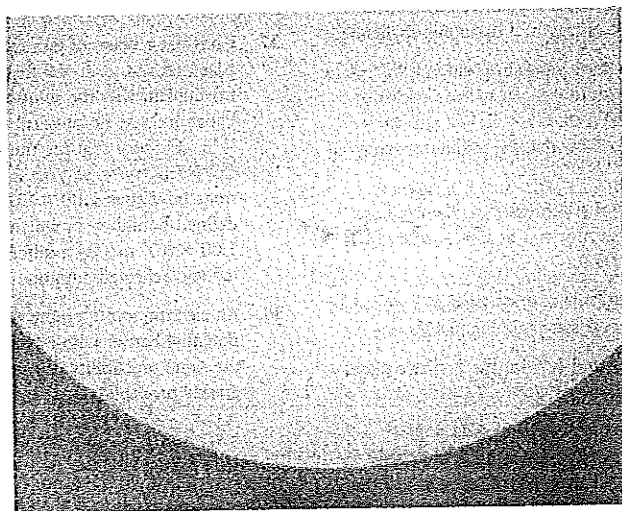


CHAPTER 6

Quantum Theory of the Hydrogen Atom



The strong magnetic fields associated with sunspots were detected by means of the Zeeman effect. Sunspots appear dark because they are cooler than the rest of the solar surface, although quite hot themselves. The number of spots varies in an 11-year cycle, and a number of terrestrial phenomena follow this cycle.

6.1 SCHRÖDINGER'S EQUATION FOR THE HYDROGEN ATOM

Symmetry suggests spherical polar coordinates

6.2 SEPARATION OF VARIABLES

A differential equation for each variable

6.3 QUANTUM NUMBERS

Three dimensions, three quantum numbers

6.4 PRINCIPAL QUANTUM NUMBER

Quantization of energy

6.5 ORBITAL QUANTUM NUMBER

Quantization of angular-momentum magnitude

6.6 MAGNETIC QUANTUM NUMBER

Quantization of angular-momentum direction

6.7 ELECTRON PROBABILITY DENSITY

No definite orbits

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What happens when an electron goes from one state to another

6.9 SELECTION RULES

Some transitions are more likely to occur than others

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How atoms interact with a magnetic field

The first problem that Schrödinger tackled with his new wave equation was that of the hydrogen atom. He found the mathematics heavy going, but was rewarded by the discovery of how naturally quantization occurs in wave mechanics: "It has its basis in the requirement that a certain spatial function be finite and single-valued." In this chapter we shall see how Schrödinger's quantum theory of the hydrogen atom achieves its results, and how these results can be interpreted in terms of familiar concepts.

6.1 SCHRÖDINGER'S EQUATION FOR THE HYDROGEN ATOM

Symmetry suggests spherical polar coordinates

A hydrogen atom consists of a proton, a particle of electric charge $+e$, and an electron, a particle of charge $-e$ which is 1836 times lighter than the proton. For the sake of convenience we shall consider the proton to be stationary, with the electron moving about in its vicinity but prevented from escaping by the proton's electric field. As in the Bohr theory, the correction for proton motion is simply a matter of replacing the electron mass m by the reduced mass m' given by Eq. (4.22).

Schrödinger's equation for the electron in three dimensions, which is what we must use for the hydrogen atom, is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad (6.1)$$

The potential energy U here is the electric potential energy

$$\text{Electric potential energy} \quad U = -\frac{e^2}{4\pi\epsilon_0 r} \quad (6.2)$$

of a charge $-e$ when it is the distance r from another charge $+e$.

Since U is a function of r rather than of x, y, z , we cannot substitute Eq. (6.2) directly into Eq. (6.1). There are two alternatives. One is to express U in terms of the cartesian coordinates x, y, z by replacing r by $\sqrt{x^2 + y^2 + z^2}$. The other is to express Schrödinger's equation in terms of the spherical polar coordinates r, θ, ϕ defined in Fig. 6.1. Owing to the symmetry of the physical situation, doing the latter is appropriate here, as we shall see in Sec. 6.2.

The spherical polar coordinates r, θ, ϕ of the point P shown in Fig. 6.1 have the following interpretations:

Spherical polar coordinates r = length of radius vector from origin O to point P

$$= \sqrt{x^2 + y^2 + z^2}$$

θ = angle between radius vector and $+z$ axis

= zenith angle

$$= \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$= \cos^{-1} \frac{z}{r}$$

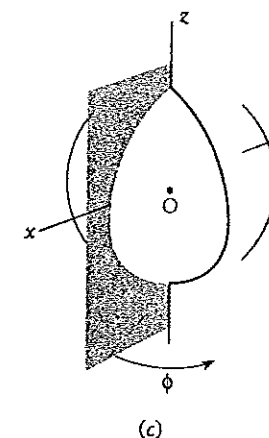
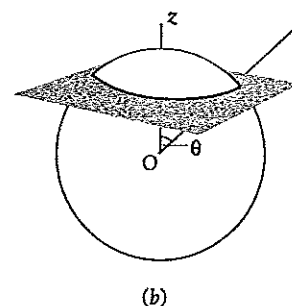
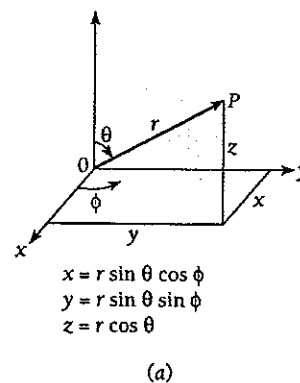


Figure 6.1 (a) Spherical polar coordinates. (b) A line of constant zenith angle θ on a sphere is a circle whose plane is perpendicular to the z axis. (c) A line of constant azimuth angle ϕ is a circle whose plane includes the z axis.

$$\begin{aligned}
\phi &= \text{angle between the projection of the radius vector in the } xy \\
&\quad \text{plane and the } +x \text{ axis, measured in the direction shown} \\
&= \text{azimuth angle} \\
&= \tan^{-1} \frac{y}{x}
\end{aligned}$$

On the surface of a sphere whose center is at O , lines of constant zenith angle θ are like parallels of latitude on a globe (but we note that the value of θ of a point is *not* the same as its latitude; $\theta = 90^\circ$ at the equator, for instance, but the latitude of the equator is 0°). Lines of constant azimuth angle ϕ are like meridians of longitude (here the definitions coincide if the axis of the globe is taken as the $+z$ axis and the $+x$ axis is at $\phi = 0^\circ$).

In spherical polar coordinates Schrödinger's equation is written

$$\begin{aligned}
\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) \\
+ \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad (6.3)
\end{aligned}$$

Substituting Eq. (6.2) for the potential energy U and multiplying the entire equation by $r^2 \sin^2 \theta$, we obtain

$$\begin{aligned}
\text{Hydrogen atom} \quad \sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) \\
+ \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \psi = 0 \quad (6.4)
\end{aligned}$$

Equation (6.4) is the partial differential equation for the wave function ψ of the electron in a hydrogen atom. Together with the various conditions ψ must obey, namely that ψ be normalizable and that ψ and its derivatives be continuous and single-valued at each point r, θ, ϕ , this equation completely specifies the behavior of the electron. In order to see exactly what this behavior is, we must solve Eq. (6.4) for ψ .

When Eq. (6.4) is solved, it turns out that three quantum numbers are required to describe the electron in a hydrogen atom, in place of the single quantum number of the Bohr theory. (In Chap. 7 we shall find that a fourth quantum number is needed to describe the spin of the electron.) In the Bohr model, the electron's motion is basically one-dimensional, since the only quantity that varies as it moves is its position in a definite orbit. One quantum number is enough to specify the state of such an electron, just as one quantum number is enough to specify the state of a particle in a one-dimensional box.

A particle in a three-dimensional box needs three quantum numbers for its description, since there are now three sets of boundary conditions that the particle's wave function ψ must obey: ψ must be 0 at the walls of the box in the x, y , and z directions independently. In a hydrogen atom the electron's motion is restricted by the inverse-square electric field of the nucleus instead of by the walls of a box, but the electron is

nevertheless free to move in three dimensions, and it is accordingly not surprising that three quantum numbers govern its wave function also.

6.2 SEPARATION OF VARIABLES

A differential equation for each variable

The advantage of writing Schrödinger's equation in spherical polar coordinates for the problem of the hydrogen atom is that in this form it may be separated into three independent equations, each involving only a single coordinate. Such a separation is possible here because the wave function $\psi(r, \theta, \phi)$ has the form of a product of three different functions: $R(r)$, which depends on r alone; $\Theta(\theta)$ which depends on θ alone; and $\Phi(\phi)$, which depends on ϕ alone. Of course, we do not really know that this separation is possible yet, but we can proceed by assuming that

Hydrogen-atom
wave function

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (6.5)$$

and then seeing if it leads to the desired separation. The function $R(r)$ describes how the wave function ψ of the electron varies along a radius vector from the nucleus, with θ and ϕ constant. The function $\Theta(\theta)$ describes how ψ varies with zenith angle θ along a meridian on a sphere centered at the nucleus, with r and ϕ constant (Fig. 6.1c). The function $\Phi(\phi)$ describes how ψ varies with azimuth angle ϕ along a parallel on a sphere centered at the nucleus, with r and θ constant (Fig. 6.1b).

From Eq. (6.5), which we may write more simply as

$$\psi = R\Theta\Phi$$

we see that

$$\begin{aligned} \frac{\partial \psi}{\partial r} &= \Theta\Phi \frac{\partial R}{\partial r} = \Theta\Phi \frac{dR}{dr} \\ \frac{\partial \psi}{\partial \theta} &= R\Phi \frac{\partial \Theta}{\partial \theta} = R\Phi \frac{d\Theta}{d\theta} \\ \frac{\partial^2 \psi}{\partial \phi^2} &= R\Theta \frac{\partial^2 \Phi}{\partial \phi^2} = R\Theta \frac{d^2 \Phi}{d\phi^2} \end{aligned}$$

The change from partial derivatives to ordinary derivatives can be made because we are assuming that each of the functions R , Θ , and Φ depends only on the respective variables r , θ , and ϕ .

When we substitute $R\Theta\Phi$ for ψ in Schrödinger's equation for the hydrogen atom and divide the entire equation by $R\Theta\Phi$, we find that

$$\begin{aligned} \frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \\ + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = 0 \quad (6.6) \end{aligned}$$

The third term of Eq. (6.6) is a function of azimuth angle ϕ only, whereas the other terms are functions of r and θ only.

Let us rearrange Eq. (6.6) to read

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \quad (6.7)$$

This equation can be correct only if both sides of it are equal to the same constant, since they are functions of different variables. As we shall see, it is convenient to call this constant m_l^2 . The differential equation for the function ϕ is therefore

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2 \quad (6.8)$$

Next we substitute m_l^2 for the right-hand side of Eq. (6.7), divide the entire equation by $\sin^2 \theta$, and rearrange the various terms, which yields

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \quad (6.9)$$

Again we have an equation in which different variables appear on each side, requiring that both sides be equal to the same constant. This constant is called $l(l+1)$, once more for reasons that will be apparent later. The equations for the functions Θ and R are therefore

$$\frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) = l(l+1) \quad (6.10)$$

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = l(l+1) \quad (6.11)$$

Equations (6.8), (6.10), and (6.11) are usually written

$$\text{Equation for } \Phi \quad \frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi = 0 \quad (6.12)$$

$$\text{Equation for } \Theta \quad \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left[l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 \quad (6.13)$$

$$\text{Equation for } R \quad \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad (6.14)$$

Each of these is an ordinary differential equation for a single function of a single variable. Only the equation for R depends on the potential energy $U(r)$.

We have therefore accomplished our task of simplifying Schrödinger's equation for the hydrogen atom, which began as a partial differential equation for a function ψ of three variables. The assumption embodied in Eq. (6.5) is evidently valid.

6.3 QUANTUM NUMBERS

Three dimensions, three quantum numbers

The first of these equations, Eq. (6.12), is readily solved. The result is

$$\Phi(\phi) = Ae^{im_l\phi} \quad (6.15)$$

As we know, one of the conditions that a wave function—and hence Φ , which is a component of the complete wave function ψ —must obey is that it have a single value at a given point in space. From Fig. 6.2 it is clear that ϕ and $\phi + 2\pi$ both identify the same meridian plane. Hence it must be true that $\Phi(\phi) = \Phi(\phi + 2\pi)$, or

$$Ae^{im_l\phi} = Ae^{im_l(\phi+2\pi)}$$

which can happen only when m_l is 0 or a positive or negative integer ($\pm 1, \pm 2, \pm 3, \dots$). The constant m_l is known as the **magnetic quantum number** of the hydrogen atom.

The differential equation for $\Theta(\theta)$, Eq. (6.13), has a solution provided that the constant l is an integer equal to or greater than $|m_l|$, the absolute value of m_l . This requirement can be expressed as a condition on m_l in the form

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

The constant l is known as the **orbital quantum number**.

The solution of the final equation, Eq. (6.14), for the radial part $R(r)$ of the hydrogen-atom wave function ψ also requires that a certain condition be fulfilled. This condition is that E be positive or have one of the negative values E_n (signifying that the electron is bound to the atom) specified by

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \left(\frac{1}{n^2} \right) = \frac{E_1}{n^2} \quad n = 1, 2, 3, \dots \quad (6.16)$$

We recognize that this is precisely the same formula for the energy levels of the hydrogen atom that Bohr obtained.

Another condition that must be obeyed in order to solve Eq. (6.14) is that n , known as the **principal quantum number**, must be equal to or greater than $l + 1$. This requirement may be expressed as a condition on l in the form

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

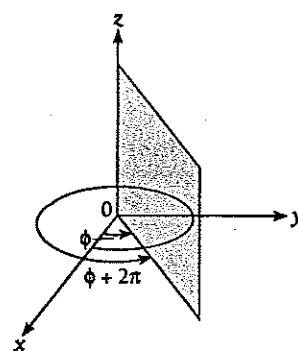


Figure 6.2 The angles ϕ and $\phi + 2\pi$ both identify the same meridian plane.

Hence we may tabulate the three quantum numbers n , l , and m together with their permissible values as follows:

$$\begin{aligned} \text{Principal quantum number} & n = 1, 2, 3, \dots \\ \text{Orbital quantum number} & l = 0, 1, 2, \dots, (n - 1) \\ \text{Magnetic quantum number} & m_l = 0, \pm 1, \pm 2, \dots, \pm l \end{aligned} \quad (6.17)$$

It is worth noting again the natural way in which quantum numbers appear in quantum-mechanical theories of particles trapped in a particular region of space.

To exhibit the dependence of R , Θ , and Φ upon the quantum numbers n , l , m , we may write for the electron wave functions of the hydrogen atom

$$\psi = R_{nl} \Theta_{lm_l} \Phi_{m_l} \quad (6.18)$$

The wave functions R , Θ , and Φ together with ψ are given in Table 6.1 for $n = 1, 2$, and 3.

Table 6.1 Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2$, and 3*

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.



Wolfgang Pauli (1900–1958) was born in Vienna and at nineteen had prepared a detailed account of special and general relativity that impressed Einstein and remained the standard work on the subject for many years. Pauli received his doctorate from the University of Munich in 1922 and then spent short periods in Göttingen, Copenhagen, and Hamburg before

becoming professor of physics at the Institute of Technology in Zurich, Switzerland, in 1928. In 1925 he proposed that four quantum numbers (what one of them governed was then unknown) are needed to characterize each atomic electron and that no two electrons in an atom have the same set of quantum numbers. This exclusion principle turned out to be the missing

link in understanding the arrangement of electrons in an atom.

Late in 1925 Goudsmit and Uhlenbeck, two young Dutch physicists, showed that the electron possesses intrinsic angular momentum, so it must be thought of as spinning, and that Pauli's fourth quantum number described the direction of the spin. The American physicist Ralph Kronig had conceived of electron spin a few months earlier and had told Pauli about it. However, because Pauli had "ridiculed the idea" Kronig did not publish his work.

In 1931 Pauli resolved the problem of the apparently missing energy in the beta decay of a nucleus by proposing that a neutral, massless particle leaves the nucleus together with the electron emitted. Two years later Fermi developed the theory of beta decay with the help of this particle (today believed to have a small mass), which he called the neutrino ("small neutral one" in Italian). Pauli spent the war years in the United States, and received the Nobel Prize in 1945.

In 1925 Wolfgang Pauli discovered the fundamental principle that governs the electronic configurations of atoms having more than one electron. His exclusion principle states that

No two electrons in an atom can exist in the same quantum state. Each electron must have a different set of quantum numbers n, l, m_l, m_s .

Pauli was led to the exclusion principle by a study of atomic spectra. The various states of an atom can be determined from its spectrum, and the quantum numbers of these states can be inferred. In the spectra of every element but hydrogen a number of lines are missing that correspond to transitions to and from states having certain combinations of quantum numbers. For instance, no transitions are observed in helium to or from the ground-state configuration in which the spins of both electrons are in the same direction. However, transitions are observed to and from the other ground-state configuration, in which the spins are in opposite directions.

In the absent state in helium the quantum numbers of *both* electrons would be $n = 1, l = 0, m_l = 0, m_s = \frac{1}{2}$. On the other hand, in the state known to exist one of the electrons has $m_s = \frac{1}{2}$ and the other $m_s = -\frac{1}{2}$. Pauli showed that every unobserved atomic state involves two or more electrons with identical quantum numbers, and the exclusion principle is a statement of this finding.

7.3 SYMMETRIC AND ANTISYMMETRIC WAVE FUNCTIONS

Fermions and bosons

Before we explore the role of the exclusion principle in detail it is interesting to look into its quantum-mechanical implications.

The complete wave function $\psi(1, 2, 3, \dots, n)$ of a system of n noninteracting particles can be expressed as the product of the wave functions $\psi(1), \psi(2), \psi(3), \dots, \psi(n)$ of the individual particles. That is,

$$\psi(1, 2, 3, \dots, n) = \psi(1) \psi(2) \psi(3) \dots \psi(n) \quad (7.5)$$

Let us use Eq. (7.5) to look into the kinds of wave functions that can be used to describe a system of two identical particles.

Suppose one of the particles is in quantum state a and the other in state b . Because the particles are identical, it should make no difference in the probability density $|\psi|^2$ of the system if the particles are exchanged, with the one in state a replacing the one in state b , and vice versa. Symbolically, we require that

$$|\psi|^2(1, 2) = |\psi|^2(2, 1) \quad (7.6)$$

The wave function $\psi(2, 1)$ that represents the exchanged particles can be either

$$\text{Symmetric} \quad \psi(2, 1) = \psi(1, 2) \quad (7.7)$$

or

$$\text{Antisymmetric} \quad \psi(2, 1) = -\psi(1, 2) \quad (7.8)$$

and still fulfill Eq. (7.6). The wave function of the system is not itself a measurable quantity, and so it can be altered in sign by the exchange of the particles. Wave functions that are unaffected by an exchange of particles are said to be **symmetric**, while those that reverse sign upon such an exchange are said to be **antisymmetric**.

If particle 1 is in state a and particle 2 is in state b , the wave function of the system is, according to Eq. (7.5),

$$\psi_I = \psi_a(1)\psi_b(2) \quad (7.9)$$

If particle 2 is in state a and particle 1 is in state b , the wave function is

$$\psi_{II} = \psi_a(2)\psi_b(1) \quad (7.10)$$

Because the two particles are indistinguishable, we have no way to know at any moment whether ψ_I or ψ_{II} describes the system. The likelihood that ψ_I is correct at any moment is the same as the likelihood that ψ_{II} is correct.

Equivalently, we can say that the system spends half the time in the configuration whose wave function is ψ_I and the other half in the configuration whose wave function is ψ_{II} . Therefore a linear combination of ψ_I and ψ_{II} is the proper description of the system. Two such combinations, symmetric and antisymmetric, are possible:

$$\text{Symmetric} \quad \psi_S = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] \quad (7.11)$$

$$\text{Antisymmetric} \quad \psi_A = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] \quad (7.12)$$

The factor $1/\sqrt{2}$ is needed to normalize ψ_S and ψ_A . Exchanging particles 1 and 2 leaves ψ_S unaffected, while it reverses the sign of ψ_A . Both ψ_S and ψ_A obey Eq. (7.6).

There are a number of important distinctions between the behavior of particles in systems whose wave functions are symmetric and that of particles in systems whose wave functions are antisymmetric. The most obvious is that in the symmetric case, both particles 1 and 2 can simultaneously exist in the same state, with $a = b$. In the antisymmetric case, if we set $a = b$, we find that

$$\psi_A = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) - \psi_a(2)\psi_a(1)] = 0$$

Hence the two particles *cannot* be in the same quantum state. Pauli found that no two electrons in an atom can be in the same quantum state, so we conclude that systems of electrons are described by wave functions that reverse sign upon the exchange of any pair of them.

Fermions and Bosons

The results of various experiments show that *all* particles which have odd half-integral spins ($\frac{1}{2}, \frac{3}{2}, \dots$) have wave functions that are antisymmetric to an exchange of any pair of them. Such particles, which include protons and neutrons as well as electrons, obey the exclusion principle when they are in the same system. That is, when they move in a common force field, each member of the system must be in a different quantum state. Particles of odd half-integral spin are often referred to as **fermions** because, as we shall learn in Chap. 9, the behavior of systems of them (such as free electrons in a metal) is governed by a statistical distribution law discovered by Fermi and Dirac.

Particles whose spins are 0 or an integer have wave functions that are symmetric to an exchange of any pair of them. These particles, which include photons, alpha particles, and helium atoms, do not obey the exclusion principle. Particles of 0 or integral spin are often referred to as **bosons** because the behavior of systems of them (such as photons in a cavity) is governed by a statistical distribution law discovered by Bose and Einstein.

There are other consequences of the symmetry or antisymmetry of particle wave functions besides that expressed in the exclusion principle. It is these consequences that make it useful to classify particles according to the natures of their wave functions rather than merely according to whether or not they obey the exclusion principle.

7.4 PERIODIC TABLE

Organizing the elements

In 1869 the Russian chemist Dmitri Mendeleev formulated the **periodic law** whose modern statement is

When the elements are listed in order of atomic number, elements with similar chemical and physical properties recur at regular intervals.

Although the modern quantum theory of the atom was many years in the future, Mendeleev was fully aware of the significance his work would turn out to have. As he