CHAPTER 7

The Hydrogen Atom

> *The atom of modern physics can be symbolized only through a partial differential equation in an abstract space of many dimensions. All its qualities are inferential; no material properties can be directly attributed to it. That is to say, any picture of the atom that our imagination is able to invent is for that very reason defective. An understanding of the atomic world in that primary sensuous fashion . . . is impossible.*
>
> **Werner Heisenberg**

In Chapter 6 we studied the Schrödinger equation and its application to several model systems. We now have the tools to apply quantum theory to real physical systems, which we will do in the next few chapters. Our first major subject is atomic physics, and we begin by applying the Schrödinger equation to the hydrogen atom. We will learn that additional quantum numbers are needed in order to explain experimental results. A couple of the sections in this chapter (sections 7.2 and 7.6) are advanced topics and may be skipped without losing continuity.

7.1 Application of the Schrödinger Equation to the Hydrogen Atom

The hydrogen atom is the first system we shall consider that requires the full complexity of the three-dimensional Schrödinger equation. To a good approximation the potential energy of the electron–proton system is electrostatic,

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{7.1}$$

We rewrite the three-dimensional time-independent Schrödinger Equation (6.43) as

$$-\frac{\hbar^2}{2m}\,\frac{1}{\psi(x, y, z)}\left[\frac{\partial^2\psi(x, y, z)}{\partial x^2} + \frac{\partial^2\psi(x, y, z)}{\partial y^2} + \frac{\partial^2\psi(x, y, z)}{\partial z^2}\right] = E - V(r) \tag{7.2}$$

As was discussed in Chapter 4, the correct mass value m to be used is the reduced mass μ of the proton and electron. We can also study other hydrogenlike (called *hydrogenic*) atoms such as He^+ or Li^{++} by inserting the appropriate μ and by replacing e^2 in Equation (7.1) with Ze^2, where Z is the atomic number.

We note that the potential $V(r)$ in Equation (7.2) depends only on the distance r between the proton and electron. To take advantage of this radial symmetry, we transform to spherical polar coordinates. The transformation is given in Figure 7.1, where the relationships between the cartesian coordinates x, y, z and the spherical polar coordinates r, θ, ϕ are shown. The transformation of Equation (7.2) into spherical polar coordinates is straightforward, but tedious. After inserting the Coulomb potential into the transformed Schrödinger equation, we have

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2\mu}{\hbar^2}(E-V)\psi=0 \tag{7.3}$$

Schrödinger equation in spherical coordinates

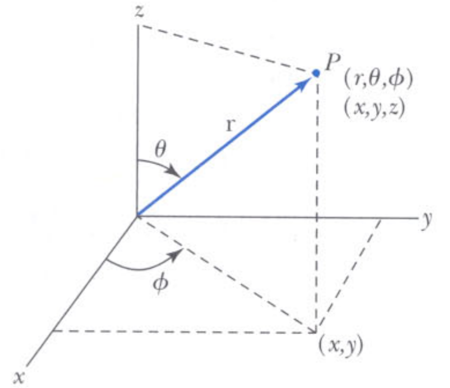
The wave function ψ is now a function of r, θ, ϕ $[\psi(r, \theta, \phi)]$, but we will write it simply as ψ for brevity. In the terminology of partial differential equations, Equation (7.3) is separable, meaning a solution may be found as a product of three functions, each depending on only one of the coordinates r, θ, ϕ. (This is exactly analogous to our separating the time-dependent part of the Schrödinger equation solution as $e^{-iEt/\hbar}$.) Let us try a solution of the form

$$\psi(r, \theta, \phi) = R(r)f(\theta)g(\phi) \tag{7.4}$$

Trial solution

This substitution allows us to separate the partial differential in Equation (7.3) into three separate differential equations, each depending on one coordinate: r, θ, or ϕ.

From Chapter 6 we have a good idea what to expect the results will look like. For each of the three differential equations we must apply appropriate boundary conditions on the functions $R(r)$, $f(\theta)$, and $g(\phi)$. This will lead



$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

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

$\theta = \cos^{-1}\frac{z}{r}$ (Polar angle)

$\phi = \tan^{-1}\frac{y}{x}$ (Azimuthal angle)

FIGURE 7.1 Relationship between spherical polar coordinates (r, θ, ϕ) and cartesian coordinates (x, y, z).

to three quantum numbers, one for each of the three separate differential equations (or one quantum number for each dimension of motion available—recall that in the previous chapter we obtained one quantum number for one-dimensional motion).

7.2 Solution of the Schrödinger Equation for Hydrogen

The first step will be to substitute the trial solution, Equation (7.4), into Equation (7.3). Then we can separate the resulting equation into three equations: one for $R(r)$, one for $f(\theta)$, and one for $g(\phi)$. The solutions to those equations will then allow us to understand the structure of the hydrogen atom, in the ground state and excited states as well.

Separation of Variables

Starting with Equation (7.4), we find the necessary derivatives to be

$$\frac{\partial\psi}{\partial r} = fg\frac{\partial R}{\partial r} \qquad \frac{\partial\psi}{\partial\theta} = Rg\frac{\partial f}{\partial\theta} \qquad \frac{\partial^2\psi}{\partial\phi^2} = Rf\frac{\partial^2 g}{\partial\phi^2} \tag{7.5}$$

We substitute these results into the Schrödinger equation (7.3) and find

$$\frac{fg}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{Rg}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{Rf}{r^2\sin^2\theta}\frac{\partial^2 g}{\partial\phi^2} + \frac{2\mu}{\hbar^2}(E-V)Rfg = 0 \tag{7.6}$$

Next we multiply both sides of Equation (7.6) by $r^2\sin^2\theta/Rfg$ and rearrange to have

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta\,(E-V) - \frac{\sin\theta}{f}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) = \frac{1}{g}\frac{\partial^2 g}{\partial\phi^2} \tag{7.7}$$

Look closely at Equation (7.7). Notice that only the variables r and θ (and their functions R and f) appear on the left side, whereas only ϕ and its function g appear on the right side. We have achieved a separation of variables, completely isolating ϕ. What does this mean? The left side of the equation cannot change as ϕ changes, because it does not contain ϕ or any function depending on ϕ. Similarly, the right side cannot change with either r or θ. The only way for this to be true is for each side of Equation (7.7) to be equal to a constant. For reasons that will be clear later, we choose to let this constant have the value $-m_\ell{}^2$. If we set the constant $-m_\ell{}^2$ equal to the right side of Equation (7.7), we have

$$\frac{1}{g}\frac{\partial^2 g}{\partial\phi^2} = -m_\ell{}^2$$

or, after rearranging,

Azimuthal equation

$$\frac{d^2 g}{d\phi^2} = -m_\ell{}^2 g \tag{7.8}$$

Notice that because ϕ is the only variable, we have replaced the partial derivative with the ordinary derivative. Because the angle ϕ in spherical coordinates corresponds to the azimuth angle in astronomy, Equation (7.8) is traditionally referred to as the **azimuthal equation.** This is just the equation of a harmonic oscillator that we have studied in introductory physics, and the solutions for $g(\phi)$ will take the form of sines and cosines.

An important restriction on the values of the quantum number m_ℓ can be obtained if we consider solutions to Equation (7.8) for the function $e^{im_\ell\phi}$. One may easily verify by direct substitution that $e^{im_\ell\phi}$ satisfies Equation (7.8) for any value of m_ℓ. However, in order to have a physically valid solution for any value of ϕ, it is necessary that the solution be single valued, that is $g(\phi) = g(\phi + 2\pi)$. This means, for example, that $g(\phi = 0) = g(\phi = 2\pi)$, which requires that $e^0 = e^{2\pi i m_\ell}$. The only way for this to be true is for m_ℓ to be zero or an integer (either positive or negative). The quantum number m_ℓ is therefore restricted to be zero or a positive or negative integer. If the sign on the right-hand side of Equation (7.8) were positive rather than negative, the solution is not physically realized, because it can't be normalized and is not single valued in ϕ. We shall defer further discussion of solutions for Equation (7.8) until later. For now it is sufficient to realize that readily obtainable solutions exist.

Now we set the left side of Equation (7.7) equal to the constant $-m_\ell^2$ and rearrange to have

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2\mu r^2}{\hbar^2}(E - V) = \frac{m_\ell^2}{\sin^2\theta} - \frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) \tag{7.9}$$

Notice that we have again achieved a successful separation of variables, with everything depending on r on the left side and everything depending on θ on the right side. We can set each side of Equation (7.9) equal to a constant, which this time we call $\ell(\ell + 1)$. Doing so with each side of the equation in succession yields (after more rearrangement) the two equations,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left(E - V - \frac{\hbar^2}{2\mu}\frac{\ell(\ell + 1)}{r^2}\right)R = 0 \tag{7.10}$$

Radial equation

and

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right) + \left(\ell(\ell + 1) - \frac{m_\ell^2}{\sin^2\theta}\right)f = 0 \tag{7.11}$$

Angular equation

where, after separation, we have again replaced the partial derivatives with the ordinary ones.

The process of separation of variables is now complete. The original Schrödinger equation has been separated into three ordinary second-order differential equations [(7.8), (7.10), and (7.11)], each containing only one variable.

Relation Between the Quantum Numbers ℓ and m_ℓ

The associated Legendre equation

Equation (7.11), which we shall call the *angular* equation, was first solved by the famous mathematician Adrien Marie Legendre (1752–1833). It is well known in the theory of differential equations as the **associated Legendre equation.** Application of the appropriate boundary conditions to Equations (7.10) and (7.11) (this process is too tedious to present here) leads to the following restrictions on the quantum numbers ℓ and m_ℓ:

$$\ell = 0, 1, 2, 3, \ldots \tag{7.12}$$
$$m_\ell = -\ell, -\ell + 1, \ldots, -2, -1, 0, 1, 2, \ldots, \ell - 1, \ell$$

That is, the quantum number ℓ must be zero or a positive integer, and the quantum number m_ℓ must be a positive or negative integer, or zero, subject to the restriction that $|m_\ell| \le \ell$. The choice of $\ell(\ell+1)$ as the constant for Equation (7.9) provides in the succinct results in Equation (7.12).

Solution of the Radial Equation

The associated Laguerre equation

Equation (7.10), appropriately called the *radial* equation, is another well-known differential equation. It is known as the **associated Laguerre equation** after the French mathematician Edmond Nicolas Laguerre (1834–1886). The solutions R to this equation that satisfy the appropriate boundary conditions are called *associated Laguerre functions.* We shall consider these solutions in some detail in Section 7.6. We can obtain some idea of how the ground-state wave function looks if we assume that the ground state has the lowest possible quantum number $\ell = 0$ of the system. Our conditions in Equation (7.12) then require that $m_\ell = 0$. Notice that $\ell = 0$ greatly simplifies the radial wave Equation (7.10) to be

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}(E-V)R=0 \tag{7.13}$$

The derivative of the bracketed expression in the first term of Equation (7.13) yields two terms by using the derivative product rule. We write out both of those terms and insert the Coulomb potential energy, Equation (7.1), to find

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\epsilon_0 r}\right)R=0 \tag{7.14}$$

Those students with some experience in solving differential equations will recognize that an exponential solution is required. We try a solution having the form

$$R = Ae^{-r/a_0}$$

where A is a normalization constant and a_0 is a constant with dimensions of length (we shall see that it was no accident that we chose the name a_0!). It is reasonable to try to verify the trial solution by inserting it into the radial equation (7.14). The first and second derivatives are

$$\frac{dR}{dr} = -\frac{1}{a_0}R \qquad \frac{d^2R}{dr^2}=\frac{R}{{a_0}^2}$$

We insert these derivatives into Equation (7.14) and rearrange terms to yield

$$\left(\frac{1}{{a_0}^2}+\frac{2\mu}{\hbar^2}E\right)+\left(\frac{2\mu e^2}{4\pi\epsilon_0\hbar^2}-\frac{2}{a_0}\right)\frac{1}{r}=0 \tag{7.15}$$

By the same reasoning that we applied in the separation of variables method, the only way for Equation (7.15) to be satisfied for *any* value of r is for *each* of the two bracketed expressions to be equal to zero. We set the second bracket term equal to zero and solve for a_0 to find

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

We see that a_0 is in fact equal to the Bohr radius [see Equation (4.24)]! Now we set the first bracket in Equation (7.15) equal to zero and solve for E to find

$$E = -\frac{\hbar^2}{2\mu {a_0}^2} = -E_0$$

Again this is equal to the Bohr result, with E_0 having the value 13.6 eV.

Because we are not prepared to deal with the full scope of the associated Laguerre functions in this book, we shall not consider higher energy states here.

Rather, we shall summarize some of the key results. The full solution to the radial wave equation requires (not surprisingly) the introduction of another quantum number, which we shall call n, such that n is a positive integer (but not zero). There is a further restriction that the quantum number ℓ can only take on values less than n. The consequences of this, along with a full consideration of allowed sets of the three quantum numbers n, ℓ, and m_ℓ, will be considered in Section 7.3. Let us note, however, that the predicted energy levels turn out to be

$$E_n = -\frac{E_0}{n^2}$$

in agreement with the Bohr result.

Solution of the Angular and Azimuthal Equations

We now return to the azimuthal Equation (7.8). We note that its solutions can be expressed in exponential form as $e^{im_\ell \phi}$ or $e^{-im_\ell \phi}$. But because the angular equation also contains the quantum number m_ℓ, solutions to the angular and azimuthal equations are linked. It is customary to group these solutions together into what are called the **spherical harmonics** $Y(\theta, \phi)$, defined as

$$Y(\theta, \phi) = f(\theta) g(\phi) \tag{7.16}$$

Spherical harmonics

The $f(\theta)$ part of the $Y(\theta, \phi)$ is always a polynomial function of $\sin\theta$ and $\cos\theta$ of order ℓ. See Table 7.1 for a listing of the normalized spherical harmonics up to $\ell = 3$.

TABLE 7.1
Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

The probability density for the electron in the hydrogen atom is given by $\psi^*\psi$, therefore, the spherical harmonics together with the radial wave function R will determine the overall shape of the probability density for the various quantum states. The total wave function $\psi(r, \theta, \phi)$ will depend on the quantum numbers n, ℓ, and m_ℓ. We can now write the wave function as

$$\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta, \phi) \tag{7.17}$$

where we indicate by the subscripts that $R(r)$ depends only on n and ℓ and $Y(\theta, \phi)$ depends only on ℓ and m_ℓ. We shall look at these wave functions again in Section 7.6.

7.3 Quantum Numbers

The three quantum numbers obtained from solving Equation (7.3) are

n	**principal quantum number**
ℓ	**orbital angular momentum quantum number**
m_ℓ	**magnetic quantum number**

Their values are obtained by applying the boundary conditions to the wave function $\psi(r, \theta, \phi)$ as discussed in Section 6.1. The restrictions imposed by the boundary conditions are

$$\begin{aligned} n &= 1, 2, 3, 4, \ldots && \text{Integer} \\ \ell &= 0, 1, 2, 3, \ldots, n-1 && \text{Integer} \\ m_\ell &= -\ell, -\ell+1, \ldots, 0, 1, \ldots, \ell-1, \ell && \text{Integer} \end{aligned} \tag{7.18}$$

These three quantum numbers must be integers. The orbital angular momentum quantum number must be less than the principal quantum number, $\ell < n$, and the magnitude of the magnetic quantum number (which may be positive or negative) must be less than or equal to the orbital angular momentum quantum number, $|m_\ell| \leq \ell$. We can summarize these conditions as

$$\begin{aligned} n &> 0 \\ \ell &< n \\ |m_\ell| &\leq \ell \end{aligned} \tag{7.19}$$

The lowest value of n is 1, and for $n = 1$, we must have $\ell = 0$, $m_\ell = 0$. For $n = 2$, we may have $\ell = 0$, $m_\ell = 0$ as well as $\ell = 1$, $m_\ell = -1, 0, +1$.

Example 7.1

What are the possible quantum numbers for a $n = 4$ state in atomic hydrogen?

Solution: The possible values of ℓ are $\ell = 0, 1, 2, 3$, because $\ell_{\text{max}} = n - 1$. For each value of ℓ, m_ℓ goes from $-\ell$ to $+\ell$.

n	ℓ	m_ℓ
4	0	0
4	1	−1, 0, 1
4	2	−2, −1, 0, 1, 2
4	3	−3, −2, −1, 0, 1, 2, 3

As yet these quantum numbers have little physical meaning to us. Let us examine each of them more carefully and try to find classical analogies where possible.

Principal Quantum Number n

The *principal quantum number n* results from the solution of the radial wave function $R(r)$ in Equation (7.4). Because the radial equation includes the potential energy $V(r)$, it is not surprising to find that the boundary conditions on $R(r)$ quantize the energy E. The result for this quantized energy is

$$E_n = \frac{-\mu}{2}\left(\frac{e^2}{4\pi\epsilon_0\hbar}\right)^2\frac{1}{n^2} = -\frac{E_0}{n^2} \tag{7.20}$$

which is precisely the value found in Chapter 4 from the Bohr theory [Equations (4.25) and (4.26)]. The energy levels of the hydrogen atom depend on the principal quantum number n only. The negative value of the energy E indicates that the electron and proton are bound together.

It is perhaps surprising that the total energy of the electron does not depend on the angular momentum. However, a similar situation occurs for planetary motion, where the energy depends on the semimajor axis of the elliptical planetary orbits and not on the eccentricity of the orbits. This peculiarity occurs for the solar system and the hydrogen atom because both the gravitational and Coulomb forces are central; they also both have inverse-square-law dependences on distance.

Orbital Angular Momentum Quantum Number ℓ

The *orbital angular momentum quantum number* ℓ is associated with the $R(r)$ and $f(\theta)$ parts of the wave function. The electron–proton system has orbital angular momentum as the particles pass around each other. Classically, this orbital angular momentum is $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ or

$$L = mv_{\text{orbital}}r \tag{7.21}$$

where v_{orbital} is the orbital velocity, perpendicular to the radius. The quantum number ℓ is related to the magnitude of the orbital angular momentum L by

$$L = \sqrt{\ell(\ell+1)}\hbar \tag{7.22}$$

This curious dependence of L on ℓ ($L^2 \sim \ell(\ell+1)$ rather than ℓ^2) is a wave phenomenon—it results from the application of the boundary conditions on $\psi(r, \theta, \phi)$. We will present a justification for it later in the section. The quantum result disagrees with the more elementary Bohr theory of the hydrogen atom, where $L = n\hbar$. This is most obvious in an $\ell = 0$ state, where $L = \sqrt{0(1)}\hbar = 0$. Apparently we will have to discard Bohr's semiclassical "planetary" model of electrons orbiting a nucleus.

In Figure 7.2 we show several classical orbits corresponding to the same total energy. For an electron in an atom, the energy depends on n; for planetary motion, the energy depends on the semimajor axis. Do not take the elliptical orbits literally for electrons; only probability functions can describe their positions, which must be consistent with the uncertainty principle. We say that a certain energy level is **degenerate** with respect to ℓ when the energy is independent of the value of ℓ (see Section 6.5). For example, the energy for an $n = 3$ level is the same for all possible values* of ℓ ($\ell = 0, 1, 2$).

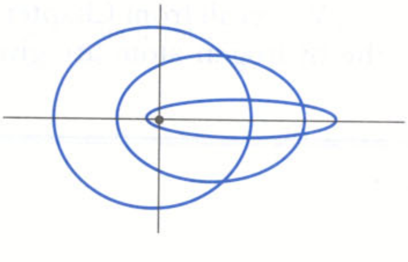


FIGURE 7.2 Various possible electron (or planetary) classical orbits. The energy depends only on the principal quantum number n and not on the angular momentum of the hydrogen atom. There is a finite probability for an $\ell = 0$ electron to be present within the nucleus. Of course, none of the planets has $\ell = 0$, and (obviously) they do not pass through the sun.

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*This statement is true for single-electron atoms like hydrogen. We will learn later in Chapter 8 that for many-electron atoms (atoms with more than 1 electron) electrons with lower ℓ values lie lower in energy for a given n value.

SPECIAL TOPIC:

RYDBERG ATOMS

Rydberg atoms are highly excited atoms with their outermost electron in a high energy level, very near ionization. They are named after Johannes Rydberg who developed the empirical relation bearing his name that produces the correct wavelengths of hydrogen atoms [Equation (3.13)]. Rydberg atoms are similar to hydrogen atoms because the highly excited electron is in such a large orbit that it stays well outside the orbits of the other electrons. A Rydberg atom of atomic number Z has an electron outside a positive core of charge $+e$[Z protons and $(Z-1)$ electrons], just like the hydrogen atom.

Even though Rydberg atoms may have properties similar to hydrogen, they have some distinctly exotic properties. For example, they are gigantic, being as much as 100,000 times larger than normal atoms. Despite being in such a highly excited energy state, they are surprisingly long lived because the selection rules do not allow them to easily decay to lower energy levels. Their lifetime can be as long as a second, which is over a million times the lifetime of a normal excited atom. On the atomic scale, these long-lived Rydberg atoms live almost forever.

We recall from Chapter 4 that the energy levels of the hydrogen atom are given by $-E_0/n^2$ and the radius is given by $n^2 a_0$, where $E_0 = 13.6$ eV and $a_0 = 5.3 \times 10^{-11}$ m. Rydberg atoms have been observed in radio astronomy measurements from outer space with n values near 400, but those produced in the laboratory are rarely larger than 100 and are more commonly studied near 30. Note that a Rydberg atom, acting like hydrogen and having $n = 400$ would have a diameter of $10^5 \times 10^{-10}$ m or 10 μm, an incredibly large atom! A transition from $n = 401 \rightarrow 400$ results in a 4×10^{-7} eV photon emission having a wavelength near 3 m, a radio wave.

Rydberg atoms can be made in the laboratory by bombarding gaseous atoms with charged particles. A revolution in their study came about, however, from the use of tunable lasers (see Chapter 10), which allows specific states to be excited by transferring a laser photon of precise energy to an electron. The density of atoms must be kept low because a collision between Rydberg atoms and normal atoms may quickly lead to de-excitation. The reason Rydberg atoms are so easily found (relatively speaking, of course) in interstellar space is because once created, a Rydberg atom has a poor chance of colliding with another atom.

The most dramatic, and most useful, property of Rydberg atoms is due to the effect of electric fields on their energy levels, called the *Stark effect*. Because of their large values of n, Rydberg atoms are highly de-

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It is customary for historical reasons to use letter names for the various ℓ values. These are

$\ell =$ 0	1	2	3	4	5	. . .
letter = s	p	d	f	g	h	. . .

These particular letter designations for the first four values resulted from empirical visual observations from early experiments: sharp, principal, diffuse, and fundamental. After $\ell = 3$, (f state), the letters generally follow alphabetical order.

Atomic states are normally referred to by the n number and ℓ letter. Thus a state with $n = 2$ and $\ell = 1$ is called a $2p$ state. Examples of other various atomic states are $1s(n = 1, \ell = 0)$, $2s(n = 2, \ell = 0)$, $4d(n = 4, \ell = 2)$, $6g(n = 6, \ell = 4)$. A state such as $2d$ is not possible, because this refers to $n = 2$ and $\ell = 2$. Our boundary conditions require $n > \ell$.

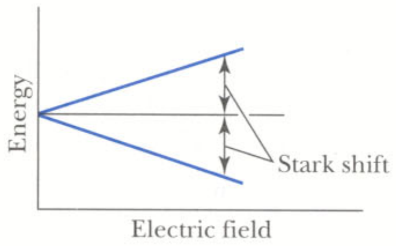

FIGURE A The thin black line represents the degenerate energy level, and the blue lines represent the maximum energy shift for a given electric field. Because of the large degeneracy, states may have many of the energies between the extremes.

generate. Remember that two states are *degenerate* when they have different quantum numbers, but have the same energy. Many states can have the same high value of n, but have different values of ℓ and m_ℓ. In highly degenerate Rydberg atoms, the Stark effect is significant because the splitting of the many energy levels varies linearly with the electric field as shown in Figure A. It requires only a weak electric field to either ionize or change the energy level of a Rydberg atom. In contrast to the electric field, a magnetic field squeezes an atom and changes its shape. This property allows the magnetic properties of Rydberg atoms to be studied under exotic situations. This area of research has received much less attention than the Stark effect.

Several applications have been proposed for Rydberg atoms besides that of fundamental atomic measurements. Detectors sensitive to electromagnetic radiation from the infrared to microwave wavelengths could be built using the very small differences between atomic energy levels in Rydberg atoms. Such long-wavelength radiation (and low frequency) is difficult to detect using normal atoms because of the larger energy differences between adjacent energy states. The use of electric fields allows the energy level differences to be fine-tuned for Rydberg atoms. Such a detector, for example, might be useful in astronomy where suitable detectors are difficult to find.

The use of Rydberg atoms has also been suggested for the separation of isotopes for uranium enrichment. A laser could be used to promote the atoms of one particular isotope, but not the others, to moderate atomic excitation, while a second laser excites the atoms of all other isotopes to highly excited states. These other atoms could then be isolated by ionization leaving the single isotope. To date, few applications* have been realized for Rydberg atoms, but they remain a useful object of experimental and theoretical inquiry.

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*D. Kleppner, M. G. Littman, and M. L. Zimmerman, *Scientific American* **244**, 130 (May 1981).

Magnetic Quantum Number m_ℓ

The orbital angular momentum quantum number ℓ determines the magnitude of the angular momentum **L**, but because **L** is a vector, it also has a direction. Classically, because there is no torque in the hydrogen atom system in the absence of external fields, the angular momentum **L** is a constant of the motion and is conserved. The solution to the Schrödinger equation for $f(\theta)$ specified that ℓ must be an integer, and therefore the magnitude of **L** is quantized.

The angle ϕ is a measure of the rotation about the z axis. The solution for $g(\phi)$ specifies that m_ℓ is an integer *and* related to the z component of the angular momentum **L**.

$$L_z = m_\ell \hbar \tag{7.23}$$

The relationship of L, L_z, ℓ, and m_ℓ is displayed in Figure 7.3 for the value $\ell = 2$. The magnitude of L is fixed ($L = \sqrt{\ell(\ell+1)}\hbar = \sqrt{6}\hbar$). Because L_z is

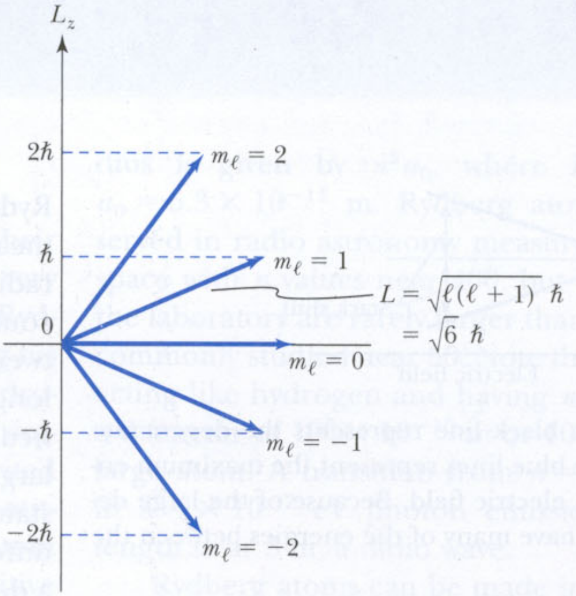

FIGURE 7.3 Schematic diagram of the relationship between **L** and L_z with the allowed values of m_ℓ.

Space quantization

quantized, only certain orientations of **L** are possible, each corresponding to a different m_ℓ (and therefore L_z). This phenomenon is called **space quantization**, because only certain orientations of **L** are allowed in space.

We can ask whether we have established a preferred direction in space by choosing the z axis. The choice of the z axis is completely arbitrary unless there is an external magnetic field to define a preferred direction in space. It is customary to choose the z axis to be along **B** if there is a magnetic field. This is why m_ℓ is called the *magnetic quantum number.*

Will the angular momentum be quantized along the x and y axes as well? The answer is that quantum theory allows **L** to be quantized along only one direction in space. Because we know the magnitude of **L**, the knowledge of a second component would imply a knowledge of the third component as well because of the relation $L^2 = L_x{}^2 + L_y{}^2 + L_z{}^2$. The following argument shows that this would violate the Heisenberg uncertainty principle: if all three components of **L** were known, then the direction of **L** would also be known. In this case we would have a precise knowledge of one component of the electron's position in space, because the electron's orbital motion is confined to a plane perpendicular to **L**. But confinement of the electron to that plane means that the electron's momentum component along **L** is *exactly* zero. This simultaneous knowledge of the same component of position and momentum is forbidden by the uncertainty principle.

Only the magnitude $|\mathbf{L}|$ and L_z may be specified simultaneously. The values of L_x and L_y should be consistent with $L^2 = L_x{}^2 + L_y{}^2 + L_z{}^2$ but cannot be specified individually. Physicists refer to the known values of L and L_z as "sharp" and the unknown L_x and L_y as "fuzzy." The angular momentum vector **L** *never* points in the z direction (see Figure 7.3) because $L = \sqrt{\ell(\ell+1)}\hbar$ and $|\mathbf{L}| > |L_z|_{\text{max}} = \ell\hbar$. Our results from solving the Schrödinger equation of the hydrogen atom are consistent with the uncertainty principle.

The space quantization just mentioned is an experimental fact. The values of L_z range from $-\ell$ to $+\ell$ in steps of 1, for a total of $2\ell + 1$ allowed values. Because there is nothing special about the three directions x, y, and z, we expect the average of the angular momentum components squared in the three directions to be the same, $\langle L_x{}^2\rangle = \langle L_y{}^2\rangle = \langle L_z{}^2\rangle$. The average value of $\langle L^2\rangle$ is equal to three times the average value of the square of any one of the components, so we choose the z component, $\langle L^2\rangle = 3\langle L_z{}^2\rangle$. To find the average value of $L_z{}^2$, we just have to sum up all the squares of the quantum numbers for L_z and divide by the total number, $2\ell + 1$.

$$\langle L^2\rangle = 3\langle L_z^2\rangle = \frac{3}{2\ell + 1}\sum_{m_\ell=-\ell}^{\ell} m_\ell^2\hbar^2 = \ell(\ell + 1)\hbar^2 \qquad (7.24)$$

where we have used a math table for the summation result. This rather simple argument to explain the $\ell(\ell + 1)$ dependence for the expectation value of L^2 (rather than using a sophisticated quantum mechanical calculation) was originally due to Richard Feynman and simplified by P. W. Milonni.*

Example 7.2

What is the degeneracy of the $n = 3$ level? That is, how many different states are contained in the energy level, $E_3 = -E_0/9$?

Solution: The energy eigenvalues for atomic hydrogen depend only on the principal quantum number n (in the absence of a magnetic field). For each value of n, there can be n different orbital angular momentum ℓ states ($\ell = 0, 1, \ldots, n - 1$). For each value of ℓ, there are $2\ell + 1$ different magnetic quantum states ($m_\ell = -\ell, -\ell + 1, \ldots, 0, 1, \ldots, +\ell$). Therefore to find the total degeneracy for $n = 3$ we have to add up all the possibilities.

n	ℓ	m_ℓ	$2\ell + 1$
3	0	0	1
3	1	$-1, 0, 1$	3
3	2	$-2, -1, 0, 1, 2$	5
			total = 9

The $n = 3$ level is degenerate (in the absence of a magnetic field) because all nine states have the same energy but different quantum numbers. Their wave functions, however, are quite different. You may notice that, in general, the degeneracy is n^2 (see Problem 16).

7.4 Magnetic Effects on Atomic Spectra—The Normal Zeeman Effect

As early as 1896 it was shown by the Dutch physicist Pieter Zeeman that the spectral lines emitted by atoms placed in a magnetic field broaden and appear to split. Sometimes a line is split into three lines (*normal* **Zeeman effect**), but often more than three lines are found (*anomalous* Zeeman effect). The normal Zeeman effect can be understood by considering the atom to behave like a small magnet and will be discussed here. The anomalous Zeeman effect is more complicated (see Section 8.3). By the 1920s considerable **fine structure** of atomic spectral lines from hydrogen and other elements had been observed.

As a rough model, think of an electron circulating around the nucleus as a circular current loop. The current loop has a magnetic moment $\mu = IA$ where the current $I = dq/dt$ is simply the electron charge ($q = -e$) divided by the period T for the electron to make one revolution ($T = 2\pi r/v$).

$$\mu = IA = \frac{q}{T}A = \frac{(-e)\pi r^2}{2\pi r/v} = \frac{-erv}{2} = -\frac{e}{2m}L \qquad (7.25)$$

where $L = mvr$ is the magnitude of the orbital angular momentum. Both the magnetic moment $\boldsymbol{\mu}$ and angular momentum $\mathbf{L}$ are vectors so that

$$\boldsymbol{\mu} = -\frac{e}{2m}\mathbf{L} \qquad (7.26)$$

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*P. W. Milonni, *Am. J. Phys.* **58**, 1012 (1990).

The Dutch physicist Pieter Zeeman (1865–1943) studied at the University of Leiden under the famous physicists H. Kamerlingh Onnes and H. A. Lorentz and received his degree in 1890. While at Leiden he showed that atomic spectral lines were split under the influence of an applied magnetic field. After his discovery he left Leiden in 1897 of the University of Amsterdam where he remained until 1935. He shared the 1902 Nobel Prize in physics with his mentor Lorentz. *AIP Emilio Segrè Visual Archives, W. F. Meggers collection.*

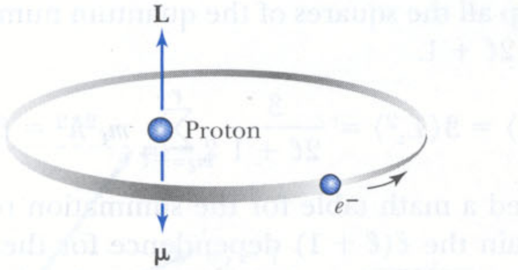

FIGURE 7.4 Representation of the orbital angular momentum **L** and magnetic moment **μ** of the hydrogen atom due to the electron orbiting the proton. The directions of **L** and **μ** are opposite because of the negative electron charge.

The relationship between **μ** and **L** is displayed in Figure 7.4.

In the absence of an external magnetic field to align them, the magnetic moments **μ** of atoms point in random directions. In classical electromagnetism, if a magnetic dipole having a magnetic moment **μ** is placed in an external magnetic field, the dipole will experience a torque $\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B}$ tending to align the dipole with the magnetic field. The dipole also has a potential energy V_B in the field given by

$$V_B = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{7.27}$$

If the system can change its potential energy, the magnetic moment will align itself with the external magnetic field.

Note the similarity with the case of the spinning top in a gravitational field. The gravitational field is not parallel to the angular momentum, and the force of gravity pulling down on the top results in a **precession** of the top about the field direction, not a falling down of the top. Precisely the same thing happens here with the magnetic moment. The angular momentum is aligned with the magnetic moment, and the torque between **μ** and **B** causes a precession of **μ** about the magnetic field (see Figure 7.4), not an alignment. The magnetic field establishes a preferred direction in space along which we customarily define the z axis. Then we have

$$\mu_z = \frac{e\hbar}{2m}\, m_\ell = \mu_B\, m_\ell \tag{7.28}$$

Bohr magneton

where $\mu_B \equiv e\hbar/2m$ is a unit of magnetic moment called a **Bohr magneton.** Because of the quantization of L_z and the fact that $L = \sqrt{\ell(\ell+1)}\hbar > m_\ell\hbar$, we cannot have $|\boldsymbol{\mu}| = \mu_z$; the magnetic moment cannot align itself exactly in the z direction. Just like the angular momentum **L**, the magnetic moment **μ** has only certain allowed quantized orientations. Note also that in terms of the Bohr magneton, $\boldsymbol{\mu} = -\mu_B \mathbf{L}/\hbar$.

Example 7.3

Determine the precessional frequency of an atom having magnetic moment **μ** in an external magnetic field **B**. This precession is known as the *Larmor precession.*

Solution: We have already seen that the torque $\boldsymbol{\tau}$ is equal to $\boldsymbol{\mu} \times \mathbf{B}$, but from mechanics we also know that the torque is $d\mathbf{L}/dt$. The torque in Figure 7.5 is perpendicular

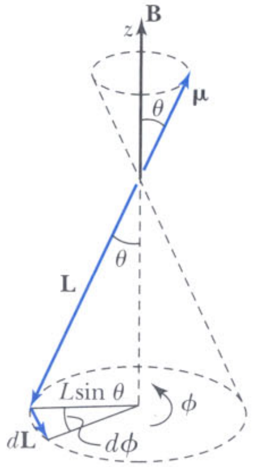

FIGURE 7.5 An atom having magnetic moment $\boldsymbol{\mu}$ feels a torque $\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B}$ due to an external magnetic field $\mathbf{B}$. This torque must also be equal to $d\mathbf{L}/dt$. The vectors $\boldsymbol{\mu}$ and $\mathbf{L}$ are antiparallel, so the vector $d\mathbf{L}/dt$ must be perpendicular to $\boldsymbol{\mu}$, $\mathbf{B}$, and $\mathbf{L}$. As shown in the figure, $d\mathbf{L}/dt$ requires both $\boldsymbol{\mu}$ and $\mathbf{L}$ to precess (angle ϕ) about the magnetic field $\mathbf{B}$.

to $\boldsymbol{\mu}$, $\mathbf{L}$, and $\mathbf{B}$ and is out of the page. This must also be the direction of the change in momentum $d\mathbf{L}$ as seen in Figure 7.5. Thus $\mathbf{L}$ and $\boldsymbol{\mu}$ precess about the magnetic field. The magnitude of $d\mathbf{L}$ is given by $L \sin\theta\, d\phi$ (see Figure 7.5). The Larmor frequency ω_L is given by $d\phi/dt$,

$$\omega_L = \frac{d\phi}{dt} = \frac{1}{L \sin\theta} \frac{dL}{dt} \tag{7.29}$$

We now insert the magnitude of $L = 2m\mu/e$ from Equation (7.26). The value of dL/dt, the magnitude of $\boldsymbol{\mu} \times \mathbf{B}$, can be determined from Figure 7.5 to be $\mu B \sin\theta$. Equation (7.29) becomes

$$\omega_L = \left(\frac{e}{2m\mu \sin\theta}\right) \mu B \sin\theta = \frac{eB}{2m} \tag{7.30}$$

What about the energy of the orbiting electron in a magnetic field? It takes work to rotate the magnetic moment away from $\mathbf{B}$. With $\mathbf{B}$ along the z direction, we have from Equations (7.16), (7.17), and (7.27)

$$V_B = -\mu_z B = +\mu_B m_\ell B \tag{7.31}$$

The potential energy is thus quantized according to the *magnetic quantum number* m_ℓ; each (degenerate) atomic level of given ℓ is split into $2\ell + 1$ different energy states according to the value of m_ℓ. The energy degeneracy of a given $n\ell$ level is removed by a magnetic field (see Figure 7.6a).

Example 7.4

What is the value of the Bohr magneton? Use that to calculate the energy difference between the $m_\ell = 0$ and $m_\ell = +1$ components in the $2p$ state of atomic hydrogen placed in an external field of 2 T.

Solution: We first find the Bohr magneton to be

$$\begin{aligned}\mu_B &= \frac{e\hbar}{2m} \\ &= \frac{(1.602 \times 10^{-19}\ \mathrm{C})(1.055 \times 10^{-34}\ \mathrm{J \cdot s})}{2(9.11 \times 10^{-31}\ \mathrm{kg})} \\ &= 9.27 \times 10^{-24}\ \mathrm{J/T}\end{aligned} \tag{7.32}$$

The international system of units has been used (T = tesla for magnetic field). The energy splitting is given by (see Figure 7.6a)

$$\Delta E = \mu_B B \Delta m_\ell \tag{7.33}$$

where $\Delta m_\ell = 1 - 0 = 1$. Hence, we have

$$\begin{aligned}\Delta E &= (9.27 \times 10^{-24}\ \mathrm{J/T})(2\ \mathrm{T}) = 1.85 \times 10^{-23}\ \mathrm{J} \\ &= 1.16 \times 10^{-4}\ \mathrm{eV}\end{aligned}$$

An energy difference of 10^{-4} eV is easily observed by optical means.

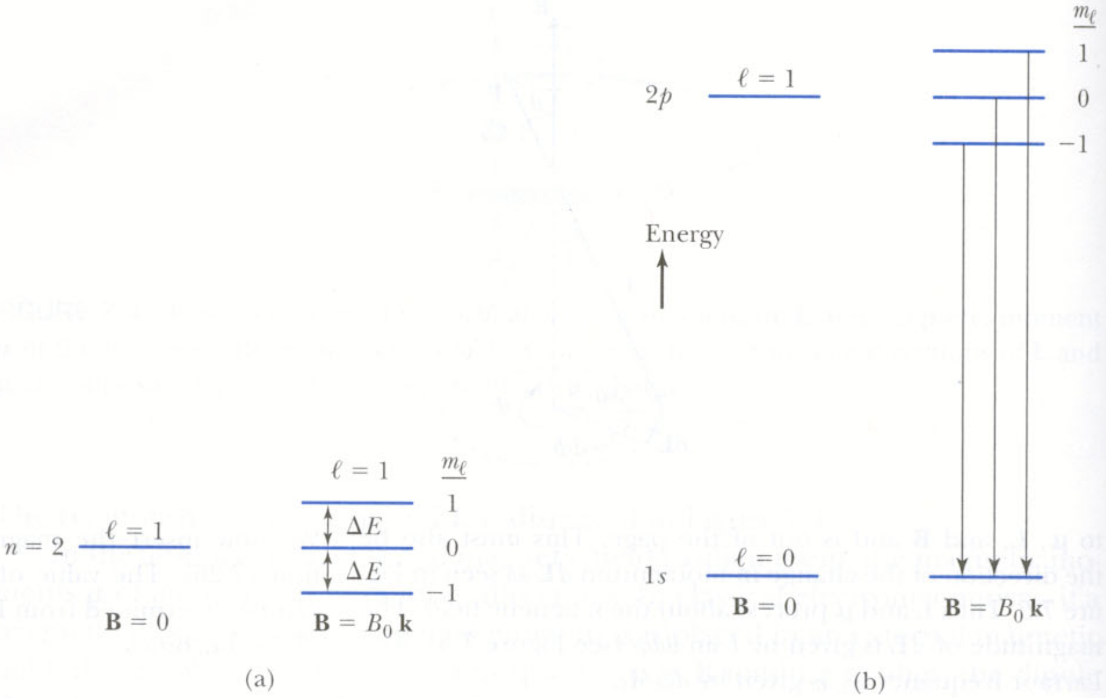

FIGURE 7.6 The normal Zeeman effect. (a) An external magnetic field removes the degeneracy of a $2p$ level and reveals the three different energy states. (b) There are now transitions with three different energies between an excited $2p$ level and the $1s$ ground state in atomic hydrogen. The energy ΔE has been grossly exaggerated along the energy scale.

The splitting of spectral lines can be partially explained by the application of external magnetic fields. This result, the normal Zeeman effect, is displayed in Figure 7.6. When a magnetic field is applied, the $2p$ level of atomic hydrogen is split into 3 different energy states with the energy difference given by Equation (7.33). A transition for an electron in the excited $2p$ level to the $1s$ ground state results in three different energy transitions as shown in Figure 7.6b. The energy differences are shown greatly exaggerated in Figure 7.6b, but as instruments were improved, such differences could be observed. The application of external magnetic fields eliminates much of the energy degeneracy, resulting in more quantized states having different energies between which electrons are

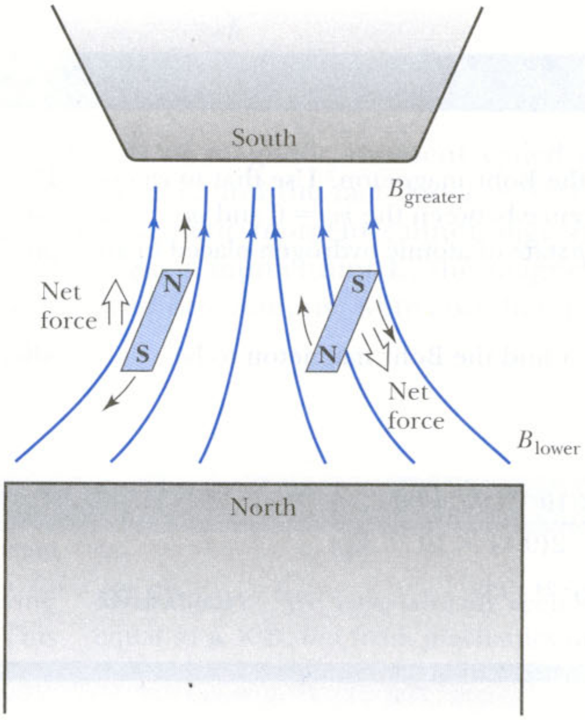

FIGURE 7.7 An inhomogeneous magnetic field is created by the smaller south pole. Two bar magnets representing atomic magnetic moments have $\boldsymbol{\mu}$ in opposite directions. Because the force on the top of the bar magnets is greater than that on the bottom, there will be a net translational force on the bar magnets (atoms).

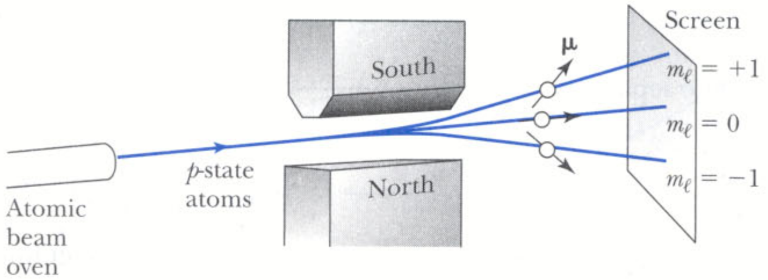

FIGURE 7.8 Schematic diagram of expected result of Stern and Gerlach experiment if atoms in a *p* state are used. Three patterns of atoms, due to $m_\ell = \pm 1, 0$, are expected on the screen. The magnet poles are arranged to produce a magnetic field gradient as shown in Figure 7.7. The experiment performed by Stern and Gerlach reported only two lines, not three (see Section 7.5).

able to move while emitting or absorbing electromagnetic radiation. We will see in Section 7.6 that the selection rule for m_ℓ will not allow more than three different lines in the normal Zeeman effect (see Problem 29).

Efforts were begun in the 1920s to detect the effects of space quantization (m_ℓ) by measuring the energy difference ΔE as in Example 7.4. In 1922 O. Stern and W. Gerlach reported the results of an experiment that clearly showed evidence for space quantization. If an external magnetic field is inhomogeneous—for example, if it is stronger at the south pole than at the north pole—then there will be a net force on a magnet placed in the field as well as a torque. This force is represented in Figure 7.7, where the net force on $\boldsymbol{\mu}$ (direction of S to N in bar magnet) is different for different orientations of $\boldsymbol{\mu}$ in the inhomogeneous magnetic field **B**.

Now if we pass an atomic beam of particles in the $\ell = 1$ state through a magnetic field along the *z* direction, we have from Equation (7.31), $V_B = -\mu_z B$, and the force on the particles is $F_z = -(dV_B/dz) = \mu_z(dB/dz)$. There will be a different force on each of the three possible m_ℓ states. A schematic diagram of the Stern-Gerlach experiment is shown in Figure 7.8. The $m_\ell = +1$ state will be deflected up, the $m_\ell = -1$ state down, and the $m_\ell = 0$ state will be undeflected.

Stern and Gerlach performed their experiment with silver atoms and observed two distinct lines, not three. This was clear evidence of space quantization, although the number of m_ℓ states is always odd $(2\ell + 1)$ and should have produced an odd number of lines if the space quantization were due to the magnetic quantum number m_ℓ.

Otto Stern (1888–1969) was born in a part of Germany that is now in Poland, where he was educated and worked in several universities until he left Germany in 1933 to avoid persecution and emigrated to the United States. He was educated and trained as a theorist, but changed to experimentation when he began his molecular beam experiments in 1920 at the University of Frankfurt with Walter Gerlach. He continued his distinguished career in Hamburg and later at Carnegie Tech in Pittsburgh. He received the Nobel Prize in 1943.
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Example 7.5

In 1927 T. E. Phipps and J. B. Taylor of the University of Illinois reported an important experiment similar to the Stern-Gerlach experiment but using hydrogen atoms instead of silver. This was done because hydrogen is the simplest atom, and the separation of the atomic beam in the inhomogeneous magnetic field would allow a clearer interpretation. The atomic hydrogen beam was produced in a discharge tube having a temperature of 663 K. The highly collimated beam passed along the *x* direction through an inhomogeneous field (of length 3 cm) having an average value of 1240 T/m along the *z* direction. If the magnetic moment of the hydrogen atom is 1 Bohr magneton, what is the separation of the atomic beam?

Solution: The force can be found from the potential energy of Equation (7.31).

$$F_z = -\frac{dV}{dz} = \mu_z \frac{dB}{dz}$$

The acceleration of the hydrogen atom along the *z* direction is $a_z = F_z/m$. The separation of the atom along the *z* direction due to this acceleration is $d = a_z t^2/2$. The time that the atom spends within the inhomogeneous field is $t = \Delta x / v_x$ where Δx is the length of the inhomogeneous field, and v_x is the constant speed of the atom within the field. The separation d is therefore found from

$$d = \frac{1}{2}\,a_z t^2 = \frac{1}{2}\left(\frac{F_z}{m}\right) t^2 = \frac{1}{2m}\left(\mu_z \frac{dB}{dz}\right)\left(\frac{\Delta x}{v_x}\right)^2$$

We know all the values needed to determine d except the speed v_x, but we do know the temperature of the hydrogen gas. The average energy of the atoms collimated along the x direction is $\frac{1}{2}\,m\langle v_x^{\,2}\rangle = \frac{3}{2}\,kT$. We calculate $\langle v_x^{\,2}\rangle$ to be

$$v_x^{\,2} = \frac{3kT}{m} = \frac{3(1.38 \times 10^{-23}\ \mathrm{J/T})(663\ \mathrm{K})}{1.67 \times 10^{-27}\ \mathrm{kg}}$$

$$= 1.64 \times 10^{7}\ \mathrm{m^2/s^2}$$

The separation d of the one atom is now determined to be

$$d = \frac{1}{2(1.67 \times 10^{-27}\ \mathrm{kg})}\left(9.27 \times 10^{-24}\frac{\mathrm{J}}{\mathrm{T}}\right)\left(1240\frac{\mathrm{T}}{\mathrm{m}}\right)$$

$$\times \frac{(0.03\mathrm{m})^2}{(1.64 \times 10^{7}\ \mathrm{m^2/s^2})} = 0.19 \times 10^{-3}\ \mathrm{m}$$

Phipps and Taylor found only two distinct lines as did Stern and Gerlach for silver atoms, and the separation of the lines from the central ray with no magnetic field was 0.19 mm as we just calculated! The total separation of the two lines (one deflected up and one down) was 0.38 mm. The mystery still remained as to why there were only two lines.

7.5 Intrinsic Spin

By the early 1920s there was clearly a problem. Wolfgang Pauli was the first to suggest that a fourth quantum number (after n, ℓ, m_ℓ) assigned to the electron might explain the anomalous optical spectra. His reasoning for four quantum numbers was based on relativity, where there are four coordinates—three space and one time. The physical significance of this fourth quantum number was not made clear.

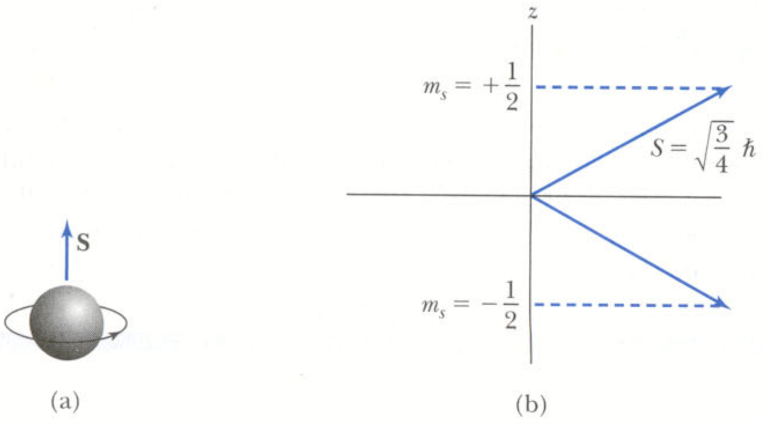
In 1925 Samuel Goudsmit and George Uhlenbeck, two young physics graduate students in Holland, proposed that *the electron must have an intrinsic angular momentum* and therefore a magnetic moment (because the electron is charged). Classically, this corresponds in the planetary model to the fact that the Earth rotates on its own axis as it orbits the sun. However, this simple classical picture runs into serious difficulties when applied to the spinning charged electron. Ehrenfest showed that the surface of the electron (or electron cloud) would have to be moving at a velocity greater than the speed of light! If such an intrinsic angular momentum exists, we must regard it as a *purely quantum-mechanical result* (see Problems 38 and 39).

Intrinsic spin quantum number

Magnetic spin quantum number

In order to explain experimental data, Goudsmit and Uhlenbeck proposed that the electron must have an **intrinsic spin quantum number** $s = 1/2$. The spinning electron reacts similarly to the orbiting electron in a magnetic field. Therefore, we should try to find quantities analogus to the angular momentum variable L, L_z, ℓ, and m_ℓ. By analogy, there will be $2s + 1 = 2(1/2) + 1 = 2$ components of the spin angular momentum vector $\mathbf{s}$. Thus the **magnetic spin quantum number** m_s has only two values, $m_s = \pm 1/2$. The electron's spin will be oriented either "up" or "down" in a magnetic field (see Figure 7.9), and the electron can never be spinning with its *magnetic moment* μ_s exactly along the z axis (the direction of the external magnetic field $\mathbf{B}$).

For each atomic state described by the three quantum numbers (n, ℓ, m_ℓ) discussed previously, there are now two distinct states, one with $m_s = +1/2$ and one with $m_s = -1/2$. These states will be degenerate in energy unless the atom is in an external magnetic field. In a magnetic field these states will have different energies due to an energy separation like that of Equation (7.33). We say the



(a)

(b)

FIGURE 7.9 (a) A purely classical schematic of the intrinsic spin angular momentum, **S**, of a spinning electron. (b) The quantization of **S**, which can have only two positions in space relative to z (direction of external magnetic field). The z component of **S** is $S_z = \pm\hbar/2$.

splitting of these energy levels by the magnetic field has removed the energy degeneracy.

Intrinsic spin angular momentum vector

Gyromagnetic ratio

The **intrinsic spin angular momentum vector S** has a magnitude of $|\mathbf{S}| = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$. The magnetic moment is $\boldsymbol{\mu}_s = -(e/m)\,\mathbf{S}$, or $-2\mu_B\mathbf{S}/\hbar$. The fact that the coefficient of $\mathbf{S}/\hbar$ is $-2\mu_B$ rather than $-\mu_B$ as with the orbital angular momentum **L** is a consequence of the theory of relativity (Dirac equation), and we will not pursue the matter further here. This numerical factor relating the magnetic moment to each angular momentum vector is called the **gyromagnetic ratio.** It is designated by the letter g with the appropriate subscript (ℓ or s), so that $g_\ell = 1$ and $g_s = 2$. In terms of the gyromagnetic ratios, then,

$$\boldsymbol{\mu}_\ell = -\frac{g_\ell \mu_B \mathbf{L}}{\hbar} = -\frac{\mu_B \mathbf{L}}{\hbar} \tag{7.34a}$$

$$\boldsymbol{\mu}_s = -\frac{g_s \mu_B \mathbf{S}}{\hbar} = -2\,\frac{\mu_B \mathbf{S}}{\hbar} \tag{7.34b}$$

The z component of **S** is $S_z = m_s\hbar = \pm\hbar/2$.

We can now understand why the experiment of Stern and Gerlach only produced two distinct lines. If the atoms were in a state with $\ell = 0$, there would be no splitting due to m_ℓ. However, there is still space quantization due to the intrinsic spin that would be affected by the inhomogeneous magnetic field. The same arguments used previously for $\boldsymbol{\mu}_\ell$ (we now use the subscript ℓ to indicate the magnetic moment due to the orbiting electron and the subscript s to indicate the magnetic moment due to intrinsic spin) can now be applied to $\boldsymbol{\mu}_s$, and the potential energy, Equation (7.27), becomes

$$V_B = -\boldsymbol{\mu}_s \cdot \mathbf{B} = +\frac{e}{m}\,\mathbf{S} \cdot \mathbf{B} \tag{7.35}$$

If we look at the hydrogen atom in the frame of the orbiting electron, we have the classical result shown in Figure 7.10. This classical picture indicates that the orbiting proton creates a magnetic field at the position of the electron. Therefore, even without an external magnetic field, the electron will feel the effects of an internal magnetic field, and Equation (7.35) predicts an energy difference depending on whether the electron's spin is up or down. Many levels are effectively split into two different states called *doublets*.

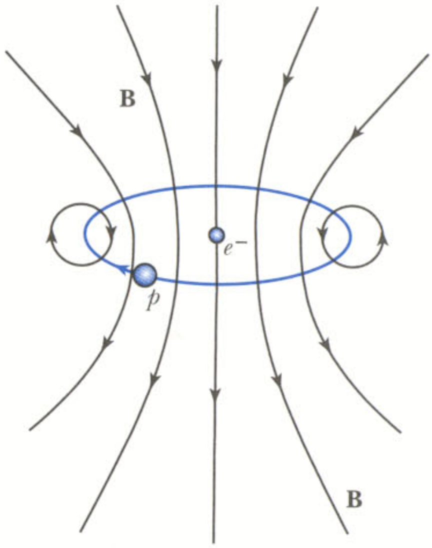


FIGURE 7.10 The hydrogen atom in the frame of reference of the electron. In this case, the orbiting proton creates a *magnetic field at the position* of the electron.

The relativistic quantum theory proposed by P. A. M. Dirac in 1928 showed that the intrinsic spin of the electron *required* a fourth quantum number as a consequence of the theory of relativity.

Example 7.6

How many distinctly different states (and therefore wave functions) exist for the 4*d* level of atomic hydrogen?

Solution: With the inclusion of the magnetic spin quantum number the number of states has multiplied. For the 4*d* level ($n = 4$, $\ell = 2$) there are $2\ell + 1 = 5$ different values of m_ℓ. For each of these $m_\ell (-2, -1, 0, 1, 2)$, there are two m_s states ($\pm 1/2$). Therefore there are 10 different possible individual states for a 4*d* level of atomic hydrogen.

Note that (in the absence of an applied magnetic field) the fourth quantum number makes the degeneracy of the *n*th quantum level $2n^2$.

7.6 Energy Levels and Electron Probabilities

We are now in a position to discuss a complete description of the hydrogen atom. Every possible state of the hydrogen atom has a distinct wave function that is specified completely by four quantum numbers: (n, ℓ, m_ℓ, m_s). In many cases the energy differences associated with the quantum numbers m_ℓ and m_s are insignificant (that is, the states are nearly degenerate), and we can describe the states adequately by *n* and ℓ alone: for example, 1*s*, 2*p*, 2*s*, 3*d*, and so on. Generally, capital letters (that is, *S*, *P*, *D*) are used to describe the orbital angular momentum of atomic states and lowercase letters (that is, *s*, *p*, *d*) to describe those for individual electrons. For hydrogen it makes little difference because each state only has a single electron, and we will use either specification.

In Figure 7.11 we show an energy-level diagram for hydrogen in the absence of an external magnetic field. The energy levels are degenerate with respect to

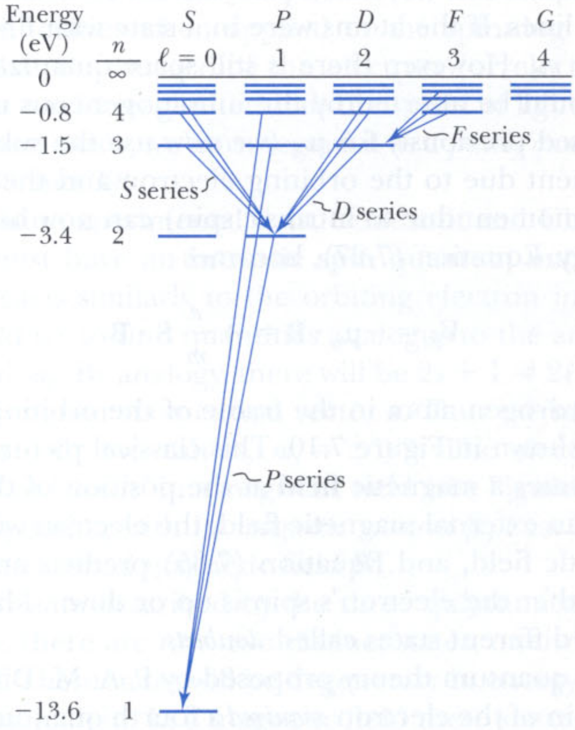


FIGURE 7.11 Energy-level diagram of hydrogen atom with no external magnetic field. Also shown are allowed photon transitions between some levels.

ℓ, m_ℓ, and m_s, but in a magnetic field this degeneracy is removed. For heavier atoms with several electrons, the degeneracy is removed—either because of internal magnetic fields within the atom or because the average potential energy due to the nucleus plus electrons is non-coulombic. In atoms with $Z > 1$ the smaller ℓ values tend to lie lower in energy for a given n (see Section 8.1). For example, in sodium or potassium, $E(4S) < E(4P) < E(4D) < E(4F)$. For hydrogen, the energy levels depend only on the principal quantum number n and are given to great accuracy by the Bohr theory.

We have previously learned that atoms emit characteristic electromagnetic radiation when they make transitions to states of lower energy. An atom in its ground state cannot emit radiation; it can absorb electromagnetic radiation, or it can gain energy through inelastic bombardment by particles, especially electrons. The atom will then have one or more of its electrons transferred to a higher energy state.

Selection Rules

Transition probabilities

We can use the wave functions obtained from the solution of the Schrödinger equation to calculate **transition probabilities** for the electron to change from one state to another. The results of such calculations show that electrons absorbing or emitting photons are much more likely to change states when $\Delta\ell = \pm 1$. Such transitions are called **allowed.** Other transitions, with $\Delta\ell \neq \pm 1$, are theoretically possible but occur with much smaller probabilities and are called **forbidden transitions.** There is no selection rule restricting the change Δn of the principal quantum number. The selection rule for the magnetic quantum number is $\Delta m_\ell = 0, \pm 1$. The magnetic spin quantum number m_s can (but need not) change between 1/2 and −1/2. We summarize the selection rules for allowed transitions:

Allowed and forbidden transitions

Selection rules

$$\begin{aligned} \Delta n &= \text{anything} \\ \Delta\ell &= \pm 1 \qquad (7.36) \\ \Delta m_\ell &= 0, \pm 1 \end{aligned}$$

Some allowed transitions are diagrammed in Figure 7.11. Notice that there are no transitions shown for $3P \rightarrow 2P$, $3D \rightarrow 2S$, and $3S \rightarrow 1S$ because those transitions violate the $\Delta\ell = \pm 1$ selection rule.

If the orbital angular momentum of the atom changes by $\hbar$ when absorption or emission of radiation takes place, we must still check that all conservation laws are obeyed. What about the conservation of angular momentum? The only external effect on the atom during the absorption or emission process is that due to the photon being absorbed or emitted. If the state of the atom changes, then the photon must possess energy, linear momentum, and angular momentum. The $\Delta\ell = \pm 1$ selection rule strongly suggests that the photon carries one unit ($\hbar$) of angular momentum. By applying quantum mechanics to Maxwell's equations, it is possible to show* that electromagnetic radiation is quantized into photons having $E = h\nu$ and intrinsic angular momentum of $\hbar$. A consequence of the photon's intrinsic angular momentum is the circular polarization of an electromagnetic wave.

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*See Leonard Schiff's *Quantum Mechanics* 3rd ed. New York: McGraw-Hill, 1968 for a discussion of both the semiclassical and quantum treatment of radiation.

Example 7.7

Which of the following transitions for quantum numbers (n, ℓ, m_ℓ, m_s) are allowed for the hydrogen atom, and if allowed, what is the energy involved?

(a) $(2, 0, 0, 1/2) \rightarrow (3, 1, 1, 1/2)$
(b) $(2, 0, 0, 1/2) \rightarrow (3, 0, 0, 1/2)$
(c) $(4, 2, -1, -1/2) \rightarrow (2, 1, 0, 1/2)$

Solution: We want to compare $\Delta\ell$ and Δm_ℓ with the selection rules of Equation (7.36). If allowed, the energies may be obtained from Equation (7.20) with $E_0 = 13.6$ eV.

(a) $\Delta\ell = +1$, $\Delta m_\ell = 1$; allowed.

$$\Delta E = E_3 - E_2 = -13.6\ \text{eV}\left(\frac{1}{3^2} - \frac{1}{2^2}\right)$$

$= 1.89$ eV, corresponding to absorption of a 1.89-eV photon.

(b) $\Delta\ell = 0$, $\Delta m_\ell = 0$; not allowed, because $\Delta\ell \neq \pm 1$.

(c) $\Delta\ell = -1$, $\Delta m_\ell = 1$; allowed. Notice that $\Delta n = -2$ and $\Delta m_s = +1$ does not affect whether the transition is allowed.

$$\Delta E = E_2 - E_4 = -13.6\ \text{eV}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$= -2.55$ eV, corresponding to emission of a 2.55-eV photon.

Probability Distribution Functions

In the Bohr theory of the hydrogen atom, the electrons were pictured as orbiting around the nucleus in simple circular (or elliptical) orbits. The position vector **r** of the electron was well defined. In the wave picture of the atom, we must use wave functions to calculate the probability distributions* of the electrons. The "position" of the electron is therefore spread over space and is not well defined. The distributions can be found by examining the separable wave functions $R(r)$, $f(\theta)$, and $g(\phi)$. The $g(\phi)$ distribution is simplest because it leads to uniform probability—all values of ϕ are equally likely. It is easy to see why. Because the azimuthal part of the wave function is always of the form $e^{im_\ell\phi}$, the probability density $\psi^*\psi$ will contain a corresponding factor of $(e^{im_\ell\phi})^* e^{im_\ell\phi} = e^{-im_\ell\phi}e^{im_\ell\phi} = e^0 = 1$.

We may use the radial wave function $R(r)$ to calculate radial probability distributions of the electron (that is, the probability of the electron being at a given r). As was discussed in Section 5.6, the probability of finding the electron in a differential volume element dV is

$$dP = \psi^*(r, \theta, \phi)\,\psi(r, \theta, \phi)\,dV \tag{7.37}$$

We are interested in finding the probability $P(r)\,dr$ of the electron being between r and $r + dr$. The differential volume element in spherical polar coordinates is

$$dV = r^2 \sin\theta\, dr\, d\theta\, d\phi$$

Therefore,

$$P(r)\,dr = r^2 R^*(r) R(r)\,dr \int_0^{\pi} |f(\theta)|^2 \sin\theta\, d\theta \int_0^{2\pi} |g(\phi)|^2\, d\phi \tag{7.38}$$

We are integrating over θ and ϕ, because we are only interested in the radial dependence. If the integrals over $f(\theta)$ and $g(\phi)$ have already been normal-

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*It may be useful at this time to review Section 5.6, where the relationships between probability and wave functions were discussed.

TABLE 7.2
Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{a_0^{3/2}}e^{-r/a_0}$
2	0	$\left(2-\frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}}\frac{2}{81\sqrt{3}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{6}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0^2}e^{-r/3a_0}$

ized to unity, the probability of finding the electron between r and $r + dr$ reduces to

$$P(r)\,dr = r^2|R(r)|^2\,dr \tag{7.39}$$

Radial probability

The first few radial wave functions are listed in Table 7.2, where a_0 = Bohr radius = 0.53×10^{-10} m. The radial probability density is

$$P(r) = r^2|R(r)|^2 \tag{7.40}$$

This probability density depends only on n and ℓ. In Figure 7.12 we display both $R(r)$ and $P(r)$ for the lowest-lying states of the hydrogen atom.

Example 7.8

Find the most probable radius for the electron of a hydrogen atom in the 1*s* and 2*p* states.

Solution: To find the most probable radial value we take the derivative of the probability density $P(r)$ with respect to r and set it equal to zero.

1*s* state:

$$\frac{d}{dr}P(r) = 0 = \frac{d}{dr}\left(\frac{4e^{-2r/a_0}}{a_0^3}r^2\right)$$

$$0 = \frac{4}{a_0^3}\left(-\frac{2}{a_0}r^2 + 2r\right)e^{-2r/a_0}$$

$$\frac{2r^2}{a_0} = 2r$$

$r = a_0$ Most probable radius for 1*s* state electron (7.41)

2*p* state:

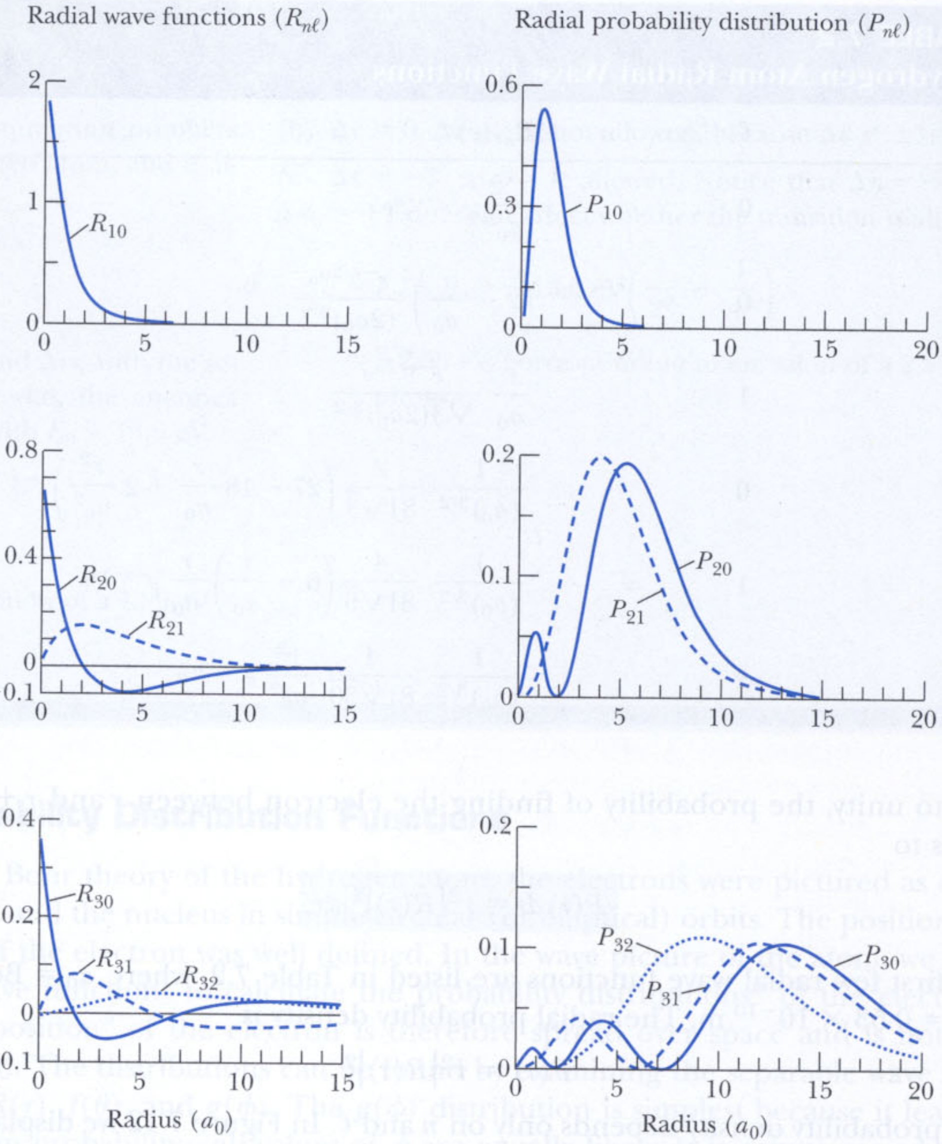
$$\frac{d}{dr}\left(\frac{e^{-r/a_0}}{3(2a_0)^3}\frac{r^4}{a_0^2}\right) = 0$$

$$\frac{1}{24a_0^5}\left(-\frac{r^4}{a_0} + 4r^3\right) = 0$$

$$\frac{r^4}{a_0} = 4r^3$$

$r = 4a_0$ Most probable radius for 2*p* state electron (7.42)

Notice that the most probable radii for the 1*s* and 2*p* states agree with the Bohr radii. This occurs only for the largest possible ℓ value for each n (see Problem 32).



(a)

(b)

FIGURE 7.12 (a) The radial wave function $R_{n\ell}(r)$ plotted as a function of radius (in units of Bohr radius a_0) for several states of the hydrogen atom. (b) The radial probability distribution $P_{n\ell}$, which gives the probability of the electron being between r and $r + dr$.

Example 7.9

Calculate the average orbital radius of a 1*s* electron in the hydrogen atom.

Solution: The expectation (or average) value of r is (see Section 6.3)

$$\langle r \rangle = \int \psi^*(r, \theta, \phi)\, r\psi(r, \theta, \phi)\, dV$$
$$= \int r\mathrm{P}(r)\, dr$$

where we have again integrated over θ and ϕ.

$$\langle r \rangle = \int_0^\infty \frac{4}{{a_0}^3}\, e^{-2r/a_0}\, r^3 dr$$

We look up this integral in Appendix 3 and find

$$\int_0^\infty r^3 e^{-2r/a_0}\, dr = \frac{3{a_0}^4}{8}$$

so that

$$\langle r \rangle = \frac{4}{{a_0}^3}\,\frac{3{a_0}^4}{8} = \frac{3}{2}\, a_0 \qquad \text{For the 1}s\text{ state electron}$$

Therefore, the average electron radius in the 1*s* state is larger than the most probable value, the Bohr radius. We can see that this result is reasonable by examining the radial probability distribution for the 1*s* state displayed in Figure 7.12. The maximum (or most probable) value occurs at a_0, but the average is greater than a_0 because of the shape of the tail of the distribution.

Example 7.10

What is the probability of the electron in the 1s state of the hydrogen atom being at a radius greater than the Bohr radius a_0?

Solution: We simply integrate the radial probability distribution from $r = a_0$ to ∞, because $P(r)$ is already normalized (that is, it has a unit probability of being somewhere between 0 and ∞).

$$\text{Probability} = \int_{a_0}^{\infty} P(r)\,dr$$

$$= \frac{4}{{a_0}^3}\int_{a_0}^{\infty} e^{-2r/a_0} r^2\,dr$$

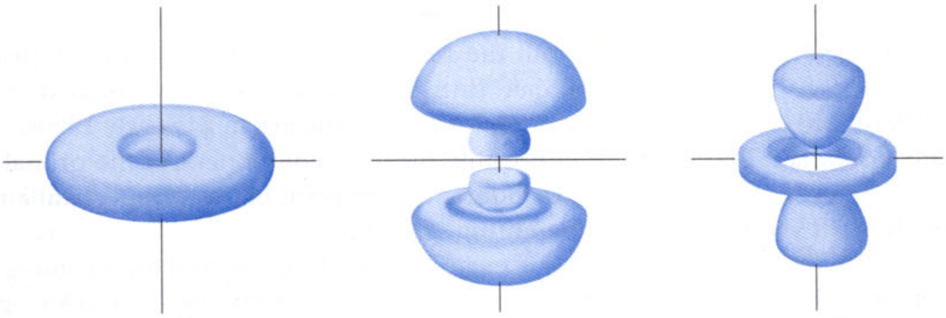
We look up the indefinite integral in Appendix 3 and evaluate to find the result

$$\text{Probability} = \frac{4}{{a_0}^3}\left(\frac{5}{4}{a_0}^3 e^{-2}\right) = 5e^{-2} = 0.68$$

The probability of the electron being outside the Bohr radius in a 1s state is greater than 50%. This explains why we found $\langle r\rangle_{1s} = 1.5\,a_0$. This result is consistent with the shape of the 1s curve in Figure 7.12b.

The probability distributions for the $\ell = 0$ state electrons are spherically symmetric, because the wave functions have no θ or ϕ dependence (see Table 7.1). For $\ell > 0$ the distributions are interesting because of the $f(\theta)$ dependence. For example, consider a p orbital. Referring to Table 7.1, we see that there are two possibilities for the angular part of the wave function. If $\ell = 1$ and $m_\ell = 0$, the Y_{10} will be a factor in the wave function, and therefore $\cos^2\theta$ will be a factor in the probability density $\psi^*\psi$. In this case the probability density will be highest near 0° and 180°, that is, near the $+z$ axis and $-z$ axis. The other possible combinations for the quantum numbers of an electron in a p orbital are $\ell = 1$ and $m_\ell = \pm 1$. Now $Y_{1\pm1}$ will go into the wave function, and hence $\sin^2\theta$ will be a factor in the probability density $\psi^*\psi$. The probability is highest at $\theta = 90°$, that is, in the xy plane. The probability distributions seen in Figure 7.13 are consistent with this analysis.

When we look at d orbitals, the situation becomes a bit more complicated, but a similar analysis will allow us to see at what angles θ the probability density is maximized. For the $\ell = 2$, $m_\ell = 0$ state, we can see that Y_{20}^2 must have a maximum around $\theta = 0°$ and 180°. Once again, these results are shown in Figure 7.13. Similarly $Y_{2\pm2}^2$ (corresponding to the $\ell = 2$, $m_\ell = \pm 2$ states) has a maximum in the xy plane. For the $\ell = 2$, $m_\ell = \pm 1$ states, we find a factor $\sin^2\theta\cos^2\theta$



$n = 2$
$\ell = 1$
$m_\ell = \pm 1$

$n = 3$
$\ell = 1$
$m_\ell = 0$

$n = 3$
$\ell = 2$
$m_\ell = 0$

FIGURE 7.13 Pictorial representation of the probability density $|\Psi(r, \theta, \phi)|^2$ for the hydrogen atom for three different electron states. There is axial symmetry about the z axis in each case. The shaded regions indicate those parts of space with the highest probability densities.

coming from $Y^2_{2\pm1}$. For these states the probability maxima are at $\theta = 45°$ and $135°$.

It is interesting to consider in which state (for a given n) the electron is closest to the origin. We can calculate $\langle r \rangle$ for the $2s$ and $2p$ states (see Problem 36) and find that the $2p$ average radius is smaller. However, because the $P(r)$ for the $2s$ state has two maxima, one with $r < a_0$, the electron in the $2s$ state will actually spend more time very close to the nucleus than will one in the $2p$ state. This effect can be seen in Figure 7.12, where the radial distribution for $P(r)$ in the $2s$ state extends farther out than that for $2p$, but there is a secondary maximum for $P(r)$ for the $2s$ state near a_0.

Summary

The Schrödinger wave theory is applied to atomic physics, beginning with the hydrogen atom. The application of the boundary conditions leads to three quantum numbers:

n	principal quantum number
ℓ	orbital angular momentum quantum number
m_ℓ	magnetic quantum number

with the values and restrictions (all are integers)

$$n = 1, 2, 3, 4, \ldots \qquad n > 0$$
$$\ell = 0, 1, 2, 3, \ldots, (n-1) \qquad \ell < n$$
$$m_\ell = -\ell, -\ell+1, \ldots, 0, 1, \ldots, \ell-1, \ell \qquad |m_\ell| \le \ell$$

The energy of the electron–proton system is quantized and depends to first order only on n. The orbital angular momentum L is quantized by $L = \sqrt{\ell(\ell+1)}\hbar$ and not by $n\hbar$ as in the Bohr theory. We use letter names *s, p, d, f, g, h*, . . . , to indicate the ℓ value for a given electron.

The z component of $\mathbf{L}$ is quantized, and $L_z = m_\ell \hbar$. This is referred to as *space quantization,* because $\mathbf{L}$ can only have certain orientations in space. In the absence of a magnetic field, the energy is degenerate with respect to ℓ and m_ℓ. In an external magnetic field each $n\ell$ level is split into $2\ell + 1$ different energy states (normal Zeeman effect).

In order to explain increasingly complex atomic spectra, a fourth quantum number was introduced by Goudsmit and Uhlenbeck. This quantum number s is related to the electron's intrinsic angular momentum, commonly referred to as *spin.* The electron spin quantum number is $s = 1/2$, and the values of the magnetic spin quantum number m_s are $\pm 1/2$. Stern and Gerlach observed in 1922 the effects of intrinsic spin, although at the time it was confused with orbital angular momentum.

The selection rules for allowed transitions for a change from one state to another are

$$\begin{aligned} \Delta n &= \text{anything} \\ \Delta \ell &= \pm 1 \\ \Delta m_\ell &= 0, \pm 1 \end{aligned} \tag{7.36}$$

The probability of finding an electron between r and $r + dr$ is $P(r)\,dr = r^2|R(r)|^2 dr$ where $R(r)$ is the radial wave function.

Questions

1. Do the radial wave functions depend on m_ℓ? Explain your reasons.
2. Would the radial wave functions be different for a potential $V(r)$ other than the Coulomb potential? Explain.
3. For what energy levels in the hydrogen atom will we not find $\ell = 2$ states?
4. What are the differences and similarities between atomic levels, atomic states, and atomic spectral lines? When do spectral lines occur?
5. Can the magnetic moment of an atom line up exactly with an external magnetic field? Explain.
6. What are the possible magnetic quantum numbers for an *f* state?
7. List all the reasons why you think a fourth quantum number (intrinsic spin) might have helped explain the complex optical spectra in the early 1920s.
8. Is it possible for the z component of the orbital magnetic moment to be zero, but not the orbital angular momentum? Explain.
9. A close examination of the spectral lines coming from starlight can be used to determine the star's magnetic field. Explain how this is possible.
10. If a hydrogen atom in the $2p$ excited state decays to the $1s$ ground state, explain how the following properties are conserved: energy, linear momentum, and angular momentum.

Problems

7.1 Application of the Schrödinger Equation to the Hydrogen Atom

1. Assume that the electron in the hydrogen atom is constrained to move only in a circle of radius *a* in the *xy* plane. Show that the separated Schrödinger equation for ϕ becomes

$$\frac{1}{a^2}\frac{d^2\psi}{d\phi^2} + \frac{2m}{\hbar^2}|E|\psi = 0$$

where ϕ is the angle describing the position on the circle. This is similar to the Bohr assumption.

2. Solve the equation in the previous problem for ψ. Find the allowed energies and angular momenta.

3. After separating the Schrödinger equation using $\psi = R(r)f(\theta)g(\phi)$, the equation for ϕ is

$$-\frac{1}{g}\frac{d^2g}{d\phi^2} = k^2$$

where $k =$ constant. Solve for $g(\phi)$ in this equation and apply the appropriate boundary conditions. Show that k must be 0 or a positive or negative integer ($k = m_\ell$, the magnetic quantum number).

4. Using the transformation equations between cartesian coordinates and spherical polar coordinates given in Figure 7.1, transform the Schrödinger Equation (7.2) from cartesian to spherical coordinates as given in Equation (7.3).

7.2 Solution of the Schrödinger Equation for Hydrogen

5. Show that the radial wave function R_{20} for $n = 2$ and $\ell = 0$ satisfies Equation (7.14). What energy E results? Is this consistent with the Bohr model?

6. Show that the radial wave function R_{21} for $n = 2$ and $\ell = 1$ satisfies Equation (7.10). What energy results? Is this consistent with the Bohr model?

7. Show that the radial wave function R_{21} for $n = 2$ and $\ell = 1$ is normalized.

8. The normalized wave function ψ for the ground state of hydrogen is given by

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0{}^3}}e^{-r/a_0}$$

Show that the wave function is normalized over all space.

7.3 Quantum Numbers

9. List all the possible quantum numbers (n, ℓ, m_ℓ) for the $n = 6$ level in atomic hydrogen.

10. For a $3p$ state give the possible values of n, ℓ, m_ℓ, L, L_z, L_x, and L_y.

11. Write down all the wave functions for the $3p$ level of hydrogen. Identify the wave functions by their quantum numbers. Use the solutions in Tables 7.1 and 7.2.

12. Prove that $\langle L^2 \rangle = \ell(\ell + 1)\hbar^2$ by actually performing the summation for Equation (7.24).

13. What is the degeneracy of the $n = 6$ shell of atomic hydrogen considering (n, ℓ, m_ℓ) and no magnetic field?

14. For a $3d$ state draw all the possible orientations of the angular momentum vector **L**. What is $L_x{}^2 + L_y{}^2$ for the $m_\ell = -1$ component?

15. What is the smallest value that ℓ may have if **L** is within 3° of the z axis?

16. Prove that the degeneracy of an atomic hydrogen state having principal quantum number n is n^2 (ignore the spin quantum number).

7.4 Magnetic Effects on Atomic Spectra—The Normal Zeeman Effect

17. Calculate the possible z components of the orbital angular momentum for an electron in a $4p$ state.

18. For hydrogen atoms in a $4d$ state what is the *maximum* difference in potential energy between atoms when placed in a magnetic field of 2.5 T? Ignore intrinsic spin.

19. Show that the wavelength difference between adjacent transitions in the normal Zeeman effect is given approximately by

$$\Delta\lambda = \frac{\lambda_0{}^2\,\mu_B B}{hc}$$

20. For hydrogen atoms in a d state sketch the orbital angular momentum with respect to the z axis. Use units of $\hbar$ along the z axis and calculate the allowed angles of μ_ℓ with respect to the z axis.

21. For a hydrogen atom in the $6f$ state, what is the minimum angle between the orbital angular momentum vector and the z axis?

22. The red Balmer series line in hydrogen ($\lambda = 656.5$ nm) is observed to split into three different spectral lines with $\Delta\lambda = 0.04$ nm between two adjacent lines when placed in a magnetic field B. What is the value of B if $\Delta\lambda$ is due to the energy splitting between two adjacent m_ℓ states?

23. A hydrogen atom in an excited $5f$ state is in a magnetic field of 3 T. How many different energy states can the electron have in the $5f$ subshell? (Ignore the magnetic spin effects.) What is the energy of the $5f$ state in the absence of a magnetic field? What will be the energy of each state in the magnetic field?

24. The magnetic field in a Stern-Gerlach experiment varies along the vertical direction as $dB_z/dz = 20$ T/cm. The horizontal length of the magnet is 7.1 cm, and the speed of the silver atoms averages 925 m/s. The mass of the silver atoms is 1.8×10^{-25} kg. Show that the z component of its magnetic moment is 1 Bohr magneton. What is the separation of the two silver atom beams as they leave the magnet?

25. An experimenter wants to separate silver atoms in a Stern-Gerlach experiment by at least 1 cm (a large separation) as they exit the magnetic field. To heat the silver she has an oven that can reach 1000°C and needs to order a suitable magnet. What should be the magnet specifications?

7.5 Intrinsic Spin

26. In an external magnetic field can the electron spin vector **S** point in the direction of **B**? Draw a diagram with $\mathbf{B} = B_0\,\mathbf{k}$ showing **S** and S_z.

27. Using all four quantum numbers (n, ℓ, m_ℓ, m_s) write down all possible sets of quantum numbers for the $5f$ state of atomic hydrogen. What is the total degeneracy?

28. Prove that the total degeneracy for an atomic hydrogen state having principal quantum number n is $2n^2$.

7.6 Hydrogen Atom Energy Levels and Electron Probabilities

29. Show that, for transitions between any two n states of atomic hydrogen, no more than three different spectral lines can be obtained for the normal Zeeman effect.

30. Find whether the following transitions are allowed, and if they are, find the energy involved and whether the photon is absorbed or emitted for the hydrogen atom: (a) $(5, 2, 1, \frac{1}{2}) \rightarrow (5, 2, 1, -\frac{1}{2})$; (b) $(4, 3, 0, \frac{1}{2}) \rightarrow (4, 2, 1, -\frac{1}{2})$; (c) $(5, 2, -2, -\frac{1}{2}) \rightarrow (1, 0, 0, -\frac{1}{2})$; (d) $(2, 1, 1, \frac{1}{2}) \rightarrow (4, 2, 1, \frac{1}{2})$.

31. In Figure 7.12, the radial distribution function $P(r)$ for the $2s$ state of hydrogen has two maxima. Find the values of r (in terms of a_0) where these maxima occur.

32. Find the most probable radial position for the electron of the hydrogen atom in the $2s$ state. Compare this value with that found for the $2p$ state in Example 7.6.

33. Sketch the probability function as a function of r for the $2s$ state of hydrogen. At what radius is the position probability equal to zero?

34. Calculate the probability of an electron in the ground state of the hydrogen atom being inside the region of the proton (radius $\approx 1 \times 10^{-15}$ m). (*Hint:* Note that $r \ll a_0$.)

35. Calculate the probability that an electron in the ground state of the hydrogen atom can be found between $0.95a_0$ and $1.05a_0$.

36. Find the expectation value of the radial position for the electron of the hydrogen atom in the $2s$ and $2p$ states.

37. Calculate the probability of an electron in the $2s$ state of the hydrogen atom being inside the region of the proton (radius $\approx 1 \times 10^{-15}$m). Repeat for $2p$ electron. (*Hint:* Note that $r \ll a_0$).

General Problems

38. Assume the following (incorrect!) classical picture of the electron intrinsic spin. Take the electrical energy of the electron to be equal to its mass energy concentrated into a spherical shell of radius R.

$$\frac{e^2}{4\pi\epsilon_0 R} = mc^2$$

Calculate R (called the *classical electron radius*). Now let this spherical shell rotate and calculate the velocity in order to obtain the electron intrinsic spin.

$$\text{Angular momentum} = I\omega = I\frac{v}{R} = \frac{\hbar}{2}$$

where I = moment of inertia of a spherical shell = $2mR^2/3$. Is the value of v obtained in this manner consistent with the theory of relativity? Explain.

39. As in the previous problem, we want to calculate the speed of the rotating electron. Now let's assume that the diameter of the electron is equal to the Compton wavelength of an electron. Calculate v and comment on the result.

40. Consider a hydrogenlike atom such as He$^+$ or Li^{++} that has a single electron outside a nucleus of charge $+Ze$. (a) Rewrite the Schrödinger equation with the new Coulomb potential. (b) What change does this new potential have on the separation of variables? (c) Will the radial wave functions be affected? Explain. (d) Will the spherical harmonics be affected? Explain.

41. For the previous problem find the wave function ψ_{100}.

42. Consider a hydrogen atom in the $3p$ state. (a) At what radius is the electron probability equal to zero? (b) At what radius will the electron probability be a maximum? (c) For $m_\ell = 1$, at what angles θ will the electron probability be equal to zero? What about for $m_\ell = -1$?

43. Consider a "muonic atom," which consists of a proton and a negative μ^-. Compute the ground state energy following the methods used for the hydrogen atom.