ \text{m}^3\ \text{cm}^{-3})(1.6 \times 10^{-19}\ \text{J eV}^{-1}) \\ &= 1.52 \times 10^{22}\ \text{cm}^{-3}\ \text{eV}^{-1} \end{aligned}$$

If δE is a small energy range (such as kT), then, by definition, $g(E)\ \delta E$ is the number of states per unit volume in δE. To find the number of states per unit volume within kT at the center of the band, we multiply g_{center} by kT or $(1.52 \times 10^{22}\ \text{cm}^{-3}\ \text{eV}^{-1})(0.026\ \text{eV})$ to get $3.9 \times 10^{20}\ \text{cm}^{-3}$. This is not a small number!

At kT above the bottom of the band, at 300 K ($kT = 0.026$ eV), we have

$$\begin{aligned} g_{0.026} &= (8\pi 2^{1/2})\left[\frac{9.1 \times 10^{-31}}{(6.626 \times 10^{-34})^2}\right]^{3/2} (0.026 \times 1.6 \times 10^{-19})^{1/2} \\ &= 6.84 \times 10^{45}\ \text{m}^{-3}\ \text{J}^{-1} \end{aligned}$$

Converting to cm^{-3} and eV^{-1} we get

$$\begin{aligned} g_{0.026} &= (6.84 \times 10^{45}\ \text{m}^{-3}\ \text{J}^{-1})(10^{-6}\ \text{m}^3\ \text{cm}^{-3})(1.6 \times 10^{-19}\ \text{J eV}^{-1}) \\ &= 1.10 \times 10^{21}\ \text{cm}^{-3}\ \text{eV}^{-1} \end{aligned}$$

Within kT, the volume density of states is

$$(1.10 \times 10^{21}\ \text{cm}^{-3}\ \text{eV}^{-1})(0.026\ \text{eV}) = 2.8 \times 10^{19}\ \text{cm}^{-3}$$

This is very close to the bottom of the band and is still very large.

EXAMPLE 4.9 TOTAL NUMBER OF STATES IN A BAND

a. Based on the overlap of atomic orbitals to form the electron wavefunction in the crystal, how many states should there be in a band?

b. The density of states function in Equation 4.10 should be written in terms of the effective mass m_e^* of electrons in the band as

$$g(E) = (8\pi 2^{1/2})\left(\frac{m_e^*}{h^2}\right)^{3/2} E^{1/2}$$

By integrating $g(E)$, estimate the total number of states in the 3*s*-band of Na and compare this with the atomic concentration. Assume that the density of states in Figure 4.23c is symmetric and the center of the band is roughly at 3 eV. Use m_e^* for Na given in Table 4.2.

SOLUTION

a. We know that when N atoms come together to form a solid, N atomic orbitals can overlap N different ways to produce N orbitals or $2N$ states in the crystal, since each orbital has two states, spin up and spin down. These states form the band.

b. To estimate the total volume density of states, we assume that the density of states $g(E)$ reaches its maximum at the center of the band $E = E_{\text{center}} = 3$ eV. Integrating $g(E)$ from the bottom of the band, $E = 0$, to the center, $E = E_{\text{center}}$, yields the number of states per unit volume up to the center of the band. This is roughly half the total number of states in the whole band, (see Figure 4.23c), that is, $\frac{1}{2}S_{\text{band}}$, where S_{band} is the number of states per unit volume in the band and is determined by

$$\frac{1}{2}S_{\text{band}} = \int_0^{E_{\text{center}}} g(E)\,dE = \frac{16\pi\, 2^{1/2}}{3}\left(\frac{m_e^*}{h^2}\right)^{3/2} E_{\text{center}}^{3/2}$$

or

$$\frac{1}{2}S_{\text{band}} = \frac{16\pi\, 2^{1/2}}{3}\left[\frac{1.2 \times 9.1 \times 10^{-31}\ \text{kg}}{(6.626 \times 10^{-34}\ \text{J s})^2}\right]^{3/2} (3\ \text{eV} \times 1.6 \times 10^{-19}\ \text{J/eV})^{3/2}$$

$$= 3.1 \times 10^{28}\ \text{m}^{-3} = 3.1 \times 10^{22}\ \text{cm}^{-3}$$

Thus

$$S_{\text{band}} = 6.2 \times 10^{22}\ \text{states cm}^{-3}$$

We must now calculate the number of atoms per unit volume in sodium. Given the density $d = 0.968$ g cm^{-3} and the atomic mass $M_{\text{at}} = 22.99$ g mol^{-1} of sodium, the atomic concentration is

$$n_{\text{Ag}} = \frac{dN_A}{M_{\text{at}}} = 2.54 \times 10^{22}\ \text{atoms cm}^{-3}$$

The density of states in the 3s band is about about 2.4 times the atomic concentration. Given the crude approximations we have used, the estimate can be considered to be reasonably close to the expected value of twice the atomic concentration for the 3*s*-band.

4.6 STATISTICS: COLLECTIONS OF PARTICLES

4.6.1 BOLTZMANN CLASSICAL STATISTICS

Given a collection of particles in random motion and colliding with each other,[7] we need to determine the concentration of particles in the energy range E to $(E + dE)$. Consider the process shown in Figure 4.27, in which two electrons with energies E_1 and E_2 interact and then move off in different directions, with energies E_3 and E_4. Let the probability of an electron having an energy E be $P(E)$, where $P(E)$ is the fraction of electrons with an energy E. Assume there are no restrictions to the electron energies, that is, we can ignore the Pauli exclusion principle. The probability of this event is then $P(E_1)P(E_2)$. The probability of the reverse process, in which electrons with energies E_3 and E_4 interact, is $P(E_3)P(E_4)$. Since we have thermal equilibrium, that is, the system is in equilibrium, the forward process must be just as likely as the reverse process, so

$$P(E_1)P(E_2) = P(E_3)P(E_4) \qquad [4.11]$$

Furthermore, the energy in this collision must be conserved, so we also need

$$E_1 + E_2 = E_3 + E_4 \qquad [4.12]$$

We can show that $P(E) = A \exp(-\beta E)$, where A and β are constants, is a solution by simply substituting this expression into Equations 4.11 and 4.12. Further, we can also show that β must be $1/kT$, where k is the Boltzmann constant and T is the temperature, by comparing the average energy calculated from using $P(E)$ with that observed in experiments.[8]

Boltzmann probability function

$$P(E) = A \exp\left(-\frac{E}{kT}\right) \qquad [4.13]$$

Equation 4.13 is the **Boltzmann probability function** and is shown in Figure 4.28. The probability of finding a particle at an energy E therefore decreases exponentially with energy. We assume, of course, that any number of particles may have a given energy E. In other words, there is no restriction such as permitting only one particle per state at an energy E, as in the Pauli exclusion principle.

Suppose that we have N_1 particles at energy level E_1 and N_2 particles at a higher energy E_2. Then, by Equation 4.13, we have

Boltzmann statistics

$$\frac{N_2}{N_1} = \exp\left(-\frac{E_2 - E_1}{kT}\right) \qquad [4.14]$$

If $E_2 - E_1 \gg kT$, then N_2 can be orders of magnitude smaller than N_1. As the temperature increases, N_2/N_1 also increases. Therefore, increasing the temperature populates the higher energy levels.

Classical particles obey the Boltzmann statistics. Whenever there are many more states (by orders of magnitude) than the number of particles, the likelihood of

[7] From Chapter 1, we can associate this with the kinetic theory of gases. The energies of the gas molecules, which are moving around randomly, are distributed according to the Maxwell–Boltzmann statistics.

[8] See Question 4.10.

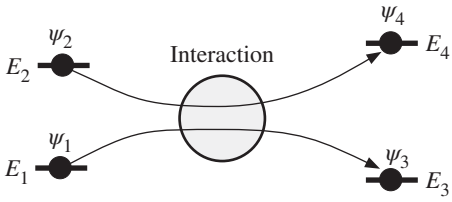


Figure 4.27 Two electrons with initial wavefunctions ψ_1 and ψ_2 at E_1 and E_2 interact and end up at different energies E_3 and E_4. Their corresponding wavefunctions are ψ_3 and ψ_4.

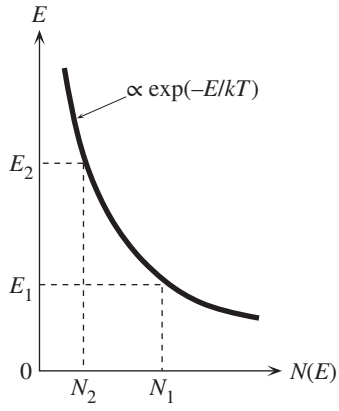


Figure 4.28 The Boltzmann energy distribution describes the statistics of particles, such as electrons, when there are many more available states than the number of particles.

two particles having the same set of quantum numbers is negligible and we do not have to worry about the Pauli exclusion principle. In these cases, we can use the Boltzmann statistics. An important example is the statistics of electrons in the conduction band of a semiconductor where, in general, there are many more states than electrons.

4.6.2 FERMI–DIRAC STATISTICS

Now consider the interaction for which no two electrons can be in the same quantum state, which is essentially obedience to the Pauli exclusion principle, as shown in Figure 4.27. We assume that we can have only one electron in a particular quantum state ψ (including spin) associated with the energy value E. We therefore need those states that have energies E_3 and E_4 to be not occupied. Let $f(E)$ be the probability that an electron is in such a state, with energy E in this new interaction environment. The forward event in Figure 4.27 requires that we have an electrons at E_1 *and* E_2 and, at the same time, E_3 *and* E_4 must be unoccupied (empty). Thus, the probability of the forward event is given by.

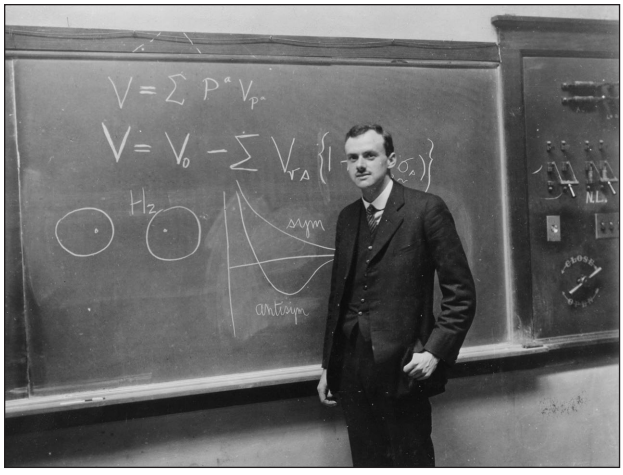
$$f(E_1)f(E_2)[1 - f(E_3)][1 - f(E_4)]$$

The square brackets represent the probability that the states with energies E_3 and E_4 are empty. In thermal equilibrium, the reverse process, the electrons with E_3 and E_4 interacting to transfer to E_1 and E_2, has just as equal a likelihood as the forward process. Thus, $f(E)$ must satisfy the equation

$$f(E_1)f(E_2)[1 - f(E_3)][1 - f(E_4)] = f(E_3)f(E_4)[1 - f(E_1)][1 - f(E_2)] \quad [4.15]$$

In addition, for energy conservation, we must have

$$E_1 + E_2 = E_3 + E_4 \quad [4.16]$$



Paul Adrien Maurice Dirac (1902–1984) received the 1933 Nobel prize for physics with Erwin Schrödinger. His first degree was in electrical engineering from Bristol University. He obtained his PhD in 1926 from Cambridge University under Ralph Fowler.

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By an "intelligent guess," the solution to Equations 4.15 and 4.16 is

$$f(E) = \frac{1}{1 + A\exp\left(\dfrac{E}{kT}\right)} \qquad [4.17]$$

where A is a constant. You can check that this is a solution by substituting Equation 4.17 into 4.15 and using Equation 4.16. The reason for the term kT in Equation 4.17 is not obvious from Equations 4.15 and 4.16. It appears in Equation 4.17 so that at sufficiently high energies Equation 4.17 becomes the same as the Boltzmann distribution in Equation 4.13 in agreement with experiments.[9] In a more rigorous approach we would use a constant $1/\beta$ instead of kT in Equation 4.17, and then show that β must be $1/kT$ by comparing the predictions based on Equation 4.17 with experiments. Letting $A = \exp(-E_F/kT)$, we can write Equation 4.17 as

Fermi–Dirac statistics

$$f(E) = \frac{1}{1 + \exp\left(\dfrac{E - E_F}{kT}\right)} \qquad [4.18]$$

where E_F is a constant called the **Fermi energy.** The probability of finding an electron in a state with energy E is given by Equation 4.18, which is called the **Fermi–Dirac function.**

The behavior of the Fermi–Dirac function is shown in Figure 4.29. Note the effect of temperature. As T increases, $f(E)$ extends to higher energies. At

[9] If N_1 and N_2 are the number of electrons at energies E_1 and E_2, then the Boltzman distribution predicts Equation (4.14) for N_1/N_2. At sufficiently high energies Equation 4.17 gives the same prediction for N_1/N_2. The reason is that at very high energies there are very few electrons compared with the available number of states at these energies so that it very unlikely that two electrons will try to occupy the same state; that is the Pauli exclusion principle is not needed and the electron statistics is simply the Boltzmann distribution.

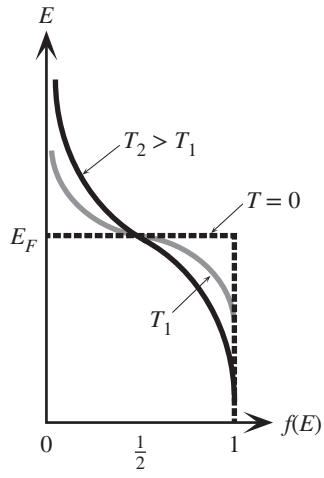


Figure 4.29 The Fermi–Dirac function $f(E)$ describes the statistics of electrons in a solid. The electrons interact with each other and the environment, obeying the Pauli exclusion principle.

energies of a few kT (0.026 eV) above E_F, $f(E)$ behaves almost like the Boltzmann function

$$f(E) = \exp\left[-\frac{(E - E_F)}{kT}\right] \qquad (E - E_F) \gg kT \qquad [4.19]$$

Above absolute zero, at $E = E_F$, $f(E_F) = \frac{1}{2}$. We define the Fermi energy as that energy for which the probability of occupancy $f(E_F)$ equals $\frac{1}{2}$. The approximation to $f(E)$ in Equation 4.19 at high energies is often referred to as the **Boltzmann tail** to the Fermi–Dirac function. Notice that the spread of $f(E)$ around E_F increases with temperature. This spread around E_F is typically several kTs.

4.7 QUANTUM THEORY OF METALS

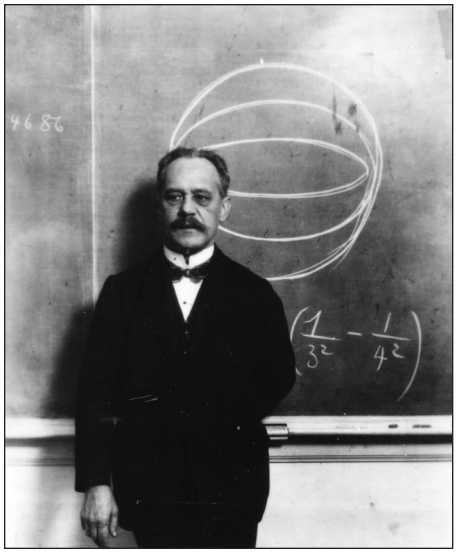
4.7.1 FREE ELECTRON MODEL[10]

We know that the number of states $g(E)$ for an electron, per unit energy per unit volume, increases with energy as $g(E) \propto E^{1/2}$. We have also calculated that the probability of an electron being in a state with an energy E is the Fermi–Dirac function $f(E)$. Consider the energy band diagram for a metal and the density of states $g(E)$ for that band, as shown in Figure 4.30a and b, respectively.

At absolute zero, all the energy levels up to E_F are full. At 0 K, $f(E)$ has the step form at E_F (Figure 4.29). This clarifies why E_F in $f(E)$ is termed the Fermi energy. At 0 K, $f(E) = 1$ for $E < E_F$, and $f(E) = 0$ for $E > E_F$, so at 0 K, E_F separates the empty and full energy levels. This explains why we restricted ourselves to 0 K or thereabouts when we introduced E_F in the band theory of metals.

At some finite temperature, $f(E)$ is *not* zero beyond E_F, as indicated in Figure 4.30c. This means that some of the electrons are excited to, and thereby occupy,

[10] The free electron model of metals is also known as the Sommerfeld model.



Arnold Johannes Wilhelm Sommerfeld (1868–1951) was responsible for the quantum mechanical free electron theory of metals covered in this section. Sommerfeld was the Director of Institute of Theoretical Physics, specially established for him, at Munich University.

AIP Emilio Segrè Visual Archives, Physics Today Collection.

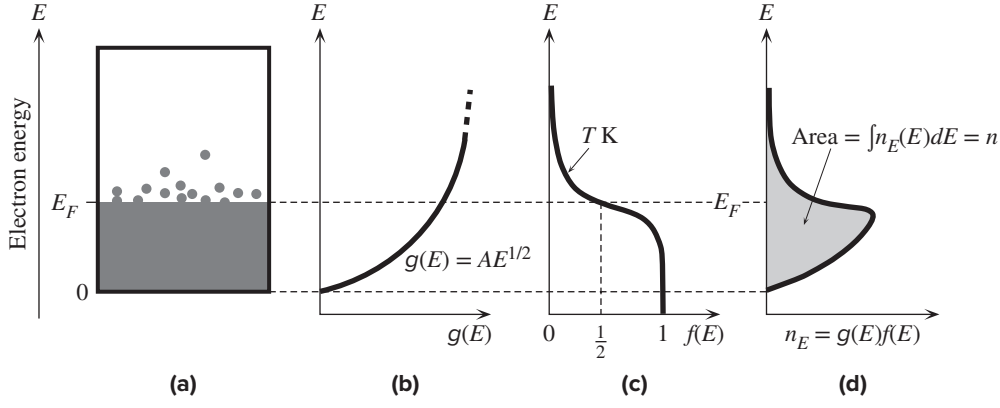


Figure 4.30 (a) Above 0 K, due to thermal excitation, some of the electrons are at energies above E_F. (b) The density of states, $g(E)$ versus E in the band. (c) The probability of occupancy of a state at an energy E is $f(E)$. (d) The product $g(E)f(E)$ is the number of electrons per unit energy per unit volume, or the electron concentration per unit energy. The area under the curve on the energy axis is the concentration of electrons in the band.

energy levels above E_F. If we multiply $g(E)$ by $f(E)$, we obtain the number of electrons per unit energy per unit volume, denoted n_E. The distribution of electrons in the energy levels is described by $n_E = g(E)f(E)$.

Since $f(E) = 1$ for $E \ll E_F$, the states near the bottom of the band are all occupied; thus, $n_E \propto E^{1/2}$ initially. As E passes through E_F, $f(E)$ starts decreasing sharply. As a result, n_E takes a turn and begins to decrease sharply as well, as depicted in Figure 4.30d. "The spread in n_E about E_F is around $4kT$. But E_F is usually a few electron volts so that the spread is actually quite narrow." (Figure 4.30(d) is exaggerated.)

In the small energy range E to $(E + dE)$, there are $n_E\,dE$ electrons per unit volume. When we sum all $n_E\,dE$ from the bottom to the top of the band, we get the total number of valence electrons per unit volume, n, in the metal, as follows:

$$n = \int_0^{\text{Top of band}} n_E\,dE = \int_0^{\text{Top of band}} g(E)f(E)\,dE \qquad [4.20]$$

Since $f(E)$ falls very sharply when $E > E_F$, we can carry the integration to $E = \infty$, rather than to $(E_F + \Phi)$, because $f \to 0$ when $E \gg E_F$. Putting in the functional forms of $g(E)$ and $f(E)$ (*e.g.*, from Equations 4.10 and 4.18), we obtain

$$n = \frac{8\pi 2^{1/2} m_e^{3/2}}{h^3} \int_0^{\infty} \frac{E^{1/2}dE}{1 + \exp\left(\dfrac{E - E_F}{kT}\right)} \qquad [4.21]$$

If we could integrate this, we would obtain an expression relating n and E_F. At 0 K, however, $E_F = E_{FO}$ and the integrand exists only for $E < E_{FO}$. If we integrate at 0 K, Equation 4.21 yields

Fermi energy at $T = 0$ K

$$E_{FO} = \left(\frac{h^2}{8m_e}\right)\left(\frac{3n}{\pi}\right)^{2/3} \qquad [4.22]$$

As an example, consider aluminum, and assume that each Al atom donates 3 electrons to the sea of conduction electrons. We can take the electron concentration $n = 3 \times$ (Concentration of Al atoms), or 6.022×10^{28} m^{-3}, and substitute this n into Equation 4.22 to find $E_{FO} = 11.7$ eV. In Example 4.7, from the soft X-ray emission spectrum in Figure 4.26, we found that the Fermi energy was approximately 12 eV. Further, we can also evaluate the speed v_F of the electrons at the Fermi level by writing $\frac{1}{2}m_e v_F^2 = E_{FO}$, which leads to $v_F = 2.0 \times 10^6$ m s^{-1}.

It may be thought that E_F is temperature independent, since it was sketched that way in Figure 4.29. However, in our derivation of the Fermi–Dirac statistics, there was no restriction that demanded this. Indeed, since the number of electrons in a band is fixed, E_F at a temperature T is implicitly determined by Equation 4.21, which can be solved to express E_F in terms of n and T. It turns out that at 0 K, E_F is given by Equation 4.22, and it changes very little with temperature. In fact, by utilizing various mathematical approximations, it is not too difficult to integrate Equation 4.21 to obtain the **Fermi energy** at a temperature T, as follows:

Fermi energy at T(K)

$$E_F(T) = E_{FO}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{FO}}\right)^2\right] \qquad [4.23]$$

which shows that $E_F(T)$ is only "slightly" temperature dependent, since $E_{FO} \gg kT$.

The Fermi energy has an important significance in terms of the average energy E_{av} of the conduction electrons in a metal. In the energy range E to $(E + dE)$, there are $n_E\,dE$ electrons with energy E. The average energy of an electron will therefore be

$$E_{\text{av}} = \frac{\int En_E\,dE}{\int n_E\,dE} \qquad [4.24]$$

If we substitute $g(E)f(E)$ for n_E and integrate, the result at 0 K is

Average energy per electron at 0 K

$$E_{\text{av}}(0) = \frac{3}{5}E_{FO} \quad [4.25]$$

Above absolute zero, the **average energy** is approximately

Average energy per electron at T(K)

$$E_{\text{av}}(T) = \frac{3}{5}E_{FO}\left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{E_{FO}}\right)^2\right] \quad [4.26]$$

Since $E_{FO} \gg kT$, the second term in the square brackets is much smaller than unity, and $E_{\text{av}}(T)$ shows only a very weak temperature dependence. Furthermore, in our model of the metal, the electrons are free to move around within the metal, where their potential energy PE is zero, whereas outside the metal, it is $E_F + \Phi$ (Figure 4.11). Therefore, their energy is purely kinetic. Thus, Equation 4.26 gives the average KE of the electrons in a metal

$$\frac{1}{2}m_e v_e^2 = E_{\text{av}} \approx \frac{3}{5}E_{FO}$$

where v_e is the root mean square (rms) speed of the electrons, which is simply called the **effective speed.** The effective speed v_e depends on the Fermi energy E_{FO} and is relatively insensitive to temperature. Compare this with the behavior of molecules in an ideal gas. In that case, the average $KE = \frac{3}{2}kT$, so $\frac{1}{2}mv^2 = \frac{3}{2}kT$. Clearly, the average speed of molecules in a gas increases with temperature.

The relationship $\frac{1}{2}mv_e^2 \approx \frac{3}{5}E_{FO}$ is an important conclusion that comes from the application of quantum mechanical concepts, ideas that lead to $g(E)$ and $f(E)$ and so on. It cannot be proved without invoking quantum mechanics. The fact that the average electronic speed is nearly constant is the only way to explain the observation that the resistivity of a metal is proportional to T (and not $T^{3/2}$), as we saw in Chapter 2.

4.7.2 CONDUCTION IN METALS

We know from our energy band discussions that in metals only those electrons in a small range ΔE around the Fermi energy E_F contribute to electrical conduction as shown in Figure 4.13c. The concentration n_F of these electrons is approximately $g(E_F)\ \Delta E$ inasmuch as ΔE is very small. All these electrons within ΔE around E_F move approximately with the Fermi speed v_F. The electron a moves to a', as shown in Figure 4.13b and c, and then it is scattered to an empty state above b'. In steady conduction, all the electrons in the energy range ΔE that are moving to the right are not canceled by any moving to the left and hence contribute to the current. An electron at the bottom of the ΔE range gains energy ΔE to move a' in a time interval Δt that corresponds to the scattering time τ. It gains a momentum Δp_x. Since $\Delta p_x/\Delta t$ = external force = eE_x, we have $\Delta p_x = \tau e E_x$. The electron a has an energy $E = p_x^2/(2m_e^*)$ which we can differentiate to obtain ΔE when the momentum changes by Δp_x,

$$\Delta E = \frac{p_x}{m_e^*}\Delta p_x = \frac{(m_e^* v_F)}{m_e^*}(\tau e E_x) = e v_F \tau E_x$$

The current J_x is due to all the electrons in the range ΔE which are moving toward the right in Figure 4.13c,

$$J_x = en_F v_F = e[g(E_F)\Delta E]v_F = e[g(E_F)ev_F\tau E_x]v_F = e^2 v_F^2 \tau g(E_F)E_x$$

The conductivity is therefore

$$\sigma = e^2 v_F^2 \tau g(E_F)$$

However, the numerical factor is wrong because Figure 4.13c considers only a hypothetical 1D crystal. In a 3D crystal, the conductivity is one-third of the conductivity value just determined:

Conductivity of Fermi-level electrons

$$\sigma = \frac{1}{3} e^2 v_F^2 \tau g(E_F) \qquad [4.27]$$

This conductivity expression is in sharp contrast with the classical expression in which all the electrons contribute to conduction. According to Equation 4.27, what is important is the density of states at the Fermi energy $g(E_F)$. For example, Cu and Mg are metals with valencies I and II. Classically, Cu and Mg atoms each contribute one and two conduction electrons, respectively, into the crystal. Thus, we would expect Mg to have higher conductivity. However, the Fermi level in Mg is where the top tail of the 3*s* band overlaps the bottom tail of the 3*p* band where the density of states is small. In Cu, on the other hand, E_F is nearly in the middle of the 4*s* band where the density of states is high. Thus, Mg has a lower conductivity than Cu.

The scattering time τ in Equation 4.27 assumes that the scattered electrons at E_F remain in the same energy band. In certain metals, there are two different energy bands that overlap at E_F. For example, in Ni (see Figure 4.68), 3*d* and 4*s* bands overlap at E_F. An electron can be scattered from the 4*s* to the 3*d* band, and vice versa. Electrons in the 3*d* band have very low drift mobilities and effectively do not contribute to conduction, so only $g(E_F)$ of the 4*s* band operates in Equation 4.27. Since 4*s* to 3*d* band scattering is an additional scattering mechanism, by virtue of Matthiessen's rule, the scattering time τ for the 4*s* band electrons is shortened. Thus, Ni has poorer conductivity than Cu.

In deriving Equation 4.27 we did not assume a particular density of states model. If we now apply the *free electron model* for $g(E_F)$ as in Equation 4.10, and also relate E_F to the total number of conduction electrons per unit volume n as in Equation 4.22, we would find that the conductivity is the same as the **Drude model,** that is,

Drude model and free electrons

$$\sigma = \frac{e^2 n \tau}{m_e} \qquad [4.28]$$

EXAMPLE 4.10 **FERMI ENERGY OF ELECTRONS IN SODIUM** Calculate the Fermi energy at 0 K and at 300 K (room temperature) for sodium. What is the speed v_F of Fermi electrons? How does this compare with the thermal velocity? The density d of Na is 0.97 g cm^{-3} and the atomic mass (atomic weight) M_{at} is 22.99 g mol^{-1}. Figure 4.31 shows the emission of soft X-rays obtained from a sodium sample that has been bombarded with electrons. The experiment is similar to that described in Example 4.7. An inner core electron is knocked out and a conduction electron falls down to fill the empty inner core state and emits an X-ray photon.

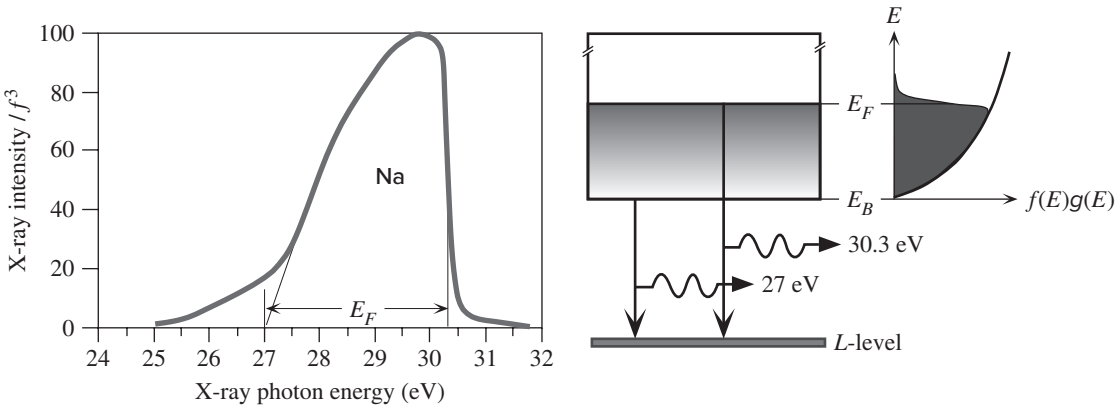


Figure 4.31 Emission of soft X-rays from a sodium sample that is bombarded by electrons (in a suitable high vacuum). An impinging electron knocks out an electron from an inner core shell (*L*-level). A conduction electron falls down and fills this space and emits an X-ray photon. The X-ray emission intensity is proportional to the number of conduction electrons available, $f(E)g(E)$, and to hf^3, a quantum mechanical transition probability. The vertical axis has been scaled to make the peak 100 percent.

| Data extracted from Cady, W.M. and Tomboulian D.H., *Physical Review* 59, 381, 1941, Table 1.

The transition probability is proportional to two factors: (a) how conduction many electrons are available at E to make the transition, that is n_E or $f(E)g(E)$, and (b) the quantum mechanical transition probability, which is proportional to $(hf)^3$. It is therefore customary to plot the measured X-ray emission intensity I divided by f^3 to indicate $f(E)g(E)$ as shown in Figure 4.31. How does your calculation compare with the experiments?

SOLUTION

Sodium (Na) is a metal in which each Na atom donates one electron to the sea of conduction electrons inside the crystal. If N_A is Avogadro's number, the concentration of electrons n is

$$n = \frac{dN_A}{M_{\text{at}}} = \frac{0.97 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{ mole}}{22.99 \text{ g mol}^{-1}} = 2.54 \times 10^{22} \text{ cm}^{-3}.$$

The Fermi energy at 0 K is given by Equation 4.22,

$$E_{FO} = \left(\frac{h^2}{8m_e}\right)\left(\frac{3n}{\pi}\right)^{2/3} = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{(8)(9.109 \times 10^{-31} \text{ kg})}\left(\frac{(3)(2.65 \times 10^{28} \text{ m}^{-3})}{\pi}\right)^{2/3}$$
$$= 5.05 \times 10^{-19} \text{ J, that is, } 3.16 \text{ eV}.$$

If we were to repeat the calculation to find E_F at 300 K, we would find that the change is in the fourth decimal place. The term $(\pi^2/12)(kT/E_{FO})^2$ in Equation 4.23 is 5.2×10^{-5}, or a decrease of 0.005 percent. In many applications, we can neglect this small change.

The examination of Figure 4.31 shows that the emitted X-ray photons have energies approximately in the range 27.0 eV to 30.3 eV. The transitions of conduction electrons from around E_F down to the *L*-level correspond to the maximum photon energy, which is 30.3 eV. The smallest emitted photon energy corresponds to a conduction electron falling from the bottom of the band to the *L*-level, which is 27.0 eV. Thus $E_F = 30.3 - 27.0 = 3.3$ eV, very close to the calculated value. (The spread of n_E around E_F is about $\sim 4kT$, that is 0.1 eV.)

We can calculate the speed of electrons at E_F from $\frac{1}{2}m_e v_{F^2} = E_{FO}$ so that $v_F = 1.05 \times 10^6$ m s^{-1}. The mean speed of all the electrons can be calculated by writing $\frac{1}{2}m_e v_e^2 = \frac{3}{5}E_{FO}$,

which leads to $v_e = 8.16 \times 10^5$ m s^{-1}. If we were to treat the electrons classically, that is, assume that they obey Boltzmann statistics, then their thermal velocity (or effective velocity) would be $\frac{1}{2}m_e v_{\text{th}}^2 = \frac{3}{2}kT$, so that $v_{\text{th}} = 1.17 \times 10^5$ m s^{-1}.

EXAMPLE 4.11

CONDUCTION IN SILVER Consider silver whose density of states $g(E)$ can be calculated by assuming a free electron model for $g(E)$ as in Equation 4.10. For silver, $E_F = 5.5$ eV, so from Equation 4.10, the density of states at E_F is $g(E_F) = 1.60 \times 10^{28}$ m^{-3} eV^{-1}. The velocity of Fermi electrons, $v_F = (2E_F/m_e)^{1/2} = 1.39 \times 10^6$ m s^{-1}. The conductivity σ of Ag at room temperature is 62.5×10^6 Ω^{-1} m^{-1}. Substituting for σ, $g(E_F)$, and v_F in Equation 4.27,

$$\sigma = 62.5 \times 10^6 = \frac{1}{3}e^2 v_F^2 \tau g(E_F) = \frac{1}{3}(1.6 \times 10^{-19})^2 (1.39 \times 10^6)^2 \tau \left(\frac{1.60 \times 10^{28}}{1.6 \times 10^{-19}}\right)$$

we find $\tau = 3.79 \times 10^{-14}$ s. The mean free path $\ell = v_F \tau = 53$ nm. The drift mobility of E_F electrons is $\mu = e\tau/m_e = 67$ cm^2 V^{-1} s^{-1}.

Silver has a valency of I, which means that the concentration of conduction electrons is n = concentration of Ag atoms = $n_{\text{Ag}} = 5.85 \times 10^{28}$ m^{-3}. Substituting for n and σ in Equation 4.28 gives

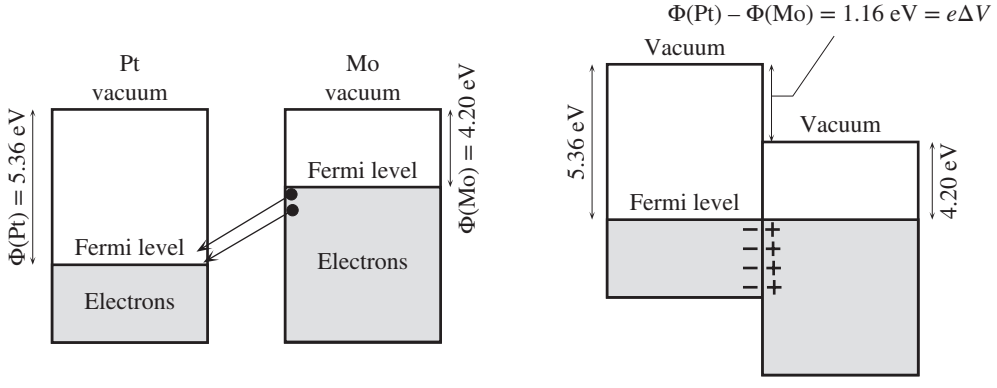
$$\sigma = 62.5 \times 10^6 = \frac{e^2 n \tau}{m_e} = \frac{(1.6 \times 10^{-19})^2 (5.85 \times 10^{28})\tau}{(9.1 \times 10^{-31})}$$

we find $\tau = 3.79 \times 10^{-14}$ s as expected because we have used the free electron model.

4.8 FERMI ENERGY SIGNIFICANCE

4.8.1 METAL–METAL CONTACTS: CONTACT POTENTIAL

Suppose that two metals, platinum (Pt) with a work function 5.36 eV and molybdenum (Mo) with a work function 4.20 eV, are brought together, as shown in Figure 4.32a. We know that in metals, all the energy levels up to the Fermi level are full. Since



(a) Electrons are more energetic in Mo, so they tunnel to the surface of Pt.

(b) Equilibrium is reached when the Fermi levels are lined up.

Figure 4.32 When two metals are brought together, there is a contact potential ΔV.

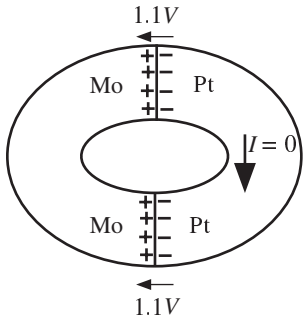


Figure 4.33 There is no current when a closed circuit is formed by two different metals, even though there is a contact potential at each contact.
The contact potentials oppose each other.

the Fermi level is higher in Mo (due to a smaller Φ), the electrons in Mo are more energetic. They therefore immediately go over to the Pt surface (by tunneling), where there are empty states at lower energies, which they can occupy. This electron transfer from Mo to the Pt surface reduces the total energy of the electrons in the Pt–Mo system, but at the same time, the Pt surface becomes negatively charged with respect to the Mo surface. Consequently, a contact voltage (or a potential difference) develops at the junction between Pt and Mo, with the Mo side being positive.

The electron transfer from Mo to Pt continues until the contact potential is large enough to prevent further electron transfer: the system reaches equilibrium. It should be apparent that the transfer of energetic electrons from Mo to Pt continues until the two Fermi levels are lined up, that is, until the Fermi level is uniform and the same in both metals, so that no part of the system has more (or less) energetic electrons, as illustrated in Figure 4.32b. Otherwise, the energetic electrons in one part of the system will flow toward a region with lower energy states. Under these conditions, the Pt–Mo system is in equilibrium. The contact voltage ΔV is determined by the difference in the work functions, that is,

$$e\ \Delta V = \Phi(\text{Pt}) - \Phi(\text{Mo}) = 5.36\ \text{eV} - 4.20\ \text{eV} = 1.16\ \text{eV}$$

We should note that away from the junction on the Mo side, we must still provide an energy of $\Phi = 4.20$ eV to free an electron, whereas away from the junction on the Pt side, we must provide $\Phi = 5.36$ eV to free an electron. This means that the vacuum energy level going from Mo to Pt has a step $\Delta\Phi$ at the junction. Since we must do work equivalent to $\Delta\Phi$ to get a free electron (*e.g.*, on the metal surface) from the Mo surface to the Pt surface, this represents a voltage of $\Delta\Phi/e$ or 1.16 V.

From the second law of thermodynamics,[11] this contact voltage cannot do work; that is, it cannot drive current in an external circuit. To see this, we can close the Pt metal–Mo metal circuit to form a ring, as depicted in Figure 4.33. As soon as we close the circuit, we create another junction with a contact voltage that is equal and opposite to that of the first junction. Consequently, going around the circuit, the net voltage is zero and the current is therefore zero.

There is a deep significance to the Fermi energy E_F, which should at least be mentioned. For a given metal the Fermi energy represents the free energy per electron

[11] By the way, the second law of thermodynamics simply says that you cannot extract heat from a system in thermal equilibrium and do work (*i.e.*, charge × voltage).

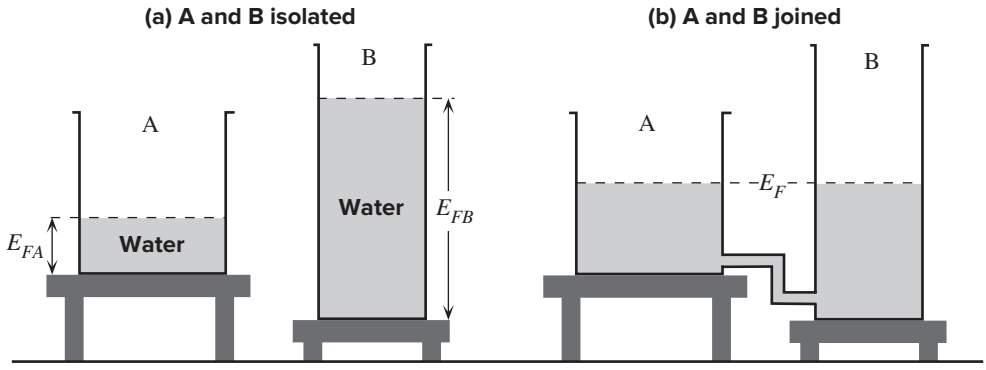


Figure 4.34 (a) Consider two different beakers A and B, filled with water up to different levels E_{FA} and E_{FB} from the bottom of each beaker, and placed on different tables. The two beakers are two independent systems, each with a certain level of water E_{FA} and E_{FB}. (b) Once the two systems are joined through a pipe, we have one combined system. Water flows from B to A until equilibrium is reached when the water level in both A and B is the same at a height E_F.

called the **electrochemical potential** μ. In other words, the Fermi energy is a measure of the potential of an electron to do electrical work ($e \times V$) or nonmechanical work, through chemical or physical processes.[12] In general, when two metals are brought into contact, the Fermi level (with respect to a vacuum) in each will be different. This difference means a difference in the chemical potential $\Delta\mu$, which in turn means that the system will do external work, which is obviously not possible. Instead, electrons are immediately transferred from one metal to the other, until the free energy per electron μ for the whole system is minimized and is uniform across the two metals, so that $\Delta\mu = 0$ or $\Delta E_F = 0$. We can guess that if the Fermi level in one metal could be maintained at a higher level than the other, by using an external energy source (*e.g.*, light or heat), for example, then the difference could be used to do electrical work.

Whenever two metals are brought together, as shown in Figure 4.32, the Fermi level E_F in the combined system is the same throughout the combined material system. We can understand the Fermi level alignment through a well-known analogy.[13] Consider two different beakers A and B, filled with water up to different levels E_{FA} and E_{FB} from the bottom of each beaker, and placed on different tables as shown in Figure 4.34a. The two beakers are two independent systems, each with a certain level of water E_{FA} and E_{FB}. Once the two systems are joined together through a pipe, as in Figure 4.34b, we have one new combined system. Water flows from B to A until *equilibrium* is reached when the water level in both A and B is the same at a height E_F. We would need external work to separate the Fermi level in the two beakers and

[12] A change in any type of *PE* can, in principle, be used to do work, that is, $\Delta(PE)$ = work done. Chemical *PE* is the potential to do nonmechanical work (*e.g.*, electrical work) by virtue of physical or chemical processes. The chemical *PE* per electron is E_F and ΔE_F = electrical work per electron.

[13] Remember that this is only an analogy, and like all analogies, you cannot push it too far. The water case relies on gravitational potential energy. Had the water levels not aligned *in equilibrium*, the difference in the heights would mean a pressure difference (or potential energy difference) and external work could be generated. Likewise, we would need to do work on the combined system to separate the water levels and upset the equilibrium.

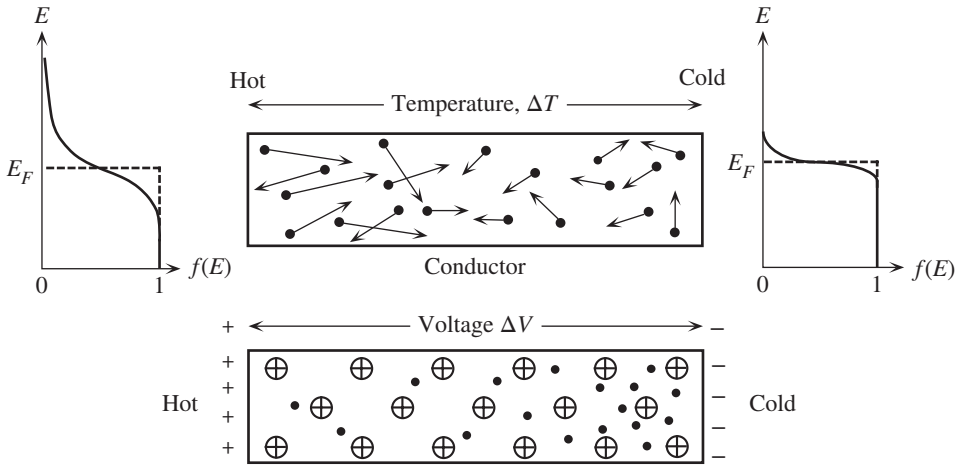


Figure 4.35 The Seebeck effect.

A temperature gradient along a conductor gives rise to a potential difference. (Note that the E_F in the hot region is not exactly the same as that in the cold region.)

upset the equilibrium. Had the two Fermi levels not aligned in equilibrium, the difference could have been used to do external work. What is important is that, in equilibrium, the Fermi level is uniform throughout the combined system as in Figure 4.34b.

4.8.2 THE SEEBECK EFFECT AND THE THERMOCOUPLE

Consider a conductor such as an aluminum rod that is heated at one end and cooled at the other end as depicted in Figure 4.35. The electrons in the hot region are more energetic and therefore have greater velocities than those in the cold region.[14]

Consequently there is a net diffusion of electrons from the hot end toward the cold end which leaves behind exposed positive metal ions in the hot region and accumulates electrons in the cold region. This situation prevails until the electric field developed between the positive ions in the hot region and the excess electrons in the cold region prevents further electron motion from the hot to the cold end. A voltage therefore develops between the hot and cold ends, with the hot end at positive potential. The potential difference ΔV across a piece of metal due to a temperature difference ΔT is called the **Seebeck effect.**[15] To gauge the magnitude of this effect we introduce a special coefficient which is defined as the potential difference developed per unit temperature difference, or

Thermoelectric power or Seebeck coefficient

$$S = \frac{dV}{dT} \qquad [4.29]$$

[14] The conduction electrons around the Fermi energy have a mean speed that has only a small temperature dependence. This small change in the mean speed with temperature is, nonetheless, significant in intuitively appreciating the thermoelectric effect. The actual effect, however, depends on the mean free path as discussed later.

[15] Thomas Seebeck observed the thermoelectric effect in 1821 using two different metals as in the thermocouple, which is the only way to observe the phenomenon. It was William Thomson (Lord Kelvin) who explained the observed effect.

Table 4.3 Seebeck coefficients of various metals

Metal	S at 27 °C ($\mu V\ K^{-1}$)	E_F (eV)	Comment
Al	−1.7	11.7	$S = aT + b/T$; $T = 190 - 700$ K $a = -3 \times 10^{-3}$ μV K^{-2}, $b = -235$ μV [1]
Au	+2.08	5.53	$S = aT + b/T$; $T = 273 - 650$ K; $a = 5.0 \times 10^{-3}$ μV K^{-2}, $b = 204$ μV [2]
Cu	+1.94	7.00	$S = aT + b/T$; $T = 70 - 900$ K $a = 5.8 \times 10^{-3}$ μV K^{-2}, $b \approx 76.4$ μV [2]
K	−13.7	2.12	[3]
Li	+11.4	4.74	[4]
Na	−6.3	3.24	[3]
Mg	−1.46	7.08	[3]
Ni	−19.5	~7.4	[3]
Pd	−10.7		[3]
Pt	−4.92	~6.0	[2]

Data extracted and combined from [1] Gripshover, R.J., et al., *Physical Review,* 163, 598 1967; [2] Roberts, R.B., *Philosophical Magazine,* 36, 91, 1977 and Roberts, R.B., *Philosophical Magazine, B,* 43, 1125, 1981; Ed. Haynes, W.M., [3] *CRC Handbook of Chemistry and Physics,* 94th Edition, 2013-2014, Boca Raton, FL: CRC Press; [4] MacDonald, D.K.C., *Thermoelectricity: An Introduction to the Principles.* Hoboken, NJ: Wiley, 1962, Figure 31. The empirical equations for Au and Cu obtained by using data from [2].

By convention, the sign of S represents the potential of the cold side with respect to the hot side. If electrons diffuse from the hot end to the cold end as in Figure 4.35, then the cold side is negative with respect to the hot side and the Seebeck coefficient is *negative* (as for aluminum).

In some metals, such as copper, this intuitive explanation fails to explain why electrons actually diffuse from the cold to the hot region, giving rise to *positive* Seebeck coefficients; the polarity of the voltage in Figure 4.35 is actually reversed for copper. The reason is that the net diffusion process depends on how the mean free path ℓ and the mean free time (due to scattering from lattice vibrations) change with the electron energy, which can be quite complicated. Typical Seebeck coefficients for various selected metals are listed in Table 4.3.

Consider two neighboring regions H (hot) and C (cold) with widths corresponding to the mean free paths ℓ and ℓ' in H and C as depicted in Figure 4.36a. Half the electrons in H would be moving in the $+x$ direction and the other half in the $-x$ direction. Half of the electrons in H therefore cross into C, and half in C cross into H. Suppose that, very roughly, the electron concentration n in H and C is about the same. The number of electrons crossing from H to C is $\frac{1}{2}n\ell$, and the number crossing from C to H is $\frac{1}{2}n\ell'$. Then,

$$\text{Net diffusion from H to C} \propto \frac{1}{2}n(\ell - \ell') \qquad [4.30]$$

Suppose that the scattering of electrons is such that ℓ increases strongly with the electron energy. Then electrons in H, which are more energetic, have a longer mean free path, that is, $\ell > \ell'$ as shown in Figure 4.36a. This means that the net

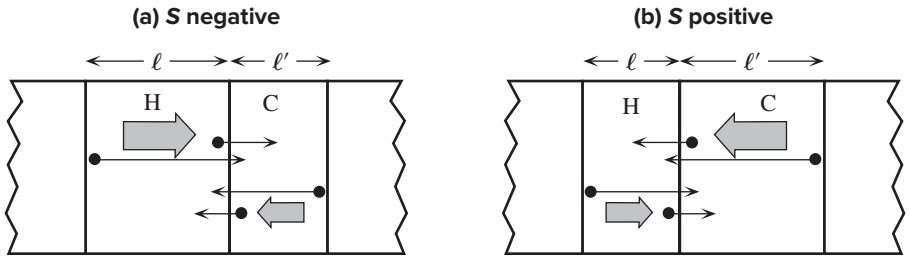


Figure 4.36 Consider two neighboring regions H (hot) and C (cold) with widths corresponding to the mean free paths ℓ and ℓ' in H and C.

Half the electrons in H would be moving in the $+x$ direction and the other half in the $-x$ direction. Half of the electrons in H therefore cross into C, and half in C cross into H.

migration is from H to C and S is negative, as in aluminum. In those metals such as copper in which ℓ decreases strongly with the energy, electrons in the cold region have a longer mean free path, $\ell' > \ell$ as shown in Figure 4.36b. The net electron migration is then from C to H and S is positive. Even this qualitative explanation is not quite correct because n is not the same in H and C (diffusion changes n) and, further, we neglected the change in the mean scattering time with the electron energy. Nonetheless, the importance of scattering processes in determining the Seebeck effect is clearly apparent.

The coefficient S is widely referred to as the **thermoelectric power** even though this term is misleading, as it refers to a voltage difference rather than power. A more appropriate recent term is the **Seebeck coefficient.** S is a material property that depends on temperature, $S = S(T)$, and is tabulated for many materials as a function of temperature. Given the Seebeck coefficient $S(T)$ for a material, Equation 4.29 yields the voltage difference between two points where temperatures are T_o and T as follows:

$$\Delta V = \int_{T_o}^{T} S\, dT \qquad [4.31]$$

Figure 4.37 shows the dependence of the Seebeck coefficient S on the temperature for aluminum and copper. While S is negative for Al it is positive for Cu. In both cases, around and above room temperature, the magnitude of S increases almost linearly with the temperature. Typical values for Al and Cu and many pure metals, as shown in Table 4.3, are only a few microvolts per 1 °C temperature difference, that is, quite small.

The thermoelectric effect involves the same electrons around the Fermi level as those that are normally involved in the electrical conduction process. We can make an intuitive argument for the magnitude of the Seebeck coefficient by considering those electrons within about kT above E_F. When an electron in the hot region at an energy $E_F + k(T + \Delta T)$ in Figure 4.35 diffuses over to the cold region where its energy is $E_F + kT$ (ignoring the slight difference in E_F), it brings with it an additional energy that is $k\Delta T$. If there are N electrons in total, then, due to Fermi–Dirac statistics, the number of electrons in the range kT above E_F is very roughly $(kT/E_F)N$. Thus, the total additional energy carried over is $(k\Delta T)(kT/E_F)N$. The energy that is

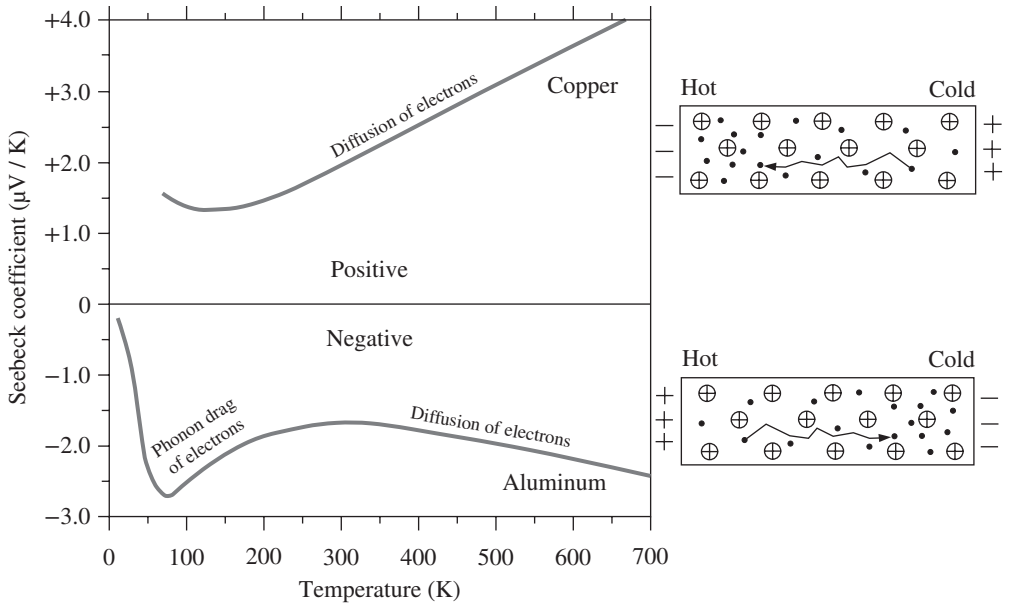


Figure 4.37 The Seebeck coefficient S of copper and aluminum as a function of temperature. While S is negative for aluminum, it is positive for copper. At sufficiently high temperatures (typically around and above room temperature), the magnitude of S increases almost linearly with T.

Data extracted and combined from Gripshover, R.J., VanZytveld, J.B., and Bass, J., *Physical Review,* 163, 598, 1967 and Roberts, R.B., *Philosophical Magazine* 36, 91, 1977 and Roberts, R.B., *Philosophical Magazine B,* 43, 1125, 1981.

transferred per electron is therefore $(k\Delta T)(kT/E_F)$. There is a built-in field or a Seebeck voltage between the two ends as shown in Figure 4.35. The change in the energy of the electron must be equivalent to $e\Delta V$, that is, the work involved in moving the electron through a potential difference of ΔV. Setting $e\Delta V = (k\Delta T)(kT/E_F)$, we can find $S = dV/dT$ as[16]

Order of magnitude of Seebeck coefficient

$$S \approx -\frac{k^2 T}{eE_F} \qquad [4.32]$$

where a negative sign has been inserted to ensure the cold end is negative for this example.

A proper explanation of the Seebeck effect has to consider how electrons around the Fermi energy E_F are scattered by lattice vibrations, crystal defects, impurities and other imperfections. Various scattering processes that typically control the conductivity also influence the diffusion of electrons in a temperature gradient and hence the Seebeck coefficient. The scattered electrons need empty states, which in turn requires that we consider how the density of states changes with the energy as well

[16] Intuitive derivations like this on the back of an envelope are quite well-known for getting the numerical factor wrong among other concerns. Further, there is nothing in this argument that relies on how the energy dependence of electron's mean free path, or the energy dependence of its scattering time, plays a role in the thermoelectric effect.

around E_F. Moreover, in certain metals such as Ni, there are overlapping partially filled bands and the Fermi level lies both inside the *s*-band and the *d*-band. An electron can be scattered from one electronic band to another, for example from the 4*s* band to the 3*d* band. For many pure metals that have the Fermi level in a simple band, the Seebeck coefficient can be described by the Mott-Jones equation that incorporates the energy dependence of the mean free path of the electrons as discussed in Example 4.12.

The Seebeck effect above arises purely from the diffusion of electrons through various scattering processes along a temperature gradient, and is called the **electron diffusion** contribution. There is one more important driving force that migrates or drags electrons through a temperature gradient. We know that lattice vibrations, that is, thermal vibrations of the atoms that make up the crystal, are important in thermal conduction in nonmetals. These thermal vibrations of the atoms set-up lattice waves that travel in the crystal and are responsible for transporting energy from the hot to the cold regions as we saw in Chapter 2. Lattice vibrations are generically called **phonons,** which will be discussed in detail later. For now, all we need to know is that lattice waves obviously also exist in metals, and lattice vibrations in the hot and cold regions will not be in equilibrium. There will be a flow of lattice waves, phonons, from the hot to the cold region. As these lattice waves collide with electrons (or vice versa), they will scatter the electrons and help push them along the temperature gradient. Thus, the collisions of phonons with electrons can cause conduction electrons to be *dragged* along with phonons and hence contribute to the potential difference. This phenomenon is called **phonon drag,** and typically becomes important at low temperatures.

Consider the S vs. T behavior for Al in Figure 4.37. The linear region above 300 K is due mainly to the diffusion of electrons. In the range 100–200 K, the phonon drag effect becomes quite important, and this increases the magnitude of the Seebeck voltage; phonons help migrate more electrons to the cold region. We can write the Seebeck coefficient S of a pure metal as arising from diffusion and phonon drag contributions as

$$S \approx aT + \frac{b}{T} \qquad [4.33]$$

Seebeck coefficient, pure metals

where a and b are constants, specific for each pure metal. The second term represents the phonon drag contribution. Equation 4.33 does not apply at very low temperatures, for example, below ~100 K for Al as can be seen from Figure 4.37.

Suppose that we try to measure the voltage difference ΔV across the aluminum rod by using aluminum connecting wires to a voltmeter as indicated in Figure 4.38a. The same temperature difference now also exists across the aluminum connecting wires; therefore an identical voltage also develops across the connecting wires, opposing that across the aluminum rod. Consequently no net voltage will be registered by the voltmeter. It is, however, possible to read a net voltage difference, if the connecting wires are of different material, that is, have a different Seebeck coefficient from that of aluminum. Then the thermoelectric voltage across this material is different than that across the aluminum rod, as in Figure 4.38b.

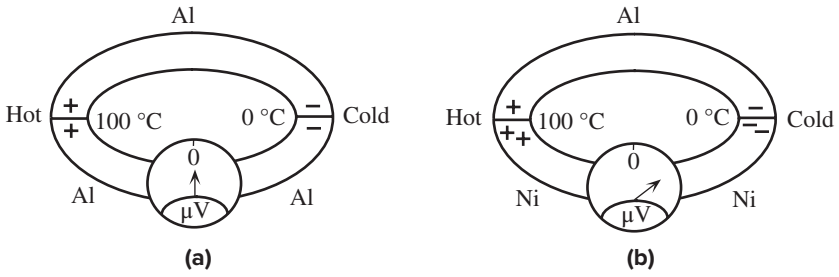


Figure 4.38 (a) If Al wires are used to measure the Seebeck voltage across the Al rod, then the net emf is zero. (b) The Al and Ni have different Seebeck coefficients. There is therefore a net emf in the Al–Ni circuit between the hot and cold ends that can be measured.

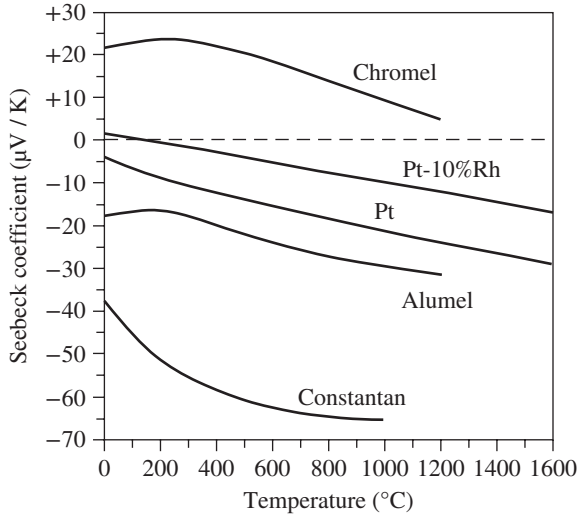


Figure 4.39 The Seebeck coefficient S versus temperature for a few metal alloys used in commercial thermocouples. (Chromel is 90%Ni-10%Cr, Alumel is 95%Ni-2%Al-2%Mn-1%Si, and constantan is 57%Cu-43%Ni.)

Data extracted from Bentley, R.E., *Handbook of Temperature Measurement Vol. 3: The Theory and Practice of Thermoelectric Thermometry.* New York, NY: Springer Publishing Co., 1998, Ch. 2.

The Seebeck effect is fruitfully utilized in the thermocouple (TC), shown in Figure 4.38b, which uses two different metals with one junction maintained at a reference temperature T_o and the other used to sense the temperature T. The voltage across each metal element depends on its Seebeck coefficient. The potential difference between the two wires will depend on $S_A - S_B$. By virtue of Equation 4.31, the electromotive force (emf) between the two wires, $V_{AB} = \Delta V_A - \Delta V_B$, is then given by

Thermocouple emf between metals A and B

$$V_{AB} = \int_{T_o}^{T} (S_A - S_B)\, dT = \int_{T_o}^{T} S_{AB}\, dT \qquad [4.34]$$

where $S_{AB} = S_A - S_B$ is defined as the **thermoelectric power for the thermocouple pair** *A–B*. S_{AB} also represents the **sensitivity** of the TC. For the chromel-alumel (K-type) TC, for example, $S_{AB} \approx 40\ \mu\text{V K}^{-1}$ at 300 K.

The Seebeck coefficients of a few TC materials are shown in Figure 4.39. The TC elements are usually chosen so that when they are used in pairs there is a large difference in their Seebeck coefficients, that is, S_{AB} is sufficiently large to generate a reasonable emf over the temperature range of interest; and with sufficient sensitivity

Table 4.4 Thermoelectric emf for metals at 100 °C and 200 °C with respect to Pt and the reference junction at 0 °C. Data compiled from various sources.

	Emf (mV)	
Material	**At 100 °C**	**At 200 °C**
Pure metals		
Aluminum, Al	0.42	1.06
Copper, Cu	0.76	1.83
Gold, Au	0.78	1.84
Iron, Fe	1.89	3.54
Nickel, Ni	−1.48	−3.10
Platinum, Pt	0	0
Silver, Ag	0.74	1.77
Tungsten, W	1.12	2.62
Alloys		
Alumel	−1.29	−2.17
Chromel	2.81	5.96
Constantan	−3.51	−7.45
Pt-10%Rh (90%Pt-10%Rh)	0.643	1.44

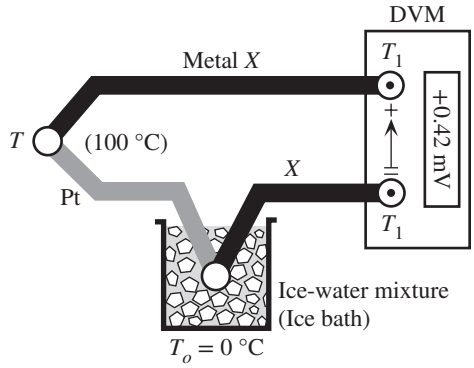


Figure 4.40 The reference junction is at T_o which is 0 °C. The temperature of both the DVM terminals is T_1 and does not affect the EMF measured. EMF depends on T and T_o only. (In this case, metal X is Al, and $T = 100$ °C and the DVM reads +0.42 mV.)

to be able to measure small temperature changes. They are also chosen for their stability and reproducibility; for example, stability against oxidation over long term use. The K-type thermocouple uses a chromel-alumel pair, and S_{AB} at 0 °C, from Figure 4.39 is 22 μV/K − (−18 μV/K) that is 40 μV/K; or an emf of 0.040 mV over a 1 °C difference around 0 °C, which can be easily measured.

The output voltage from a TC pair obviously depends on the two metals used. Instead of tabulating the emf from all possible pairs of materials in the world, which would be a challenging task, engineers have tabulated the emfs available when a given material is used with a reference metal which is chosen to be platinum. The reference junction is kept at 0 °C (273.16 K), which corresponds to a mixture of ice and water. The emf generated is then measured as a function of the junction temperature T as shown in Figure 4.40. The temperature (T_1) of the two junctions at the voltmeter must be kept the same and do not affect the emf. (Why?). Some typical materials and their emfs are listed in Table 4.4.

According to Equation 4.34, the emf V_{AB} generated by a TC depends on the integration of S_{AB}, that is $S_A - S_B$. In many cases, the individual Seebeck coefficients depend linearly on the temperature, at least, over some temperature range. Thus, we would expect S_{AB} to depend linearly on T so that we can write $S_{AB} \approx a_0 + a_1 T$, where a_0 and a_1 are constants. We can now integrate S_{AB} in Equation 4.34 from T_o to T to find that V_{AB} has a quadratic dependence on the temperature difference,

$$V_{AB} \approx c_1 \Delta T + c_2 \Delta T^2 \qquad [4.35]$$

Thermocouple equation

where $\Delta T = T - T_o$, is the temperature with respect to the reference temperature T_o (273.16 K), and c_1 and c_2 are new constants for a given pair of TC materials; the so-called thermocouple coefficients.

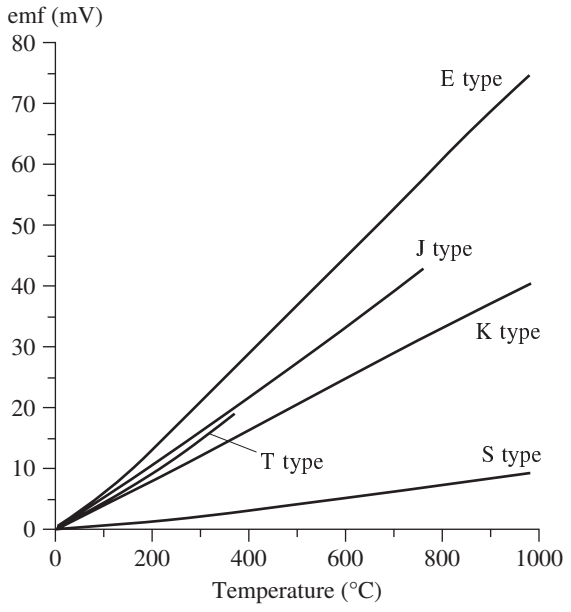


Figure 4.41 Output emf versus temperature (°C) for various thermocouples between 0 °C and 1000 °C.

The inference from Equation 4.35 is that the emf output from the thermocouple wires does not depend linearly on the temperature difference ΔT unless S_{AB} is constant (*i.e.,* $a_1 = 0$). Figure 4.41 shows the emf output versus temperature for various thermocouples. At 0 °C, by definition, the TC emf is zero. The K-type thermocouple, the chromel-alumel pair, is a widely employed general-purpose thermocouple up to about 1250 °C.

EXAMPLE 4.12 **MOTT–JONES EQUATION** The simplest expression for the Seebeck coefficient for a pure metal that has its Fermi level in a single energy band is given by the **Mott–Jones equation,** that is

Mott–Jones equation

$$S \approx -\frac{\pi^2 k^2 T}{3eE_F} x \qquad [4.36]$$

where E_F is the Fermi energy of the electrons, and x is a numerical parameter that characterizes the energy dependence of the mean free path of the electron. For example, if the mean free path decreases with electron's energy then x is negative. Apply this equation to Cu and Al and obtain x for these two metals.

SOLUTION

The Al case is relatively straightforward since Table 4.3 gives S for Al as $aT + b/T$ where $a = -3.0 \times 10^{-3}$ μV K^{-2}, $b = -235$ μV. The aT term represents the diffusion of electrons and corresponds to Equation 4.36 above. (The b/T term is the phonon drag contribution.) Thus,

$$-\frac{\pi^2 k^2}{3eE_F} x = a = -3.0 \times 10^{-3} \times 10^{-6} \text{ V K}^{-2}$$

and substituting $E_F = 11.7$ eV from Table 4.1, and the values for k and e we find $x = +1.43$.

In the case of Cu, from Table 4.3, $a = +5.8 \times 10^{-3}$ μV K^{-2}. Thus,

$$-\frac{\pi^2 k^2}{3eE_F}x = a = +5.8 \times 10^{-3} \times 10^{-6} \text{ V K}^{-2}$$

and substituting $E_F = 7.0$ eV from Table 4.1 we find $x = -1.66$.

EXAMPLE 4.13

Consider the thermocouple configuration shown in Figure 4.40 where the reference junction is at T_o, the probe junction is at T and the two measuring ends of the thermocouple are connected to the voltmeter terminals which are at a temperature T_1. Show that the emf measured is independent of T_1? What is your conclusion?

SOLUTION

Each thermocouple end that is connected to the voltmeter forms a junction. We therefore have two junctions at the voltmeter terminals. Provided that these two junctions are at the same temperature T_1, the measured emf is indeed independent of T_1. Consider the voltage developed across each element in Figure 4.40 and then add these going from the top voltmeter terminal (at T_1), around the circuit, from T_1 to T to T_o to T_1 at the bottom terminal, that is,

$$\begin{aligned}\text{Emf at voltmeter} &= \int_{T_1}^{T} S_X dT + \int_{T}^{T_o} S_{\text{Pt}} dT + \int_{T_o}^{T_1} S_X dT \\ &= \int_{T_o}^{T} S_X dT - \int_{T_o}^{T} S_{\text{Pt}} dT = \int_{T_o}^{T} (S_X - S_{\text{Pt}}) dT\end{aligned}$$

where it is clear that the measured emf depends only on the temperature of the two junctions T_o and T and the integral of the difference of the Seebeck coefficients, $S_X - S_{\text{Pt}}$; a distinct advantage in temperature measurements. Further, if a point or a region within a TC element is heated or cooled, the emf remains unchanged. We can run the TC wires through any temperature region and the emf measured will depend only on temperatures T and T_o of the two junctions.[17] It is assumed that each TC wire material is homogeneous.

EXAMPLE 4.14

COPPER-CONSTANTAN THERMOCOUPLE Consider a copper-constantan (a Cu and Ni alloy) thermocouple pair. The Seebeck coefficient of Cu is in Table 4.3 and the Seebeck coefficient of constantan (CuNi alloy) between 273 − 650 K can be described approximately by a second order polynomial of the form

$$S_{\text{CuNi}} = a_0 + a_1 T + a_2 T^2$$

where $a_0 = -8.63$ μV K^{-1}, $a_1 = -0.1258$ μV K^{-2}, $a_2 = 7.92 \times 10^{-5}$ μV K^{-3}, and T is in K. If one junction is at 0 °C, and the other at 200 °C, what is the emf generated? Calculate the TC voltage using the emf values of Cu and constantan against Pt in Table 4.4 at 200 °C.

SOLUTION

The voltage developed between the copper and constantan thermocouple with one junction at T_o (reference) and the other at T is given by

$$V = \int_{T_o}^{T} (S_{\text{Cu}} - S_{\text{CuNi}}) dT$$

[17] The general proof is left as an exercise, using arguments along the above lines of thought.

We can substitute $S_{Cu} = aT + b/T$ with a and b from Table 4.3 and S_{CuNi} that is given above, and carry out the integration with the result that the emf V at T is

$$V = -a_0(T - T_o) + \frac{1}{2}(a - a_1)(T^2 - T_o^2) - \frac{1}{3}a_2(T^3 - T_o^3) + b\ln(T/T_o)$$

We can now substitute all the values for the coefficients as well as $T_o = 273$ K and $T = 200 + 273 = 473$ K to find,

$$\begin{aligned} V = &-(-8.63\ \mu\text{V K}^{-1})(473\ \text{K} - 273\ \text{K}) \\ &+ (1/2)[0.53 \times 10^{-3} - (-0.1258)\ \mu\text{V K}^{-2}](473^2\ \text{K}^2 - 273^2\ \text{K}^2) \\ &- (1/3)(7.92 \times 10^{-5}\ \mu\text{V K}^{-3})(473^3\ \text{K}^3 - 273^3\ \text{K}^3) + (76.4\ \mu\text{V})\ln(472/273) \\ = &\ 9{,}291\ \mu\text{V} \quad \text{or} \quad 9.291\ \text{mV} \end{aligned}$$

If we were to check standard copper-constantan thermocouple tables we would find $V = 9.286$ mV, so that our calculation is to within ~0.05% in this case. (The reason for the unusually good agreement is that the values of S we have used for Cu and constantan are reasonably well known in this temperature range.)

From Table 4.4, $V_{Cu\text{-}Pt} = 1.83$ mV whereas $V_{CuNi\text{-}Pt} = -7.45$ mV, so that

$$V_{Cu\text{-}CuNi} = V_{Cu\text{-}Pt} - V_{CuNi\text{-}Pt} = 1.83\ \text{mV} - (-7.45\ \text{mV}) = 9.28\ \text{mV}$$

4.9 THERMIONIC EMISSION AND VACUUM TUBE DEVICES

4.9.1 THERMIONIC EMISSION: RICHARDSON–DUSHMAN EQUATION

Even though most of us view vacuum tubes as electrical antiques, their basic principle of operation (electrons emitted from a heated cathode) still finds application in cathode ray and X-ray tubes and various RF microwave vacuum tubes, such as triodes, tetrodes, klystrons, magnetrons, and traveling wave tubes and amplifiers. Therefore, it is useful to examine how electrons are emitted when a metal is heated.

When a metal is heated, the electrons become more energetic as the Fermi–Dirac distribution extends to higher temperatures. Some of the electrons have sufficiently large energies to leave the metal and become free. This situation is self-limiting because as the electrons accumulate outside the metal, they prevent more electrons from leaving the metal. (Put differently, emitted electrons leave a net positive charge behind, which pulls the electrons in.) Consequently, we need to replenish the "lost" electrons and collect the emitted ones, which is done most conveniently using the vacuum tube arrangement in a closed circuit, as shown in Figure 4.42a. The cathode, heated by a filament, emits electrons. A battery connected between the cathode and the anode replenishes the cathode electrons and provides a positive bias to the anode to collect the thermally emitted electrons from the cathode. The vacuum inside the tube ensures that the electrons do not collide with the air molecules and become dispersed, with some even being returned to the cathode by collisions. Therefore, the vacuum is essential. The current due to the flow of emitted electrons from the cathode to the anode depends on the anode voltage as indicated in Figure 4.42b. The current increases with the anode voltage until, at sufficiently high voltages, all the