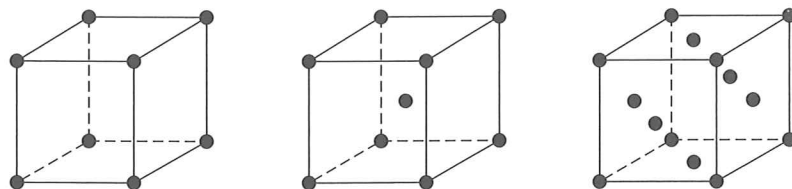


Question 3

- (a) Diamond and zinc blende crystal structures are both composed of a Bravais lattice with a two-atom basis. Circle the correct unit cell for this Bravais lattice.



- (b) Which statement below is true?

1. GaAs has a *diamond / zinc blende* crystal structure.
2. Si has a *diamond / zinc blende* crystal structure.

Question 4

Give some examples of zero-dimensional, one-dimensional, two-dimensional, and three-dimensional defects in a semiconductor.

Question 5

- (a) What is the difference between a primitive cell and a unit cell? What is the utility of both concepts?
- (b) What is the difference between a lattice and a crystal? How many different 1-D lattices can you have?

Question 6

Consider growing InAs on the following crystal substrates: InP, AlAs, GaAs, and GaP. For which case would the *critical thickness* of the InAs layer be greatest? You may use Fig. 1-13 from your text.

GaP / GaAs / AlAs / InP

Chapter 2**Atoms and Electrons****OBJECTIVES**

1. Understand the wave-particle duality of nature in quantum mechanics
2. Study the Bohr model of atoms
3. Apply the Schrödinger equation to simple problems
4. Understand the electronic structure of atoms and the periodic table
5. Understand how semiconductor properties are determined

Since this book is primarily an introduction to solid state devices, it would be preferable not to delay this discussion with subjects such as atomic theory, quantum mechanics, and electron models. However, the behavior of solid state devices is directly related to these subjects. For example, it would be difficult to understand how an electron is transported through a semiconductor device without some knowledge of the electron and its interaction with the crystal lattice. Therefore, in this chapter we shall investigate some of the important properties of electrons, with special emphasis on two points: (1) the electronic structure of atoms, and (2) the interaction of atoms and electrons with excitation, such as the absorption and emission of light. By studying electron energies in an atom, we lay the foundation for understanding the influence of the lattice on electrons participating in current flow through a solid. Our discussions concerning the interaction of light with electrons form the basis for later descriptions of changes in the conductivity of a semiconductor with optical excitation, properties of light-sensitive devices, and lasers.

First, we shall investigate some of the experimental observations which led to the modern concept of the atom, and then we shall give a brief introduction to the theory of quantum mechanics. Several important concepts will emerge from this introduction: the electrons in atoms are restricted to certain energy levels by quantum rules; the electronic structure of atoms is determined from these quantum conditions; and this "quantization" defines certain allowable transitions involving absorption and emission of energy by the electrons.

2.1 INTRODUCTION TO PHYSICAL MODELS

The main effort of science is to describe what happens in nature, in as complete and concise a form as possible. In physics this effort involves observing natural phenomena, relating these observations to previously established theory, and finally establishing a physical model for the observations. For example, we can explain the behavior of a spring-supported weight moving up and down periodically after an initial displacement, because the differential equations describing such a simple harmonic motion have been established by Newtonian classical mechanics.

When a new physical phenomenon is observed, it is necessary to find out how it fits into the established models and “laws” of physics. In the vast majority of cases this involves a direct extension of the mathematics of well-established models to the particular conditions of the new problem. In fact, it is not uncommon for a scientist or engineer to predict that a new phenomenon should occur before it is actually observed, simply by a careful study and extension of existing models and laws. The beauty of science is that natural phenomena are not isolated events but are related to other events by a few analytically describable laws. However, it does happen occasionally that a set of observations cannot be described in terms of existing theories. In such cases it is necessary to develop models which are based as far as possible on existing laws, but which contain new aspects arising from the new phenomena. Postulating new physical principles is a serious business, and it is done only when there is no possibility of explaining the observations with established theory. When new assumptions and models are made, their justification lies in the following question: “Does the model describe precisely the observations, and can reliable predictions be made based on the model?” The model is good or poor depending on the answer to this question.

In the 1920s it became necessary to develop a new theory to describe phenomena on the atomic scale. A long series of careful observations had been made that clearly indicated that many events involving electrons and atoms did not obey the classical laws of mechanics. It was necessary, therefore, to develop a new kind of mechanics to describe the behavior of particles on this small scale. This new approach, called *quantum mechanics*, describes atomic phenomena very well and also properly predicts the way in which electrons behave in solids—our primary interest here. Through the years, quantum mechanics has been so successful that now it stands beside the classical laws as a valid description of nature.

A special problem arises when students first encounter the theory of quantum mechanics. The problem is that quantum concepts are largely mathematical in nature and do not involve the “common sense” quality associated with classical mechanics. At first, many students find quantum concepts difficult, not so much because of the mathematics involved, but because they feel the concepts are somehow divorced from “reality.” This is a reasonable reaction, since ideas which we consider to be real or intuitively satisfying are usually based on our own observation. Thus the classical laws of motion are easy to understand because we observe bodies in motion every day. On the

other hand, we observe the effects of atoms and electrons only indirectly, and naturally we have very little feeling for what is happening on the atomic scale. It is necessary, therefore, to depend on the facility of the theory to predict experimental results rather than to attempt to force classical analogs onto the nonclassical phenomena of atoms and electrons.

Our approach in this chapter will be to investigate the important experimental observations that led to the quantum theory, and then to indicate how the theory accounts for these observations. Discussions of quantum theory must necessarily be largely qualitative in such a brief presentation, and those topics that are most important to solid state theory will be emphasized here. Several good references for further individual study are given at the end of this chapter.

2.2 EXPERIMENTAL OBSERVATIONS

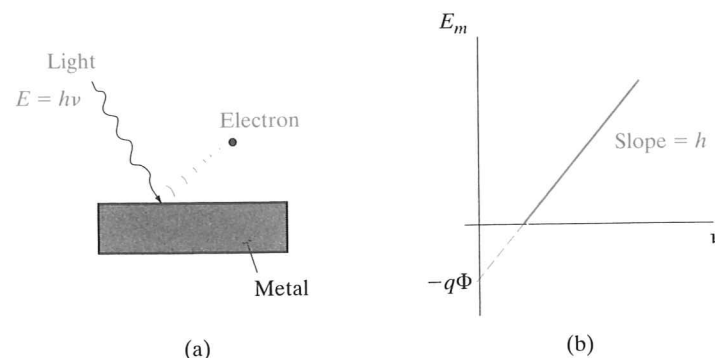
The experiments that led to the development of quantum theory were concerned with the interaction of light and matter. On the one hand, there were phenomena such as interference or diffraction which clearly indicated that light has a wave character as proposed by Huygens, in contrast to the particle or *corpuscular* view of light proposed by Newton. But on the other hand, many experiments at the turn of the 20th century clearly showed that a new theory of light was needed.

2.2.1 The Photoelectric Effect

An important observation by Planck indicated that radiation from a heated sample, known as blackbody radiation, is emitted in discrete units of energy called *quanta*; the energy units were described by $h\nu$, where ν is the frequency of the radiation, and h is a quantity now called Planck's constant ($h = 6.63 \times 10^{-34}$ J-s). Soon after Planck developed this hypothesis, Einstein interpreted an important experiment that clearly demonstrated the discrete nature (*quantization*) of light. This experiment involved absorption of optical energy by the electrons in a metal and the relationship between the amount of energy absorbed and the frequency of the light (Fig. 2-1). Let us suppose that monochromatic light is incident on the surface of a metal plate in a vacuum. The electrons in the metal absorb energy from the light, and some of the electrons receive enough energy to be ejected from the metal surface into the vacuum. This phenomenon is called the *photoelectric effect*. If the energy of the escaping electrons is measured, a plot can be made of the maximum energy as a function of the frequency ν of the incident light (Fig. 2-1b).

One simple way of finding the maximum energy of the ejected electrons is to place another plate above the one shown in Fig. 2-1a and then create an electric field between the two plates. The potential necessary to retard all electron flow between the plates gives the energy E_m . For a particular frequency of light incident on the sample, a maximum energy E_m is observed

Figure 2-1
The photoelectric effect: (a) electrons are ejected from the surface of a metal when exposed to light of frequency ν in a vacuum; (b) plot of the maximum kinetic energy of ejected electrons vs. frequency of the incoming light.



for the emitted electrons. The resulting plot of E_m vs. ν is linear, with a slope equal to Planck's constant. The equation of the line shown in Fig. 2-1b is

$$E_m = h\nu - q\Phi \quad (2-1)$$

where q is the magnitude of the electronic charge. The quantity Φ (volts) is a characteristic of the particular metal used. When Φ is multiplied by the electronic charge, an energy (joules) is obtained which represents the minimum energy required for an electron to escape from the metal into a vacuum. The energy $q\Phi$ is called the *work function* of the metal. These results indicate that the electrons receive an energy $h\nu$ from the light and lose an amount of energy $q\Phi$ in escaping from the surface of the metal.

This experiment demonstrates clearly that Planck's hypothesis was correct—light energy is contained in discrete units rather than in a continuous distribution of energies. Other experiments also indicate that, in addition to the wave nature of light, the quantized units of light energy can be considered as localized packets of energy, called *photons*. (Interestingly, this is reminiscent of the Newtonian picture.) We get the Planck relationship

$$E = h\nu \quad (2-2a)$$

Some experiments emphasize the wave nature of light, while other experiments reveal the discrete nature of photons. This wave-particle duality is fundamental to quantum processes and does not imply an ambiguity in the theory. Based on the wave-particle duality of light, Louis de Broglie proposed that particles of matter (such as electrons) similarly could manifest a wave character in certain experiments. This observation was confirmed by the diffraction of electrons by the periodic array of atoms in a crystal observed by Davisson and Germer. De Broglie proposed that a particle of momentum $p = mv$ has a wavelength given by

$$\lambda = h/p = h/mv \quad (2-2b)$$

The Planck and de Broglie relationships are fundamental in quantum physics and are valid for *all* situations and objects, including photons and

electrons. They connect the wave description of phenomena (frequency and wavelength) to a particle description (energy and momentum).

The relation between frequency and wavelength, known as the *dispersion relationship*, however, is *not* the same for different objects. For example, for photons, the wavelength (λ) is related to frequency by $\lambda = c/\nu$, where c is the speed of light. For electrons, it is a different relationship, known as the band structure, as discussed in Chapter 3.

2.2.2 Atomic Spectra

One of the most valuable experiments of modern physics is the analysis of absorption and emission of light by atoms. For example, an electric discharge can be created in a gas, so that the atoms begin to emit light with wavelengths characteristic of the gas. We see this effect in a neon sign, which is typically a glass tube filled with neon or a gas mixture, with electrodes for creating a discharge. If the intensity of the emitted light is measured as a function of wavelength, one finds a series of sharp lines rather than a continuous distribution of wavelengths. By the early 1900s the characteristic spectra for several atoms were well known. A portion of the measured emission spectrum for hydrogen is shown in Fig. 2-2, in which the vertical lines represent the positions of observed emission peaks on the wavelength scale. Photon energy $h\nu$ is then related to wavelength by the dispersion relation $\lambda = c/\nu$.

The lines in Fig. 2-2 appear in several groups labeled the *Lyman*, *Balmer*, and *Paschen* series after their early investigators. Once the hydrogen spectrum was established, scientists noticed several interesting relationships among the lines. The various series in the spectrum were observed to follow certain empirical forms:

$$\text{Lyman: } \nu = cR\left(\frac{1}{1^2} - \frac{1}{n^2}\right), \quad n = 2, 3, 4, \dots \quad (2-3a)$$

$$\text{Balmer: } \nu = cR\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \quad n = 3, 4, 5, \dots \quad (2-3b)$$

$$\text{Paschen: } \nu = cR\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \quad n = 4, 5, 6, \dots \quad (2-3c)$$

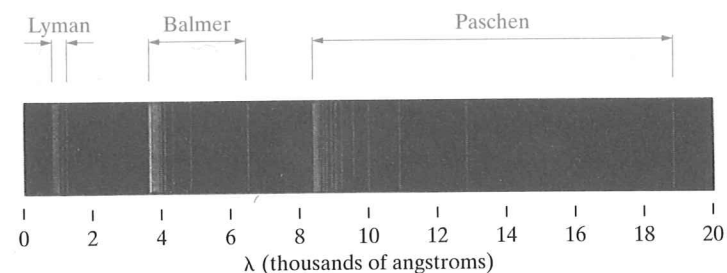
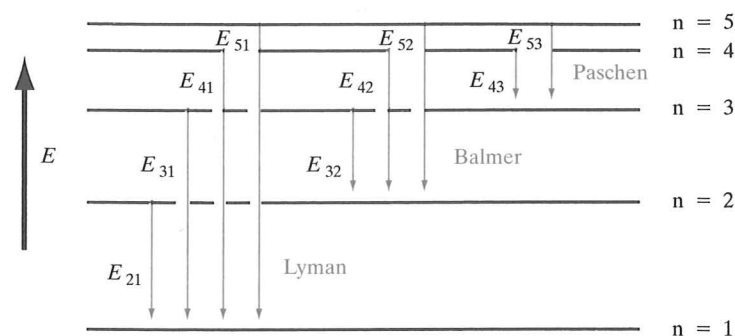


Figure 2-2
Some important lines in the emission spectrum of hydrogen.

Figure 2-3
Relationships
among photon en-
ergies in the hy-
drogen spectrum.

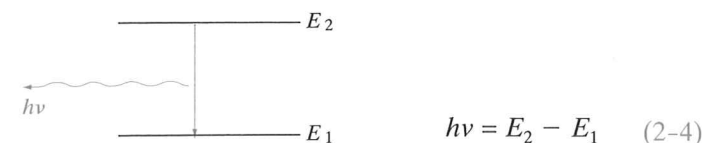


where R is a constant called the Rydberg constant ($R = 109,678 \text{ cm}^{-1}$). If the photon energies $h\nu$ are plotted for successive values of the integer n , we notice that each energy can be obtained by taking sums and differences of other photon energies in the spectrum (Fig. 2-3). For example, E_{42} in the Balmer series is the difference between E_{41} and E_{21} in the Lyman series. This relationship among the various series is called the *Ritz combination principle*. Naturally, these empirical observations stirred a great deal of interest in constructing a comprehensive theory for the origin of the photons given off by atoms.

2.3 THE BOHR MODEL

The results of emission spectra experiments led Niels Bohr to construct a model for the hydrogen atom, based on the mathematics of planetary systems. If the electron in the hydrogen atom has a series of planetary-type orbits available to it, it can be excited to an outer orbit and then can fall to any one of the inner orbits, giving off energy corresponding to one of the lines of Fig. 2-3. To develop the model, Bohr made several postulates:

1. Electrons exist in certain stable, circular orbits about the nucleus. This assumption implies that the orbiting electron does not give off radiation as classical electromagnetic theory would normally require of a charge experiencing angular acceleration; otherwise, the electron would not be stable in the orbit but would spiral into the nucleus as it lost energy by radiation.
2. The electron may shift to an orbit of higher or lower energy, thereby gaining or losing energy equal to the difference in the energy levels (by absorption or emission of a photon of energy $h\nu$).

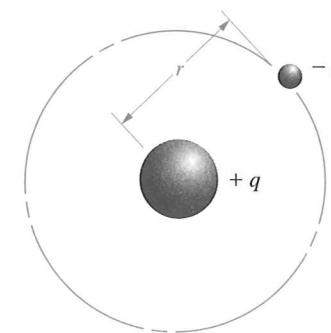


3. The angular momentum p_θ of the electron in an orbit is always an integral multiple of Planck's constant divided by 2π ($h/2\pi$ is often abbreviated \hbar for convenience). This assumption,

$$p_\theta = n\hbar, \quad n = 1, 2, 3, 4, \dots \quad (2-5)$$

is necessary to obtain the observed results of Fig. 2-3. Although Bohr proposed this *ad hoc* relationship simply to explain the data, one can see that this is equivalent to having an integer number of de Broglie wavelengths fit within the circumference of the electron orbit (Prob. 2.2). These were called *pilot waves*, guiding the motion of the electrons around the nucleus. The de Broglie wave concept provided the inspiration for the Schrödinger wave equation in quantum mechanics discussed in Section 2.4.

If we visualize the electron in a stable orbit of radius r about the proton of the hydrogen atom, we can equate the electrostatic force between the charges to the centripetal force:



$$-\frac{q^2}{Kr^2} = -\frac{mv^2}{r} \quad (2-6)$$

where $K = 4\pi\epsilon_0$ in MKS units, m is the mass of the electron, and v is its velocity. From assumption 3 we have

$$p_\theta = mvr = n\hbar \quad (2-7)$$

Since n takes on integral values, r should be denoted by r_n to indicate the n th orbit. Then Eq. (2-7) can be written

$$m^2 v^2 = \frac{n^2 \hbar^2}{r_n^2} \quad (2-8)$$

Substituting Eq. (2-8) in Eq. (2-6) we find that

$$\frac{q^2}{K r_n^2} = \frac{1}{m r_n} \approx \frac{n^2 \hbar^2}{r_n^2} \quad (2-9)$$

$$r_n = \frac{K^2 n^2 \hbar^2}{m q^2} \quad (2-10)$$

for the radius of the n th orbit of the electron. Now we must find the expression for the total energy of the electron in this orbit, so that we can calculate the energies involved in transitions between orbits.

From Eqs. (2-7) and (2-10) we have

$$v = \frac{n \hbar}{m r_n} \quad (2-11)$$

$$v = \frac{n \hbar q^2}{K n^2 \hbar^2} = \frac{q^2}{K n \hbar} \quad (2-12)$$

Therefore, the kinetic energy of the electron is

$$\text{K. E.} = \frac{1}{2} m v^2 = \frac{m q^4}{2 K^2 n^2 \hbar^2} \quad (2-13)$$

The potential energy is the product of the electrostatic force and the distance between the charges:

$$\text{P. E.} = -\frac{q^2}{K r_n} = -\frac{m q^4}{K^2 n^2 \hbar^2} \quad (2-14)$$

Thus the total energy of the electron in the n th orbit is

$$E_n = \text{K. E.} + \text{P. E.} = -\frac{m q^4}{2 K^2 n^2 \hbar^2} \quad (2-15)$$

The critical test of the model is whether energy differences between orbits correspond to the observed photon energies of the hydrogen spectrum. The transitions between orbits corresponding to the Lyman, Balmer, and Paschen series are illustrated in Fig. 2-4. The energy difference between orbits n_1 and n_2 is given by

$$E_{n_2} - E_{n_1} = \frac{m q^4}{2 K^2 \hbar^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2-16)$$

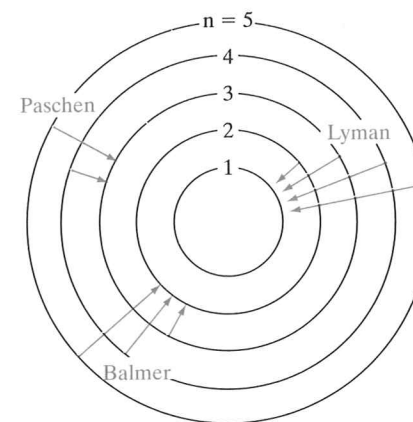


Figure 2-4
Electron orbits
and transitions in
the Bohr model
of the hydrogen
atom. Orbit spac-
ing is not drawn
to scale.

The frequency of light given off by a transition between these orbits is

$$\nu_{21} = \left[\frac{m q^4}{2 K^2 \hbar^2} \right] \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2-17)$$

The factor in brackets is essentially the Rydberg constant R times the speed of light c . A comparison of Eq. (2-17) with the experimental results summed up by Eq. (2-3) indicates that the Bohr theory provides a good model for electronic transitions within the hydrogen atom, as far as the early experimental evidence is concerned.

Whereas the Bohr model accurately describes the gross features of the hydrogen spectrum, it does not include many fine points. For example, experimental evidence indicates some splitting of levels in addition to the levels predicted by the theory. Also, difficulties arise in extending the model to atoms more complicated than hydrogen. Attempts were made to modify the Bohr model for more general cases, but it soon became obvious that a more comprehensive theory was needed. However, the partial success of the Bohr model was an important step toward the eventual development of the quantum theory. The concept that electrons are quantized in certain allowed energy levels, and the relationship of photon energy and transitions between levels, had been established firmly by the Bohr theory.

The principles of quantum mechanics were developed from two different points of view at about the same time (the late 1920s). One approach, developed by Heisenberg, utilizes the mathematics of matrices and is called *matrix mechanics*. Independently, Schrödinger developed an approach utilizing a wave equation, now called *wave mechanics*. These two mathematical formulations appear to be quite different. However, closer examination

reveals that beyond the formalism, the basic principles of the two approaches are the same. It is possible to show, for example, that the results of matrix mechanics reduce to those of wave mechanics after mathematical manipulation. We shall concentrate here on the wave mechanics approach, since solutions to a few simple problems can be obtained with it, involving less mathematical discussion.

2.4.1 Probability and the Uncertainty Principle

It is impossible to describe with absolute precision events involving individual particles on the atomic scale. Instead, we must speak of the average values (*expectation values*) of position, momentum, and energy of a particle such as an electron. It is important to note, however, that the uncertainties revealed in quantum calculations are not based on some shortcoming of the theory. In fact, a major strength of the theory is that it describes the probabilistic nature of events involving atoms and electrons. The fact is that such quantities as the position and momentum of an electron *do not exist* apart from a particular uncertainty. The magnitude of this inherent uncertainty is described by the *Heisenberg uncertainty principle*:¹

In any measurement of the position and momentum of a particle, the uncertainties in the two measured quantities will be related by

$$(\Delta x)(\Delta p_x) \geq \hbar/2 \quad (2-18)$$

Similarly, the uncertainties in an energy measurement will be related to the uncertainty in the time at which the measurement was made by

$$(\Delta E)(\Delta t) \geq \hbar/2 \quad (2-19)$$

These limitations indicate that simultaneous measurement of position and momentum or of energy and time are inherently inaccurate to some degree. Of course, Planck's constant h is a rather small number (6.63×10^{-34} J-s), and we are not concerned with this inaccuracy in the measurement of x and p_x for a truck, for example. On the other hand, measurements of the position of an electron and its speed are seriously limited by the uncertainty principle.

One implication of the uncertainty principle is that we cannot properly speak of *the* position of an electron, for example, but must look for the "probability" of finding an electron at a certain position. Thus one of the important results of quantum mechanics is that a *probability density function* can be

¹This is often called the *principle of indeterminacy*.

obtained for a particle in a certain environment, and this function can be used to find the expectation value of important quantities such as position, momentum, and energy. We are familiar with the methods for calculating discrete (single-valued) probabilities from common experience. For example, it is clear that the probability of drawing a particular card out of a random deck is $1/52$, and the probability that a tossed coin will come up heads is $1/2$. The techniques for making predictions when the probability varies are less familiar, however. In such cases it is common to define a probability of finding a particle within a certain volume. Given a probability density function $P(x)$ for a one-dimensional problem, the probability of finding the particle in a range from x to $x + dx$ is $P(x)dx$. Since the particle will be *somewhere*, this definition implies that

$$\int_{-\infty}^{\infty} P(x)dx = 1 \quad (2-20)$$

if the function $P(x)$ is properly chosen. Equation (2-20) is implied by stating that the function $P(x)$ is *normalized* (i.e., the integral equals unity).

To find the average value of a function of x , we need only multiply the value of that function in each increment dx by the probability of finding the particle in that dx and sum over all x . Thus the average value of $f(x)$ is

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x)P(x)dx \quad (2-21a)$$

If the probability density function is not normalized, this equation should be written

$$\langle f(x) \rangle = \frac{\int_{-\infty}^{\infty} f(x)P(x)dx}{\int_{-\infty}^{\infty} P(x)dx} \quad (2-21b)$$

2.4.2 The Schrödinger Wave Equation

There are several ways to develop the wave equation by applying quantum concepts to various classical equations of mechanics. One of the simplest approaches is to consider a few basic postulates, develop the wave equation from them, and rely on the accuracy of the results to serve as a justification of the postulates. In more advanced texts these assumptions are dealt with in more convincing detail.

Basic Postulates

1. Each particle in a physical system is described by a wave function $\Psi(x, y, z, t)$. This function and its space derivative ($\partial\Psi/\partial x + \partial\Psi/\partial y + \partial\Psi/\partial z$) are continuous, finite, and single valued.

2. In dealing with classical quantities such as energy E and momentum p , we must relate these quantities with abstract quantum mechanical operators defined in the following way:

Classical variable	Quantum operator
x	x
$f(x)$	$f(x)$
$p(x)$	$\frac{\hbar}{j} \frac{\partial}{\partial x}$
E	$-\frac{\hbar}{j} \frac{\partial}{\partial t}$

and similarly for the other two directions.

3. The probability of finding a particle with wave function Ψ in the volume $dx dy dz$ is $\Psi^* \Psi dx dy dz$.² The product $\Psi^* \Psi$ is normalized according to Eq. (2-20) so that

$$\int_{-\infty}^{\infty} \Psi^* \Psi dx dy dz = 1$$

and the average value $\langle Q \rangle$ of any variable Q is calculated from the wave function by using the operator form Q_{op} defined in postulate 2:

$$\langle Q \rangle = \int_{-\infty}^{\infty} \Psi^* Q_{op} \Psi dx dy dz$$

Once we find the wave function Ψ for a particle, we can calculate its average position, energy, and momentum, within the limits of the uncertainty principle. Thus, a major part of the effort in quantum calculations involves solving for Ψ within the conditions imposed by a particular physical system. We notice from assumption 3 that the probability density function is $\Psi^* \Psi$, or $|\Psi|^2$.

The classical equation for the energy of a particle can be written:

$$\text{Kinetic energy} + \text{potential energy} = \text{total energy} \quad (2-22)$$

$$\frac{1}{2m} p^2 + V = E$$

² Ψ^* is the complex conjugate of Ψ , obtained by reversing the sign on each j . Thus, $(e^{jx})^* = e^{-jx}$.

In quantum mechanics we use the operator form for these variables (postulate 2); the operators are allowed to operate on the wave function Ψ . For a one-dimensional problem Eq. (2-22) becomes³

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x) \Psi(x, t) = -\frac{\hbar}{j} \frac{\partial \Psi(x, t)}{\partial t} \quad (2-23)$$

which is the Schrödinger wave equation. In three dimensions the equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi = -\frac{\hbar}{j} \frac{\partial \Psi}{\partial t} \quad (2-24)$$

where $\nabla^2 \Psi$ is

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

The wave function Ψ in Eqs. (2-23) and (2-24) includes both space and time dependencies. It is common to calculate these dependencies separately and combine them later. Furthermore, many problems are time independent, and only the space variables are necessary. Thus we try to solve the wave equation by breaking it into two equations by the technique of separation of variables. Let $\Psi(x, t)$ be represented by the product $\psi(x)\phi(t)$. Using this product in Eq. (2-23) we obtain

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} \phi(t) + V(x) \psi(x) \phi(t) = -\frac{\hbar}{j} \psi(x) \frac{\partial \phi(t)}{\partial t} \quad (2-25)$$

Now the variables can be separated to obtain the time-dependent equation in one dimension,

$$\frac{d\phi(t)}{dt} + \frac{jE}{\hbar} \phi(t) = 0 \quad (2-26)$$

and the time-independent equation,

$$\frac{d^2 \psi(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad (2-27)$$

We can show that the separation constant E corresponds to the energy of the particle when particular solutions are obtained, such that a wave function ψ_n (eigenfunction) corresponds to a particle energy E_n (eigenenergy).

These equations are the basis of wave mechanics. From them we can determine the wave functions for particles in various simple systems. For calculations involving electrons, the potential term $V(x)$ usually results from an electrostatic or magnetic field.

³The operational interpretation of $(\partial/\partial x)^2$ is the second-derivative form $\partial^2/\partial x^2$; the square of j is -1 .

2.4.3 Potential Well Problem

It is quite difficult to find solutions to the Schrödinger equation for most realistic potential fields. One can solve the problem with some effort for the hydrogen atom, for example, but solutions for more complicated atoms are hard to obtain. There are several important problems, however, which illustrate the theory without complicated manipulation. The simplest problem is the potential energy well with infinite boundaries. Let us assume a particle is trapped in a potential well with $V(x)$ zero except at the boundaries $x = 0$ and L , where it is infinitely large (Fig. 2-5a):

$$\begin{aligned} V(x) &= 0, & 0 < x < L \\ V(x) &= \infty, & x = 0, L \end{aligned} \quad (2-28)$$

Inside the well we set $V(x) = 0$ in Eq. (2-27):

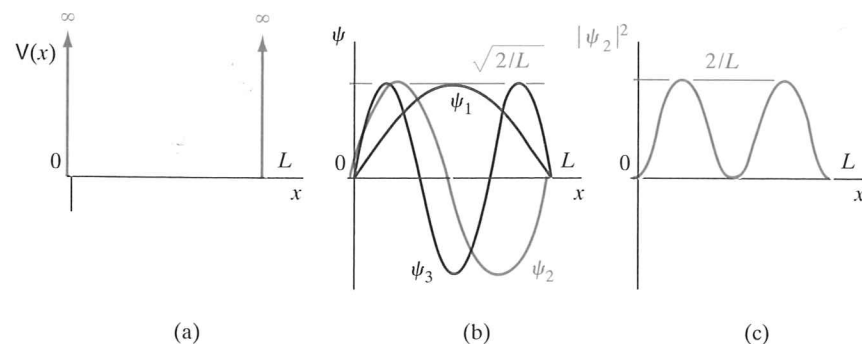
$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} E\psi(x) = 0, \quad 0 < x < L \quad (2-29)$$

This is the wave equation for a free particle; it applies to the potential well problem in the region with no potential $V(x)$.

Possible solutions to Eq. (2-29) are $\sin kx$ and $\cos kx$, where k is $\sqrt{2mE}/\hbar$. In choosing a solution, however, we must examine the boundary conditions. The only allowable value of ψ at the walls is zero. Otherwise, there would be a nonzero $|\psi|^2$ outside the potential well, which is impossible because a particle cannot penetrate an infinite barrier. Therefore, we must choose only the sine solution and define k such that $\sin kx$ goes to zero at $x = L$:

$$\psi = A \sin kx, \quad k = \frac{\sqrt{2mE}}{\hbar} \quad (2-30)$$

Figure 2-5
The problem of a particle in a potential well: (a) potential energy diagram; (b) wave functions in the first three quantum states; (c) probability density distribution for the second state.



The constant A is the amplitude of the wave function and will be evaluated from the normalization condition (postulate 3). If ψ is to be zero at $x = L$, then k must be some integral multiple of π/L :

$$k = \frac{n\pi}{L}, \quad n = 1, 2, 3, \dots \quad (2-31)$$

From Eqs. (2-30) and (2-31) we can solve for the total energy E_n for each value of the integer n :

$$\frac{\sqrt{2mE_n}}{\hbar} = \frac{n\pi}{L} \quad (2-32)$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad (2-33)$$

Thus for each allowable value of n the particle energy is described by Eq. (2-33). We notice that the *energy is quantized*. Only certain values of energy are allowed. The integer n is called a *quantum number*; the particular wave function ψ_n and corresponding energy state E_n describe the *quantum state* of the particle.

The quantized energy levels described by Eq. (2-33) appear in a variety of small-geometry structures encountered in semiconductor devices. We shall return to this potential well problem (often called the “particle in a box” problem) in later discussions.

The constant A is found from postulate 3:

$$\int_{-\infty}^{\infty} \psi^* \psi dx = \int_0^L A^2 \left(\sin \frac{n\pi}{L} x \right)^2 dx = A^2 \frac{L}{2} \quad (2-34)$$

Setting Eq. (2-34) equal to unity we obtain

$$A = \sqrt{\frac{2}{L}}, \quad \psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \quad (2-35)$$

The first three wave functions ψ_1, ψ_2, ψ_3 are sketched in Fig. 2-5b. The probability density function $\psi^* \psi$, or $|\psi|^2$, is sketched for ψ_2 in Fig. 2-5c.

Given a plane wave $\psi = A \exp(jk_x x)$, what is the expectation value for p_x , the x -component of momentum?

EXAMPLE 2-1

SOLUTION

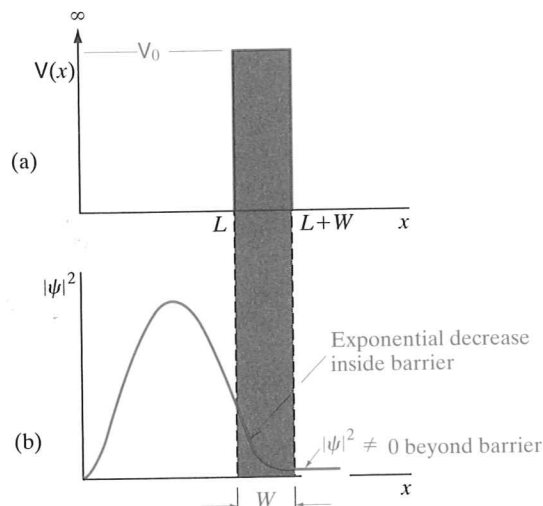
$$\langle p_x \rangle = \frac{\int_{-\infty}^{\infty} A^* e^{-jk_x x} \left(\frac{\hbar}{j} \frac{\partial}{\partial x} \right) A e^{jk_x x} dx}{\int_{-\infty}^{\infty} |A|^2 e^{-jk_x x} e^{jk_x x} dx} = (\hbar k_x) \text{ after normalization}$$

If we try to evaluate these integrals directly, we run into the problem that both numerator and denominator tend to infinity, because an *ideal* plane wave is strictly not a normalizable wave function. The trick to use is to choose the limits of integration from, say, $-L/2$ to $+L/2$ in a region of length L . The factor L cancels out in the numerator and denominator. Then we can consider L approaches infinity. For wave functions that are normalizable, such a mathematical “trick” does not have to be used.

2.4.4 Tunneling

The wave functions are relatively easy to obtain for the potential well with infinite walls, since the boundary conditions force ψ to zero at the walls. A slight modification of this problem illustrates a principle that is very important in some solid state devices—the quantum mechanical *tunneling* of an electron through a barrier of finite height and thickness. Let us consider the potential barrier of Fig. 2-6. If the barrier is not infinite, the boundary conditions do not force ψ to zero at the barrier. Instead, we must use the condition that ψ and its slope $d\psi/dx$ are continuous at each boundary of the barrier (postulate 1). Thus ψ must have a nonzero value within the barrier and also on the other side. Since ψ has a value to the right of the barrier, $\psi^*\psi$ exists there also, implying that there is some probability of finding the particle beyond the barrier. We notice that the particle does not go over the barrier; its total energy is assumed to be less than the barrier height V_0 . The mechanism by which the particle “penetrates” the barrier is called tunneling. However, no classical analog, including classical descriptions of tunneling through barriers, is appropriate for this effect. Quantum mechanical

Figure 2-6
Quantum mechanical tunneling:
(a) potential barrier of height V_0 and thickness W ; (b) probability density for an electron with energy $E < V_0$, indicating a non-zero value of the wave function beyond the barrier.



tunneling is intimately bound to the uncertainty principle. If the barrier is sufficiently thin, we cannot say with certainty that the particle exists only on one side. However, the wave function amplitude for the particle is reduced by the barrier as Fig. 2-6 indicates, so that by making the thickness W greater, we can reduce ψ on the right-hand side to the point that negligible tunneling occurs. Tunneling is important only over very small dimensions, but it can be of great importance in the conduction of electrons in solids, as we shall see in Chapters 5, 6, and 10.

A novel electronic device called the resonant tunneling diode has been developed. This device operates by tunneling electrons through “particle in a potential well” energy levels of the type described in Section 2.4.3.

The Schrödinger equation describes accurately the interactions of particles with potential fields, such as electrons within atoms. Indeed, the modern understanding of atomic theory (the modern atomic *models*) comes from the wave equation and from Heisenberg’s matrix mechanics. It should be pointed out, however, that the problem of solving the Schrödinger equation directly for complicated atoms is extremely difficult. In fact, only the hydrogen atom is generally solved directly; atoms of atomic number greater than one are usually handled by techniques involving approximations. Many atoms such as the alkali metals (Li, Na, etc.), which have a neutral core with a single electron in an outer orbit, can be treated by a rather simple extension of the hydrogen atom results. The hydrogen atom solution is also important in identifying the basic selection rules for describing allowed electron energy levels. These quantum mechanical results must coincide with the experimental spectra, and we expect the energy levels to include those predicted by the Bohr model. Without actually working through the mathematics for the hydrogen atom, in this section we shall investigate the energy level schemes dictated by the wave equation.

2.5 ATOMIC STRUCTURE AND THE PERIODIC TABLE

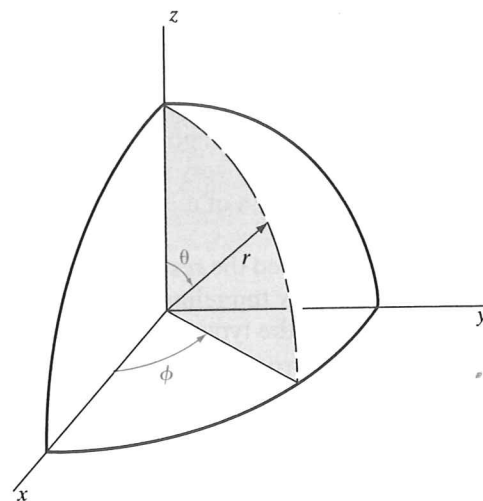
2.5.1 The Hydrogen Atom

Finding the wave functions for the hydrogen atom requires a solution of the Schrödinger equation in three dimensions for a coulombic potential field. Since the problem is spherically symmetric, the spherical coordinate system is used in the calculation (Fig. 2-7). The term $V(x, y, z)$ in Eq. (2-24) must be replaced by $V(r, \theta, \phi)$, representing the Coulomb potential which the electron experiences in the vicinity of the proton. The Coulomb potential varies only with r in spherical coordinates

$$V(r, \theta, \phi) = V(r) = -(4\pi\epsilon_0)^{-1} \frac{q^2}{r} \quad (2-36)$$

as in Eq. (2-14).

Figure 2-7
The spherical co-
ordinate system.



When the separation of variables is made, the time-independent equation can be written as

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (2-37)$$

Thus the wave functions are found in three parts. Separate solutions must be obtained for the r -dependent equation, the θ -dependent equation, and the ϕ -dependent equation. After these three equations are solved, the total wave function ψ is obtained from the product.

As in the simple potential well problem, each of the three hydrogen atom equations gives a solution which is quantized. Thus we would expect a quantum number to be associated with *each* of the three parts of the wave equation. As an illustration, the ϕ -dependent equation obtained after separation of variables is

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0 \quad (2-38)$$

where m is a quantum number. The solution to this equation is

$$\Phi_m(\phi) = Ae^{jm\phi} \quad (2-39)$$

where A can be evaluated by the normalization condition, as before:

$$\int_0^{2\pi} \Phi_m^*(\phi)\Phi_m(\phi)d\phi = 1 \quad (2-40)$$

$$A^2 \int_0^{2\pi} e^{-jm\phi} e^{jm\phi} d\phi = A^2 \int_0^{2\pi} d\phi = 2\pi A^2 \quad (2-41)$$

Thus the value of A is

$$A = \frac{1}{\sqrt{2\pi}} \quad (2-42)$$

and the ϕ -dependent wave function is

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{jm\phi} \quad (2-43)$$

Since values of ϕ repeat every 2π radians, Φ should repeat also. This occurs if m is an integer, including negative integers and zero. Thus the wave functions for the ϕ -dependent equation are quantized with the following selection rule for the quantum numbers:

$$m = \dots, -3, -2, -1, 0, +1, +2, +3, \dots \quad (2-44)$$

By similar treatments, the functions $R(r)$ and $\Theta(\theta)$ can be obtained, each being quantized by its own selection rule. For the r -dependent equation, the quantum number n can be any positive integer (not zero), and for the θ -dependent equation the quantum number l can be zero or a positive integer. However, there are interrelationships among the equations which restrict the various quantum numbers used with a single wave function ψ_{nlm} :

$$\psi_{nlm}(r, \theta, \phi) = R_n(r)\Theta_l(\theta)\Phi_m(\phi) \quad (2-45)$$

These restrictions are summarized as follows:

$$n = 1, 2, 3, \dots \quad (2-46a)$$

$$l = 0, 1, 2, \dots, (n-1) \quad (2-46b)$$

$$m = -l, \dots, -2, -1, 0, +1, +2, \dots, +l \quad (2-46c)$$

In addition to the three quantum numbers arising from the three parts of the wave equation, there is an important quantization condition on the "spin" of the electron. Investigations of electron spin employ the theory of relativity as well as quantum mechanics; therefore, we shall simply state that the intrinsic angular momentum s of an electron with ψ_{nlm} specified is

$$s = \pm \frac{\hbar}{2} \quad (2-47)$$

That is, in units of \hbar , the electron has a spin of $\frac{1}{2}$, and the angular momentum produced by this spin is positive or negative depending on whether the electron is "spin up" or "spin down." The important point for our discussion is that each allowed energy state of the electron in the hydrogen atom is uniquely described by four quantum numbers: n, l, m and s .⁴

⁴In many texts, the numbers we have called m and s are referred to as m_l and m_s , respectively.

Using these four quantum numbers, we can identify the various states which the electron can occupy in a hydrogen atom. The number n , called the *principal* quantum number, specifies the “orbit” of the electron in Bohr terminology. Of course, the concept of orbit is replaced by probability density functions in quantum mechanical calculations. It is common to refer to states with a given principal quantum number as belonging to a *shell* rather than an orbit.

There is considerable fine structure in the energy levels about the Bohr orbits, due to the dictates of the other three quantum conditions. For example, an electron with $n = 1$ (the first Bohr orbit) can have only $l = 0$ and $m = 0$ according to Eq. (2-46), but there are two spin states allowed from Eq. (2-47). For $n = 2$, l can be 0 or 1, and m can be $-1, 0$, or $+1$. The various allowed combinations of quantum numbers appear in the first four columns of Table 2-1. From these combinations it is apparent that the electron in a hydrogen atom can occupy any one of a large number of excited states in addition to the lowest (*ground*) state ψ_{100} . Energy differences between the various states properly account for the observed lines in the hydrogen spectrum.

2.5.2 The Periodic Table

The quantum numbers discussed in Section 2.5.1 arise from the solutions to the hydrogen atom problem. Thus the energies obtainable from the wave functions are unique to the hydrogen atom and cannot be extended to more complicated atoms without appropriate alterations. However, the quantum number selection rules are valid for more complicated structures, and we can use these rules to gain an understanding of the arrangement of atoms in the periodic table of chemical elements. Without these selection rules, it is difficult to understand why only two electrons fit into the first Bohr orbit of an atom, whereas eight electrons are allowed in the second orbit. After even the brief discussion of quantum numbers given above, we should be able to answer these questions with more insight.

Before discussing the periodic table, we must be aware of an important principle of quantum theory, the *Pauli exclusion principle*. This rule states that no two electrons in an interacting system⁵ can have the same set of quantum numbers n, l, m, s . In other words, only two electrons can have the same three quantum numbers n, l, m , and those two must have opposite spin. The importance of this principle cannot be overemphasized; it is basic to the electronic structure of all atoms in the periodic table. One implication of this principle is that by listing the various combinations of quantum numbers, we can determine into which shell each electron of a complicated atom fits, and how many electrons are allowed per shell. The quantum states summarized in Table 2-1 can be

⁵An interacting system is a system in which electron wave functions overlap—in this case, an atom with two or more electrons.

Table 2-1 Quantum numbers to $n = 3$ and allowable states for the electron in a hydrogen atom: The first four columns show the various combinations of quantum numbers allowed by the selection rules of Eq. (2-46); the last two columns indicate the number of allowed states (combinations of n, l, m , and s) for each l (subshell) and n (shell, or Bohr orbit).

n	l	m	s/ħ	Allowable states in subshell	Allowable states in complete shell	
1	0	0	$\pm \frac{1}{2}$	2	2	
2	0	0	$\pm \frac{1}{2}$	2	8	
	1	-1	$\pm \frac{1}{2}$	6		
		0	$\pm \frac{1}{2}$			
1		$\pm \frac{1}{2}$				
3	0	0	$\pm \frac{1}{2}$	2	18	
	1	-1	$\pm \frac{1}{2}$	6		
		0	$\pm \frac{1}{2}$			
		1	$\pm \frac{1}{2}$			
	2	-2	$\pm \frac{1}{2}$	10		
		-1	$\pm \frac{1}{2}$			
		0	$\pm \frac{1}{2}$			
		1	$\pm \frac{1}{2}$			
		2	$\pm \frac{1}{2}$			
		$\pm \frac{1}{2}$				

used to indicate the electronic configurations for atoms in the lowest energy state.

In the first electronic shell ($n = 1$), l can be only zero since the maximum value of l is always $n - 1$. Similarly, m can be only zero since m runs from the negative value of l to the positive value of l . Two electrons with opposite spin can fit in this ψ_{100} state; therefore, the first shell can have at most two electrons. For the helium atom (atomic number $Z = 2$) in the ground state, both electrons will be in the first Bohr orbit ($n = 1$), both will have $l = 0$ and $m = 0$, and they will have opposite spin. Of course, one or both of the He atom electrons can be excited to one of the higher energy states of Table 2-1 and subsequently relax to the ground state, giving off a photon characteristic of the He spectrum.

As Table 2-1 indicates, there can be two electrons in the $l = 0$ subshell, six electrons when $l = 1$, and ten electrons for $l = 2$. The electronic configurations of various atoms in the periodic table can be deduced from this list of allowed states. The ground state electron structures for a number of atoms are listed in Table 2-2. There is a simple shorthand notation for

Table 2-2 Electronic configurations for atoms in the ground state.

		$n = 1$ $l = 0$	2 0 1	3 0 1 2	4 0 1
Atomic number (Z)	Ele- ment	1s	2s 2p	3s 3p 3d	4s 4p
		Number of electrons			
1	H	1			$1s^1$
2	He	2			$1s^2$
3	Li	helium core, 2 electrons	1		$1s^2 2s^1$
4	Be		2		$1s^2 2s^2$
5	B		2 1		$1s^2 2s^2 2p^1$
6	C		2 2		$1s^2 2s^2 2p^2$
7	N		2 3		$1s^2 2s^2 2p^3$
8	O		2 4		$1s^2 2s^2 2p^4$
9	F		2 5		$1s^2 2s^2 2p^5$
10	Ne		2 6		$1s^2 2s^2 2p^6$
11	Na	neon core, 10 electrons	1		[Ne] $3s^1$
12	Mg		2		$3s^2$
13	Al		2 1		$3s^2 3p^1$
14	Si		2 2		$3s^2 3p^2$
15	P		2 3		$3s^2 3p^3$
16	S		2 4		$3s^2 3p^4$
17	Cl		2 5		$3s^2 3p^5$
18	Ar		2 6		$3s^2 3p^6$
19	K	argon core, 18 electrons		1	[Ar] $4s^1$
20	Ca			2	$4s^2$
21	Sc			1	$3d^1 4s^2$
22	Ti			2	$3d^2 4s^2$
23	V			3	$3d^3 4s^2$
24	Cr			5	$3d^5 4s^1$
25	Mn			5	$3d^5 4s^2$
26	Fe			6	$3d^6 4s^2$
27	Co			7	$3d^7 4s^2$
28	Ni			8	$3d^8 4s^2$
29	Cu			10	$3d^{10} 4s^1$
30	Zn			10	$3d^{10} 4s^2$
31	Ga			10	$3d^{10} 4s^2 4p^1$
32	Ge			10	$3d^{10} 4s^2 4p^2$
33	As			10	$3d^{10} 4s^2 4p^3$
34	Se			10	$3d^{10} 4s^2 4p^4$
35	Br			10	$3d^{10} 4s^2 4p^5$
36	Kr			10	$3d^{10} 4s^2 4p^6$

electronic structures which is commonly used instead of such a table. The only new convention to remember in this notation is the naming of the *l* values:

$l = 0, 1, 2, 3, 4, \dots$
 s, p, d, f, g, \dots

This convention was created by early spectroscopists who referred to the first four spectral groups as sharp, principal, diffuse, and fundamental. Alphabetical order is used beyond *f*. With this convention for *l*, we can write an electron state as follows:

6 electrons in the 3*p* subshell
 $(n = 3) \quad 3p^6 \quad (l = 1)$

For example, the total electronic configuration for Si (*Z* = 14) in the ground state is

$1s^2 2s^2 2p^6 3s^2 3p^2$

We notice that Si has a closed Ne configuration (see Table 2-2) plus four electrons in an outer *n* = 3 orbit ($3s^2 3p^2$). These are the four valence electrons of Si; two valence electrons are in an *s* state and two are in a *p* state. The Si electronic configuration can be written [Ne] $3s^2 3p^2$ for convenience, since the Ne configuration $1s^2 2s^2 2p^6$ forms a closed shell (typical of the inert elements).

Figure 2-8a shows the orbital model of a Si atom, which has a nucleus consisting of 14 protons (with a charge of +14) and neutrons, 10 core electrons in shells *n* = 1 and 2, and 4 valence electrons in the 3*s* and 3*p* subshells. Figure 2-8b shows the energy levels of the various electrons in the coulombic potential well of the nucleus. Since unlike charges attract each other, there is an attractive potential between the negatively charged electrons and the positively charged nucleus. As indicated in Eq. (2-36), a Coulomb potential varies as 1/*r* as a function of distance from the charge, in this case the Si nucleus. The potential energy gradually goes to zero when we approach infinity. We end up getting “particle-in-a-box” states for these electrons in this potential well, as discussed in Section 2.4.3 and Eq. (2-33). Of course, in this case the shape of the potential well is not rectangular, as shown in Fig. 2-5a, but coulombic, as shown in Fig. 2-8b. Therefore, the energy levels have a form closer to those of the H atom as shown in Eq. (2-15), rather than in Eq. (2-33).

If we solve the Schrödinger equation for the Si atom as we did in Section 2.5.1 for the H atom, we can get the radial and angular dependence of the wavefunctions or “orbitals” of the electrons. Let us focus on the valence shell, *n* = 3, where we have two 3*s* and two 3*p* electrons. It turns out that the 3*s* orbital is spherically symmetric with no angular dependence, and is positive everywhere. It can hold 2 electrons with opposite spin according to the Pauli

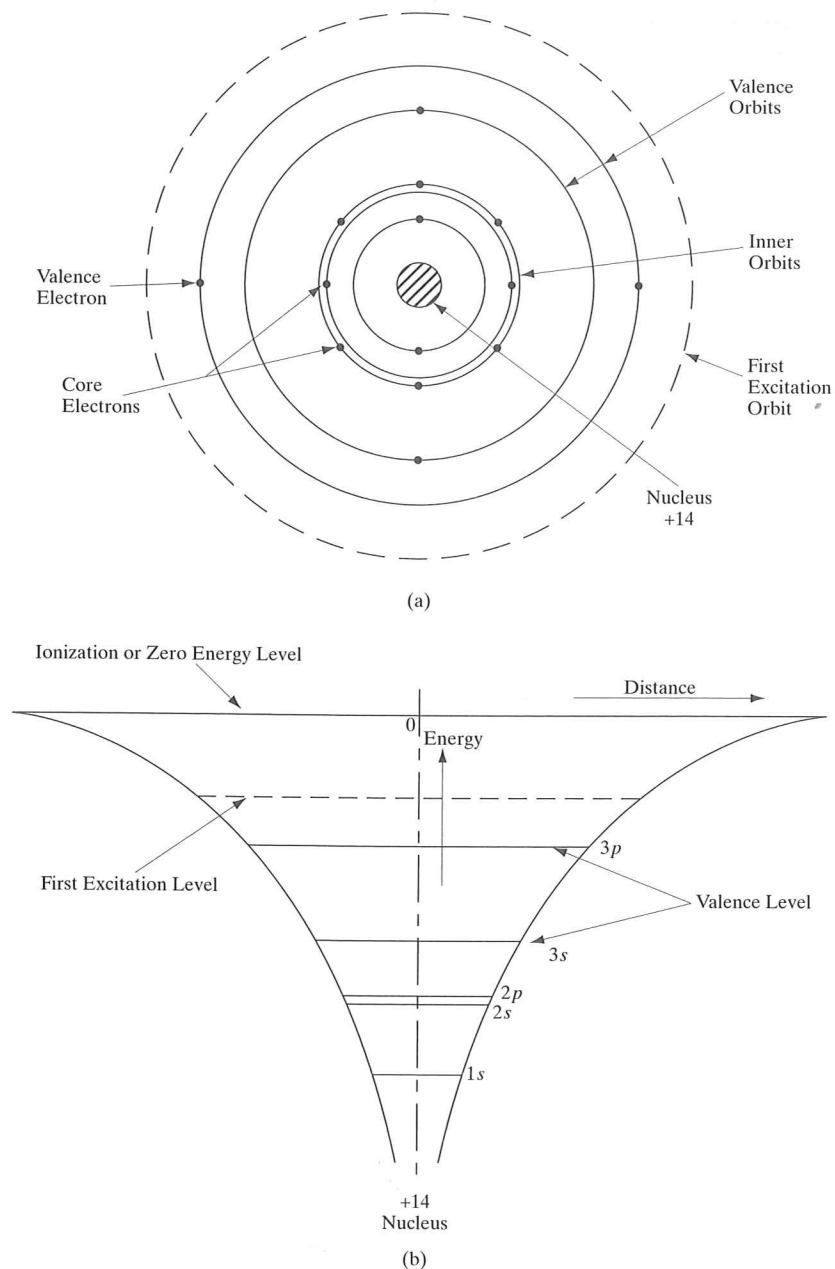


Figure 2-8

Electronic structure and energy levels in a Si atom: (a) The orbital model of a Si atom showing the 10 core electrons ($n = 1$ and 2), and the 4 valence electrons ($n = 3$); (b) energy levels in the coulombic potential of the nucleus are also shown schematically.

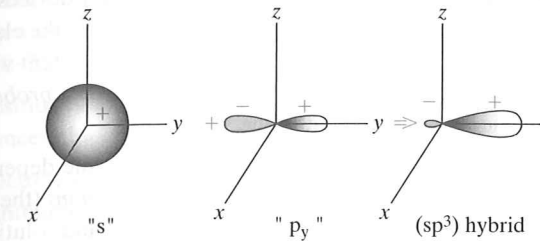


Figure 2-9

Orbitals in a Si atom: The spherically symmetric "s" type wave functions or orbitals are positive everywhere, while the three mutually perpendicular "p" type orbitals (p_x , p_y , p_z) are dumbbell shaped and have a positive lobe and a negative lobe. The four sp^3 "hybridized" orbitals, only one of which is shown here, point symmetrically in space and lead to the diamond lattice in Si.

principle. There are $3p$ -orbitals which are mutually perpendicular. These are shaped like dumbbells with a positive lobe and a negative lobe (Fig. 2-9). The $3p$ subshell can hold up to 6 electrons, but in the case of Si has only 2. Interestingly, in a Si crystal when we bring individual atoms very close together, the s - and p -orbitals overlap so much that they lose their distinct character, and lead to four mixed sp^3 orbitals. The negative part of the p orbital cancels the s -type wavefunction, while the positive part enhances it, thereby leading to a "directed" bond in space. As shown in Fig. 2-9, these *linear combinations of atomic orbitals (LCAO)* or "hybridized" sp^3 orbitals point symmetrically in space along the 4 tetragonal directions (see Fig. 1-9). In Chapter 3 we shall see that these "directed" chemical bonds are responsible for the tetragonal diamond or zinc blende lattice structure in most semiconductors. They are also very important in the understanding of energy bands, and in the conduction of charges in these semiconductors.

The column IV semiconductor Ge ($Z = 32$) has an electronic structure similar to Si, except that the four valence electrons are outside a closed $n = 3$ shell. Thus the Ge configuration is $[\text{Ar}] 3d^{10}4s^24p^2$. There are several cases in Table 2-2 that do not follow the most straightforward choice of quantum numbers. For example, we notice that in K ($Z = 19$) and Ca ($Z = 20$) the $4s$ state is filled before the $3d$ state; in Cr ($Z = 24$) and Cu ($Z = 29$) there is a transfer of an electron back to the $3d$ state. These exceptions, required by minimum energy considerations, are discussed more fully in most atomic physics texts.

2.1 In classical physics, *matter* (including electrons) was described as *particles* by Newtonian mechanics, while *light* was described as *waves*, consistent with phenomena such as interference and diffraction of light.

2.2 Phenomena such as blackbody radiation and the photoelectric effect forced Planck and Einstein to introduce a *particle* aspect to light (photons). Analysis of atomic spectra then led Bohr and de Broglie to analogously introduce a *wave aspect* to *subatomic particles* such as electrons. This led to a *wave-particle duality* and a *quantum mechanical* description of nature by Heisenberg and Schrödinger.

SUMMARY

- 2.3 To understand how electrons move in semiconductor devices or interact with light, we need to determine a *complex wave function* of the electron. The wave function has to be mathematically well behaved, consistent with the interpretation that the *wave function magnitude squared is the probability density* of finding the electron in space and time.
- 2.4 We get the wave function by solving Schrödinger's time-dependent partial differential equation. The application of *boundary conditions* (the potential energy profile) allows certain (proper) *eigenfunctions* as valid solutions, with corresponding *eigenenergies*, determined by *allowed quantum numbers*. Results of physical measurements are *no longer deterministic* (as in classical mechanics), but *probabilistic*, with an *expectation* value given by an average using the wave function of appropriate quantum mechanical *operators* corresponding to physical quantities.
- 2.5 Application of these principles to the simplest atom (H) introduces four quantum numbers— n , l , m , and s , which are subject to appropriate quantum mechanical rules. Extrapolating these ideas to more complicated atoms such as Si leads to the idea of electronic structure and the *periodic table*, if we apply the *Pauli exclusion principle* that one can have a maximum of one electron for one set of these quantum numbers.

PROBLEMS

- 2.1 (a) Sketch a simple vacuum tube device and the associated circuitry for measuring E_m in the photoelectric effect experiment. The electrodes can be placed in a sealed glass envelope.
- (b) Sketch the photocurrent I vs. retarding voltage V that you would expect to measure for a given electrode material and configuration. Make the sketch for several intensities of light at a given wavelength.
- (c) The work function of platinum is 4.09 eV. What retarding potential will be required to reduce the photocurrent to zero in a photoelectric experiment with Pt electrodes if the wavelength of incident light is 2440 Å? Remember that an energy of $q\Phi$ is lost by each electron in escaping the surface.
- 2.2 Show that the third Bohr postulate, Eq. (2-5), is equivalent to an integer number of de Broglie waves fitting within the circumference of a Bohr circular orbit.
- 2.3 (a) Show that the various lines in the hydrogen spectrum can be expressed in angstroms as

$$\lambda(\text{\AA}) = \frac{911n_1^2n^2}{n^2 - n_1^2}$$

where $n_1 = 1$ for the Lyman series, 2 for the Balmer series, and 3 for the Paschen series. The integer n is larger than n_1 .

- (b) Calculate λ for the Lyman series to $n = 5$, the Balmer series to $n = 7$, and the Paschen series to $n = 10$. Plot the results as in Fig. 2-2. What are the wavelength limits for each of the three series?

- 2.4 Show that the calculated Bohr expression for frequency of emitted light in the hydrogen spectrum, Eq. (2-17), corresponds to the experimental expressions, Eq. (2-3).
- 2.5 (a) The position of an electron is determined to within 1 Å. What is the minimum uncertainty in its momentum?
- (b) An electron's energy is measured with an uncertainty of 1 eV. What is the minimum uncertainty in the time over which the measurement was made?
- 2.6 What is the de Broglie wavelength (in Å) of an electron at 100 eV? What is the wavelength for electrons at 12 keV, which is typical of electron microscopes? Comparing this to visible light, comment on the advantages of electron microscopes.
- 2.7 A sample of radioactive material undergoes decay such that the number of atoms $N(t)$ remaining in the unstable state at time t is related to the number N_0 at $t = 0$ by the relation $N(t) = N_0 \exp(-t/\tau)$. Show that τ is the average lifetime $\langle t \rangle$ of an atom in the unstable state before it spontaneously decays. Equation (2-21b) can be used with t substituted for x .
- 2.8 We define a potential well having energies V as a function of position x , as follows: $V = \infty$ for $x = -0.5$ nm to 0; $V = 0$ eV for $x = 0$ to 5 nm; $V = 10$ eV for $x = 5$ to 6 nm, and $V = 0$ for $x > 6$ nm and $x < -0.5$ nm. We put an electron with energy 7 eV in the region x , between 0 and 5 nm. What is the probability of finding the electron at $x < 0$ nm? Is the probability of finding the electron at $x > 6$ nm zero or nonzero? What is this probability for $x > 6$ nm if the electron was described by classical mechanics and not quantum mechanics?
- 2.9 An electron is described by a plane-wave wave function $\psi(x,t) = Ae^{i(10x+3y-4t)}$. Calculate the expectation value of a function defined as $\{4p_x^2 + 2p_z^3 + 7E/m\}$, where m is the mass of the electron, p_x and p_z are the x and z components of momentum, and E is energy. (Give values in terms of the Planck constant.)
- 2.10 A particle is trapped in the ground state (lowest energy level) of a potential well of width L . To understand how the particle is localized, a common measure is the standard deviation Δx defined by $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$, where $\langle x^2 \rangle$ and $\langle x \rangle$ are the expectation values of x^2 and x , respectively. Find the uncertainty Δx in the position of the particle in terms of length L and estimate the minimum uncertainty in the momentum of the particle, using the Heisenberg uncertainty principle in terms of L and the Planck's constant h . Note: $\frac{2}{L} \int_0^L x \left(\sin \frac{\pi x}{L} \right)^2 dx = 0.5L$ and $\frac{2}{L} \int_0^L x^2 \left(\sin \frac{\pi x}{L} \right)^2 dx = 0.28L$.
- 2.11 Calculate the first three energy levels for an electron in a quantum well of width 10 Å with infinite walls.
- 2.12 Schematically show the number of electrons in the various subshells of an atom with the electronic shell structure $1s^2 2s^2 2p^4$ and an atomic weight of 21. Indicate how many protons and neutrons there are in the nucleus. Is this atom chemically reactive, and why?

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SELF QUIZ Question 1

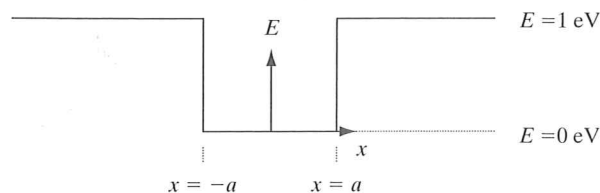
Decide whether *each* of the following one-dimensional functions defined between the limits x approaches negative infinity and x approaches positive infinity is an allowed quantum mechanical wave function (circle one answer in each case):

1. $\Psi(x) = C$ for $-|a| < x < |a|$; $\Psi(x) = 0$ otherwise **allowed / not allowed**
2. $\Psi(x) = C(e^{x/a} + e^{-x/a})$ **allowed / not allowed**
3. $\Psi(x) = C \exp(-x^2/|a|)$ **allowed / not allowed**

where both C and a are nonzero and finite constants.

Question 2

Consider the finite potential well sketched below.

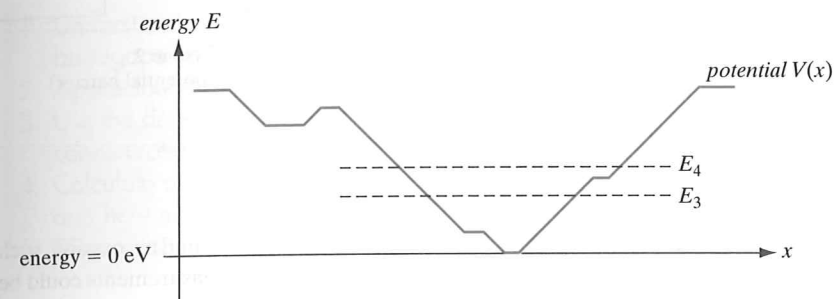


1. Can the measured value of a particle's energy in the well be 0 eV?
2. If the particle has an energy of $E < 1$ eV, can the measured value of the particle's position be $|x| > a$?

Question 3

- (a) For a particle in the following potential well of minimum potential energy equal to 0 eV, could the ground state eigenenergy E_1 of the particle be equal to zero? Circle one choice below.

yes / no / not enough information provided



- (b) Given the 3rd and 4th most energetic eigenstates of energies as shown above, is it possible under any circumstances that the expectation value of the particle's energy could be exactly $0.5(E_3 + E_4)$? (Do not assume the particle is in an energy eigenstate.) Circle one choice below.

yes / no / not enough information provided

- (c) Consider the following *continuous, smooth, and normalizable* wavefunction $\Psi(x)$. Is this wave function an allowed quantum mechanical wave function for a particle (currently) above the potential $V(x)$ of part (a)? (Circle one.)

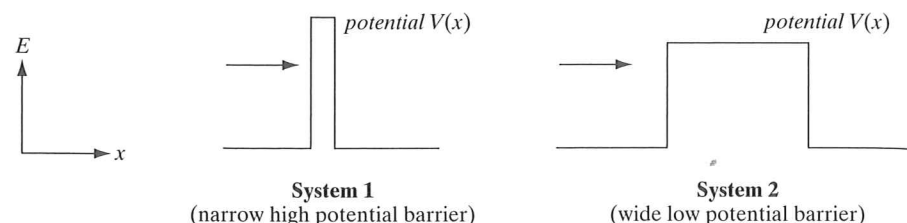
yes / no / can't tell



Question 4

Consider quantum mechanical particles incident from the left having well-defined energy as indicated by the vertical positions of the arrows, in the two systems shown below. Will the probability of being reflected be greater for the incident particle in System 1 than for the incident particle in System 2? Circle one choice below.

yes / no / not enough information provided

**Question 5**

Suppose five precise measurements were made on a particle in rapid succession, such that the time evolution of the particle wave function *between* measurements could be neglected, in the following order: (1) position, (2) momentum, (3) momentum, (4) position, (5) momentum. If the results of the first two measurements were x_o and p_o , respectively, what would be the results of the next three measurements (circle one each)?

measurement (3): momentum p_o / unknown

measurement (4): position x_o / unknown

measurement (5): momentum p_o / unknown

Question 6

If the photoelectric effect were governed by classical physics rather than quantum mechanics, what would be result of the following experiments:

- By changing the intensity of the incident radiation, what would happen to the energy and number of ejected electrons?
- How about changing the frequency of the light?

Chapter 3**Energy Bands and Charge Carriers in Semiconductors****OBJECTIVES**

- Understand conduction and valence energy bands, and how bandgaps are formed
- Appreciate the idea of doping in semiconductors
- Use the density of states and Fermi Dirac statistics to calculate carrier concentrations
- Calculate drift currents in an electric field in terms of carrier mobility, and how mobility is affected by scattering
- Discuss the idea of "effective" masses

In this chapter we begin to discuss the specific mechanisms by which current flows in a solid. In examining these mechanisms we shall learn why some materials are good conductors of electric current, whereas others are poor conductors. We shall see how the conductivity of a semiconductor can be varied by changing the temperature or the number of impurities. These fundamental concepts of charge transport form the basis for later discussions of solid state device behavior.

In Chapter 2 we found that electrons are restricted to sets of discrete energy levels within atoms. Large gaps exist in the energy scale in which no energy states are available. In a similar fashion, electrons in solids are restricted to certain energies and are not allowed at other energies. The basic difference between the case of an electron in a solid and that of an electron in an isolated atom is that in the solid the electron has a *range*, or *band*, of available energies. The discrete energy levels of the isolated atom spread into bands of energies in the solid because in the solid the wave functions of electrons in neighboring atoms overlap, and an electron is not necessarily localized at a particular atom. Thus, for example, an electron in the outer orbit of one atom feels the influence of neighboring atoms, and its overall wave function is altered. Naturally, this influence affects the potential energy term and the boundary conditions in the Schrödinger equation, and we would

**3.1
BONDING
FORCES AND
ENERGY BANDS
IN SOLIDS**