

# Chapter 6: Quantum Theory of the Hydrogen Atom

- The first problem that Schrödinger tackled with his new wave equation was that of the hydrogen atom.
- 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.”

## 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.

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

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

The potential energy  $U$  here is the electric potential energy

**Electric potential energy**

$$U = -\frac{e^2}{4\pi\epsilon_0 r}$$

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.
  1. One is to express  $U$  in terms of the cartesian coordinates  $x, y, z$  by replacing  $r$  by

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

2. The other is to express Schrödinger's equation in terms of the spherical polar coordinates  $r, \theta, \phi$  defined in Fig. 6.1.

The spherical polar coordinates  $r, \theta, \phi$  of the point  $P$  shown in Fig. 6.1 have following interpretations:

**Spherical polar coordinates**  $r =$  length of radius vector from origin  $O$  to point  $P$   
 $= \sqrt{x^2 + y^2 + z^2}$

$\theta =$  angle between radius vector and  $+z$  axis  
 $=$  zenith angle

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

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

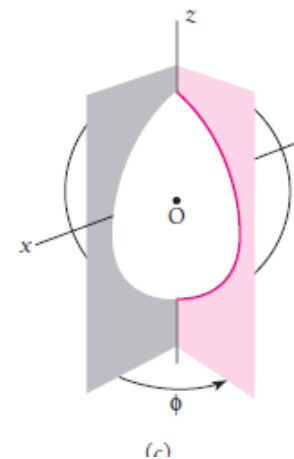
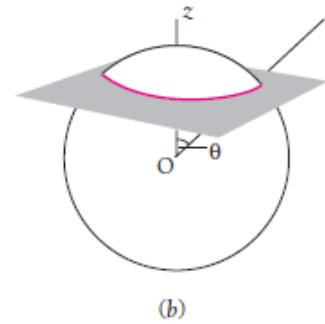
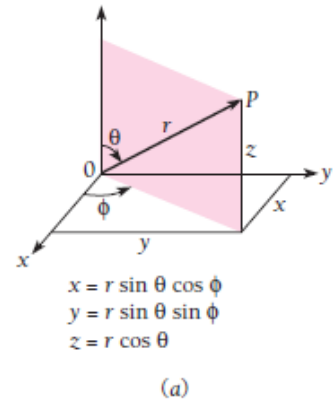


Figure 6.1 (a) Spherical polar coordinates.  
 (b) A line of constant zenith angle  $\theta$  on a sphere is a circle whose plane is perpendicular to the  $z$  axis.  
 (c) A line of constant azimuth angle  $\phi$  is a circle whose plane includes the  $z$  axis.

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

In spherical polar coordinates Schrödinger's equation is written

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

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

**Hydrogen atom**

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

- Equation (6.4) is the partial differential equation for the wave function  $\psi$  of the electron in a hydrogen atom.
- Together with the various conditions  $\psi$  must obey,
  - $\psi$  be normalizable
  - $\psi$  and its derivatives be continuous and single-valued at each point  $r, \theta, \phi$  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  $\psi$ .
- 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  $\psi$  must obey:
  - $\psi$  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.

## 6.2 SEPARATION OF VARIABLES

- A differential equation for each variable.
- Here the wave function  $\psi(r, \theta, \phi)$  has the form of a product of three different functions:
  1.  $R(r)$  which depends on  $r$  alone;
  2.  $\Theta(\theta)$  which depends on  $\theta$  alone;
  3.  $\Phi(\phi)$  which depends on  $\phi$  alone.

**Hydrogen-atom  
wave function**

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

- The function  $R(r)$  describes how the wave function  $\psi$  of the electron varies along a radius vector from the nucleus, with  $\theta$  and  $\phi$  constant.
  - The function  $\Theta(\theta)$  describes how  $\psi$  varies with zenith angle  $\theta$  along a meridian on a sphere centered at the nucleus, with  $r$  and  $\phi$  constant (Fig. 6.1c).
  - The function  $\Phi(\phi)$  describes how  $\psi$  varies with azimuth angle  $\phi$  along a parallel on a sphere centered at the nucleus, with  $r$  and  $\theta$  constant (Fig. 6.1b).
- 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  $R$ ,  $\Theta$ , and  $\Phi$  depends only on the respective variables  $r$ ,  $\theta$ , and  $\phi$ .

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

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

- The third term of Eq. (6.6) is a function of azimuth angle  $\phi$  only, whereas the other terms are functions of  $r$  and  $\theta$  only.

Let us rearrange Eq. (6.6) to read

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

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  $\Phi$  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  $\Theta$  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

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

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

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

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  $U(r)$ .

### 6.3 QUANTUM NUMBERS

- Three dimensions, three quantum numbers.
- The first of these equations, Eq. (6.12), is readily solved. The result is

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

- From Fig. 6.2, it is clear that  $\phi$  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 ( $\pm 1, \pm 2, \pm 3, \dots$ ).

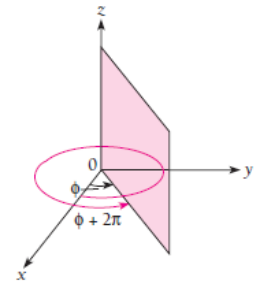


Figure 6.2 The angles  $\phi$  and  $\phi+2\pi$  both identify the same meridian plane.

- 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  $m_l$ .

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

- 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 also requires that a certain condition be fulfilled.

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

- 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  $l+1$ .

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

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

<b>Principal quantum number</b>	$n = 1, 2, 3, \dots$	
<b>Orbital quantum number</b>	$l = 0, 1, 2, \dots, (n - 1)$	(6.17)
<b>Magnetic quantum number</b>	$m_l = 0, \pm 1, \pm 2, \dots, \pm l$	

- The electron wave functions of the hydrogen atom

$$\psi = R_{nl}\Theta_{lm_l}\Phi_{m_l}$$

**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	$\pm 1$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
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	$\pm 1$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
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	$\pm 1$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	$\pm 2$	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

\*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.

### Example 6.1

Find the ground-state electron energy  $E_1$  by substituting the radial wave function  $R$  that corresponds to  $n=1, l=0$  into Eq. (6.14).

#### Solution

From Table 6.1 we see that  $R = (2/a_0^{3/2})e^{-r/a_0}$ . Hence

$$\frac{dR}{dr} = \left(\frac{2}{a_0^{5/2}}\right)e^{-r/a_0}$$

and

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) = \left( \frac{2}{a_0^{7/2}} - \frac{4}{a_0^{5/2}r} \right) e^{-r/a_0}$$

Substituting in Eq. (6.14) with  $E = E_1$  and  $l = 0$  gives

$$\left[ \left( \frac{2}{a_0^{7/2}} + \frac{4mE_1}{\hbar^2 a_0^{3/2}} \right) + \left( \frac{me^2}{\pi\epsilon_0 \hbar^2 a_0^{3/2}} - \frac{4}{a_0^{5/2}} \right) \frac{1}{r} \right] e^{-r/a_0} = 0$$

Each parenthesis must equal 0 for the entire equation to equal 0. For the second parenthesis this gives

$$\frac{me^2}{\pi\epsilon_0 \hbar^2 a_0^{3/2}} - \frac{4}{a_0^{5/2}} = 0$$

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

which is the Bohr radius  $a_0 = r_1$  given by Eq. (4.13)—we recall that  $\hbar = h/2\pi$ . For the first parenthesis,

$$\frac{2}{a_0^{7/2}} + \frac{4mE_1}{\hbar^2 a_0^{3/2}} = 0$$

$$E_1 = -\frac{\hbar^2}{2ma_0^2} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}$$

which agrees with Eq. (6.16).

## 6.4 PRINCIPAL QUANTUM NUMBER

- Quantization of energy.
- Two quantities are conserved -that is, maintain a constant value at all times- in planetary motion:
  - the scalar total energy
  - the vector angular momentum of each planet.
- Classically the total energy can have any value whatever, but it must, of course, be negative if the planet is *to be trapped* permanently in the solar system.
- In the quantum theory of the hydrogen atom the electron energy is also a constant, but while it may have any positive value (corresponding to an ionized atom), the only negative values the electron can have are specified by the formula  $E_n = E_1/n^2$ .
- The quantization of electron energy in the hydrogen atom is therefore described by the **principal quantum number**  $n$ .

## 6.5 ORBITAL QUANTUM NUMBER

- Quantization of angular-momentum magnitude.
- The kinetic energy  $KE$  of the electron has two parts,  $KE_{\text{radial}}$  due to its motion toward or away from the nucleus, and  $KE_{\text{orbital}}$  due to its motion around the nucleus.
- The potential energy  $U$  of the electron is the electric energy
- Hence the total energy of the electron is

$$U = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$E = KE_{\text{radial}} + KE_{\text{orbital}} + U = KE_{\text{radial}} + KE_{\text{orbital}} - \frac{e^2}{4\pi\epsilon_0 r}$$

Inserting this expression for  $E$  in Eq. (6.14) we obtain, after a slight rearrangement,

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[ \text{KE}_{\text{radial}} + \text{KE}_{\text{orbital}} - \frac{\hbar^2 l(l+1)}{2mr^2} \right] R = 0 \quad (6.19)$$

If the last two terms in the square brackets of this equation cancel each other out, we shall have what we want: a differential equation for  $R(r)$  that involves functions of the radius vector  $r$  exclusively.

We therefore require that

$$\text{KE}_{\text{orbital}} = \frac{\hbar^2 l(l+1)}{2mr^2} \quad (6.20)$$

Since the orbital kinetic energy of the electron and the magnitude of its angular momentum are respectively

$$\text{KE}_{\text{orbital}} = \frac{1}{2} m v_{\text{orbital}}^2 \quad L = m v_{\text{orbital}} r$$

we may write for the orbital kinetic energy

$$\text{KE}_{\text{orbital}} = \frac{L^2}{2mr^2}$$

Hence, from Eq. (6.20),

$$\frac{L^2}{2mr^2} = \frac{\hbar^2 l(l+1)}{2mr^2}$$

**Electron angular momentum**

$$L = \sqrt{l(l+1)} \hbar \quad (6.21)$$

With the orbital quantum number  $l$  restricted to the values

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

### Designation of Angular-Momentum States

It is customary to specify electron angular-momentum states by a letter, with  $s$  corresponding to  $l = 0$ ,  $p$  to  $l = 1$ , and so on, according to the following scheme:

<b>Angular-momentum states</b>	$l = 0$	$1$	$2$	$3$	$4$	$5$	$6$	$\dots$
	$s$	$p$	$d$	$f$	$g$	$h$	$i$	$\dots$

- This peculiar code originated in the empirical classification of spectra into series called **sharp, principal, diffuse**, and **fundamental** which occurred before the theory of the atom was developed.
- Thus, an  $s$  state is one with no angular momentum, a  $p$  state has the angular moment,  $\sqrt{2}\hbar$  and so forth.

- The combination of the total quantum number with the letter that represents orbital angular momentum provides a convenient and widely used notation for atomic electron states.
- In this notation, a state in which  $n=2, l=0$  is a 2s state, for example, and one in which  $n=4, l=2$  is a 4d state. Table 6.2 gives the designations of electron states in an atom through  $n=6, l=5$ .

**Table 6.2** Atomic Electron States

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1s					
$n = 2$	2s	2p				
$n = 3$	3s	3p	3d			
$n = 4$	4s	4p	4d	4f		
$n = 5$	5s	5p	5d	5f	5g	
$n = 6$	6s	6p	6d	6f	6g	6h

### 6.6 MAGNETIC QUANTUM NUMBER

- Quantization of angular-momentum direction. The orbital quantum number  $l$  determines the magnitude  $L$  of the electron's angular momentum  $\mathbf{L}$ .
- However, angular momentum, like linear momentum, is a vector quantity, and to describe it completely means that its direction be specified as well as its magnitude. (see Fig. 6.3)
- What possible significance can a direction in space have for a hydrogen atom? The answer becomes clear when we reflect that an electron revolving about a nucleus is a minute current loop and has a magnetic field like that of a magnetic dipole.
- Hence an atomic electron that possesses angular momentum interacts with an external magnetic field  $\mathbf{B}$ .

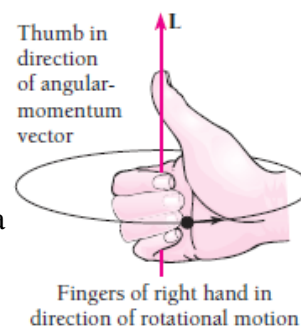


Figure 6.3 The right-hand rule for angular momentum.

- The magnetic quantum number  $m_l$  specifies the direction of  $\mathbf{L}$  by determining the component of  $\mathbf{L}$  in the field direction. This phenomenon is often referred to as **space quantization**.
- If we let the magnetic-field direction be parallel to the  $z$  axis, the component of  $\mathbf{L}$  in this direction is

$$\text{Space quantization} \quad L_z = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l \quad (6.22)$$

The possible values of  $m_l$  for a given value of  $l$  range from  $+l$  through 0 to  $-l$ , so that the number of possible orientations of the angular-momentum vector  $\mathbf{L}$  in a magnetic field is  $2l + 1$ . When  $l = 0$ ,  $L_z$  can have only the single value of 0; when  $l = 1$ ,  $L_z$  may be  $\hbar$ , 0, or  $-\hbar$ ; when  $l = 2$ ,  $L_z$  may be  $2\hbar$ ,  $\hbar$ , 0,  $-\hbar$ , or  $-2\hbar$ ; and so on.

- The space quantization of the orbital angular momentum of the hydrogen atom is shown in Fig. 6.4.
- An atom with a certain value of  $m_l$  will assume the corresponding orientation of its angular momentum  $\mathbf{L}$  relative to an external magnetic field if it finds itself in such a field.
- In the absence of an external magnetic field, the direction of the  $z$  axis is arbitrary.
- What must be true is that the component of  $\mathbf{L}$  in any direction we choose is  $m_l \hbar$ .
- What an external magnetic field does is to provide an experimentally meaningful reference direction.

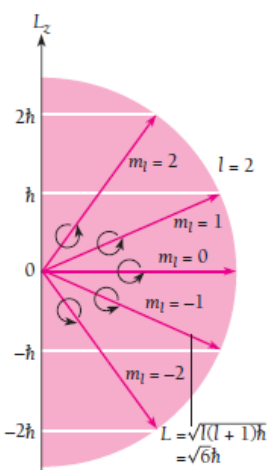


Figure 6.4 Space quantization of orbital angular momentum. Here the orbital quantum number is  $l=2$  and there are accordingly  $2l+1=5$  possible values of the magnetic quantum number  $m_l$ , with each value corresponding to a different orientation relative to the  $z$ -axis.



## 6.7 ELECTRON PROBABILITY DENSITY

- No definite orbits.
- In Bohr's model of the hydrogen atom the electron is visualized as revolving around the nucleus in a circular path. This model is pictured in a spherical polar coordinate system in Fig. 6.7.
- It implies that if a suitable experiment were performed, the electron would always be found a distance of  $r=n^2a_0$  from the nucleus and in the equatorial plane  $\theta=90^\circ$ , while its azimuth angle  $\phi$  changes with time.
- The quantum theory of the hydrogen atom modifies the Bohr model in two ways:

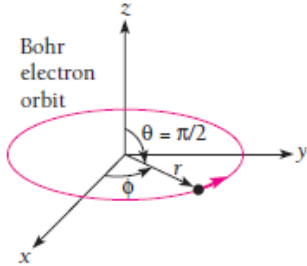


Figure 6.7 The Bohr model of the hydrogen atom in a spherical polar coordinate system.

1 No definite values for  $r$ ,  $\theta$ , or  $\phi$  can be given, but only the relative probabilities for finding the electron at various locations. This imprecision is, of course, a consequence of the wave nature of the electron.

2 We cannot even think of the electron as moving around the nucleus in any conventional sense since the probability density  $|\psi|^2$  is independent of time and varies from place to place.

The probability density  $|\psi|^2$  that corresponds to the electron wave function  $\psi = R\Theta\Phi$  in the hydrogen atom is

$$|\psi|^2 = |R|^2|\Theta|^2|\Phi|^2 \quad (6.23)$$

- From Eq. (6.15) we see that the azimuthal wave function is given by

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

The azimuthal probability density  $|\Phi|^2$  is therefore

$$|\Phi|^2 = \Phi^*\Phi = A^2e^{-im_l\phi}e^{im_l\phi} = A^2e^0 = A^2$$

- The likelihood of finding the electron at a particular azimuth angle  $\phi$  is a constant that does not depend upon  $\phi$  at all.
- The electron's probability density is symmetrical about the  $z$  axis regardless of the quantum state it is in, and the electron has the same chance of being found at one angle  $\phi$  as at another.
- The radial part  $R$  of the wave function, in contrast to  $\Phi$ , not only varies with  $r$  but does so in a different way for each combination of quantum numbers  $n$  and  $l$ .
- Figure 6.8 contains graphs of  $R$  versus  $r$  for 1s, 2s, 2p, 3s, 3p, and 3d states of the hydrogen atom.
  - Evidently  $R$  is a maximum at  $r=0$  -that is, at the nucleus itself- for all  $s$  states, which correspond to  $L=0$  since  $l=0$  for such states.
  - The value of  $R$  is zero at  $r=0$  for states that possess angular momentum.

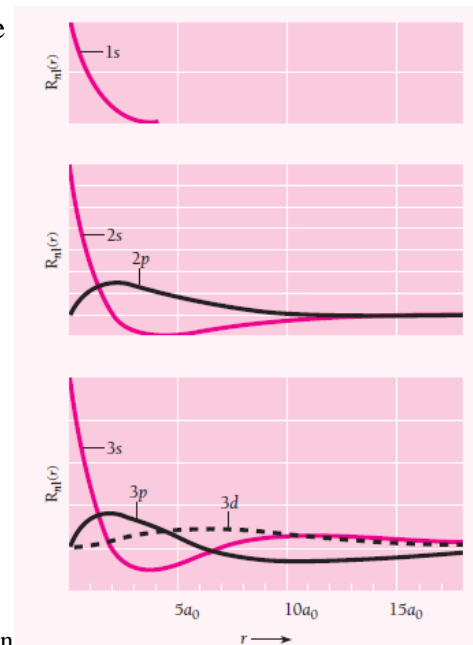


Figure 6.8 The variation with distance from the nucleus of the radial part of the electron wave function in hydrogen for various quantum states. The quantity  $a_0=0.053$  nm is the radius of the first Bohr orbit.

## Probability of Finding the Electron

The *probability density* of the electron at the point  $r, \theta, \phi$  is proportional to  $|\psi|^2$ , but the *actual probability* of finding it in the infinitesimal volume element  $dV$  there is  $|\psi|^2 dV$ . In spherical polar coordinates (Fig. 6.9),

$$\begin{aligned} dV &= (dr) (r d\theta) (r \sin \theta d\phi) \\ \text{Volume element} &= r^2 \sin \theta dr d\theta d\phi \end{aligned} \quad (6.24)$$

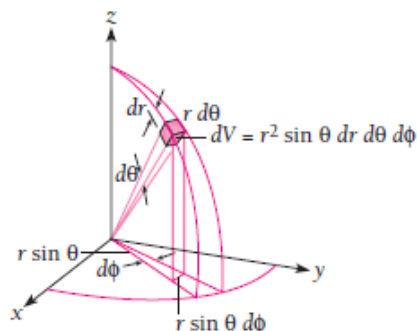


Figure 6.9 Volume element  $dV$  in spherical polar coordinates.

- As  $\Theta$  and  $\Phi$  are normalized functions, the actual probability  $P(r)dr$  of finding the electron in a hydrogen atom somewhere in the spherical shell between  $r$  and  $r+dr$  from the nucleus is

$$\begin{aligned} P(r) dr &= r^2 |R|^2 dr \int_0^\pi |\Theta|^2 \sin \theta d\theta \int_0^{2\pi} |\Phi|^2 d\phi \\ &= r^2 |R|^2 dr \end{aligned} \quad (6.25)$$

- Equation (6.25) is plotted in Fig. 6.11 for the same states whose radial functions  $R$  were shown in Fig. 6.8. The curves are quite different as a rule.
- The most probable value of  $r$  for a  $1s$  electron turns out to be exactly  $a_0$ , the orbital radius of a ground-state electron in the Bohr model.

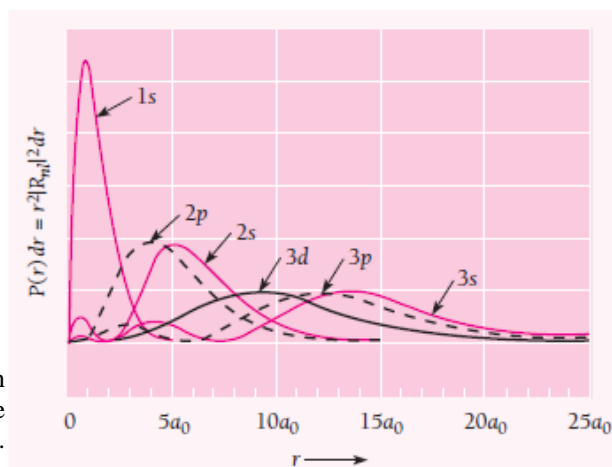


Figure 6.11 The probability of finding the electron in a hydrogen atom at a distance between  $r$  and  $r+dr$  from the nucleus for the quantum states of Fig. 6.8.

### Example 6.2

Verify that the average value of  $1/r$  for a  $1s$  electron in the hydrogen atom is  $1/a_0$ .

#### Solution

The wave function of a  $1s$  electron is, from Table 6.1,

$$\psi = \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}}$$

Since  $dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$  we have for the expectation value of  $1/r$

$$\begin{aligned} \left\langle \frac{1}{r} \right\rangle &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \left( \frac{1}{r} \right) |\psi|^2 \, dV \\ &= \frac{1}{\pi a_0^3} \int_0^\infty r e^{-2r/a_0} \, dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \end{aligned}$$

The integrals have the respective values

$$\int_0^\infty r e^{-2r/a_0} \, dr = \left[ \frac{a_0^2}{4} e^{-2r/a_0} - \frac{r}{2} e^{-2r/a_0} \right]_0^\infty = \frac{a_0^2}{4}$$

$$\int_0^\pi \sin\theta \, d\theta = [-\cos\theta]_0^\pi = 2$$

$$\int_0^{2\pi} d\phi = [\phi]_0^{2\pi} = 2\pi$$

Hence

$$\left\langle \frac{1}{r} \right\rangle = \left( \frac{1}{\pi a_0^3} \right) \left( \frac{a_0^2}{4} \right) (2)(2\pi) = \frac{1}{a_0}$$

### Example 6.3

How much more likely is a 1s electron in a hydrogen atom to be at the distance  $a_0$  from the nucleus than at the distance  $a_0/2$ ?

### Solution

According to Table 6.1 the radial wave function for a 1s electron is

$$R = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

From Eq. (6.25) we have for the ratio of the probabilities that an electron in a hydrogen atom be at the distances  $r_1$  and  $r_2$  from the nucleus

$$\frac{P_1}{P_2} = \frac{r_1^2 |R_1|^2}{r_2^2 |R_2|^2} = \frac{r_1^2 e^{-2r_1/a_0}}{r_2^2 e^{-2r_2/a_0}}$$

Here  $r_1 = a_0$  and  $r_2 = a_0/2$ , so

$$\frac{P_{a_0}}{P_{a_0/2}} = \frac{(a_0)^2 e^{-2}}{(a_0/2)^2 e^{-1}} = 4e^{-1} = 1.47$$

The electron is 47 percent more likely to be  $a_0$  from the nucleus than half that distance (see Fig. 6.11).

## 6.9 SELECTION RULES

- Some transitions are more likely to occur than others.
- The general condition necessary for an atom in an excited state to radiate is that the integral

$$\int_{-\infty}^{\infty} x \psi_n \psi_m^* \, dx \quad (6.34)$$

not be zero, since the intensity of the radiation is proportional to it.

- Transitions for which this integral is finite are called **allowed transitions**, while those for which it is zero are called **forbidden transitions**.

In the case of the hydrogen atom, three quantum numbers are needed to specify the initial and final states involved in a radiative transition. If the principal, orbital, and magnetic quantum numbers of the initial state are  $n', l', m_l'$ , respectively, and those of the final state are  $n, l, m_l$ , and  $u$  represents either the  $x, y$ , or  $z$  coordinate, the condition for an allowed transition is

**Allowed transitions** 
$$\int_{-\infty}^{\infty} u \psi_{n,l,m_l} \psi_{n',l',m_l'}^* dV \neq 0 \quad (6.35)$$

where the integral is now over all space. When  $u$  is taken as  $x$ , for example, the radiation would be that produced by a dipole antenna lying on the  $x$  axis.

- It is found that the only transitions between states of different  $n$  that can occur are
  - those in which the orbital quantum number  $l$  changes by  $+1$  or  $-1$
  - and the magnetic quantum number  $m_l$  does not change or changes by  $+1$  or  $-1$ .
- That is, the condition for an allowed transition is that

**Selection rules** 
$$\Delta l = \pm 1 \quad (6.36)$$

$$\Delta m_l = 0, \pm 1 \quad (6.37)$$

The change in total quantum number  $n$  is not restricted. Equations (6.36) and (6.37) are known as the **selection rules** for allowed transitions (Fig. 6.13).

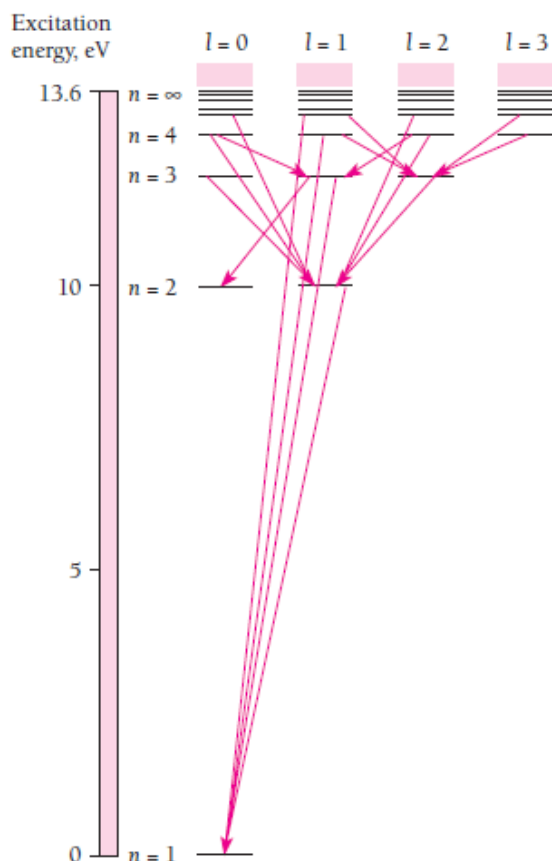


Figure 6.13 Energy-level diagram for hydrogen showing transitions allowed by the selection rule  $\Delta l = \pm 1$ . In this diagram, the vertical axis represents excitation energy above the ground state.

### 6.10 ZEEMAN EFFECT

- How atoms interact with a magnetic field.
- In an external magnetic field  $\mathbf{B}$ , a magnetic dipole has an amount of potential energy  $U_m$  that depends upon both the magnitude of its magnetic moment and the orientation of this moment with respect to the field (Fig. 6.15).
- The torque on a magnetic dipole in a magnetic field of flux density  $B$  is  $\tau = \mu B \sin \theta$ .

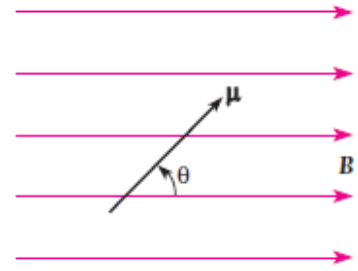


Figure 6.15 A magnetic dipole of moment  $\mu$  at the angle  $\theta$  relative to a magnetic field  $B$ .

- Set  $U_m = 0$  when  $\theta = \pi/2 = 90^\circ$ , that is, when  $\mu$  is perpendicular to  $B$ .
- The potential energy at any other orientation of  $\mu$  is equal to the external work that must be done to rotate the dipole from  $\theta_0 = \pi/2$  to the angle  $\theta$  that corresponds to that orientation.

Hence

$$\begin{aligned}
 U_m &= \int_{\pi/2}^{\theta} \tau \, d\theta = \mu B \int_{\pi/2}^{\theta} \sin \theta \, d\theta \\
 &= -\mu B \cos \theta
 \end{aligned}
 \tag{6.38}$$

When  $\mu$  points in the same direction as  $B$ , then  $U_m = -\mu B$ , its minimum value.

- The magnetic moment of a current loop has the magnitude

$$\mu = IA$$

where  $I$  is the current and  $A$  the area it encloses. An electron that makes  $f$  rev/s in a circular orbit of radius  $r$  is equivalent to a current of  $-ef$  (since the electronic charge is  $-e$ ), and its magnetic moment is therefore

$$\mu = -ef\pi r^2$$

Because the linear speed  $v$  of the electron is  $2\pi fr$  its angular momentum is

$$L = mvr = 2\pi mfr^2$$

Comparing the formulas for magnetic moment  $\mu$  and angular momentum  $L$  shows that

#### Electron magnetic moment

$$\mu = -\left(\frac{e}{2m}\right)L \tag{6.39}$$

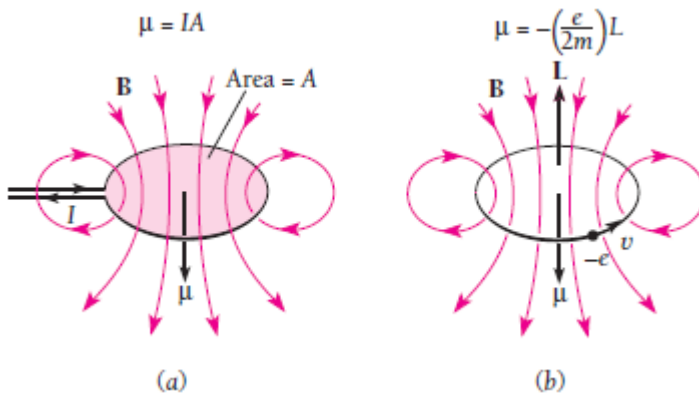


Figure 6.16 (a) Magnetic moment of a current loop enclosing area  $A$ . (b) Magnetic moment of an orbiting electron of angular momentum  $L$ .

**Magnetic energy** 
$$U_m = m_l \left( \frac{e\hbar}{2m} \right) B \quad (6.41)$$

The quantity  $e\hbar/2m$  is called the **Bohr magneton**:

**Bohr magneton** 
$$\mu_B = \frac{e\hbar}{2m} = 9.274 \times 10^{-24} \text{ J/T} = 5.788 \times 10^{-5} \text{ eV/T} \quad (6.42)$$

- In a magnetic field, then, the energy of a particular atomic state depends on the value of  $m_l$  as well as on that of  $n$ .
- A state of total quantum number  $n$  breaks up into several substates when the atom is in a magnetic field, and their energies are slightly more or slightly less than the energy of the state in the absence of the field.
- This phenomenon leads to a “splitting” of individual spectral lines into separate lines when atoms radiate in a magnetic field. The spacing of the lines depends on the magnitude of the field.
- The splitting of spectral lines by a magnetic field is called the *Zeeman effect* (first observed in 1896). The Zeeman effect is a vivid confirmation of space quantization.

Because  $m_l$  can have the  $2l + 1$  values of  $+l$  through 0 to  $-l$ , a state of given orbital quantum number  $l$  is split into  $2l + 1$  substates that differ in energy by  $\mu_B B$  when the atom is in a magnetic field. However, because changes in  $m_l$  are restricted to  $\Delta m_l = 0, \pm 1$ , we expect a spectral line from a transition between two states of different  $l$  to be split into only three components, as shown in Fig. 6.17. The **normal Zeeman effect** consists of the splitting of a spectral line of frequency  $\nu_0$  into three components whose frequencies are

**Normal Zeeman effect** 
$$\begin{aligned} \nu_1 &= \nu_0 - \mu_B \frac{B}{h} = \nu_0 - \frac{e}{4\pi m} B \\ \nu_2 &= \nu_0 \\ \nu_3 &= \nu_0 + \mu_B \frac{B}{h} = \nu_0 + \frac{e}{4\pi m} B \end{aligned} \quad (6.43)$$

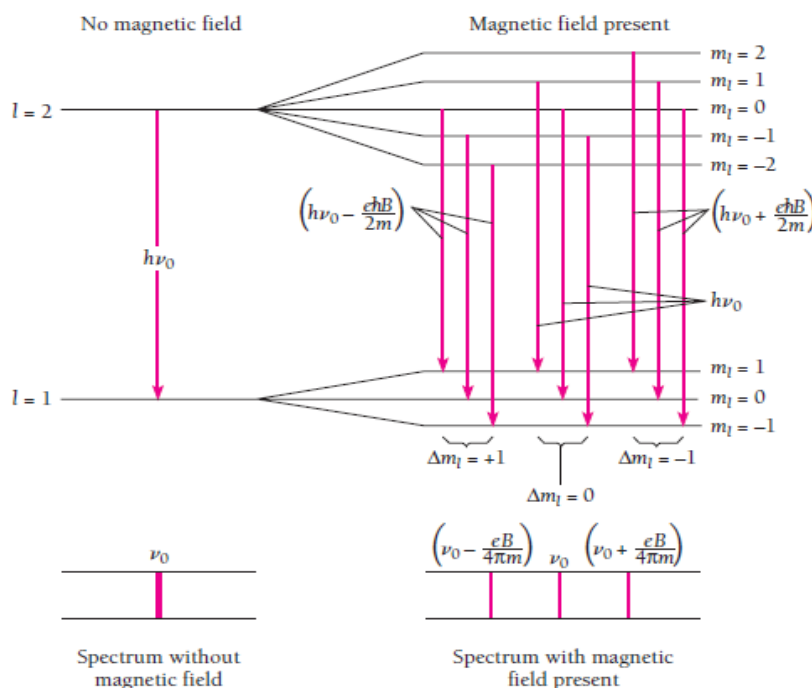


Figure 6.17 In the normal Zeeman effect a spectral line of frequency  $\nu_0$  is split into three components when the radiating atoms are in a magnetic field of magnitude  $\mathbf{B}$ . One component is  $\nu_0$  and the others are less than and greater than  $\nu_0$  by  $U_m$ . There are only three components because of the selection rule  $\Delta m_l = 0, \pm 1$ .

### Example 6.4

A sample of a certain element is placed in a 0.300 T magnetic field and suitably excited. How far apart are the Zeeman components of the 450-nm spectral line of this element?

### Solution

The separation of the Zeeman components is

$$\Delta\nu = \frac{eB}{4\pi m}$$

Since  $\nu = c/\lambda$ ,  $d\nu = -c d\lambda/\lambda^2$ , and so, disregarding the minus sign,

$$\begin{aligned}\Delta\lambda &= \frac{\lambda^2 \Delta\nu}{c} = \frac{eB\lambda^2}{4\pi mc} \\ &= \frac{(1.60 \times 10^{-19} \text{ C})(0.300 \text{ T})(4.50 \times 10^{-7} \text{ m})^2}{(4\pi)(9.11 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m/s})} \\ &= 2.83 \times 10^{-12} \text{ m} = 0.00283 \text{ nm}\end{aligned}$$