1

Nature and Types of Solid Materials

Do not worry about your difficulties in Mathematics, I can assure you mine are still greater.

Albert Einstein

1.1 Introduction

In this chapter, we will learn about the fundamental nature of solids and how their defining properties are associated with quantum mechanical concepts of electrons and their energy. The exposure to the most essential concepts of solid-state physics will greatly help us in understanding the nature of electroceramics and the multiple physical phenomena they can exhibit that form the basis for a large number of novel device applications that impact electronic and sensor technology. We have purposely tried to avoid the intricacies of mathematical models in describing these concepts because the goal here is not to produce another book on solid-state physics but rather to make use of the essential features of various theoretical models in understanding the transport properties of electrons, uniqueness of semiconductors, and the scientific basis behind the dielectric properties of materials.

1.2 Defining Properties of Solids

Solids can be broadly classified as conductors, semiconductors, and insulators of which dielectrics are a subset. Another important group of solids are classified as high temperature superconductors. Because of the unique physical mechanisms involved in the origin of superconductivity, these materials are of a special category and will be treated as an independent class of materials. We will devote a section on superconductivity later in this chapter. So far as the other three groups are concerned, we can differentiate between them on the basis of their defining properties. For example, a conductor is defined by its capacity to facilitate the transport of an electrical current associated with the inherent material property that we call resistance. Similarly a semiconductor is defined by its energy gap (also, called bandgap) and a dielectric by its dielectric property. We discuss in this chapter, the origin of these properties and how they add uniqueness to materials.

1.2.1 Electrical Conductance (G)

All materials tend to resist the flow of an electric current by virtue of its built-in resistance. The magnitude
of current, \( I \), is dictated by the resistance, \( R \) (or, conductance, \( G \) ) when a voltage, \( V \), is applied between the two ends of a solid sample. This relationship is given by the famous law of physics universally known as the Ohm's law that was conceived in 1825–1826 by Gerog Ohm of Germany. It states that the current \( (J) \) generated between the two fixed points of a conductor (such as a metal) is directly proportional to the potential applied and inversely proportional to its resistance. Mathematically, it is expressed as Eq. (1.1).

\[
I = \frac{V}{R} = GV
\]

Here \( G \) being the conductance that is simply the inverse of resistance. From the above equation, we can conclude that \( I \) increases as \( R \) decreases or it increases with the increase in conductivity \( G \). The resistance \( (R) \) changes as two reference points between which it is measured is changed. For example, it increases with the increase in the distance between the reference points and decreases if the distance between these points is reduced. That means that the resistance (or, conductance) is dependent upon the geometry of the sample. In other words, neither resistance nor conductance is the intrinsic property of the sample under consideration. Unless we can develop the concept of intrinsic resistance of a material, we would not be able develop theoretical models that are independent of sample geometry. To accomplish this goal, let us introduce now a parameter which we shall call resistivity. It is defined as follows:

\[
\rho = R \left( \frac{A}{L} \right)
\]

Here \( \rho \) is the resistivity, \( L \) the sample length, and \( A \) the cross-sectional area. The unit of the resistivity is \( \Omega \cdot m \). We can see from the above equation that the resistivity becomes an intrinsic property of materials. No two materials would have the same value of resistivity.

While defining the resistivity, we assumed the sample to be uniform in which the current flows uniformly. However, in reality that may not always be the case. We therefore need to develop a more basic definition of resistivity. We can imagine that an electric field prevails inside the sample when it experiences a potential difference between any two fixed points. It is actually the electric field \( (E) \) that enables the current flow within the sample, and therefore, the resistivity must be associated with the current density \( (J) \) that exists within the sample. We can then redefine the resistivity with respect to \( E \) and \( J \) as in Eq. (1.3).

\[
\rho = \left( \frac{V}{T} \right) \cdot \left( \frac{A}{J} \right) = \frac{E}{J}
\]

The inverse of the resistivity is called conductivity \( (\sigma) \) and its unit is \( S \cdot m^{-1} \) or \( (\Omega \cdot m)^{-1} \). Replacing the resistivity with conductivity, we can rewrite Eq. (1.3) in its alternative formulation as follows:

\[
J = \sigma E
\]

Metals have the highest conductivity among all solids, and it is greater than \( 10^5 \) \( (S \cdot m^{-1}) \). In comparison, in semiconductors, it varies from \( 10^{-6} < \sigma < 10^5 \) \( (S \cdot m^{-1}) \). The dielectrics have very small conductivity that is smaller than \( 10^{-6} \) \( (S \cdot m^{-1}) \). Based on this information, we can now distinguish between the three types of solids as in Eq. (1.5).

\[
\sigma_{\text{metal}} \gg \sigma_{\text{semiconductor}} \gg \sigma_{\text{dielectric}}
\]

In Table 1.1, a list of materials with their electrical conductivity is presented.

### 1.2.2 Bandgap, \( E_g \)

The defining property of a semiconductor is its energy bandgap that exists between the valence band and the conduction band. The width of the bandgap is expressed in electron volt with the symbol of \( E_g \). The unit of electron volts for energy is defined as the work done in accelerating an electron through 1 V of potential difference. For converting 1 J of energy to electron volts, we need to divide it by the charge of an electron that is \( 1.602 \times 10^{-19} \) C.

The concept of energy being in bands of solids instead of just being discrete is based on the band theory of solids to which we will introduce our readers later in this chapter. For the time being, let us be satisfied with the assumption that electrons and other charge carriers (e.g., holes) can reside only in the valence band or the conduction band. It is forbidden for any charge carrier to be found in the bandgap at absolute zero. The Fermi–Dirac distribution function (also known as F-D

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrical conductivity, ( \sigma ) ( (S \cdot m^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (Al)</td>
<td>( 3.5 \times 10^7 )</td>
</tr>
<tr>
<td>Carbon (graphene)</td>
<td>( 1.00 \times 10^8 )</td>
</tr>
<tr>
<td>Carbon (diamond)</td>
<td>( \approx 10^{-13} )</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>( 5.96 \times 10^7 )</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>( 4.10 \times 10^7 )</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>( 6.30 \times 10^7 )</td>
</tr>
<tr>
<td>Platinum (Pt)</td>
<td>( 9.43 \times 10^6 )</td>
</tr>
<tr>
<td>Germanium (Ge)</td>
<td>( 2.17 ) (depends on doping)</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>( 1.56 \times 10^{-3} ) (depends on doping)</td>
</tr>
<tr>
<td>Gallium arsenide (GaAs)</td>
<td>( 1.00 \times 10^{-8} ) to ( 10^3 )</td>
</tr>
</tbody>
</table>
statistics) with its enormous importance to the quantum nature of solids completely excludes the possibility that any electron can be found in the bandgap. Not only that, this theory also predicts that at absolute zero (0 K), all electrons are frozen in valence band, and the conduction band is completely empty. We will deal also with this magnificent theory later in this chapter. However, it is also probable that some electrons might get sufficient kinetic energy to escape the valence band and migrate to the conduction band. But this probability is allowed only at temperature \(\gg 0 \text{K}\) according to the F-D statistics.

In general, metals have almost no bandgap, whereas insulators have large bandgaps. The bandgaps of semiconductors lie between these two extremes. If the bandgap is greater than 2 eV, the material is thought to be an insulator, though this notion is not always supported by facts. For example, there are many semiconductors with \(E_g > 2\) eV, and they are classified as wide bandgap semiconductors and not insulators.

The semiconductors are normally classified as narrow bandgap, midlevel bandgap, and wide bandgap. In Figure 1.1, a qualitative picture of bandgap is given, which can serve for distinguishing among metals, semiconductors, and dielectrics.

We see in Figure 1.1 that dielectrics have much larger bandgaps than semiconductors, whereas metals have no bandgap at all. In fact, the two bands merge in metals causing an overlapped region, where electrons are shared by the two bands. We also find in this figure that besides the bandgap, there is another parameter labeled as Fermi level, which lies between the upper (conduction band) and lower (valence band) energy bands. It is defined as the sum of the potential energy and kinetic energy. For convenience, for example, in discussing the semiconductor properties, the potential energy is set at zero corresponding to the bottom of the valence band.

It is important to know that all solids have Fermi energy, and its location with respect to the bandgap is commonly referred to as Fermi level. We can now summarize that

\[E_{g, \text{dielectric}} \gg E_{g, \text{semiconductor}} \gg E_{g, \text{metal}}\]  

In Table 1.2, values for the bandgap for some common semiconductor materials is given at 300 K.

### 1.2.3 Permeability, \(\varepsilon\)

From Figure 1.1, we can also conclude based on the arguments advanced in the previous section that the large bandgap of a dielectric material would inhibit the electrical conduction since it would be difficult for electrons to gain sufficient energy to overcome the bandgap at room temperature. This is certainly consistent with our everyday experience that dielectrics are very poor carriers of electricity. However, one need to remember that theoretically even the best of dielectric can conduct electricity when subjected to a large potential difference, but the magnitude of the resulting current would be so small as to be of any practical interest.

The defining property of a dielectric material is the permittivity, which is also known by its other name of dielectric constant with the universal symbol of \(\varepsilon\). All materials will get polarized when subjected to an electric

<table>
<thead>
<tr>
<th>Materials</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.661</td>
</tr>
<tr>
<td>Si</td>
<td>1.12</td>
</tr>
<tr>
<td>InSb</td>
<td>0.17</td>
</tr>
<tr>
<td>InP</td>
<td>1.344</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.424</td>
</tr>
</tbody>
</table>

Source: From http://hyperphysics.phy-astr.gsu.edu/hbase/hph.html.
field. We know that the relationship between the electric displacement \(D\), and the electric field \(E\) is given by the fundamental equation of electromagnetics which states that

\[
D = \varepsilon_0 E + P
\]

(1.7)

where \(\varepsilon_0\) is the permittivity of vacuum with the value of \(8.85 \times 10^{-12} \text{ F m}^{-1}\) and \(P\) the electric field-induced polarization. At low electric field, the product \(\varepsilon_0 E\) is a very small number, and therefore, we can approximate \(D \approx P\). Therefore, for low electric fields, Eq. (1.7) takes the form of Eq. (1.8).

\[
P \approx \varepsilon_r \varepsilon_0 E
\]

(1.8)

The parameter \(\varepsilon_r\) is the relative dielectric constant that is a unitless quantity and is equal to \(\varepsilon \cdot \varepsilon_0^{-1}\), where \(\varepsilon\) is the permittivity of the material. The permittivity is specific to a material similar to the electrical conductivity. Therefore, we can also use this parameter to distinguish between the three types of solids as shown in the relationship in Eq. (1.9).

\[
\varepsilon_{r, \text{dielectric}} \gg \varepsilon_{r, \text{semiconductor}} \gg \varepsilon_{r, \text{metal}}
\]

(1.9)

In Table 1.3, a list of relative dielectric constant \(\varepsilon_r\) for selected materials is presented.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Dielectric constant, (\varepsilon_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>1</td>
</tr>
<tr>
<td>Air</td>
<td>1.00059</td>
</tr>
<tr>
<td>Mica</td>
<td>3–6</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>3.18</td>
</tr>
<tr>
<td>Germanium (Ge)</td>
<td>16</td>
</tr>
<tr>
<td>Strontium titanate (SrTiO₃)</td>
<td>310</td>
</tr>
<tr>
<td>Titanium dioxide (TiO₂)</td>
<td>173</td>
</tr>
</tbody>
</table>

Source: From http://hyperphysics.phy-astr.gsu.edu/hbase/hph.html.

We can easily visualize a picture in which a traveling electron will encounter thermally generated phonons in a crystal lattice and then will acquire an average velocity that is also called the drift velocity, \(v_d\). But what are phonons and where do they come from? It is quantum mechanical concept and refers to the unit of vibrational energy originating from the oscillations of atoms within a crystal lattice. The atomic oscillations increase with increasing temperature resulting in larger number of thermally generated phonons. Phonons are the counterpart of photons and both being quantum mechanical concepts. They are the two main types of elementary particles associated with solids.

The magnitude of the drift velocity will be proportional to the applied electric field. The coefficient of proportionality is called the electron mobility \(\mu_e\). Alternatively, it can also be defined with the help of the following equation:

\[
\mu_e = \left( \frac{\Delta v_d}{\Delta E} \right)
\]

(1.10)

The electron mobility is a very important property and plays a vital role in designing a transistor. Materials with larger values of mobility are desired because that translates to faster transistors. We will discuss this parameter again in Chapter 7. Its unit is \(\text{m}^2 \text{V}^{-1} \text{s}^{-1}\).

We can easily visualize that electrical conductivity \(\sigma_e\) and electron mobility \(\mu_e\) to be related somehow. We can in fact find this relationship simply by assuming that there are \(n\) number of electrons involved and their transport from one point to another is facilitated by the onset of mobility \(\mu_e\) and the applied electric field \(E\) such that

\[
\sigma_e = ne\mu_e
\]

(1.11)

where \(e\) is obviously the electronic charge. Equation (1.11) is the standard expression and gains a special importance while dealing with semiconductor materials where the conductivity is the sum of the contributions made by electrons and holes. This is discussed also in Chapter 7.

### 1.3 Fundamental Nature of Electrical Conductivity

We defined in Eq. (1.4) the electric current, \(I\). This derivation was based on geometrical considerations of a sample of finite size and length. The question now arises what causes the onset of current and how do we understand its true nature. To accomplish this goal, we need to consider that the current is generated when electrons move from one point to another under the influence of an applied electric field. Such a movement will obviously involve a velocity and mobility.

### 1.4 Temperature Dependence of Electrical Conductivity

Resistivity of solids is highly temperature-dependent. Strong thermal dependence of resistivity is exhibited by metals and semiconductors. However, their trends are opposite to each other. They are displayed in Figure 1.2. We can see here that metal resistivity first remains constant in the low temperature regime until a temperature is reached above which it starts increasing rapidly as the temperature increases. At high temperature regime, it follows approximately a linear relationship with temperature yielding a positive temperature coefficient of
resistivity \( \frac{\Delta \rho}{\Delta T} = \eta \). The semiconductor resistivity, on the other hand, increases rapidly with decreasing temperature following an exponential thermal dependence. At sufficiently low temperatures, all semiconductors become good insulators. At higher temperatures, its resistivity decreases at a vastly reduced rate such that the change is almost monotonous. Resistivity of a typical insulator follows qualitatively the same temperature dependence as semiconductors. Obviously, the resistivity of an insulator is much greater than that of semiconductors as can be concluded from Figure 1.1.

In Figure 1.2, we have included the temperature dependence of resistivity also for a superconductor simply to demonstrate the distinction one can make between metals, semiconductors, and superconductors based on the behavior of their electrical resistivity with temperature. In superconductors, the resistivity goes through a phase change at a critical temperature, called the superconducting transition point below which a normal metal becomes superconducting. Its resistance vanishes and the material acquires infinite conductivity and remains in the superconducting state so long as temperature remains below the transition point. Above the critical temperature, it loses its superconducting nature and behaves like a normal metal. The thermal behavior of solids, as shown in Figure 1.2, can be easily explained on the basis of physics as describe below.

### 1.4.1 Case of Metals

The thermal behavior of electrical resistivity of metals can be expressed empirically by Matthiessen’s rule that

\[
\rho_{\text{net}} = \rho_0 + \rho(T)
\]

is given by Eq. (1.12).

\[
\eta = \frac{R - R_0}{R(T - T_0)} = \frac{\Delta R}{\Delta T} \cdot \frac{1}{R}
\]

### 1.4.2 Case of Semiconductors

For intrinsic semiconductor, the conduction can only take place when electrons closest to the surface of the bandgap acquire sufficient energy to escape the bandgap and reach the conduction band. The temperature dependence of the resistivity \( \rho \) is given by Eq.(1.14).

\[
\rho = \rho_0 \exp \left( -\frac{E_g}{2k_B T} \right)
\]

### Table 1.4 Temperature coefficient of resistivity (\( \eta \)) of some common metals.

<table>
<thead>
<tr>
<th>Metals</th>
<th>( \eta \times 10^{-3} ) (per °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver, Ag</td>
<td>3.8</td>
</tr>
<tr>
<td>Copper, Cu</td>
<td>3.9</td>
</tr>
<tr>
<td>Gold, Au</td>
<td>3.4</td>
</tr>
<tr>
<td>Aluminum, Al</td>
<td>4.3</td>
</tr>
<tr>
<td>Iron, Fe</td>
<td>6.5</td>
</tr>
<tr>
<td>Tungsten, W</td>
<td>4.5</td>
</tr>
<tr>
<td>Platinum, Pt</td>
<td>3.92</td>
</tr>
</tbody>
</table>

Nichrome is an alloy of Ni and Cr.

Source: From http://hyperphysics.phy-astr.gsu.edu/hbase/hph.html.
In Eq (1.14), \( \rho_0 \) is the temperature-independent part of the resistivity, \( E_g \) the bandgap, and \( k_B \) the Boltzmann constant. Equation (1.14) tells us that the resistivity of a semiconductor material increases exponentially as the temperature decreases. This can be seen from Figure 1.2 as well.

### 1.4.3 Frequency Spectrum of Permittivity (or Dielectric Constant)

So far we have paid more attention to metals and semiconductor, while discussing the nature of electrical conductivity. Let us now consider the case of an insulator. We may recall that even a standard semiconductor material can become a good insulator when cooled to very low temperatures. The electrical conductivity is of no special interest while discussing the nature of insulators. It is the dielectric constant, or polarizability, that is of greater interest for understanding the dielectric nature of electroceramics. Comparatively speaking, electroceramics show much higher permittivity than semiconductors. Equation (1.7) gives us an expression for the displacement \( (D) \) when an insulator is subjected to an external electric field \( (E) \). Permittivity is strongly dependent upon the frequency of the applied electric field. Permittivity measured at any frequency \( (\omega) \) consists of real and imaginary components as shown in Eq. (1.15).

\[
\epsilon(\omega) = \epsilon'(\omega) + j\epsilon''(\omega) \quad (1.15)
\]

Here \( \epsilon(\omega) \) is the measured permittivity at frequency \( (\omega) \), \( \epsilon'(\omega) \) the real part and \( \epsilon''(\omega) \) the imaginary part. The real part is related to the stored electrical energy of the medium such as a capacitor, and imaginary part is related to the dissipation of the energy which is also called the energy lost. The ratio between the two components defines the loss tangent. Loss tangent is also referred to as \( \tan \delta \) and is a measure of the efficiency of a capacitor device. Taking into consideration the loss angle, \( \delta \), Eq. (1.15) can also be expressed as in Eq. (1.16).

\[
\epsilon = \frac{P}{E}(\cos \delta + j \sin \delta) \quad (1.16)
\]

There are three types of permittivity that are dipolar, atomic, and electronic. Their presence is distinctly noticeable when \( \omega \) changes from low frequencies to optical frequencies covering the frequency spectrum of microwave, infrared, visible, and then finally ultra-violet as shown in Figure 1.3.¹ The dipolar part dominates between \( 10^3 < \omega < 10^9 \) Hz and ceases to exist once the microwave range (\( \approx 10^{11} - 13 \) Hz) sets in. Then the ionic polarization begins and it persists for approximately \( 10^{12} < \omega < 10^{13} \) Hz. The electronic polarization is the only polarization that prevails in the optical regime of \( 10^{14} < \omega < 10^{17} \) Hz. Notice that both the ionic and electronic components go through a resonance that occurs approximately at \( \omega \approx 10^{12} \) Hz and at \( \omega \approx 10^{15} \) Hz, respectively. Comparatively speaking, dipolar polarization, \( P_d \), is much larger than the ionic polarization, \( P_i \), or electronic polarization, \( P_e \).

We find a strong resonance of ionic polarization in the infrared (IR) regime covering the frequency range between 300 GHz and 430 THz (equivalent wave lengths being 700–10⁶ nm). The imaginary dielectric constant, \( \epsilon'' \) also undergoes pronounced resonances at frequencies corresponding to the resonances of the real part of three types of polarization. We furthermore notice that the

¹ [https://en.wikipedia.org/wiki/Permittivity](https://en.wikipedia.org/wiki/Permittivity)
imaginary part decreases with increasing frequency and the largest change occurs in the dipolar region. What actually causes the onset of these polarizations? We shall discuss this now.

The **dipolar polarization** that is also known as orientation polarization is randomly oriented dipoles in the absence of an electric field. However, when an external electric field is applied, these dipoles orient themselves in the direction of the field. At frequencies (\( \omega \)) below \( 10^{11} \) Hz the applied field can induce periodic rotation. At moderately high fields, the rotations become rapid and energy is absorbed as heat. This is the basis for microwave heating. As can be seen from Figure 1.3, this polarization dominates in the frequency domain covering \( 0 < \omega < 10^{11} \) Hz.

At moderately high frequencies, molecules may not rotate because the high energy that is absorbed results in the emergence of the resonance peaks. On the application of electric field with frequencies in the microwave domain (\( 10^{11} < \omega < 10^{13} \) Hz), small displacements of ions from their equilibrium positions can result. As a consequence, a net dipole moment can be induced. These dipoles will absorb energy that like in the previous case will give rise to resonance. Such a response is mostly present in the infrared region. The **electronic polarization**, on the other hand, sets in at the optical frequencies with \( \omega > 10^{14} \). The dipolar and ionic polarizations are negligible at optical frequencies because of the inertia of molecules to respond to optical frequencies. At optical frequencies, the square of the refractive index, \( n^2 \), is the value of the relative dielectric with good accuracy. Some examples are given in Table 1.5.

Then there is another type of polarization that occurs only in heterogeneous materials such as in a ceramic where grain boundaries are present or at the interface such as material–metallic electrode interface. Its origin lies in the limited movements of charges under the influence of an applied electric field at very low frequencies. Charges accumulate at the grain boundaries or at the interfaces giving rise to **interfacial polarization**. This effect has no fundamental value but is of considerable importance to electronic technology.

### Table 1.5 Comparison of refractive index and permittivity for some materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>( \epsilon_r )</th>
<th>( n^2 )</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond, C</td>
<td>5.7</td>
<td>5.85</td>
<td>Electronic</td>
</tr>
<tr>
<td>Germanium, Ge</td>
<td>16</td>
<td>16.73</td>
<td>Electronic</td>
</tr>
<tr>
<td>Sodium chloride, NaCl</td>
<td>5.9</td>
<td>2.37</td>
<td>Electronic and ionic</td>
</tr>
<tr>
<td>Water, H₂O</td>
<td>80</td>
<td>1.77</td>
<td>Electronic, ionic and dipolar</td>
</tr>
</tbody>
</table>

### 1.5 Essential Elements of Quantum Mechanics

We are well familiar with the fact that quantum mechanics is a powerful branch of physics that provides us with the requisite tools for understanding the physical phenomenon that cannot be adequately described by classical physics. Since its emergence in the early twentieth century, it has dominated the field of solid-state sciences of which electroceramics is a part. In this section, we will try to appreciate the essential concepts that form the pillars of quantum mechanics leading to a better understanding of the physical properties of electroceramic materials. Of particular interest are the concepts of Planck’s radiation law, Einstein’s photoelectric effect, Bohr’s theory of the hydrogen atom, de Broglie principle of duality of matter and waves, Schrödinger’s equations, Heisenberg’s uncertainty principle, and the quantum mechanical interpretation of the periodic table of elements.

#### 1.5.1 Planck’ Radiation Law

Until 1900, classical physics could explain satisfactorily most of the physical phenomena observed. However, a time came when it was not possible to explain some of experimental results using the concepts of classical physics. One of them was the true nature of emitted radiation from a black body. Ideally, a black body is a perfect radiator and an absorber of energy at all electromagnetic wavelengths. Energy is considered to be continuous according to classical physics. However, physicists at the time failed to explain black body radiation using the concepts of classical physics. In 1901, Max Planck of Germany took a bold step and postulated that light energy is not continuous, but rather it exists in discrete packets which he called quanta. The emitted energy (\( E \)) is proportional to the frequency of emitted radiation (\( \nu \)).

\[
E = n \hbar \nu
\]

(1.17)

where \( n = 1, 2, 3, \ldots \) and \( \hbar \) Planck’s constant which is equal to \( 6.625 \times 10^{-34} \) Js.

This simple equation tells us that the radiated energy from a black body can only assume values in integral steps of \( \hbar \nu \) with \( n = 1, 2, 3, \ldots \). In the vocabulary of quantum mechanics, such a situation is described as quantized. That makes radiative energy a quantized parameter that is one of the cornerstones of quantum mechanics. The concept of quantization plays a vital role in quantum mechanics. With this assumption, Planck was finally able to explain successfully the nature of radiated energy from a black body. Planck received Nobel Prize in Physics in 1918 for this very fundamental
contribution. Equation (1.17) can be written in other forms as well; one of them being as in Eq. (1.18).

\[ E = n\hbar \frac{h}{2\pi} (2\pi v) = n\hbar \omega \]  \hspace{1cm} (1.18)

The symbols \( \hbar \) and \( \omega \) are reduced Planck’s constant and angular frequency, respectively. From Eq. (1.18), it follows that the photon energy, \( E_{ph} \), between any two successive quantum number is given by

\[ E_{ph} = nhv - (n - 1)hv = \hbar \omega \]  \hspace{1cm} (1.19)

It is interesting that neither Planck nor Einstein later, in explaining the photoelectric effect, used the word “photon” in place of “light quanta.” It was Gilbert N. Lewis, an American Physical Chemist, who coined the word “photon” in 1926 to describe light quanta. Ever since, this word has been in use universally to mean light quanta.

1.5.2 Photoelectric Effect

The photoelectric effect was discovered by Heinrich Hertz of Germany in 1887 while experimenting with electromagnetic waves whose existence he conclusively proved. Electromagnetic waves were theoretically predicted in 1864 by James Clark Maxwell of England in his celebrated “electromagnetic theory of light.” It was Heinrich Hertz of Germany who had discovered the photoelectric effect in 1887 while illuminating metallic surfaces with ultraviolet light. He noticed during his experiments, the emission of bursts of sparks. It is the same Hertz who had also discovered radio waves and experimentally showed the existence of electromagnetic waves predicted by Maxwell. Today, in his honor, Hz (Hertz) is used as the unit for frequency.

The photoelectric effect phenomenon could not be explained on the basis of classical physics. It offered a dilemma to the physicist of the time and remained unexplained until 1905 when Albert Einstein successfully explained the effect for which he received the Nobel Prize in Physics in 1921. It is interesting to note that though he had earlier developed the “special theory of relativity” that gained him international stature and respect, it was his work on the photoelectric effect that was recognized by the Nobel Committee and not the celebrated “special theory of relativity.” The photoelectric effect is defined as the emission of electrons or other charged particles from a material when irradiated by light of suitable frequency. This effect can be observed by doing a simple experiment with the setup similar to the one shown in Figure 1.4.

When a cathode made of a metal is irradiated by photons (light quanta of Planck) of suitable energy, electrons are emitted. These electrons are collected at the positively charged anode resulting in the onset of a photocurrent, \( I_{ph} \). However, the emission can take place only when the Einstein’s equation of electron emissivity is obeyed which states that

\[ h\nu = \Omega_{max} + W \]  \hspace{1cm} (1.20)

Here \( \Omega_{max} \) is the maximum kinetic energy of the emitted particles and \( W \) the work function which is a material constant. From this equation, we can infer that for photoemission to set in the threshold energy equivalent to \( W \) must be overcome. That is \( W \) must be equal to the photon energy of \( h\nu_0 \), where \( \nu_0 \) is the frequency corresponding to the threshold energy. Then Eq. (1.20) takes the form of Eq. (1.21).

\[ \Omega_{max} = h(\nu - \nu_0) \]  \hspace{1cm} (1.21)

Equation (1.21) tells us that the maximum kinetic energy of emitted electrons is directly proportional to frequency with the slope of the straight-line giving us the experimental determination of the value of Planck’s constant, \( h \). This is another important implication of Einstein’s equation of photoemission. In Figure 1.5,
the maximum kinetic energy as a function of radiation frequency for three arbitrary metals (M-1, M-2, and M-3) is plotted. We can easily find that the slope of the plots gives us the value of the Planck's constant. The intercepts on the x-axis gives the values of the threshold frequencies for the three metals, respectively, which are labeled as \( \nu_1, \nu_2, \) and \( \nu_3. \) The intercepts on the negative side of the y-axis and identified as \( \Omega_1, \Omega_2, \) and \( \Omega_3 \) are the potentials that must be applied to stop the photoelectric effect entirely. It is important to remember that photoemission is a frequency-dependent function and is independent of the photo-current, \( I_{ph}. \)

When a voltage, \( V > 0 \) is applied in the circuit of Figure 1.4 the photocurrent, \( I_{ph}, \) will be amplified and similarly a negative potential will make it smaller. This is shown in Figure 1.6. From this figure, we also find that the photocurrent increases with the increase in the intensity of light. However, the process of photoemission itself remains unaffected by the intensity of light.

As the positive potential increases, the photocurrent is first amplified and keeps on increasing until it begins to saturate. However, exactly the opposite happens when the sample is biased with a negative potential. The photocurrent, as expected, becomes smaller and finally disappears completely when the photoemission stops. This characteristic negative potential, \( -V_s, \) is called the “stopping potential.” The work done by an electron in transporting against the “stopping potential” must be equal to its maximum kinetic energy, \( \Omega_{\text{max}}. \) Substituting it in Eq. (1.21), we get Eq. (1.22).

\[
\nu_1 \Omega_{\text{max}} = \hbar \nu - W = \frac{\Omega}{\epsilon} - W. \tag{1.22}
\]

When \( V \) approaches the stopping potential, the photoemission stops so that for \( \nu = 0, V_s = -\frac{W}{\epsilon}. \) In Figure 1.5, the intercepts along the y-axis at \( v = 0 \) correspond to kinetic energies at the stopping potentials which are

\[
\Omega_1 \equiv \frac{W_{\text{max}}}{\epsilon}, \quad \Omega_2 \equiv \frac{W_{\text{max}}}{\epsilon}, \text{ and } \quad \Omega_3 \equiv \frac{W_{\text{max}}}{\epsilon}. \]

This enables us to determine the work function of a metal accurately because \( V \) can be measured more accurately than the kinetic energy.

Work function is an important physical parameter that plays crucial roles in solid-state electronics, field emission, thermodynamics, and chemical processes. It is defined as the minimum energy required for an electron to escape from the surface of a solid to reach the vacuum level. By convention the energy of the vacuum level is assigned the value of infinity. Its experimentally determined values vary from one technique to another depending upon the method used. We present its value for some selected group of metals which are commonly used in electronics. A list is presented in Table 1.6. There are many good applications based on the photoelectric effect. Some of them are night vision devices, image sensors, and photomultipliers.

### Exercise 1.1

In a photoelectric effect experiment, a polished surface of Ca with work function of 2.9 eV is radiated with the ultraviolet (UV) radiation having the wavelength of 250 nm. What is the velocity of the emitted electrons?

**Solution**

We have from Eq. (1.20) \( \Omega_{\text{max}} = \hbar \nu - W = \frac{\Omega}{\epsilon} - W. \) Here, \( \Omega_{\text{max}} \) is the maximum kinetic energy of the emitted electron, \( c = \text{velocity of light} = 3 \times 10^8 \text{ m s}^{-1}, \hbar = \text{Planck’s constant} = 6.63 \times 10^{-34} \text{ J s}, \) \( W \) the work function of Ca = 2.9 eV. Substituting these values in Eq. (1.20) we get

\[
\Omega_{\text{max}} = \left( \frac{3 \times 10^8 \times 6.63 \times 10^{-34}}{1.60 \times 10^{-19} \times 250 \times 10^{-9}} \right) - 2.9 = 2.1 \text{ eV}
\]

Now, \( \Omega_{\text{max}} = \frac{1}{2} m_e (\nu_0)^2 \) where \( m_e = 9.1 \times 10^{-31} \text{ kg}. \)

### Table 1.6 Work function of some commonly used metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Work function, ( W ) (eV)</th>
<th>Average value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver, Ag</td>
<td>4.26–4.74</td>
<td>4.50</td>
</tr>
<tr>
<td>Aluminum, Al</td>
<td>4.06–4.26</td>
<td>4.16</td>
</tr>
<tr>
<td>Gold, Au</td>
<td>5.1–5.47</td>
<td>5.29</td>
</tr>
<tr>
<td>Copper, Cu</td>
<td>4.53–5.10</td>
<td>4.82</td>
</tr>
<tr>
<td>Platinum, Pt</td>
<td>5.12–5.93</td>
<td>5.53</td>
</tr>
<tr>
<td>Palladium, Pd</td>
<td>5.22–5.6</td>
<td>5.41</td>
</tr>
<tr>
<td>Iron, Fe</td>
<td>4.67–4.81</td>
<td>4.74</td>
</tr>
</tbody>
</table>

Substituting this for $\Omega_{\text{max}}$, we get the maximum velocity, $v_m$, for emitted electron to be

$$v_m = \sqrt{\frac{2\Omega_m}{m_e}} = 8.6 \times 10^5 \text{ m s}^{-1}$$

1.5.3 Bohr’s Theory of Hydrogen Atom

In 1911, Lord (Ernest) Rutherford of England (originally, from New Zealand; Nobel Prize in Chemistry in 1909) proposed a model for an atom in which he compared an atom to an ultra-miniaturized prototype of our solar system. According to this model, an atom consists of a nucleus that is surrounded by a number of orbits. The entire mass of the atom is densely packed at the core of the nucleus that consists of many subatomic particles of which neutrons and protons are just two examples. Protons are positively charged, whereas neutron is electrically neutral. Both of them are of approximately equal mass, and each is roughly 1840 times heavier than an electron with the mass of $9.1 \times 10^{-31}$ kg. The atomic number, $Z$, of an element is equal to the number of protons residing at the nucleus. A very strong Colombian force between the proton and the electron holds the atom together and gives stability to the structure.

Niels Henrik David Bohr, a Danish physicist, used Rutherford’s model of atomic structure to develop his model of the hydrogen atom. Here $p^+$ and $e^-$ represent the positively charged protons and negatively charged electrons, respectively. It also shows the energy emitted by the electron when transiting between the orbits $n = 1, 2, 3$.

Since the orbits are quantized, its energies must also have only the integral values of 1, 2, 3, etc. According to this, he made use of the concept of quantized photon energy proposed earlier by Planck. Bohr made three assumptions:

Assumption 1: The electrons can traverse around the orbits but without emitting or absorbing any radiation. The order of orbits in an atom, beginning with the first orbit nearest the nucleus, follow the ascending order of the principal quantum number, $n$, which can only have only the integral values of 1, 2, 3, …

Assumption 2: The electrons can transit from one orbit to another. Because the energy of each orbit is different, during the process of transition, the electrons can either absorb or emit radiation in order to satisfy the law of conservation of energy. In either case, Planck’s radiation law must prevail, and such the photon energy must be equal to $hv$.

Assumption 3: The angular momentum, $L$, is quantized and can have only the values equal to integral multiples of $\hbar$. This was his boldest assumption and has the same importance as Planck’s quantized energy. Quantized $L$ is called the orbital quantum number.

Mathematically, we can express the third assumption in the form of Eq. (1.24).

$$L_n = m_e r_n^2 \omega_n = \frac{n\hbar}{2\pi}$$

(1.24)

where $m_e$ is the electron mass, $r_n$ the radius of the $n$th circular orbit, $\omega_n$ its angular velocity and $\hbar = \left(\frac{\hbar}{2\pi}\right)$. It follows from Eq. (1.24) that $\omega_n = \frac{n\hbar}{m_e r_n^2}$. That gives us $r_n = \left(\frac{n\hbar}{m_e \omega_n}\right)^{\frac{1}{2}}$. Using this relationship, Bohr accurately calculated the radii of the orbits and their respective angular momenta for different spectral series, and these calculations were found to be in agreement with experimentally determined values. In Figure 1.7, the Bohr’s model of hydrogen atom is shown. Here $p^+$ and $e^-$ represent the positively charged protons and negatively charged electrons, respectively. It also shows the energy emitted by the electron when transiting between the orbits $n = 1, 2, 3$.

Since the orbits are quantized, its energies must also be quantized, which would lead to the onset of discrete spectra. In the emission and absorption processes, photons are involved whose energy is quantized. Therefore, the change in energy during the transition from one orbit to another must satisfy the following condition.

$$\Delta E = h\nu = E_f - E_i$$

(1.25)

where $E_i$ and $E_f$ refer to the energies of the initial and final orbits involved in the transition.

We know that the hydrogen atom is the simplest element of the periodic table having the atomic number, $Z = 1$. Bohr’s elaborate calculation resulted in the
It should also be recognized that in spite of the success of Bohr’s theory in explaining the spectrum of the hydrogen atom and giving us the concept of the quantization of angular momentum it has some fundamental flaws. For example, it is in violation of the Heisenberg Uncertainty Principle, and it cannot explain the Zeeman Effect when the spectral lines split up in several components in the presence of a magnetic field.

1.5.4 Matter–Wave Duality: de Broglie Hypothesis

Planck gave the concept of energy being quantized, Einstein gave the concept of photons that can behave like a particle yet has no mass, and Bohr advanced quantum mechanics that was in its infancy by proposing the angular momentum to be quantized. All these groundbreaking concepts point to the particle-like behavior of light that was well established to be wave-like by electromagnetic theory. This leads us to the question of how can a particle (such as an electron) also acquire wave-like characteristics?

The answer was provided by Louis de Broglie of France in 1923 in his famous hypothesis of matter–wave duality. This led to the development of the famous Schrödinger’s equation that firmly anchored quantum mechanics as the new physics. de Broglie based his hypothesis on two well-established results. He considered Einstein’s matter–energy equation and Planck’s theory of light quanta.

Einstein’s matter–energy equation states that

\[ E = mc^2 \]  

(1.30)

And Planck’s law of radiation says that

\[ E = h\nu \]  

(1.31)

de Broglie argued that since particles and waves have the same traits, the two energies must be equal. Combining these two equations Eq. (1.32) results.

\[ m_e c^2 = h\nu \]  

(1.32)

Considering that the real particles, such as an electron, cannot acquire the velocity equal to the velocity of light, we need to modify the above equation slightly to use it for real particles. Let us assume that we are dealing with electrons with the mass, \( m_e \) and velocity, \( v_e \). Furthermore, we can substitute for the frequency \( \left( \frac{v_e}{\lambda_e} \right) \), where \( \lambda_e \) is the wavelength associated with an electron. These manipulations result in Eq. (1.33).

\[ \lambda_e = \frac{\hbar}{m_e v_e} = \frac{\hbar}{2\pi} \left( \frac{2\pi}{p_e} \right) = \frac{2\pi\hbar}{p_e} \]  

(1.33)

where \( p_e \) is the momentum of the electron. We can also write Eq. (1.33) as Eq. (1.34) which is the standard form
of de Broglie’s relationship.

\[ p_e = \frac{\hbar}{\lambda_e} = \hbar k_e \quad (1.34) \]

where \( k_e \) is the wave number which by definition is \( \left( \frac{2\pi}{\lambda_e} \right) \).

This simple equation derived from another two very simple equations may look humble, but it has far-reaching consequences in solid-state physics and electronics. de Broglie was awarded the Nobel Prize in Physics in 1929 for this contribution. Its experimental proof was given by Clinton Davisson and Lester Germer, both American Physicists, in 1925 confirming the wave nature of electron. For this contribution, they too shared the Nobel Prize in Physics in 1937.

### 1.5.5 Schrödinger’s Wave Equation

What Newton’s laws of motion and his concept of conservation of energy are to classical physics so is the Schrödinger’s equation to quantum mechanics. He is one of the giants of physics of the twentieth century and belongs to the class of Sir Isaac Newton. The matter–wave duality hypothesis of de Broglie is the nucleating factor for Schrödinger’s equation. Schrödinger argued that since particles can have a wavelength associated with them, they must be represented by a wave equation.

Schrödinger’s equation predicts the future behavior of electrons in a dynamic frame work. It is the probability of finding an electron in events to come. A partial differential equation describes how the quantum state of a quantum system changes with time. This is the cornerstone of quantum mechanics that opened up multiple avenues to evolve and advance. It was formulated in 1926 by Erwin Schrödinger, a brilliant theoretical physicist of Austria. It earned him, of course, the Nobel Prize in Physics in 1933. It should be remembered that there is no formal derivation of Schrödinger’s equation. It is intuitive and Schrödinger simply wrote it. It was immediately accepted by other geniuses of his time and has never been challenged. One of the greatest theoretical physicists of our time, Richard Feynman, is quoted to have said, “Where did we get that from? It is not possible to derive it from anything you know. It came out of the mind of Schrödinger?”

Let us now write the one-dimensional form of Schrödinger’s equation.

\[ \frac{d^2\psi}{dx^2} + \frac{2m_e}{\hbar^2}(E - V)\psi = 0 \quad (1.35) \]

Here \( \psi \) is the wave function, \( E \) the total energy, and \( V \) the potential energy. The kinetic energy of the electron then is equal to \( (E - V) \).

In its three-dimensional form, Eq. (1.35) becomes Eq. (1.36) on substituting the first term on the left side with the Laplacian operator \( \nabla^2 \).

\[ \nabla^2\psi + \frac{2m_e}{\hbar^2}(E - V)\psi = 0 \quad (1.36) \]

The question now arises about the exact nature of the Schrödinger’s wave function, \( \psi \). What is it, and how is it significant in a real physical system? The answer is provided by Max Born (Nobel Prize in Physics in 1954) of Germany in 1926. He postulated that the quantity \( |\psi|^2 \) must represent the probability of finding an electron in a unit volume at the time at which the wave function, \( \psi \), is being considered. Alternatively, \( |\psi|^2 \) predicts the presence of an electron in a space, \( dv \). That amounts to normalizing the wave function as in Eq. (1.37).

\[ \int_{-\infty}^{+\infty} |\psi|^2 dv = 1 \quad (1.37) \]

Equation (1.37) sets the boundary conditions that the solutions for wave function, \( \psi \), must obey. The other boundary conditions imposed on the wave functions are (i) they must be continuous and (ii) mathematically well behaved. This amounts to telling us that \( \psi(x) \) must be a continuously varying function of \( x \) and its first derivative with respect to \( x \), \( d\psi/dx \), must also be a continuous function of \( x \).

Another form of the Schrödinger’s equation can be represented using the Hamiltonian operator that is the sum of the kinetic and potential energy in quantum mechanics. The operator is named after Sir William Hamilton, a reputed physicist of Ireland who lived in the nineteenth century. He is best known for the development of Hamiltonian mechanics that is essentially the reformulation of Newton’s mechanics. If \( T \) is the kinetic energy and \( V \) the potential energy, then the corresponding Hamiltonian takes the form of Eq. (1.38).

\[ \hat{H} = \hat{T} + \hat{V} \quad (1.38) \]

Here the potential energy operation \( \hat{V} \) is equivalent to the space and time variants of the potential energy, \( V \). The momentum, \( p \), in operator form is written as:

\[ \hat{p} = -i\hbar \nabla \quad (1.39) \]

Similarly, the kinetic energy operator form is as in Eq. (1.40).

\[ \hat{T} = \frac{\hat{p}^2}{2m_e} = -\frac{\hbar^2}{2m_e} \nabla^2 \quad (1.40) \]

Substituting these two equations in Eq. (1.38), we get the Hamiltonian operator, \( \hat{H} \), as in Eq. (1.41).

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 + V(r, t) \quad (1.41) \]
We can now rewrite the time-independent Schrödinger’s
equation in terms of the Hamiltonian \( \hat{H} \), as

\[
\hat{H}\psi_i = E_i\psi_i
\]  
(1.42)

Here \( \psi_i \) is called the eigenfunctions and \( E_i \) the eigenvalues
of energy.

The Hamiltonian operator also lead us to the
time-dependent Schrödinger’s equation which is given by Eq. (1.43).

\[
\dot{\hat{H}}\psi = i\hbar\left( \frac{\delta\psi}{\delta t} \right)
\]  
(1.43)

The probability of finding an electron in the volume element \( \text{d}x\text{d}y\text{d}z \) at a time \( t \) is then given by

\[
|\psi(x, y, z, t)|^2\text{d}x\text{d}y\text{d}z
\]

Exercise 1.2
Express the time-independent Schrödinger’s equation in terms of the momentum.

Solution
We have the standard form of the time-independent
Schrödinger’s equation containing the energy term in
Eq. (1.36).

\( (E - V) \) is the kinetic energy \( T \) of the electron; then it
follows from Eq. (1.36) hat

\[
\nabla^2\psi = -\left[ \frac{\hbar^2}{2m_e} T \right] \psi
\]  
(a)

Equation (b) gives us the kinetic energy in term of the
momentum, \( p_e \) of the electron.

\[
T = \text{k.e.} = \frac{1}{2}m_ev^2 = \frac{1}{2}\left( \frac{m_e^2v^2}{m_e} \right) = \frac{p_e^2}{2m_e}
\]  
(b)

Substituting this in Eq. (a) and after a little rearrange-
ment, we get Eqs. (c) and (d).

\[
\nabla^2\psi = -\left[ \frac{\hbar^2}{2m_e} \left( \frac{p_e^2}{2m_e} \right) \right] \psi = -\left[ \left( \frac{\hbar}{2m_e} \right)^2 \right] \psi
\]  
(c)

\[
\nabla^2\psi = -\left( \frac{\hbar p_e}{2m_e} \right)^2 \psi
\]  
(d)

Equation (d) is the momentum form of Eq. (1.36).

1.5.6 Heisneberg’s Uncertainty Principle
We learned in the previous section that the Schrödinger’s
equation is statistical in nature and can predict the proba-
bility of an event happening but cannot predict accurately
either the position of an electron or its velocity. Similarly,
it is not possible to predict either the momentum in a
particular space in which the electron finds itself nor the
energy it might acquire in a particular instant of time.
The reason being that the uncertainty principle forbids
the measurements of two complimentary parameters concurrently with arbitrary accuracy. The theory was
developed by Werner Heisenberg (Nobel Prize in Physics
in 1932) of Germany in 1927.

The essence of this theory is that the product of two complimentary variables cannot be less than a constant
value. For example, if position \( x \) and momentum \( p \) are
considered, then the uncertainty in position \( \Delta x \) and
momentum \( \Delta p \) is given by the following inequality.

\[
\Delta x \times \Delta p \geq \hbar \approx 10^{-34} \text{ Js}
\]  
(1.44)

Similarly, the uncertainty in energy \( E \) and time \( t \) can be
expressed as follows:

\[
\Delta E \times \Delta t \geq \hbar \approx 10^{-34} \text{ Js}
\]  
(1.45)

One can draw the conclusion that if one tries to
measure one physical parameter with arbitrarily high
precision, the uncertainty in measuring the other conjugate parameter becomes larger. The more the particle
becomes smaller such as atomic and subatomic particles,
the accuracy in determining their two complimentary
variables cannot exceed the limits of \( \approx 10^{-34} \) set by the
uncertainty principle. One should remember that it
is not a reflection on the inaccuracy of measurement
instruments or the methods used for experimentation. It
is simply inherent in the quantum mechanical interpre-
tation of nature. As the particles approach macroscopic
scales, the uncertainty decreases drastically. To illustrate
this point, let us consider a mass \( m \), which is \( 10^3 \) times
greater than the mass of an electron. If the velocity of
the particle is \( v \), its momentum \( p = mv \) and \( \Delta p = m\Delta v \).
Substituting this in Eq. (1.44) for \( \Delta P \), we get Eq. (1.45).

\[
\frac{\Delta x \times \Delta v}{10^3m_e} \approx 10^{-4} \text{ J s kg}^{-1}
\]  
(1.46)

The uncertainty has decreased by 1000-fold for a
macroscopic system whose characteristics can be deter-
mined individually with greater accuracy. Nevertheless,
it is to be learned from Eq. (1.46) that both the velocity
of a particle and its position cannot be measured with
arbitrary accuracy at the same instant.

1.6 Quantum Numbers
The wave function, \( \psi \), describes the probability of finding
an electron at certain energy levels within an atom. Since
it is associated with an electron in an atom it is also
called the atomic orbital. It defines a region in space in
which the probability of finding an electron is high. To
every such electron, there are four quantum numbers
associated with it which are its defining characteristics.
We have already discussed two of them; the principal
quantum number, \( n \), and the orbital quantum number, \( l \).
The other two are magnetic quantum number, \( m_l \), and the spin quantum number, \( s \). We now describe all four in some detail.

I. **Principal quantum number, \( n \):** Allowed values are only integers ranging from 1 to \( \infty \). It determines the total energy of the electron; and the number of orbitals \((-2n^2)\) having different energy levels.

II. **Orbital quantum number, \( l \):** Allowed values are from 0 to \((n-1)\).

The second quantum number is the orbital quantum number and is directly associated with the principal quantum number, \( n \). It is also referred to as angular momentum quantum number and azimuthal quantum number. We already discussed previously that it also is allowed to have only integral values. It divides the shells into smaller group of subshells identified by letters such as \( s \), \( p \), \( d \), \( f \), etc. The origin of such a nomenclature lies in optical spectroscopy where the emission or absorption processes were identified as \( s \) (sharp), \( p \) (principal), \( d \) (diffused), \( f \) (fundamental), \( g \) (ground), etc. After the discovery of quantum mechanics, it was realized that these spectral series correspond to specific values of the orbital quantum numbers as shown in Table 1.7.

The term “subshells” are preferred by chemists, whereas physicists prefer the term “orbitals.” The other designation assigned to the subshells or orbitals with certain values of \( l \) are called the Bohr designation of atomic subshells with the letter of \( K \), \( L \), \( M \), \( N \), etc. This designation is followed by experts of X-ray diffraction. The total number of orbitals (or subshells) is given by \( 2n^2 \). That is, there are two orbitals for \( n = 1 \); 8 for \( n = 2 \), 18 for \( n = 3 \), 32 for \( n = 4 \), and so forth. Table 1.7 lists them all.

If \( n = 1 \), then \( l = 0 \), the orbital is called \( 1s \); if \( n = 2 \) and \( l = 0 \), the orbital is called \( 2s \); and if \( n = 3 \) and \( l = 0 \), the orbital is \( 3s \). Other identifiers follow the same logic. So far as the orbital energy \( (E) \) is concerned, it increases with increasing orbital quantum number, \( l \). It follows the sequence: \( E_s < E_p < E_d < E_f \).

Their relative energy levels follow the sequence of \( 1s < 2s < 2p < 3s < 3p < 3d < 4s < 4p < 4d < 5f < 5s \) – and so forth.

III. **Magnetic quantum number, \( m_l \):** Its allowed values are \( m_l = 0 \) to \( \pm l \) with total number of \( m_l \) being \( (2l + 1) \).

From Amperé’s law, we know that a moving charge generates an electric current which in turn can induce a magnetic field when enclosed in a loop (such as an orbit). That is the reason that this quantum number is called the magnetic quantum number and as such it is supposed to be directional. It can assume any of the \((2l + 1)\) different directions. This was indeed shown to be the case experimentally by Otto Stern and Walther Gerlach, both German physicists, in 1922. They confirmed that the magnetic moments are quantized and can orient only in certain directions. For this ground breaking work Stern was recognized with the Nobel Prize in Physics in 1943, but Gerlach was excluded apparently because of his association with the Nazi Regime.

IV. **Spin quantum number, \( s \):** Allowed values \(+\frac{1}{2} \) or \(-\frac{1}{2} \).

In an atomic system, electrons can reside in different orbits. They are allowed to move around the orbit while at the same time spinning around its own axis. A spinning electron generates a magnetic field with two well defined orientations. These orientations are designated as either “up (↑)” or “down (↓).” Alternatively, it can only have the values of \( ±\frac{1}{2} \).

In Table 1.8, we present a list of values for orbital and magnetic quantum numbers with respect to the values of the principal quantum number. Their resulting spectrographic and Bohr designations are also given there.

### 1.7 Pauli Exclusion Principle

The four quantum numbers define a wave function of an electron fully and completely. They define its quantum state, its energy, and almost any other characteristics associated with it. The orbital quantum number, \( l \), and magnetic quantum number, \( m_l \), can each have multiple values for any fixed value of the principal quantum numbering as outlined in Table 1.8. What happens when there are a large number of electrons present in a system? This can cause an enormous challenge to sort out their quantum states leading to utter confusion.

This is where the selection rule conceived by Wolfgang Pauli of Austria in 1925 comes to our rescue. This rule is universally known as the Pauli’s Exclusion Principle for which he received the Nobel Prize in Physics in 1945. It states that: *No two electrons in an atom can have exactly the same set of four quantum number; the spins must be antiparallel.* This simply means that there can be two electrons for each combination of \( n, l, \) and \( m_l \), but their spin orientations must be antiparallel. Following this rule, we can assign 2 electrons to each s-state, 6 to each p-state, 10 to each d-state, 14 to each f-state, and

<table>
<thead>
<tr>
<th>Orbital quantum number, ( l )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral series</td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>f</td>
<td>g</td>
</tr>
</tbody>
</table>
Table 1.8 Relationship between $n$, $l$, and $m_l$, and their spectrographic and Bohr designations.

<table>
<thead>
<tr>
<th>Principal quantum number, $n$</th>
<th>Orbital quantum number, $l$</th>
<th>Magnetic quantum number, $m_l$</th>
<th>Number of values for magnetic quantum number, $m_l$</th>
<th>Electrons per orbital $= 2n^2$</th>
<th>Spectrographic designation</th>
<th>Bohr designation of shells</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>1s</td>
<td>K</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>2s</td>
<td>L</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\pm 1$</td>
<td>3</td>
<td>6</td>
<td>2p</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>$\pm 1$</td>
<td>5</td>
<td>10</td>
<td>3p</td>
<td>M</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\pm 1$</td>
<td>5</td>
<td>10</td>
<td>4p</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>$\pm 1, \pm 2$</td>
<td>7</td>
<td>14</td>
<td>4f</td>
<td></td>
</tr>
</tbody>
</table>


so forth. They vary in arithmetic progression with four being the common difference. It is important to note that this selection rule is not arbitrary, rather it is based on sound mathematical principles of quantum relativistic physics. A full mathematical treatment of Pauli exclusion principle is beyond the scope of this book.

### 1.8 Periodic Table of Elements

The periodic table of elements was originally developed by the Russian chemist with the name of Dmitri Mendeleev in 1869. He arranged all the elements known until that time (about 60) in rows and columns according to their atomic weight and chemical properties. Many more elements have since been discovered since, and they all can be arranged in the periodic table on the basis of their atomic numbers, chemical properties, and electronic configurations. The periodic table is an indispensable tool available to scientists and engineers engaged in the study of chemical systems and materials. The modern periodic table consists of eight columns and seven rows.

To take the full benefit of the subject matter covered in this section, it is advisable that readers should have a modern copy of the periodic table readily available. There are many sources from which one can get a good copy of the Periodic Table. The NIST (National Institute of Standards and Technology) in the United States may be a reliable source.

The discovery of quantum numbers greatly shaped the periodic table resulting in advancement to the fields of chemistry, physics, and materials science. Elements found in the same column are referred to as belonging to the same group such as Groups I, II, III, IV, V, etc., as they are similar in their chemical properties. There are a total of eight groups, many of which are subdivided in A and B subgroups in many of today’s periodic tables. The rows in the periodic table are called periods. There are seven periods in which elements are arranged with increasing values of atomic numbers. For example, hydrogen with its atomic number ($Z$) of 1 is the first element of the periodic table, then comes He with $Z = 2$ followed by lithium with $Z = 3$, and so on. Currently, the highest atomic number of $Z = 118$ belonging to the artificially synthesized ununoctium (also known as eka-radon) with the chemical symbol of Uuo. It is radioactive and very unstable. With its discovery in 2002, the seventh period of the periodic table is complete and a new period begins. The heaviest naturally found element is uranium-238 (U-238) with $Z = 92$. It is a well-established radioactive material with the half-life time of $\approx 4.5$ billion years. The heaviest stable element is bismuth (Bi) with $Z = 83$ and density $= 11.34 \text{ g cm}^{-3}$.

Each element has its unique atomic electronic configuration based on the number of the principal quantum number, $n$, its atomic number, and the number of electrons in each orbit as dictated by the Pauli exclusion principle. For example, our lightest element is hydrogen with $Z = 1$ only and its electronic configuration is written as $1s^1$. The rule for writing the electronic configuration of an element can be described as follows: “The integer on the left refers to the value on the principal quantum number, $n$, followed by the orbital (s, p, d, f, etc.) and then a superscript giving the number of electrons found in each orbital.” The filling sequence follows in the order of s, p, d, f, etc.

The electrons in the outermost orbital are technically called the valence electrons. The valence electrons play a decisive role in initiating a chemical reaction and in
forming chemical bonds between atoms which makes a structure stable. They can be shared with other atoms giving rise to chemical bonds known as ionic, metallic, and covalent. The concept of valence electrons is also very important to solid-state sciences, materials science, and electroceramics because they help us in developing models and theories for understanding electronic properties and physical phenomena displayed by materials.

Following the rule stated above, electrons in an atom can be divided between different orbitals. Let us now write electronic configurations for the second and third elements of the periodic table. The second element is He \((Z = 2)\), and its electronic configuration is \(1s^2\), and the third element Li \((Z = 3)\) has the configuration of \(1s^22s^1\) which is equivalent to \([\text{He}]2s^1\). This short cut simply tells us that the first two \(s\)-electrons of Li have the same configuration as He and the third electron moves to the higher orbital. This makes it easier to assign electronic configurations of elements with higher values of atomic numbers.

Let us now consider the elements of the Group VIII that is the home of the seven noble gases. Each of them represents the completion of the period in which they reside and the beginning of the next period. We present their electronic configuration in Table 1.9.

These elements are called the noble gases because they are to a great extent chemically inert. They represent the configurations with maximum allowable electrons in each subshell leaving no vacancy at all.

We stated already that many of the physical properties and phenomena exhibited by materials can be best explained based on the value of the valence electrons present. The tables that follow include some elements are of great interest (Table 1.10).

Notice that each of these elements have just one \(s\)-valence electrons and represents the beginning of a new group. Chemically, the alkali metals are highly reactive (Tables 1.11–1.13).

Ga and In also form very important semiconductor materials when alloyed with certain members of Group V. Al, of course, is a heavily used metal for transmission of electrical power and makes good contacts with semiconductors and dielectrics (Table 1.14).

There is large number of elements classified as transition metals, and they are found in Groups III through VIII. We include here in our table only those found in the fourth period with \(Z = 22–29\). They are characterized by the occupancy of their 3-d subshell. They exhibit interesting magnetic properties. Chemically, they have multiple oxidation states (Table 1.15).

Fe, Co, and Ni are the only 3-d elements that are also strongly ferromagnetic (FM). Ti and Mn are paramagnetic (PM), Cr is antiferromagnetic (AFM), whereas the magnetic nature of V is unknown but as \(V_2O_5\) it is

<table>
<thead>
<tr>
<th>Table 1.9</th>
<th>Elements of Group VIII.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>Helium, He</td>
</tr>
<tr>
<td>Atomic number, (Z)</td>
<td>2</td>
</tr>
<tr>
<td>Atomic electronic configuration</td>
<td>(1s^2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 1.10</th>
<th>Group I – alkali metals.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>Lithium, Li</td>
</tr>
<tr>
<td>Atomic number, (Z)</td>
<td>3</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>([\text{He}]2s^1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 1.11</th>
<th>Group IIA – alkali earth metals.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>Beryllium, Be</td>
</tr>
<tr>
<td>Atomic number, (Z)</td>
<td>4</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>([\text{He}]2s^2)</td>
</tr>
</tbody>
</table>

Here the valence electrons are \(2s\) electrons.
Nature and Types of Solid Materials

Table 1.12 Group II B—important industrial materials.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Zinc, Zn</th>
<th>Cadmium, Cd</th>
<th>Mercury, Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number, Z</td>
<td>30</td>
<td>48</td>
<td>80</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>[Ar]3d^{10}4s^{2}</td>
<td>[Kr]4d^{10}5s^{2}</td>
<td>[Xe]4f^{14}5d^{10}6s^{2}</td>
</tr>
<tr>
<td>Significant physical properties</td>
<td>Industrial material when alloyed with Group VI elements, it becomes a good semiconductor. Examples: ZnS, ZnSe, and ZnTe</td>
<td>Industrial material when alloyed with Group VI elements, it becomes a good semiconductor. Examples: CdS, CdSe, and CdTe</td>
<td>First material in which superconductivity was discovered, when alloyed with Te, it becomes a semiconductor</td>
</tr>
</tbody>
</table>

They form alloys with Group VI elements to become good semiconductors.

Table 1.13 Group III—an important group of elements used for doping Group IV semiconductors and for making contacts.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Boron, B</th>
<th>Aluminum, Al</th>
<th>Gallium, Ga</th>
<th>Indium, In</th>
<th>Thallium, Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number, Z</td>
<td>5</td>
<td>13</td>
<td>31</td>
<td>49</td>
<td>81</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>[He]2s^{2}2p^{1}</td>
<td>[Ne]3s^{2}3p^{1}</td>
<td>[Ar]3d^{10}4s^{2}4p^{1}</td>
<td>[Kr]4d^{10}5s^{2}5p^{1}</td>
<td>[Xe]4f^{14}5d^{10}6s^{2}6p^{1}</td>
</tr>
</tbody>
</table>

Table 1.14 Group IV—a very interesting group that begins with highly conductive element (C) and ends with one of the heaviest elements (Pb) which also becomes a superconductor at low temperatures.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Carbon, C</th>
<th>Silicon, Si</th>
<th>Germanium, Ge</th>
<th>Tin, Sn</th>
<th>Lead, Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number, Z</td>
<td>6</td>
<td>14</td>
<td>32</td>
<td>50</td>
<td>82</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>[He]2s^{2}2p^{2}</td>
<td>[Ne]3s^{2}3p^{2}</td>
<td>[Ar]3d^{10}4s^{2}4p^{2}</td>
<td>[Kr]4d^{10}5s^{2}5p^{2}</td>
<td>[Xe]4f^{14}5d^{10}6s^{2}6p^{2}</td>
</tr>
<tr>
<td>Significant physical property</td>
<td>Highly conductive: in diamond form, it is an excellent semiconductor material</td>
<td>Leading elemental semiconductor: king of microelectronics</td>
<td>Very good elemental semiconductor material; acquires excellent properties when alloyed with silicon</td>
<td>An important industrial material; exhibits superconductivity at low temperatures</td>
<td>Heavily used in industrial products, becomes a superconductor at low temperatures: when alloyed with Titania, it becomes ferroelectric/nonlinear dielectric material</td>
</tr>
</tbody>
</table>

Table 1.15 Some important transition metals (found in the fourth period).

<table>
<thead>
<tr>
<th>Element</th>
<th>Titanium, Ti</th>
<th>Vanadium, V</th>
<th>Chromium, Cr</th>
<th>Manganese, Mn</th>
<th>Iron, Fe</th>
<th>Cobalt, Co</th>
<th>Nickel, Ni</th>
<th>Copper, Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number, Z</td>
<td>22</td>
<td>23</td>
<td>24</td>
<td>25</td>
<td>26</td>
<td>27</td>
<td>28</td>
<td>29</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>[Ar]3d^{2}4s^{2}</td>
<td>[Ar]3d^{3}4s^{2}</td>
<td>[Ar]3d^{4}4s^{2}</td>
<td>[Ar]3d^{5}4s^{2}</td>
<td>[Ar]3d^{6}4s^{2}</td>
<td>[Ar]3d^{7}4s^{2}</td>
<td>[Ar]3d^{8}4s^{2}</td>
<td>[Ar]3d^{10}4s^{2}</td>
</tr>
<tr>
<td>Magnetic characteristics</td>
<td>PM</td>
<td>V_{2}O_{5} is DM</td>
<td>AFM</td>
<td>PM</td>
<td>FM</td>
<td>FM</td>
<td>FM</td>
<td>DM</td>
</tr>
</tbody>
</table>

diamagnetic (DM). Copper is also diamagnetic and has completely filled 3d-subshell that excludes the presence of ferromagnetism. All other members of the transition metal period have partially filled 3d-subshell.

Rare earth elements: These are also transition elements and are found in the sixth period. They are also called the lanthanides. Some examples of rare earths are cerium, Ce (Z = 58); neodymium, Nd (Z = 60);
samarium, Sm \((Z = 62)\); europium, Eu \((Z = 63)\); and gadolinium, Gd \((Z = 64)\).

**Radioactive elements**: Elements of the seventh period are called the actinides or radioactive elements. They are also classified as transition elements. Some of these include the following thorium, Th \((Z = 90)\); uranium, U \((Z = 92)\); plutonium, Pu \((Z = 94)\), and americium, Am \((Z = 95)\).

### 1.9 Some Important Concepts of Solid-State Physics

#### 1.9.1 Ceramic Superconductivity

The superconductivity was discovered in 1911 at the University of Leiden in the Netherlands by Heike Kamerlingh Onnes. He was awarded the Nobel Prize in Physics in 1913 for the production of very low temperatures. It was in mercury that he found the resistance became nonexistent when cooled to 4.2 K. He also discovered superconductivity properties in lead and tin. The table that follows lists the ground-breaking advancement in the field of superconductivity since its discovery. Since 1911 until 1987 superconductivity was found mostly in metallic systems at very low temperatures. It was in 1987 that superconductivity was observed for the first time in ceramic compounds at relatively high temperatures. This landmark discovery dramatically changed the field of superconductivity from being a curiosity of fundamental science to be of great importance to technology. Some of these issues we discuss in this section. The nature of this book does not allow us to discuss this topic in detail. However, interested readers may wish to consult a good book on superconductivity for advanced studies; we recommend the book by Orlando and Delin [2]. This field has produced a number of Nobel laureates. We list them in Table 1.16.

As already stated until 1985, superconductivity was observed only in metals and their alloys with the uppermost critical temperature of 20 K. Then it increased to 35 K with the discovery of superconductivity in a ceramic sample of Ba–La–Cu-oxide. The discovery was made in January of 1986 at IBM Zurich Laboratories by Georg Bednorz and K. Alex Müller who were awarded Nobel Prize in Physics in 1987. This landmark discovery was a paradigm shift in solid-state physics for two reasons: first, the critical point for superconductivity crossed the boiling point of Ne \((27 K \approx -246{\degree}C)\) and second, the superconductivity was found in a ceramic system against all prevailing concepts of physics at the time. By now many more oxide superconductors have been discovered, and we list some of them in Table 1.17.

It is interesting that the crystal structure of these oxides happen to be perovskite \((ABO_3)\), which is the leading group in which prominent nonlinear dielectrics such as ferroelectrics are found.

So far as an explanation of this interesting physical phenomenon is concerned, there is only one unified theory that can explain superconductivity and even that is not

---

**Table 1.16** List of Nobel Prize in Physics awarded for superconductivity.

<table>
<thead>
<tr>
<th>Name</th>
<th>Year</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heike Kamerlingh Onnes</td>
<td>1913</td>
<td>Discovery of superconductivity</td>
</tr>
<tr>
<td>John Bardeen, Leon N. Cooper, and J. Robert Schrieffer</td>
<td>1972</td>
<td>BCS theory of superconductivity</td>
</tr>
<tr>
<td>Leo Esaki, Ivar Giæver, and Brian D. Josephson</td>
<td>1973</td>
<td>Josephson tunneling effect</td>
</tr>
<tr>
<td>Georg Bednorz and K. Alex Müller</td>
<td>1987</td>
<td>High temperature superconductivity (ceramic superconductivity)</td>
</tr>
<tr>
<td>Alexi A. Abrikosov, Vitaly L. Ginzburg, and Anthony J. Leggett</td>
<td>2003</td>
<td>Theory of superconductivity and superfluids</td>
</tr>
</tbody>
</table>

**Table 1.17** List of some ceramic superconductor materials.

<table>
<thead>
<tr>
<th>Ceramic superconductors</th>
<th>Critical point, (T_c) (K)</th>
<th>Number of Cu–O planes/unit cell</th>
<th>Crystal structure</th>
<th>Crystal unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>123 YBCO ((\text{YBa}_2\text{Cu}_3\text{O}_7))</td>
<td>93</td>
<td>2</td>
<td>Perovskite</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>2122 BCSCO ((\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_8))</td>
<td>85</td>
<td>2</td>
<td>Perovskite</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>2223 BCSCO ((\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}<em>3\text{O}</em>{10}))</td>
<td>110</td>
<td>3</td>
<td>Perovskite</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>2223 TCBCO ((\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}<em>3\text{O}</em>{14}))</td>
<td>125</td>
<td>3</td>
<td>Perovskite</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>1223 HBCCO ((\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8))</td>
<td>134</td>
<td>3</td>
<td>Perovskite</td>
<td>Tetragonal</td>
</tr>
</tbody>
</table>

Note all critical points are above the liquid nitrogen temperature of 77 K (\(-196{\degree}C\)).

Source: https://en.m.wikipedia.org/wiki/Hightemperature_Superconductivity. Licensed under CC BY 3.0.
adequate to handle the superconductivity found in oxide systems. In 1972, almost 60 years after the discovery of superconductivity, a macroscopic theory was developed by three American Physicists named John Bardeen, Leon Cooper, and J. Robert Schrieffer that has been successful in explaining the superconductivity found in metallic systems at low temperatures. The theory is also known as BCS theory, and the three physicists were awarded Nobel Prize in Physics in 1972 for developing this elegant theory. This was the second Nobel Prize for John Bardeen, the first one was for the discovery of transistors in 1956.

The BCS theory requires a sound knowledge of advanced physics and therefore is beyond the scope of this textbook. The central point of this theory is the concept of so-called Cooper pairs. In the superconducting phase Cooper pairs can form when two electrons couple with antiparallel spins. Cooper pairs can behave differently than single electrons that must obey the Pauli Exclusion Principle, whereas the Cooper pairs behave more like bosons that can condense in the same energy levels. The Cooper pairs are also called superconducting electrons. Though the BCS theory has been very successful in explaining conventional superconductivity satisfactorily, it appears not to be applicable to ceramic superconductivity. Various groups of theoreticians are currently working on this problem, and we hope one day soon we might have a good theory of superconductivity found in electroceramics.

1.9.2 Superconductivity and Technology

Superconductivity is a unique physical phenomenon poised to play a vital role in the evolution of new technology. A large number of devices and applications have been proposed based on magnetic and electronic properties of superconductivity that we will discuss subsequently in this chapter. Production of very high magnetic fields, Josephson junctions, and superconducting quantum interference device (SQUID) magnetometers are so far the most established technologies based on low temperature superconducting materials. They operate only at cryogenic temperatures. However, a large number of applications, from highly sophisticated to straightforward and simple, have been proposed based on ceramic superconductors with critical temperatures far above cryogenic temperatures. For these proposals to be more useful, and commercially viable, room-temperature superconducting materials have to be discovered. The hope is pinned on new ceramic materials because it will be possible to produce them in high volumes and in high quality at reasonable costs.

Superconducting magnets can produce fields far greater than those generated by the most powerful electromagnets. Currently, the highest sustained magnetic fields achieved are about $8.3 \times 10^5$ G by niobium–titanium (Nb–Ti) superconducting magnets that operate at the extremely low temperature of 1.9 K. The magnetic fields are measured in the units of Tesla and Gauss, and they are abbreviated as T and G, respectively. Superconducting magnets are universally used in magnetic resonance imaging (MRI) machines that is a powerful diagnostic tool indispensable to health professionals as well as of great significance to scientists for new discoveries. One of the most intriguing aspects of these magnets is the onset of persistent currents. Once the magnet is energized the windings of Nb–Ti become superconducting closed loops at about 1.9 K giving rise to a persistent current following the Faraday’s law of induction. This law states that a magnetic field can induce a current in a conducting loop according to $L \frac{dI}{dt} = -a \left( \frac{dL}{dt} \right)$ where $L$ is the inductance, $I$ the current, and $B$ the magnetic flux. The current generated in a superconducting loop can flow for months even in the absence of an external magnetic field. At this point, the external power supply can be turned off, and the magnetic field is sustained by the persistent current. We will learn more about it later while studying the magnetic properties of superconducting materials.

Another very powerful superconducting device is the SQUID magnetometer based on the Josephson junction effect that establishes the tunneling of the Cooper pairs. There are many other unique applications based on this effect, and we will discuss some of them when we study the Josephson effect.

1.10 Signature Properties of Superconductors

Temperature, magnetic field, and pressure are three external agents that can greatly alter the fundamental nature of a superconducting material by switching them from normal phase to superconducting phase, and vice versa. Infinite electrical conductivity and the onset of diamagnetism below a critical temperature are the two most important properties of a superconductor material. We discuss both these properties in the next sections here. It is known that a large number of elements of the periodic table become superconducting at a critical temperature and a critical pressure. Recently, it has been reported that H$_3$S becomes superconducting with a critical temperature ($T_C$) of 203 K at 150 GPa of pressure. This is the highest transition point reported so far for

---

2 Reported in Physics Today of July 2016 about this discovery made by Mikhail Eremetes and his team at the Max Planck Institute of Chemistry in Germany.
any superconducting material. \( \text{H}_2\text{S} \) belongs to the same family of chemicals as hydrogen sulfide (\( \text{H}_2\text{S} \)) which is present in almost any chemistry laboratory and has a noxious smell.

### 1.10.1 Thermal Behavior of Resistivity of a Superconductor

Superconductivity can be defined most simply by stating that below a critical temperature a superconductor completely loses its resistivity resulting in the conductivity to be infinite. The critical temperature is also known as critical point or superconducting transition temperature or even superconducting transition point. Its universal symbol is \( T_C \). The temperature dependence of resistance of a superconductor material is presented in Figure 1.8.

Here we find two distinct phases to exist: one above the critical point, \( T > T_C \), and the other below this point. As we can see from the figure, a superconducting material goes from its normal state at \( T > T_C \) to its superconducting state at \( T < T_C \) undergoing a phase change at \( T = T_C \). The transition from the normal state to the superconducting state is governed by the relationship described by Eq. (1.47).

\[
\sigma \approx \frac{C}{T - T_C} 
\]  

(1.47)

When \( T = T_C \) the conductivity, \( \sigma \), is infinite. Thermodynamically, it is a phase change of the second order. Equation (1.47) is the standard form of the Curie–Weiss law that is obeyed by ferromagnetic and ferroelectric materials where we also encounter similar phase transitions at their respective critical temperatures called the Curie temperatures, \( T_C \). We will learn about ferroelectricity and ferromagnetism in the other chapters in this book.

The state of infinite conductivity persists so long as the temperature is below the critical point of \( T_C \). It is a significant result and obviously of great importance to power transmission technology. All metals lose part of the original electric power by Joule heating \( \approx I^2R \) due to a nonzero resistance. Over the course of time, this loss can be significant. The hope is that one day we will be able to use superconducting wires instead of metallic wires to transmit electric power from one point to another and thereby completely eliminate the loss of power.

We can easily imagine the benefit of such a system to consumers and industry. This dream can only be fulfilled if a room temperature superconducting material is discovered. Today, we are not there, but science is working diligently to reach that goal post. The discovery of ceramic superconductor has given us a roadmap to reach this destination and the race is intense.

### 1.10.2 Magnetic Nature of Superconductivity: Meissner–Ochsenfeld Effect

We concluded in the previous section that all superconductors become ideal conductors (\( \sigma \to \infty \)) below their critical temperatures. They also become ideal diamagnetic materials (magnetic susceptibility, \( \chi = -1 \)) in the superconducting phase. This remarkable property was confirmed by the Meissner–Ochsenfeld effect, which is referred erroneously in many circles only as the Meissner effect. The Meissner–Ochsenfeld effect was discovered in Germany in 1933 by Walther Meissner and Robert Ochsenfeld. It states that in the superconducting phase, the magnetic flux lines are expelled after it reaches a certain depth below the surface. This is called the London penetration depth and is associated with the superconducting electron density. It decays exponentially within the interior of the superconducting phase. Once the London penetration depth is reached, the magnetic field stops penetrating the sample, which then becomes an ideal diamagnetic material. Diamagnetism is characterized by the capacity of a material to oppose the penetration of magnetic flux lines below its surface. This is in contrast to the nature of a ferromagnetic or a paramagnetic material in which magnetic flux lines can penetrate unopposed. The Meissner–Ochsenfeld effect cannot be explained by classical physics, and the explanation is provided by quantum mechanics establishing the fact that the superconductivity is a quantum mechanical phenomenon. Mathematically, the London-penetrating depth is given by

\[
\lambda_L = \left( \frac{e_m c^2}{ne^2} \right)^{1/2}
\]  

(1.48)
where \( n \) is the superconducting electron density. The parameters \( \epsilon_0 \), \( c \), \( m_e \), and \( e \) are physical constants as defined already above.

Another critical property associated with superconductivity is called the coherence length. It is related to the energy gap and the Fermi velocity of the superconducting phase. It bears no relationship with the London penetration depth. Both the coherence length and the London penetration depth have been experimentally determined for a number of superconducting materials. Its magnitude usually is in the nanometers range.

The Meissner–Ochsenfeld effect can be demonstrated easily by cooling a 123 YBCO ceramic sample below its critical point using liquid nitrogen (\( \approx 77 \) K). Once superconductivity sets in, the sample becomes diamagnetic facilitating the levitation of a magnet in air above the sample surface, which can be seen in Figure 1.9. As expected, the magnetic flux lines are expelled resulting in the magnetic levitation. In Figure 1.9, the double levitation was achieved by floating a ceramic magnet on top of another magnet.\(^3\)

It is not only the temperature that defines the superconducting phase. Also under the influence of an external magnetic field, \( H \), the superconducting phase can switch to the normal phase. The magnitude of the field that can induce this phase change in called the critical magnetic field (\( H_c \)), and it is found to be strongly temperature-dependent as we can see from Figure 1.10. Here, each combination of \( H_{c1} \) - \( T_1 \) and \( H_{c2} \) - \( T_2 \) is capable of inducing switching of the superconducting phase to the normal phase.

At absolute zero, the critical magnetic field, \( H_c \), reaches its maximum value of \( (H_0) \). Experimentally, it has been established by studying a large array of superconducting materials that the temperature-dependence of the critical magnetic field is described by Eq. (1.49).

\[
H_c = H_0 \left(1 - \left(\frac{T}{T_C}\right)^2\right)
\]  

We can conclude from Figure 1.10 that at any temperature below the superconducting critical temperature, \( T_C \), the superconducting phase can be destroyed by the application of a magnetic field greater than the critical field, \( H_c \). This observation plays an important role in designing a superconducting magnet that can produce very large fields without being plagued by any loss of power as is the case for normal electromagnets using metallic wires.

Exercise 1.3
Find the temperature at which the superconducting phase will switch to the normal phase if the needed critical field, \( H_c \), is 80% of the maximum field, \( H_0 \) and the critical temperature of the superconducting material is 90 K.

Solution
From Figure 1.10, we can infer that \( H_c < H_0 \) and \( T < T_c \) in Eq. (1.49). By substituting the values of the parameter given in the problem in this equation, we find that: \( \frac{T}{T_0} = \sqrt{0.2} \). That is, \( T = 40.5 \) K.

Another very interesting result of the Meissner–Ochsenfeld effect is the fact that a persistent current can be produced in the superconducting phase that can last for months even in the absence of an applied magnetic field. It is estimated that it can last for approximately \( 10^5 \) years. This phenomenon cannot be understood with the help of the electromagnetic theory. It is found that

\(^3\) R.K. Pandey, unpublished results. This experiment was done in the Electronic Materials Labs of Electrical and Computer engineering department at Texas A&M University circa 1989.
it is a quantum mechanical phenomenon just like the superconductivity itself. This is because of the flux quantization in the superconducting phase. The quantized flux, \( \phi \), is given by the following equation:

\[
\phi \approx n \left( \frac{\hbar}{2e} \right) \quad \text{with } n = 1, 2, 3, \ldots \quad (1.50)
\]

Here, \( \hbar \) and \( e \) are Planck’s constant and electronic charge, respectively. From the above equation, we see that \( \phi \) can assume values only as \( \phi_1 = \hbar/2e \), \( \phi_2 = \hbar/e \), \( \phi_3 = 3\hbar/2e \), and so on. The first quantized flux, \( \phi_1 \), is called the fluxoid and normally written as \( \phi_0 \). Its numerical value is \( 2.068 \times 10^{-15} \text{ T m}^2 \) (or Wb). In the superconducting phase, the magnetic flux can exist only discretely in units of the fluxoid. This is a remarkable result originating from the Meissner–Ochsenfeld effect. Quantization of magnetic flux is another unique property of a superconducting material and is an important consideration in designing a superconducting magnet. It also plays an important role in finding applications of the Josephson junction in high-speed data transfer. We will describe the Josephson effect in the next section.

1.10.3 Josephson Effect

It was in 1962 that Brain David Josephson of Great Britain predicted theoretically the tunneling of Copper pairs in a junction sandwiched between two superconducting arms. This is a macroscopic quantum phenomenon universally associated with the onset of a current because of tunneling through a junction by the Copper pairs. The uniqueness of the effect lies in the fact that the tunneling current flows even when no potential is applied to the junction. One should be careful in not confusing the tunneling current associated with Copper pairs with the persistent current we discussed with respect to superconducting magnets.

The Josephson junction is also known as a weak link in engineering. The Josephson effect is the basis for such practical and very important devices as SQUID magnetometers, superconducting qubits, rapid single flux quantum (RSFQ) digital electronics that can operate at very high speeds with minimal of power consumption, oscillators, and voltage calibrators. The standard for 1 V is based on the Josephson effect. Apparently NIST produces this standard by connecting thousands of Josephson junctions in series. Josephson was awarded the Nobel Prize in Physics in 1973 for his landmark prediction of the tunneling by Copper pairs. Electron tunneling is one of the landmark contributions of quantum mechanics. It is based on the fundamental idea of the matter–wave nature of electrons as predicted by de Broglie.

There are two types of tunneling effects: one being metal–insulator–superconductor with the acronym of M-I-S tunneling; and the other the superconductor–insulator–superconductor (S-I-S) tunneling. The idea for the first type of tunneling was advanced by Ivar Giaever, a Norwegian-American physicist. He showed experimentally the electron tunneling through a junction sandwiched between a normal metal and superconductor in 1960, and so it is appropriately called the Giaever tunneling. He shared the Nobel Prize in Physics with Leo Esaki and Brian Josephson in 1973 for the tunneling phenomena in solids.

A typical configuration for an M-I-S or S-I-S tunneling is shown in Figure 1.11. Let us first discuss the M-I-S tunneling process. In the M-I-S experiment, the upper sample is a normal metal. When a current, \( I \), is injected in the junction, its transport first follows the path from a metal to an insulator. If the insulation layer is thick, no voltage drop will occur in the configuration. If it is, however, between 1 and 2 nm, then the electrons can acquire sufficient energy to overcome the barrier and reach the superconducting part of the structure and then finally exit it to complete the circuit. If the superconductor is in the normal phase (\( T > T_C \)), then the \( I-V \) relationship will be governed by the Ohm’s law as shown in Figure 1.12 by the dashed line.

But when the superconducting arm is kept at \( T < T_C \), then the electron tunneling will happen manifesting itself in the appearance of a tunneling current at the apparent potential equivalent to \( \left( \frac{\Delta}{2} \right) \) where \( \Delta \) is the bandgap of the superconductor and \( e \) the electron charge. The structure will remain in this state as long as \( T < T_C \). As soon as the superconductor reverts back to its normal phase, the tunneling current will disappear and we will be left with the ohmic \( I-V \) characteristics of the device.

Now let us discuss the S-I-S tunneling that is the backbone of the Josephson effect. If we replace the metal in the upper arm of the structure of Figure 1.11 with a superconducting material that is identical to the superconducting material in the lower arm of the configuration, then
we will have a Josephson junction. Once again, we apply a current to the structure, but this time we do not have normal electrons available to give us as the characteristic ohmic plot. Noting happens no matter how large a current we inject so long as the structure is at \( T > T_c \). As soon as the samples are cooled to \( T < T_c \) we notice the appearance of a current, \( \pm I_c \), even when \( V \approx 0 \) which is a situation unique to superconductivity because there is no resistance present in the superconducting state and therefore ohmic current does not exist. This is shown in Figure 1.13.

The current that develops at \( V \approx 0 \) is the result of the Cooper pair tunneling through the very thin insulating barrier. This current is called the Josephson current; it was he who on the basis of the famous BCS (Bardeen, Cooper, and Schrieffer) theory of superconductivity predicted that the probability of Cooper pairs tunneling through a barrier is the same as that of an electron. It is an ordered coherent process in which a macroscopic wave function travels from one superconductor to the other. The experimental proof of the Josephson junction was provided by Phillip Anderson and John Rowell, both of the USA, in 1963.

But what are the Cooper pairs? In the BCS theory, Leon Cooper argued that in the superconducting phase, two electrons with anti-parallel spin bind loosely to form a pair and move with the same speed, but in opposite directions. This assumption is the core of the BCS theory which successfully explained the quantum nature of superconductivity.

Now back to the Josephson junction story. After the development of the Josephson current, the Cooper pairs wander until they gain sufficient energy to overcome the bandgap, \( \Delta \). At that point, the binding energy of the Cooper pairs breaks down releasing the normal electrons to travel through the barrier. As soon as \( V \approx \frac{2\Delta}{e} \), the current appears, which is the result of the normal electron tunneling while the structure is maintained in the superconducting phase by keeping the temperature \( T < T_c \). The tunneling occurs at \( V = \pm \frac{2\Delta}{e} \) positions as shown in Figure 1.13.

We now need to understand the very nature of the Josephson current, \( \pm I_c \). We know that this is the current that develops even when there is no potential applied to the circuit. But it has one limitation; it cannot keep on increasing in magnitude uncontrolled. As soon as it reaches a critical value, it stops increasing and a voltage appears at the junction. The structure switches from a state of zero voltage to a state of a finite voltage. This is the basis for high-speed digital electronics with superior attributes than those found in the best of semiconductor devices that dominate the present-day field of microelectronics. A Josephson junction can be manipulated by the applications of a potential, both DC and AC, as well as by a magnetic field resulting in some interesting applications. Let us briefly examine some of these cases.

**Case I: Application of a DC potential**

If the potential is of such a magnitude that it exceeds the value of \( \left( \frac{2\Delta}{e} \right) \), the Cooper pairs will disintegrate into two normal electrons giving rise to the tunneling effect as shown in Figure 1.13. However, if the equivalent energy, \( E \leq \frac{2\Delta}{e} \), the Cooper pairs will be retained intact but will begin to oscillate back and forth emitting electromagnetic waves with a specified frequency. This is the basis for fabricating oscillators that are extremely accurate and can be integrated in many applications.
Case II: Application of an AC potential
If instead of a DC potential, we now subject the Josephson junction to an electromagnetic field, then we will naturally induce an AC potential across the junction. Since frequency can be measured more accurately than a voltage, AC modulated Josephson junctions are used for producing very accurate voltmeters, some of which are used for calibrating other voltmeters.

Case III: Application of an external magnetic field
The Josephson junctions are extremely sensitive to even the smallest magnetic field applied to it. This unique response to the magnetic field is exploited in the design and construction of the world’s most sensitive magnetometer universally known as the SQUID. They are so sensitive that they can even detect the feeble and very weak magnetic fields present in organs such as the human heart ($10^{-13}$ T $\approx 0.1 \mu$G) and brain ($10^{-15}$ T $\approx 10$ nG). These highly sensitive magnetometers are indispensable tools for scientific studies requiring determination of extremely small magnetic fields. The magnetic response of the Josephson junction resulted in the discovery of quantized magnetic flux that is defined in Eq. (1.50). Some caution should be exercised when referring to the Bohr magneton, $\mu_B$, and quantized magnetic fluxoid, $\phi_0$. Bohr magneton refers to the magnetic moment of an electron having a value of $9.274 \times 10^{-21}$ J T$^{-1}$, whereas the fluxoid is the magnetic flux ($B$) at the quantized level corresponding to the first principal quantum number ($n = 1$). Both are physical constants.

1.11 Fermi–Dirac Distribution Function
The F-D distribution function or F-D-statistics is a beautiful piece of theoretical work and impacts solid-state physics and solid-state electronics in a very significant way. It helps us in understanding how the population and depopulation of quantum energy states vary with temperature which becomes instrumental in understanding the properties of conductors and semiconductors at a thermal equilibrium. Before this powerful theory was published in 1926 first by Enrico Fermi of Italy and soon after that by Paul Dirac of England, it was not possible to fully understand the contributions made by electrons in the specific heat of solid and magnetic susceptibility. Classical physics was not at all in the position to solve these physical properties of solids. The picture changed drastically once the Pauli exclusion principle became the accepted fact of life from 1925 onward. Fermi and Dirac applied the restrictions imposed on electrons by the Pauli exclusion principle and were successful in developing the F-D statistics. Both received the Nobel Prize in Physics, Dirac with Schrödinger in 1933 and Fermi in 1938, but not for the development of the F-D statistics.

The objective of the F-D statistics are twofold: (i) To find the number of particles in each energy state at thermodynamic equilibrium and (ii) To find the number of electrons (also called particles in statistical environments) between the neighboring energy states of $E$ and $E + \Delta E$.

In solids, we are dealing with a large number of particles at any one time (for example, $\approx 10^{26}$ mol$^{-1}$), and at a thermal equilibrium, the properties of solids are dependent upon factors such as the Coulomb potential between each pair of electrons, Coulomb interactions between electrons and protons at the nucleus and the appropriate solution of Schrödinger equation for each set under consideration. We can easily visualize what a daunting task it would be without resorting to statistical methods.

There are two statistical models that are useful when dealing with solids: (i) The classical model of Maxwell–Boltzmann statistics and (ii) the F-D distribution of quantum statistics. Now let us examine the fundamental difference between the particles dealt with by each of these two types of statistical models.

The classical model of Maxwell–Boltzmann: Here, the particles are assumed to be atoms, ions, and molecules. They are distinguishable from each other because they do not interact mutually, and their energy is continuous. All phenomena dealing with the classical particles at thermal equilibrium can be explained satisfactorily by the classical model.

The quantum mechanical model of F-D: This model is applicable to electrons that obey the Pauli exclusion principle with spin being $\pm \frac{1}{2}$. They are indistinguishable from each other because they can electrostatically interact mutually. Since they are subjected to restrictions imposed by the principles of quantum mechanics, their energy states must be considered degenerate which means that they are not continuous but discrete. The electrons that obey the F-D-distribution function are called fermions. It was Dirac himself who coined the name fermions; apparently in honor of Enrico Fermi. Thermal properties of metals and semiconductors are the two prime examples where the F-D statistics is applicable.

The degeneracy is defined by the number of magnetic quantum number for each state. For example, when $l = 1$, the state is $p$ and $m_l = 0, \pm 1$. By definition this is a three-fold degenerate state. Similarly when $m_l$ has five values (for $l = 2$ and state being $d$) the degeneracy is fivefold. By inference, then when $l = 0$, the state is $s$, and there are no corresponding values for $m_l$; then the energy is said to be single-fold degenerate.
Besides the F-D statistics, there is another quantum statistics called the Bose–Einstein distribution function. Here the particles are also indistinguishable, but with integral values of spin. These particles are called bosons. This model is used for those cases where bosons are the particles. Atomic and nuclear physics as well as chemistry take full advantage of this model.

Now let us try to make some mathematical distinction between these three statistical models. For this, we consider that there are $N_i$ particles that must be distributed in $E_i$ energy states at the thermal equilibrium with temperature $T$.

For classical particles that obey the M-B statistics, the formulation of Eq. (1.51) is used.

$$N_i = A \exp \left( -\frac{E_i}{k_B T} \right)$$  \hspace{1cm} (1.51)

where $A$ is a constant and $k_B$ the Boltzmann constant.

Generalization of the above expression can be done by using the concept of probability, $f(E)$, which simply tells us the statistical probability of finding a particle with energy, $E$. Then we can convert the above equation into Eq. (1.52).

$$f(E) = A \exp \left( -\frac{E}{k_B T} \right) \approx \frac{A}{\exp \left( \frac{E}{k_B T} \right)}$$  \hspace{1cm} (1.52)

When, however, degeneracy is present as is the case with quantum statistics, we can express the probability simply by defining the probability as: $f(E) \approx \left( \frac{N_i}{g_i} \right)$. The probability functions for the two quantum statistics can then be expressed as in Eqs. (1.53) and (1.54).

$$f(E) = \frac{1}{A \exp \left( \frac{E}{k_B T} \right) + 1} \text{ for F-D statistics}$$

$$f(E) = \frac{1}{A \exp \left( \frac{E}{k_B T} \right) - 1} \text{ for B-E statistics}$$  \hspace{1cm} (1.53) \hspace{1cm} (1.54)

Having made the distinctions between the three types of statistical models, we need to concentrate now on the F-D statistics that is of paramount importance to our needs. Let us consider once again that there are $N_i$ electrons to be distributed in $E_i$ available energy states having degeneracy of $g_i$ when the system is in thermodynamic equilibrium at temperature, $T$. Then the general formulation of the F-D statistics is described by the expression of Eq. (1.55).

$$N_i = \frac{A g_i \exp \left( -\frac{E_i}{k_B T} \right)}{1 + A \exp \left( -\frac{E_i}{k_B T} \right)}$$  \hspace{1cm} (1.55)

Let us at this point introduce two new terms, the Fermi function, $F(E)$ which is nothing else than a substitute for the general term probability, $f(E) = (N_i/g_i)$, and the Fermi energy, $E_F$. We are using the term Fermi function, $F(E)$, and not the general term of probability, $f(E)$, just to be consistent with the convention. By setting $A = \exp \left( \frac{E_F}{k_B T} \right)$, and after some rearrangement, we can rewrite Eq. (1.55) as Eq. (1.56).

$$F(E) = \frac{1}{\left( \exp \frac{E - E_F}{k_B T} \right) + 1}$$  \hspace{1cm} (1.56)

What is the Fermi energy ($E_F$) but what exactly does it mean? While dealing with semiconductor materials we constantly encounter the terms Fermi energy and Fermi level, and it is not uncommon to confuse one with the other. It is important to distinguish between them for the sake of accuracy.

Fermi energy is defined as the difference in kinetic energy that exists between the highest and the lowest occupied quantum states at absolute zero temperature ($T = 0$ K). In general, the lowest occupied state is defined as the state with zero kinetic energy. In semiconductors, the lowest energy state corresponds to the top of the valence band, whereas for metals it is the bottom of the conduction band. The Fermi energy is the kinetic energy, whereas the Fermi level is the sum of both the kinetic energy and the potential energy. Furthermore, Fermi energy is always defined with respect to absolute zero temperature, whereas the Fermi level can be referred to at any temperature. In contrast to the Fermi energy, the Fermi level for a metal at absolute zero corresponds to the highest occupied state.

Let us now go back to Eq. (1.56) and interpret its importance. We discuss three specific conditions which are the following:

**Case I:** When $T = 0$ K and $E_i < E_F$, the exponential term in the denominator becomes $\approx 0$ making $F(E) = 1$. That means that all energy states are fully occupied below the Fermi energy.

**Case II:** When $T = 0$ K and $E_i > E_F$. The exponential term now approaches $\approx 0$ rendering $F(E) = 0$. This means that all energy states above $E_F$ are totally empty.

**Case III:** If $E_i = E_F$, then $F(E) = \frac{1}{2}$. This means that the probability of occupancy at $E_i = E_F$ is always 50% no matter what the temperature at equilibrium might be.
Case IV: At high temperatures, $E_i - E_F \ll k_B T$. Then Eq. (1.56) reduces to

$$F(E) = \exp \left\{ - \left( \frac{E_i - E_F}{k_B T} \right) \right\} \approx \exp \left( - \frac{\Delta E}{k_B T} \right)$$

(1.57)

We can easily recognize it as another way for writing the M-B distribution function (see Eq. (1.52)). We infer from this that at sufficiently large thermal energies, the F-D statistics yields the same result as the M-B statistics. This then means that at elevated thermal equilibrium, electrons can be statistically described by the M-B distribution just as we would do for the atoms, ions, and molecules.

Case V: For very low temperatures but above $T = 0$ K, if $E_F - E_i \gg k_B T$, then the Fermi function is given by

$$F(E) \approx 1 - \exp \left( \frac{E_i - E_F}{k_B T} \right) \approx 1$$

(1.58)

This simply means that even at very low temperatures, the probability of occupation is 100%, which is the same as at $T = 0$ K (see Case I above).

Figure 1.14 is the typical plot for the F-D distribution. This, in fact, gives us the graphical picture of all the five cases we just discussed. Notice that the transfer of fermions from the upper half of the curve to the lower half occurs when $T > 0$ K and passes through the 50% point of the $F(E)$ axis. The population-depopulation of energy states must go through the $\frac{1}{2}$ point. This situation will reproduce itself time, and again, as the temperature rises and more and more electrons migrate from the upper half of the plot to its lower half. The probability of 100% occupancy of all available energy states is guaranteed at absolute zero. The Fermi energy, $E_F$, can now be defined also as the cut-off point between the populated and depopulated energy states.

We have so far discussed the conditions for population and depopulation of energy states according to the F-D statistics. Now we need to examine: (i) How many energy states might be there between the energy levels $E$ and $E + dE$ and (ii) What is the quantitative nature of the Fermi energy, $E_F$.

The technical term for the number of energy states found between the $E$ and $E + dE$ levels is density of states, $Z(E)dE$. The calculation to find a mathematical expression for $Z(E)$ is quite involved. We shall leave it for Chapter 7, where we will study the essential elements of semiconductors. The concept of density of states plays an important role in understanding the physical principles involved on semiconductor devices and therefore it will be more beneficial to deal with this topic there. For the time being, let us just give its mathematical formulation which is shown in Eq. (1.59).

$$Z(E)dE = \left( \frac{4\pi V (2m_e)^{\frac{3}{2}}}{h^3} \right) \cdot E^{\frac{3}{2}} \cdot dE = A \cdot E^{\frac{3}{2}} \cdot dE$$

(1.59)

where $V =$ the volume with $N$ number of electrons contained therein, $m_e$ and $h$ being the electron mass and the Planck constant, respectively. $A$ is a constant containing all the parameters under the square brackets. The numerical expression for the Fermi energy can be derived from the density of state, $Z(E)dE$ and is given by Eq. (1.60).

$$E_F \approx \left( \frac{\hbar^2}{8m_e} \right) \cdot \left( \frac{3N}{\pi V} \right)^{\frac{2}{3}} \approx \frac{\hbar^2}{8m_e} \left( \frac{3n}{\pi} \right)^{\frac{2}{3}}$$

(1.60)

Here $n =$ number of electrons per unit volume.

The temperature corresponding to the Fermi energy is called the Fermi temperature, $T_F$, and the velocity with which the electrons travel at the Fermi energy is called the Fermi velocity, $V_F$. The Fermi temperature is defined as $T_F \approx \left( \frac{E_F}{k_B} \right)$ and the Fermi velocity as $V_F \approx \left( \frac{p_F}{m_e} \right)$, where $p_F$ is the Fermi momentum which is equal to $\sqrt{2m_e E_F}$. The values of these parameters for some common metals is given in Table 1.18 [3].

Exercise 1.4
Consider a system with fivefold degeneracy and number of electrons to distribute in these energy states are only 3. Find the permissible distribution function, $\Omega$.

**Solution**

For the first electrons, there are five choices available; for the second there are four choices, and for the third there are three choices. The distribution function is then:

$$\Omega = \frac{5.4.3}{3!} = \frac{5!}{3!2!} = 10$$

---

Figure 1.14 Fermi–Dirac distribution plot: Fermi function vs. energy at $T = 0$ and $T > 0$. 

---
Table 1.18  Fermi energy, Fermi temperature, and Fermi velocity for some common metals [3].

<table>
<thead>
<tr>
<th>Metal</th>
<th>$E_F$, Fermi energy (eV)</th>
<th>$T_F$, Fermi temperature $\times 10^4$ (K)</th>
<th>$V_F$, Fermi velocity $\times 10^6$ (m S$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>3.24</td>
<td>3.77</td>
<td>1.07</td>
</tr>
<tr>
<td>Cu</td>
<td>7.00</td>
<td>8.16</td>
<td>1.57</td>
</tr>
<tr>
<td>Ag</td>
<td>5.49</td>
<td>6.38</td>
<td>1.39</td>
</tr>
<tr>
<td>Au</td>
<td>5.53</td>
<td>6.42</td>
<td>1.40</td>
</tr>
<tr>
<td>Al</td>
<td>11.7</td>
<td>13.6</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Exercise 1.5
Consider the case of sodium with atomic weight is 23, density equal to 0.968 g cm$^{-3}$, and the electronic configuration [Ne]3s. Calculate its Fermi energy, Fermi temperature, and Fermi velocity.

Solution
The Fermi energy can be found using Eq. (1.60) and from its value then we can calculate the other two parameters. The electronic configuration tells us that Na is monovalent. Therefore, the number of atoms per unit volume is simply given by $n = \frac{dN_A}{d}$, where $d$ is the density, $N_A = \text{Avogadro’s number} = 6.0 \times 10^{23}$ per atomic weight, $A$ (here $A$ is grams per mole). Substituting for these parameters in Eq. (1.60) we get

$$n = \frac{dN_A}{A} = \frac{(0.968 \times 6.02 \times 10^{23})}{23} \approx 2.54 \times 10^{21} \text{ cm}^{-3}$$

Substituting it then in Eq. (1.60) and dividing the value of Fermi energy obtained in joules by electron charge ($=1.60 \times 10^{-19}$ C), we get $E_F = 3.38$ eV for Na. This is in agreement by 96% of the experimentally obtained value of 3.24 eV.

The Fermi velocity, $v_F$ is obtained by using the relationship $v_F \approx \sqrt{\frac{m_e}{m_i}} E_F$. Substituting for $m_e$ and $E_F$, we get $v_F = 1.11 \times 10^6$ m s$^{-1}$. Note $E_F$ needs to be multiplied by electron charge to convert it from electron volts to joules.

Finally, the Fermi temperature $T_F \approx \frac{E_F}{k_B} \approx \frac{(3.24 \times 1.6 \times 10^{-19})}{1.38 \times 10^{-23}} \approx 3.75 \times 10^4$ K.

In conclusion, the calculated values for Na are $E_F = 3.24$ eV, $V_F = 1.11 \times 10^6$ m S$^{-1}$ and $T_F = 3.75 \times 10^4$ K. These values are in good agreement with the values reported in literature.

1.12 Band Structure of Solids
The free electron theory is capable of explaining almost all physical phenomena associated with metals. But it fails when it comes to insulators and semiconductors. In metals electrons are supposed to be free so that they can cause electrical conduction to take place. This is not the case for insulators where the electrons are bound and not free to roam around to produce electrical conduction. A similar picture we can visualize for semiconductors which by definition are bad insulators. The failure of the free electron theory made it essential to find a suitable theoretical model that could explain the basic nature of solids other than metals. So far we have learned that discrete energy states exist in single atoms, but the picture is very different when many atoms are involved as is the case of solids. A solid can be visualized in which positive and negative ions are present simultaneously and the electrons are bound. When separation between two atoms becomes infinitesimally small, the available energy states lose their respective discrete states and form bands. This is the consequence of the Pauli Exclusion Principle.

Three theoretical models are often used in solid-state sciences to understand how these energy bands originate in solids. They are Kronig–Penney model, Ziman model, and Feynman model. Each of them explains the physical mechanisms for the formation of allowed and forbidden bands. But they all require solid skills in mathematical manipulations. We will not go into those details here and will limit ourselves to some simpler approach that would satisfy our needs. That would be the approach by considering a simplified version of the Kronig–Penney model. This model was developed in 1931 by Ralph Kronig of Germany and William Penney of England.

The solids in this model are treated as a highly ordered periodic three-dimensional structure built on the basis of unit cells that repeat themselves in space. Each cell is identical in every respect to the other. We will recognize such a well-defined solid to be nothing else than a highly symmetric crystal lattice. To simplify the calculation Kronig and Penney considered the case of a one dimensional lattice of atoms. In such an arrangement, the atoms will experience the effects of periodic potentials varying with the lattice period. Figure 1.15 gives a graphical...
representation of this concept. Here the atoms are found along the $x$-axis with the period of $a$.

By careful analysis of the time-independent Schrödinger equation, we can find the eigenfunctions and eigenvalues that would satisfy the mathematical conditions for the electrons in the potential field with the period of $a$. The wave function that would satisfy this condition was proposed by Felix Bloch of Switzerland, and it is expressed mathematically as follows:

$$\psi_{nk}(r) = \exp(ik \cdot r)u_{nk}(r)$$  \hspace{1cm} (1.61)

where $k$ is the wave vector and $u_k(r)$ is the periodicity of the lattice such that $u_k(R + r) \approx u_k(r)$, where $R$ is defined as the position vector capable of generating an infinite number of lattice points. The concept of a position vector is related to the reciprocal lattice in crystallography. We will visit this topic in Chapter 4, where we well cover the essential elements of crystallography. The parameter $n$ is as always equal to an integer, 1, 2, 3, … For each value of $k$, there could be multiple solutions for the Schrödinger equation corresponding to the values of $n$. If $u_{nk}(r) = 0$ and $n = 1$ then Eq. (1.61) reduces to $\psi_k(r) \approx \exp(ik \cdot r)$, which represents a plane wave of a free electron.

The most important results that follow from the Kronig–Penney model are (i) Presence of forbidden and allowed energy bands in a solid; (ii) Switch from one energy state to another is discontinuous; and (iii) The discontinuity occurs at $k = \pm n \left( \frac{\pi}{a} \right)$. Notice that it also tells us that in solids, the wave vectors are also quantized. With respect to these values of $k$, the Schrödinger’s wave function can be given by Eqs. (1.62) and (1.63).

$$\psi_1 = \exp \left( i \frac{n \pi x}{a} \right) + \exp \left( -i \frac{n \pi x}{a} \right)$$

$$\psi_1 = 2 \cos \left( \frac{n \pi x}{a} \right)$$  \hspace{1cm} (1.62)

$$\psi_2 = \exp \left( i \frac{n \pi x}{a} \right) - \exp \left( -i \frac{n \pi x}{a} \right)$$

$$\psi_2 = 2 \sin \left( \frac{n \pi x}{a} \right)$$  \hspace{1cm} (1.63)

For $\psi_1$ the maxima occurs when $x = 0, a, 2a, \ldots, na$. Exactly, at these values of $x$, the minima for the wave function $\psi_2$ occur. From this, we can infer that there are two values of wave function for the same value of $k$, indicating that for the same values of $k$, there could be two values of energy, $E$, as well. We present graphically these results in the $E$–$k$ diagram as depicted in Figure 1.16.

We find in this figure that for each set of $k$, there is a corresponding allowed energy band. Sandwiched between the successive allowed energy bands, there are the forbidden energy bands where no electrons are allowed to reside. The first allowed band is called the first Brillouin zone; similarly the second and third bands are called the second and third Brillouin zones, respectively. They are named after the French physicist with the name of Léon Nicolas Brillouin who made valuable fundamental contributions of in many fields of physics.

Theoretically, it is possible to have infinite number of bands and as such an infinite number of energy states. But because of the limited number of electrons available in all types of solids, in reality there are only a few allowed and forbidden energy bands. The most important bands relevant to solid-state electronics and optics are the

![Figure 1.16 E–k diagram showing allowed and forbidden energy bands in a solid.](image-url)
Nature and Types of Solid Materials

valence band, conduction band, and the bandgap. We all are familiar with these bands as they are the fundamental nature of semiconducting materials. Of course, the same picture prevails also in insulators. In metals, however, the conduction band overlaps the valence band eliminating the possibility of the presence of a bandgap. The Fermi level is found in the forbidden gap of semiconductors and insulators, but it is buried inside one of the allowed bands for metals and semimetals. This is what we find in Figure 1.1.

Glossary

**Allowed band** In solids according to quantum mechanics, energy states exist in bands and are not discrete as is the case with electrons in an isolated atom.

**Bandgap** It is the energy band that is sandwiched, for example, in a semiconductor material, between the valence band and conduction band. No electrons are allowed to find themselves in this band. Therefore, it is also called the forbidden gap. It width is measured in electron volt.

**Brillouin zones** The allowed energy bands in a solid are grouped as the first allowed band, the second allowed band, the third allowed band, and so forth. They are also referred to as the first Brillouin zone, the second Brillouin zone, the third Brillouin zone, respectively. Léon Nicolas Brillouin (1869–1969) was a brilliant French physicist who gave the concept of Brillouin zones in a crystal lattice. He made also many more ground-breaking contributions.

**Cooper pairs** In superconducting materials, electrons form pairs with antiparallel spins and do not obey Pauli Exclusion Principle like the normal electrons. Leon N. Cooper, one of the recipients of Nobel Prize in Physics in 1972 with John Bardeen and Robert Schrieffer, showed that the Cooper pairs are responsible for the superconductivity phenomenon.

**Critical field** It refers to the critical magnetic field that can induce switching of the superconducting state into normal state. This is a signature property of a superconducting material.

**Critical point** The critical temperature at which a superconducting material becomes a normal conductor. This is the other signature property of a superconducting material.

**Fermi energy** This is the difference in kinetic energy between the highest and lowest occupied states of solid at absolute zero (0 K). This is the characteristic property of all solids and plays a vital role in describing the fundamental nature of metals and semiconductors at a thermal equilibrium.

**Fermi level** By definition is the sum of the kinetic energy and potential energy of electrons in a solid. Unlike Fermi energy, it can be referred to at any temperature. In semiconductor, it is common to refer to Fermi level instead of Fermi energy. Here the bottom of the valence band corresponds to the potential energy equal to zero. Then the Fermi level for an intrinsic semiconductor becomes equal to the width between the bottom of the valence band and the position of the Fermi level in the bandgap. Fermi level changes with temperature and also with the doping level of the extrinsic semiconductor.

**Forbidden band** The energy band in which no electrons are supposed to be present. Same as the bandgap of a semiconductor material.

**Frequency spectrum** Dielectric constant vs. frequency plot of an insulator in which the dipolar, ionic, and electronic components of the permittivity are identified.

**Josephson effect** It is the physical phenomenon specific to superconductors which was discovered by Brian David Josephson of England in 1962. The effect describes the tunneling of the Cooper pairs through a very thin insulating layer sandwiched between two superconducting layers. It has many practical applications including detecting extremely small magnetic fields.

**Magnetic levitation** When a normal material becomes superconducting below the critical temperature, its acquired diamagnetism prevents the penetration of magnetic fluxes within the superconducting material. As a result fluxes are expelled back causing a magnet to be levitated above the superconducting surface and being suspended in air (as in Figure 1.9). This also has many applications and represents another signature property of a superconductor.

**Matter–wave-duality** This is the true nature of an electron as proposed by Louis de Broglie of France in 1923. According to his hypothesis, an electron can behave simultaneously as a particle and a wave. This concept is the cornerstone of quantum mechanics, and it has led to the discovery of the celebrated Schrödinger equation. de Broglie received the Nobel Prize in Physics in 1929 for this contribution.

**Persistent current** A current generated by a magnetic field in a superconducting ring that can persist for a very long time even after the originating magnetic field is withdrawn.

**Phonon** In a crystal lattice, temperature can set up oscillations of atoms. The unit to measure the
resulting vibrational energy is referred to as phonons and is a quantum mechanical concept. It is considered to be an elementary particle associated with a solid and is used to describe a mechanical wave. **Phonon** What a phonon is to a mechanical wave so is a photon to an electromagnetic wave, or more precisely, to an optical wave. It is a quantum of energy associated with light and originally introduced by Planck.

**Potential field** In a solid with perfectly ordered lattice and periodicity in space, the potential energy can vary from a minimum to a maximum value. This facilitated the discovery of allowed and forbidden energy bands in a solid using the model proposed by Kronig and Penney.

**Quantization** In quantum mechanics, when a parameter can assume values in steps of 1, 2, 3, … (equivalent to the value of the principal quantum number, \( n \)), then the parameters are called quantized. Some examples are orbital quantum number, \( l \); Planck’s photon energy, \( h \nu \); and magnetic flux, \( \phi \), in superconducting state.

**Quantum numbers** A set of four numbers identified as principal quantum number \( (n) \), orbital quantum number \( (l) \), magnetic quantum number \( (m_l) \), and spin quantum number \( (\pm 1/2) \) are jointly referred to as quantum numbers. They are used to describe the quantum mechanical properties of an electron.

**SQUID** It is the abbreviation for “superconducting quantum interference device” that is based on the Josephson junction. These are very precise magnetometers capable of detecting extremely small magnetic fields.

**Superconductivity** A special class of physical phenomenon occurring in solids below a certain temperature is called superconductivity. As the name suggests a superconducting material has zero resistance and as such infinite conduction. Such materials can deliver lossless electrical power \( (P = I^2R) \) at a long distance and as such they possess enormous technical value for mankind.

**Work function** It is a material parameter of enormous scientific and technical importance. Its commonly used symbol is \( W \), and it can be defined in many different ways. For example, in a photoelectric experiment, it is the threshold energy that must be exceeded by the photon energy radiating a metallic surface before electrons can be emitted. It is also measured in electron volts. Its general definition is the following: this is the energy that an electron must acquire before it can escape a surface in order to reach its ultimate destination that is the vacuum level with infinite energy.

### Problems

1. **Consider a sample of GaAs with the following dimensions: length = 5 mm, width = 1 mm, and thickness = 1 mm. The electrical conductivity of GaAs is \( 1 \times 10^{-8} \) S m\(^{-1}\). Assume that the two parallel faces (5 mm long) are fully metallized. Find the electric field that must be applied to generate a current density of 1 \( \mu \)A m\(^{-2}\).**

2. **Using the values of the dielectric constant given in Table 1.3 calculate the polarization that develops when 10 V is applied to a cube sample of 1 mm dimension of Ge, SrTiO\(_3\), and TiO\(_2\). Comment on the result.**

3. **Find the maximum kinetic energy with which the electrons will emit when the samples of metals listed in Table 1.6 are irradiated by a UV light of 0.2 \( \mu \)m wavelength. Comment on your result.**

4. **Find the stopping potential for photoemission for all the metals listed in Table 1.6 when the samples are irradiated by a UV light of 0.2 \( \mu \)m wavelength.**

5. **Describe the mechanism for population and depopulation of states involved in Fermi–Dirac statistics. Find the temperature at which there is 1% probability that a state with the energy of 0.1 eV above the Fermi energy will be occupied by an electron. Comment on your result.**

6. **Find the velocity and the momentum of the electron with de Broglie wavelength of 1 nm. Comment on your result.**

7. **Describe the Pauli exclusion principle and show how it leads to the quantum mechanical interpretation of the Periodic table of elements.**
References


Further Reading
