

or to $n\lambda$, where n is an integer (but not zero). Thus

$$2\pi r = n\lambda = \frac{nh}{mv} \quad (2-9)$$

Clearly, Eq. (2-9) is identical with the Bohr condition [Eq. (2-5)].

Wave Mechanics Schrödinger carried the implication of the wave nature of the electron further and developed a branch of physics called *wave mechanics*, or *quantum mechanics*. He argued that, if De Broglie's concept is correct, it should be possible to deduce the properties of an electron system from a mathematical relationship such as the wave equation of electromagnetic theory, optics, mechanical vibrations, etc. Such a wave equation is

$$\nabla^2\phi - \frac{1}{v^2} \frac{\partial^2\phi}{\partial t^2} = 0 \quad (2-10)$$

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and v is the velocity of the wave, and t is time. The physical meaning of ϕ depends upon the problem under consideration. It may be one component of electric field, the mechanical displacement, the pressure, etc., depending upon the physical problem. We can eliminate the time variable by assuming a solution of the form

$$\phi(x, y, z, t) = \psi(x, y, z)e^{j\omega t} \quad (2-11)$$

where $\omega = 2\pi f$ is the angular frequency. Then Eq. (2-10) becomes

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0 \quad (2-12)$$

where $\lambda \equiv v/f =$ the wavelength. From De Broglie's relationship [Eq. (2-8)],

$$\frac{1}{\lambda^2} = \frac{p^2}{h^2} = \frac{2m}{h^2}(W - U) \quad (2-13)$$

where use has been made of the fact that the kinetic energy $p^2/2m$ is the difference between the total energy W and the potential energy U . Substituting Eq. (2-13) in (2-12) gives the time-independent Schrödinger equation

$$\nabla^2\psi + \frac{8\pi^2m}{h^2}(W - U)\psi = 0 \quad (2-14)$$

The ψ in Eq. (2-14) is called the *wave function*, and it must describe the behavior of the particle. But what is the physical meaning of ψ ? It is found that the proper interpretation of ψ is that it is a quantity whose square gives the probability of finding the electron. In other words, $|\psi|^2 dx dy dz$ is proportional to the probability that the electron is in the volume $dx dy dz$ at the point $P(x, y, z)$ in space. The wave function ψ must be normalized, that is, $\iiint |\psi|^2 dx dy dz$ over all space equals unity, indicating that the probability of

finding the electron somewhere must be unity. Quantum mechanics makes no attempt to locate a particle at a precise point P in space, but rather the Schrödinger equation determines only the probability that the electron is to be found in the neighborhood of P .

The potential energy $U(x, y, z)$ specifies the physical problem at hand. For the electron in the hydrogen atom, $U = -e^2/4\pi\epsilon_0 r$, whereas for a crystal, it is a complicated periodic function of space. The solution of Schrödinger's equation, subject to the proper boundary conditions, yields the allowed total energies W_n (called *characteristic values*, or *eigenvalues*) of the particle and the corresponding wave functions ψ_n (called *eigenfunctions*). Except for the very simplest potential functions (as in Sec. 3-6), there is considerable mathematical complexity in solving for ψ . Hence we shall not obtain the solution of the Schrödinger equation for the hydrogen atom, but shall state the important result that such a solution leads to precisely the energy levels given in Eq. (2-3) which were obtained from the simpler Bohr picture of the atom.

2-9 ELECTRONIC STRUCTURE OF THE ELEMENTS

The solution of the Schrödinger equation for hydrogen or any multielectron atom need not have radial symmetry. The wave functions may be a function of the azimuthal and polar angles as well as of the radial distance. It turns out that, in the general case, four quantum numbers are required to define the wave function. The total energy, the orbital angular momentum, the component of this angular momentum along a fixed axis in space, and the electron spin are quantized. The four quantum numbers are identified as follows:

1. The *principal quantum number* n is an integer 1, 2, 3, . . . and determines the total energy associated with a particular state. This number may be considered to define the size of the classical elliptical orbit, and it corresponds to the quantum number n of the Bohr atom.

2. The *orbital angular momentum quantum number* l takes on the values 0, 1, 2, . . . , $(n - 1)$. This number indicates the shape of the classical orbit. The magnitude of this angular momentum is $\sqrt{l(l+1)}(h/2\pi)$.

3. The *orbital magnetic number* m_l may have the values 0, ± 1 , ± 2 , . . . , $\pm l$. This number gives the orientation of the classical orbit with respect to an applied magnetic field. The magnitude of the component of angular momentum along the direction of the magnetic field is $m_l(h/2\pi)$.

4. *Electron spin*. In order to explain certain spectroscopic and magnetic phenomena, Uhlenbeck and Goudsmit, in 1925, found it necessary to assume that, in addition to traversing its orbit around the nucleus, the electron must also rotate about its own axis. This intrinsic electronic angular momentum is called *electron spin*. When an electron system is subjected to a magnetic field, the spin axis will orient itself either parallel or antiparallel to the direc-

tion of the field. The spin is thus quantized to one of two possible values. The electronic angular momentum is given by $m_s(h/2\pi)$, where the *spin quantum number* m_s may assume only two values, $+\frac{1}{2}$ or $-\frac{1}{2}$.

The Exclusion Principle The periodic table of the chemical elements (given in Appendix C) may be explained by invoking a law enunciated by Pauli in 1925. He stated that *no two electrons in an electronic system can have the same set of four quantum numbers, n , l , m_l , and m_s* . This statement that no two electrons may occupy the same quantum state is known as the *Pauli exclusion principle*.

Electronic Shells All the electrons in an atom which have the same value of n are said to belong to the same *electron shell*. These shells are identified by the letters K, L, M, N, \dots , corresponding to $n = 1, 2, 3, 4, \dots$, respectively. A shell is divided into *subshells* corresponding to different values of l and identified as s, p, d, f, \dots , corresponding to $l = 0, 1, 2, 3, \dots$, respectively. Taking account of the exclusion principle, the distribution of electrons in an atom among the shells and subshells is indicated in Table 2-1. Actually, seven shells are required to account for all the chemical elements, but only the first four are indicated in the table.

There are two states for $n = 1$ corresponding to $l = 0$, $m_l = 0$, and $m_s = \pm\frac{1}{2}$. These are called the $1s$ states. There are two states corresponding to $n = 2$, $l = 0$, $m_l = 0$, and $m_s = \pm\frac{1}{2}$. These constitute the $2s$ subshell. There are, in addition, six energy levels corresponding to $n = 2$, $l = 1$, $m_l = -1, 0$, or $+1$, and $m_s = \pm\frac{1}{2}$. These are designated as the $2p$ subshell. Hence, as indicated in Table 2-1, the total number of electrons in the L shell is $2 + 6 = 8$. In a similar manner we may verify that a d subshell contains a maximum of 10 electrons, an f subshell a maximum of 14 electrons, etc.

The atomic number Z gives the number of electrons orbiting about the nucleus. Let us use superscripts to designate the number of electrons in a particular subshell. Then sodium, Na, for which $Z = 11$, has an electronic configuration designated by $1s^2 2s^2 2p^6 3s^1$. Note that Na has a single electron in the outermost unfilled subshell, and hence is said to be monovalent. This

TABLE 2-1 Electron shells and subshells

Shell	K		L			M			N				
	1	2	3			4							
n	0	0	1	0	1	2	0	1	2	3			
l	s	s	p	s	p	d	s	p	d	f			
Subshell	2	2	6	2	6	10	2	6	10	14			
Number of electrons	2	8		18			32						

TABLE 2-2 Electronic configuration in Group IVA

Element	Atomic number	Configuration
C	6	$1s^2 2s^2 2p^2$
Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$

same property is possessed by all the alkali metals (Li, Na, K, Rb, and Cs), which accounts for the fact that these elements in the same group in the periodic table (Appendix C) have similar chemical properties.

The inner-shell electrons are very strongly bound to an atom, and cannot be easily removed. That is, the electrons closest to the nucleus are the most tightly bound, and so have the lowest energy. Also, atoms for which the electrons exist in closed shells form very stable configurations. For example, the inert gases He, Ne, Ar, Kr, and Xe all have either completely filled shells or, at least, completely filled subshells.

Carbon, silicon, germanium, and tin have the electronic configurations indicated in Table 2-2. Note that each of these elements has completely filled subshells except for the outermost p shell, which contains only two of the six possible electrons. Despite this similarity, carbon in crystalline form (diamond) is an insulator, silicon and germanium solids are semiconductors, and tin is a metal. This apparent anomaly is explained in the next section.

2-10 THE ENERGY-BAND THEORY OF CRYSTALS

X-ray and other studies reveal that most metals and semiconductors are crystalline in structure. A crystal consists of a space array of atoms or molecules (strictly speaking, ions) built up by regular repetition in three dimensions of some fundamental structural unit. The electronic energy levels discussed for a single free atom (as in a gas, where the atoms are sufficiently far apart not to exert any influence on one another) do not apply to the same atom in a crystal. This is so because the potential U in Eq. (2-14), characterizing the crystalline structure, is now a periodic function in space whose value at any point is the result of contributions from every atom. When atoms form crystals it is found that the energy levels of the inner-shell electrons are not affected appreciably by the presence of the neighboring atoms. However, the levels of the outer-shell electrons are changed considerably, since these electrons are shared by more than one atom in the crystal. The new energy levels of the outer electrons can be determined by means of quantum mechanics, and it is found that coupling between the outer-shell electrons of the atoms results in a *band* of closely spaced energy states instead of the

widely separated energy levels of the isolated atom (Fig. 2-2). A qualitative discussion of this energy-band structure follows.

Consider a crystal consisting of N atoms of one of the elements in Table 2-2. Imagine that it is possible to vary the spacing between atoms without altering the type of fundamental crystal structure. If the atoms are so far apart that the interaction between them is negligible, the energy levels will coincide with those of the isolated atom. The outer two subshells for each element in Table 2-2 contain two s electrons and two p electrons. Hence, if we ignore the inner-shell levels, then, as indicated to the extreme right in Fig. 2-2a, there are $2N$ electrons completely filling the $2N$ possible s levels, all at the same energy. Since the p atomic subshell has six possible states, our imaginary crystal of widely spaced atoms has $2N$ electrons, which fill only one-third of the $6N$ possible p states, all at the same level.

If we now decrease the interatomic spacing of our imaginary crystal (moving from right to left in Fig. 2-2a), an atom will exert an electric force on its neighbors. Because of this coupling between atoms, the atomic-wave functions overlap, and the crystal becomes an electronic system which must obey the Pauli exclusion principle. Hence the $2N$ degenerate s states must spread out in energy. The separation between levels is small, but since N is very large ($\sim 10^{23} \text{ cm}^{-3}$), the total spread between the minimum and maximum energy may be several electron volts if the interatomic distance is decreased sufficiently. This large number of discrete but closely spaced energy levels is called an *energy band*, and is indicated schematically by the lower shaded

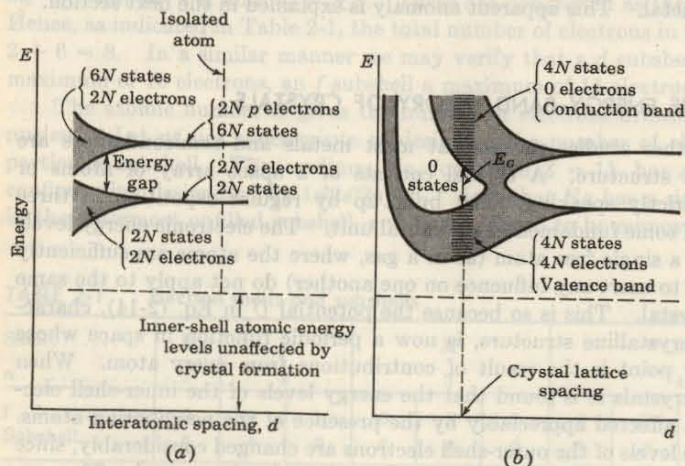


Fig. 2-2 Illustrating how the energy levels of isolated atoms are split into energy bands when these atoms are brought into close proximity to form a crystal.

region in Fig. 2-2a. The $2N$ states in this band are completely filled with $2N$ electrons. Similarly, the upper shaded region in Fig. 2-2a is a band of $6N$ states which has only $2N$ of its levels occupied by electrons.

Note that there is an energy gap (a forbidden band) between the two bands discussed above and that this gap decreases as the atomic spacing decreases. For small enough distances (not indicated in Fig. 2-2a but shown in Fig. 2-2b) these bands will overlap. Under such circumstances the $6N$ upper states merge with the $2N$ lower states, giving a total of $8N$ levels, half of which are occupied by the $2N + 2N = 4N$ available electrons. At this spacing each atom has given up four electrons to the band; these electrons can no longer be said to orbit in s or p subshells of an isolated atom, but rather they belong to the crystal as a whole. In this sense the elements in Table 2-2 are tetravalent, since they contribute four electrons each to the crystal. The band these electrons occupy is called the *valence band*.

If the spacing between atoms is decreased below the distance at which the bands overlap, the interaction between atoms is indeed large. The energy-band structure then depends upon the orientation of the atoms relative to one another in space (the crystal structure) and upon the atomic number, which determines the electrical constitution of each atom. Solutions of Schrödinger's equation are complicated, and have been obtained approximately for only relatively few crystals. These solutions lead us to expect an energy-band diagram somewhat as pictured⁴ in Fig. 2-2b. At the crystal-lattice spacing (the dashed vertical line), we find the valence band filled with $4N$ electrons separated by a forbidden band (no allowed energy states) of extent E_G from an empty band consisting of $4N$ additional states. This upper vacant band is called the *conduction band*, for reasons given in the next section.

2-11 INSULATORS, SEMICONDUCTORS, AND METALS

A very poor conductor of electricity is called an *insulator*; an excellent conductor is a *metal*; and a substance whose conductivity lies between these extremes is a *semiconductor*. A material may be placed in one of these three classes, depending upon its energy-band structure.

Insulator The energy-band structure of Fig. 2-2b at the normal lattice spacing is indicated schematically in Fig. 2-3a. For a diamond (carbon) crystal the region containing no quantum states is several electron volts high ($E_G \approx 6 \text{ eV}$). This large forbidden band separates the filled valence region from the vacant conduction band. The energy which can be supplied to an electron from an applied field is too small to carry the particle from the filled into the vacant band. Since the electron cannot acquire externally applied energy, conduction is impossible, and hence diamond is an *insulator*.

Semiconductor A substance for which the width of the forbidden energy region is relatively small ($\sim 1 \text{ eV}$) is called a *semiconductor*. Graphite, a

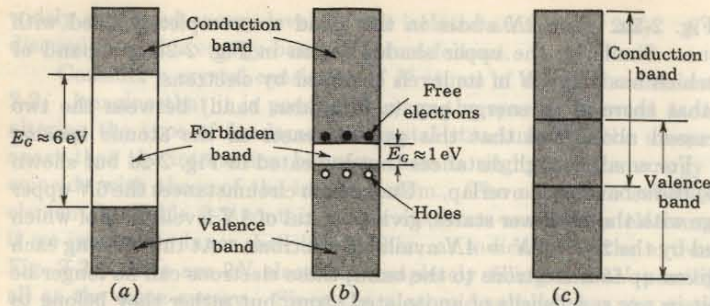


Fig. 2-3 Energy-band structure of (a) an insulator, (b) a semiconductor, and (c) a metal.

crystalline form of carbon but having a crystal symmetry which is different from diamond, has such a small value of E_G , and it is a semiconductor. The most important practical semiconductor materials are germanium and silicon, which have values of E_G of 0.785 and 1.21 eV, respectively, at 0°K. Energies of this magnitude normally cannot be acquired from an applied field. Hence the valence band remains full, the conduction band empty, and these materials are insulators at low temperatures. However, the conductivity increases with temperature, as we explain below, and for this reason these substances are known as *intrinsic semiconductors*.

As the temperature is increased, some of these valence electrons acquire *thermal* energy greater than E_G and hence move into the conduction band. These are now free electrons in the sense that they can move about under the influence of even a small applied field. These free, or conduction, electrons are indicated schematically by dots in Fig. 2-3b. The insulator has now become slightly conducting; it is a *semiconductor*. The absence of an electron in the valence band is represented by a small circle in Fig. 2-3b, and is called a *hole*. The phrase "holes in a semiconductor" therefore refers to the empty energy levels in an otherwise filled valence band.

The importance of the hole is that it may serve as a carrier of electricity, comparable in effectiveness with the free electron. The mechanism by which a hole contributes to conductivity is explained in Sec. 5-1. We also show in Chap. 5 that if certain impurity atoms are introduced into the crystal, these result in allowable energy states which lie in the forbidden energy gap. We find that these impurity levels also contribute to the conduction. A semiconductor material where this conduction mechanism predominates is called an *extrinsic (impurity) semiconductor*.

Since the band-gap energy of a crystal is a function of interatomic spacing (Fig. 2-2), it is not surprising that E_G depends somewhat on temperature. It has been determined experimentally that E_G for silicon decreases with

temperature at the rate of 3.60×10^{-4} eV/°K. Hence, for silicon,⁵

$$E_G(T) = 1.21 - 3.60 \times 10^{-4}T \quad (2-15)$$

and at room temperature (300°K), $E_G = 1.1$ eV. Similarly, for germanium,⁶

$$E_G(T) = 0.785 - 2.23 \times 10^{-4}T \quad (2-16)$$

and at room temperature, $E_G = 0.72$ eV.

Metal The band structure of a crystal may contain no forbidden energy region, so that the valence band merges into an empty band, as indicated in Fig. 2-3c. Under the influence of an applied electric field the electrons may acquire additional energy and move into higher energy states. Since these mobile electrons constitute a current, this substance is a conductor, and the empty region is the conduction band. A *metal* is characterized by a band structure containing overlapping valence and conduction bands.

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