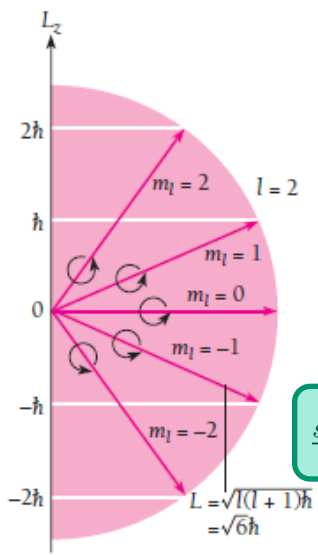


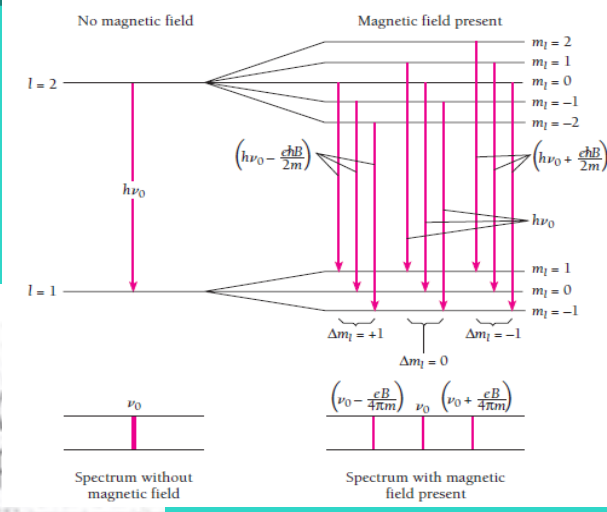
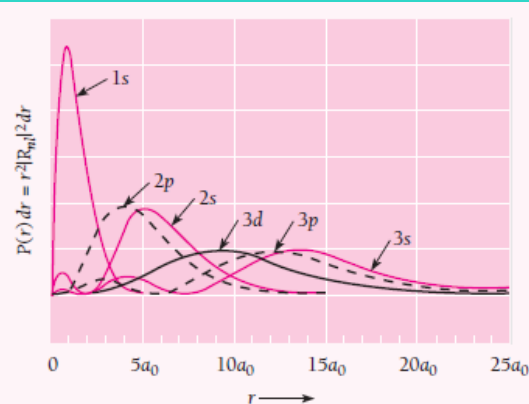
$$\int_{-\infty}^{\infty} u \psi_{n,l,m_l} \psi_{n',l',m_l'}^* dV \neq 0$$



Chapter 6

Quantum Theory of the Hydrogen Atom

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



6.1 SCHRÖDINGER'S EQUATION FOR THE HYDROGEN ATOM

Symmetry suggests spherical polar coordinates

6.2 SEPARATION OF VARIABLES

A differential equation for each variable

6.3 QUANTUM NUMBERS

Three dimensions, three quantum numbers

6.4 PRINCIPAL QUANTUM NUMBER

Quantization of energy

6.5 ORBITAL QUANTUM NUMBER

Quantization of angular-momentum magnitude

6.6 MAGNETIC QUANTUM NUMBER

Quantization of angular-momentum direction

6.7 ELECTRON PROBABILITY DENSITY

No definite orbits

6.8 RADIATIVE TRANSITIONS

What happens when an electron goes from one state to another

6.9 SELECTION RULES

Some transitions are more likely to occur than others

6.10 ZEEMAN EFFECT

How atoms interact with a magnetic field

- 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.
- 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

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

The potential energy U here is the electric potential energy

$$U = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad (6.2 \text{ Electric potential energy})$$

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

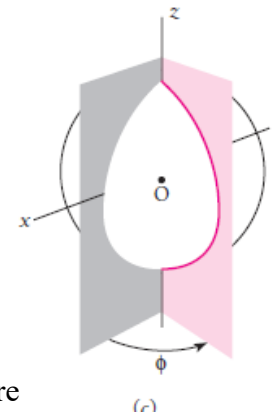
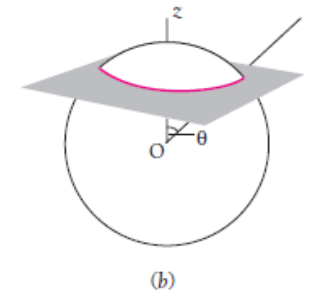
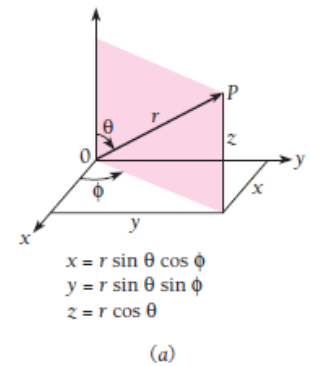


Figure 6.1 (a) Spherical polar coordinates. (b) A line of constant zenith angle θ on a sphere is a circle whose plane is perpendicular to the z axis. (c) A line of constant azimuthal angle ϕ is a circle whose plane includes the z axis.

- Since U is a function of r rather than of x, y, z, we cannot substitute Eq. (6.2) directly into Eq. (6.1). 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, θ , ϕ defined in Fig. 6.1.

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

$$r = \text{length of radius vector from origin } O \text{ to point } P$$

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

$$\theta = \text{angle between radius vector and } +z\text{-axis}$$

$$= \text{zenith angle}$$

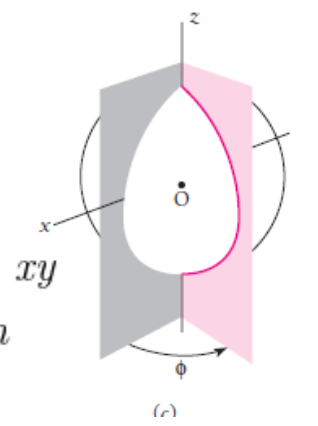
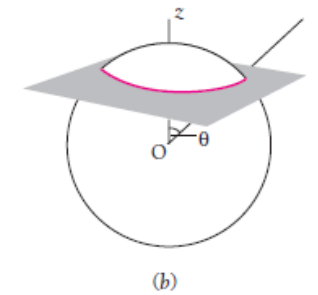
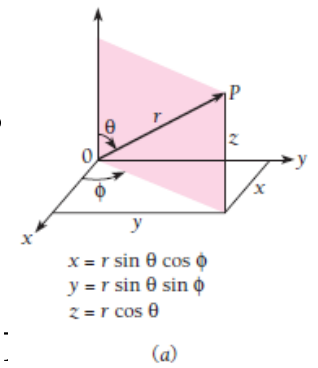
$$= \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}} = \cos^{-1} \frac{z}{r}$$

$$\phi = \text{angle between the projection of the radius vector in the } xy \text{ plane and the } +x\text{-axis, measured in the direction shown}$$

$$= \text{azimuth angle}$$

$$= \tan^{-1} \frac{y}{x}$$

(Spherical polar coordinates)



6.1 Schrödinger's Equation for the Hydrogen Atom

- 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

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} + E \right) \psi = 0 \quad (6.4)$$

- Equation (6.4) is the partial differential equation for the wave function ψ of the electron in a hydrogen atom.
- Together with the various conditions ψ must obey:
 - ψ be normalizable
 - ψ and its derivatives be continuous and single-valued at each point r, θ, ϕ
- This equation completely specifies the behavior of the electron.

In order to see exactly what this behavior is, we must solve Eq. (6.4) for ψ .

- A particle in a *three-dimensional box needs three quantum numbers* for its description, since there are now three sets of boundary conditions that the particle's wave function ψ must obey:
 - ψ must be 0 at the walls of the box in the x, y, and z directions independently.
 - In a hydrogen atom the electron's motion is restricted by the inverse-square electric field of the nucleus instead of by the walls of a box.
- *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 θ alone;
 3. $\Phi(\phi)$ which depends on ϕ alone.

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

(6.5 Hydrogen atom wave function)

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

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

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

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

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

(6.6)

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

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

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

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

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 $l(l+1)$. The equations for the functions Θ and R are therefore

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

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

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

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

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

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

- 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 $U(r)$.

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

From Fig. 6.2, it is clear that ϕ and $\phi+2\pi$ both identify the same meridian plane.

(6.15)

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

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 ($\pm 1, \pm 2, \pm 3, \dots$).

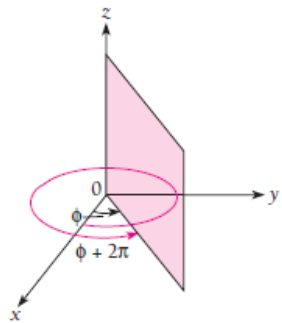


Figure 6.2 The angles ϕ and $\phi+2\pi$ both identify the same meridian plane.

- 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 . $m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$
- 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

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

- 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_l together with their permissible values as follows:

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

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

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2 = 5.292 \times 10^{-11}$ 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

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

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

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

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).

- *Quantization of energy.*
- Two quantities are conserved (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_{radial} due to its motion toward or away from the nucleus, and KE_{orbital} due to its motion around the nucleus.
- The potential energy U of the electron is the electric energy $U = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$
- Hence the total energy of the electron is

$$E = KE_{\text{radial}} + KE_{\text{orbital}} + U = KE_{\text{radial}} + KE_{\text{orbital}} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

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

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

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

$$KE_{\text{orbital}} = \frac{\hbar^2 l(l+1)}{2mr^2} = \frac{1}{2} m v_{\text{orbital}}^2 = \frac{L^2}{2mr^2} \text{ with } L = m v_{\text{orbital}} \quad (6.20)$$

$$\Rightarrow \frac{L^2}{2mr^2} = \frac{\hbar^2 l(l+1)}{2mr^2} \Rightarrow L = \sqrt{l(l+1)} \hbar, \quad l = 0, 1, 2, \dots, (n-1) \quad (6.21 \text{ Electron angular momentum})$$

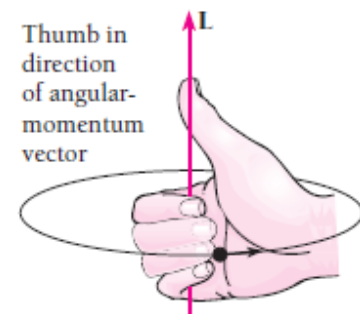
6.5 Orbital Quantum Number: Designation of Angular-Momentum States

Angular- momentum states	$l = 0$	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 and one in which $n=4, l=2$ is a 4d state.

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



Thumb in direction of angular-momentum vector
Fingers of right hand in direction of rotational motion

Figure 6.3 The right-hand rule for angular momentum..

- *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 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} .**
- 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.***

6.6 Magnetic Quantum Number

- If we let the magnetic-field direction be parallel to the z-axis, the component of L in this direction is $L_z = m_l \hbar$ $m_l = 0, \pm 1, \pm 2, \dots, \pm l$ (6.22 Space quantization)
- The number of possible orientations of the angular-momentum vector L in a magnetic field is $2l+1$. (When $l=2$, L_z may be $2\hbar, \hbar, 0, -\hbar, -2\hbar$).
- The space quantization of the orbital angular momentum of the hydrogen atom is show in Fig. 6.4.
- An atom with a certain value of m_l will assume the corresponding orientation of its angular momentum 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 L in any direction we choose is $m_l \hbar$.*
- What an external magnetic field does is to provide an experimentally meaningful reference direction.

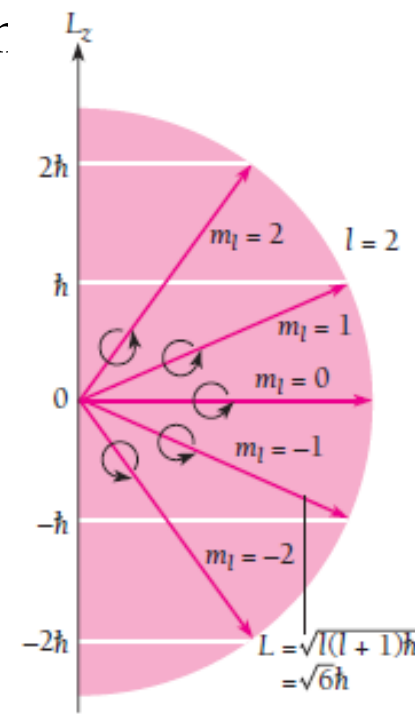


Figure 6.4 Space quantization of orbital angular momentum. Here the orbital quantum number is $l=2$ and there are accordingly $2l+1=5$ possible values of m_l .

- *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 ϕ changes with time.

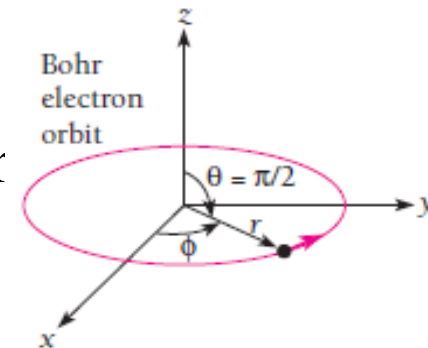


Figure 6.7 The Bohr model of the hydrogen atom in a spherical polar coordinate system.

The quantum theory of the hydrogen atom modifies the Bohr model in two ways:

1. No definite values for r , θ , ϕ or ψ can be given, but only the relative probabilities for finding the electron at various locations. This imprecision is 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.

6.7 Electron Probability Density

- The *probability density* $|\psi|^2$ that corresponds to the electron wave function $\psi = R\Theta\Phi$ in the hydrogen atom is $|\psi|^2 = |R|^2|\Theta|^2|\Phi|^2$ (6.23)
- The likelihood of finding the electron at a particular azimuth angle ϕ is a constant that does not depend upon ϕ at all. ($\Phi(\phi) = Ae^{im_l\phi}$)
 - 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 ϕ as at another.
- The radial part R of the wave function, in contrast to Φ , 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.

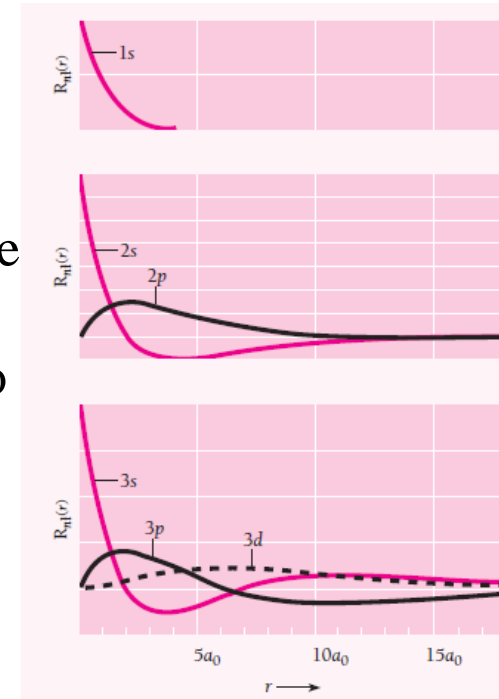


Figure 6.8 The Bohr model of the hydrogen atom in a spherical polar coordinate system.

6.7 Electron Probability Density: Probability of Finding the Electron

- The *probability density* of the electron at the point r, θ, ϕ , 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)

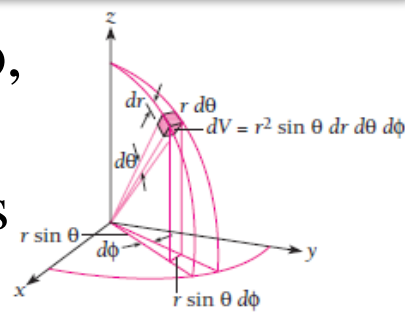


Figure 6.9 Volume element dV in spherical polar coordinates

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

- As Θ and Φ 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

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

- Equation (6.25) is plotted in Fig. 6.11 for the same states whose radial functions R were shown in Fig. 6.8.
- The 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.

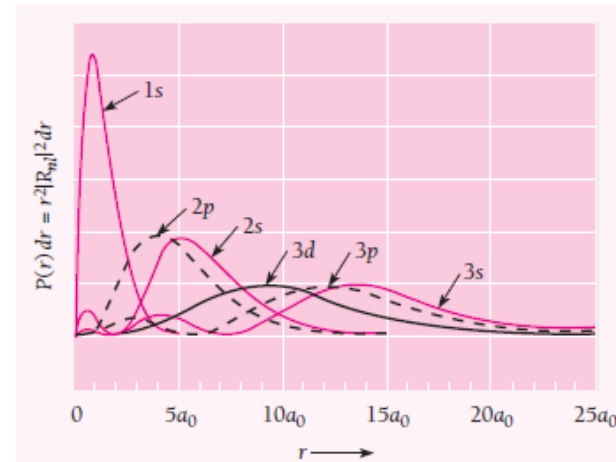


Figure 6.11 The probability of finding the electron in a hydrogen atom at a distance between r and $r+dr$ from the nucleus for the quantum states of Fig. 6.8.

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,

$$\psi = \frac{e^{-r/a_0}}{\sqrt{\pi}a_0^{3/2}}$$

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

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

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

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

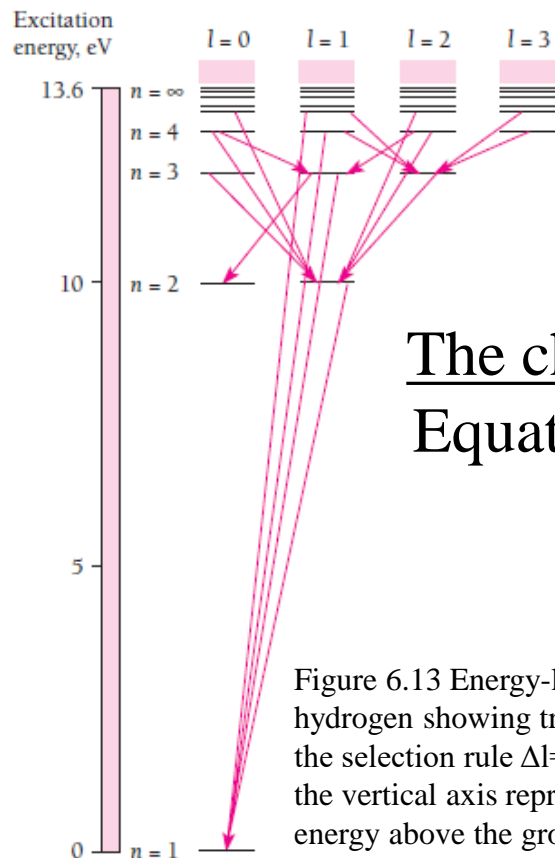
The electron is 47 percent more likely to be a_0 from the nucleus than half that distance (see Fig. 6.11).

- *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 $\int_{-\infty}^{\infty} x\psi_n\psi_m^*dx$ (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

$$\int_{-\infty}^{\infty} u\psi_{n,l,m_l}\psi_{n',l',m_l'}^*dV \neq 0$$

(6.25 Allowed transitions)

- 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**



$$\text{Selection rules } \Delta l = \pm 1 \quad (6.36)$$

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

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.

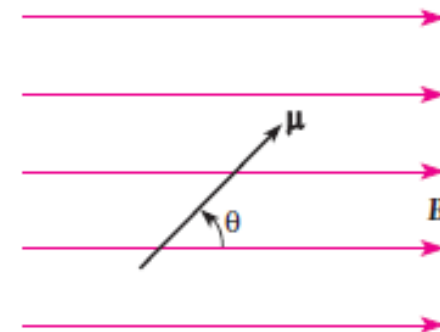


Figure 6.15 A magnetic dipole of moment μ at the angle θ relative to a magnetic field B .

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

$$U_m = \int_{\pi/2}^{\theta} \tau d\theta = \mu B \int_{\pi/2}^{\theta} \sin\theta d\theta = -\mu B \cos\theta \quad (6.38)$$

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

6.10 Zeeman Effect

- 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 $-ef$, and its magnetic moment is therefore

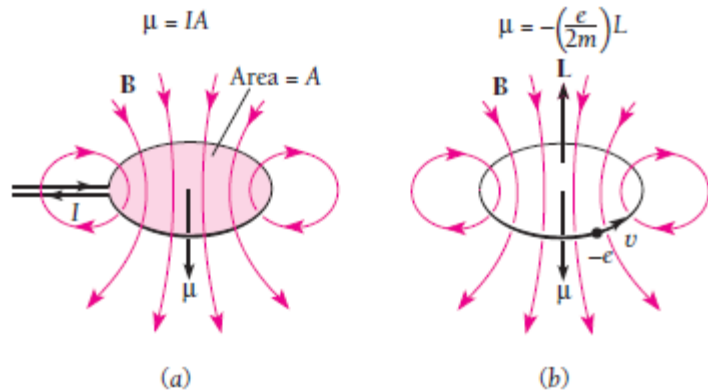
$$\mu = -ef\pi r^2$$

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

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

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

$$\mu = -\left(\frac{e}{2m}\right) L \quad (6.39 \text{ Electron magnetic moment})$$



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

$$\mu_B = \frac{e\hbar}{2m} = 9.274 \times 10^{-24} \text{ V/T} = 5.788 \times 10^{-5} \text{ eV/T}$$

(6.42 Bohr magneton)

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

- In a magnetic field, 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.

6.10 Zeeman Effect

- 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 ν_0 into three components whose frequencies are

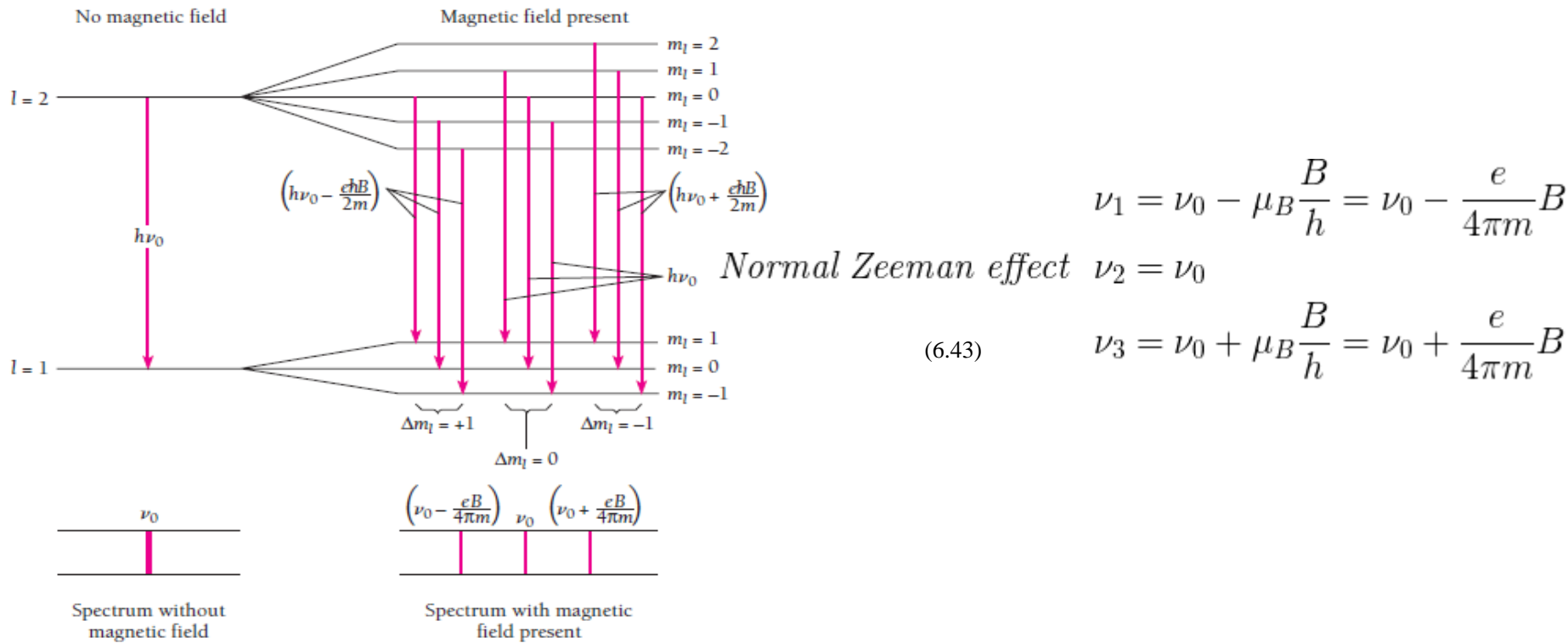


Figure 6.17 In the normal Zeeman effect a spectral line of frequency ν_0 is split into three components when the radiating atoms are in a magnetic field of magnitude \mathbf{B} . One component is ν_0 and the others are less than and greater than ν_0 by U_m . There are only three components because of 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,

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

1. Find the normalization constant of the ground state wave function for a particle trapped in the one-dimensional Coulomb potential energy.

One dimensional Coulomb potential energy: $U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$; in 1D: $r \rightarrow x$
 $\psi \rightarrow \psi(x)$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - \frac{e^2}{4\pi\epsilon_0 x} \psi = E\psi \quad \left\{ \begin{array}{l} \text{BCs} \\ \psi \rightarrow 0 \text{ as } x \rightarrow \infty \\ \psi \rightarrow 0 \text{ as } x = 0 \end{array} \right. \quad \left\{ \begin{array}{l} \text{Solution:} \\ \psi(x) = Ax e^{-bx} \end{array} \right. \quad \left\{ \begin{array}{l} b = \frac{me^2}{4\pi\epsilon_0 \hbar^2} = \frac{1}{a_0} \\ E = -\frac{me^4}{32\pi^2\epsilon_0^2 \hbar^2} = -\frac{\hbar^2 b^2}{2m} \end{array} \right.$$

$\Rightarrow \int_0^{\infty} |\psi(x)|^2 dx = A^2 \int_0^{\infty} x^2 e^{-2bx} dx = 1$

From Integral Table: $\int_0^{\infty} x^n e^{-cx} dx = \frac{n!}{c^{n+1}} \quad ; \quad c = 2b = 2/a_0$
 $n = 2$

$\rightarrow A^2 \frac{2!}{(2/a_0)^3} = 1 \rightarrow \underline{\underline{A = 2a_0^{-3/2}}}$

prove that!!

2. In the ground state of an electron bound in a one-dimensional Coulomb potential energy, what is the probability to find the electron located between $x = 0$ and $x = a_0$?

$$\psi(x) = \frac{2}{\sqrt{a_0^3}} x e^{-bx} ; P(0:a_0) = \int_0^{a_0} |\psi|^2 dx = \int_0^{a_0} \frac{4}{a_0^3} x^2 e^{-2bx} dx = \frac{4}{a_0^3} \int_0^{a_0} x^2 e^{-2x/a_0} dx$$

Integral Table: $\int x^n e^{-cx} dx = -\frac{e^{-cx}}{c} \left(x^n + \frac{nx^{n-1}}{c} + \frac{n(n-1)x^{n-2}}{c^2} + \dots + \frac{n!}{c^n} \right)$ $\left. \begin{matrix} n=2 \\ c=2/a_0 \end{matrix} \right\}$

$$\rightarrow P = \frac{4}{a_0^3} \left[-\frac{e^{-2x/a_0}}{2/a_0} \left(x^2 + \frac{2x}{2/a_0} + \frac{2}{(2/a_0)^2} \right) \right]_0^{a_0} = \underline{\underline{0.323}}$$

3. An electron in a hydrogen atom is in a 3d state. What is the most probable radius at which to find it? (Hint: use $P(r)$ not $P(r)dr$ and then to find the maximum set the derivative $dP(r)/dr$ to zero.)

$$\begin{aligned}
 &\text{From Table 6.1; } R_{3,2}(r) = \frac{4}{81\sqrt{30}a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \\
 &\rightarrow P(r) = r^2 R_{3,2}^2(r) = r^2 \frac{16}{81^2 30 a_0^3} \frac{r^4}{a_0^4} e^{-2r/3a_0} \Rightarrow \frac{dP(r)}{dr} = 0 \\
 &\Rightarrow \frac{16}{81^2 30 a_0^7} \left(\frac{d}{dr} \left(r^6 e^{-2r/3a_0} \right) \right) = \frac{16}{81^2 30 a_0^7} \left(6r^5 e^{-2r/3a_0} - \frac{2}{3a_0} r^6 e^{-2r/3a_0} \right) \\
 &= \frac{16}{81^2 30 a_0^7} \left(6 - \frac{2}{3a_0} r \right) r^5 e^{-2r/3a_0} = 0 \Rightarrow 6 - \frac{2}{3a_0} r = 0 \Rightarrow \underline{\underline{r = 9a_0}}
 \end{aligned}$$

4. Prove that the most likely distance from the origin of an electron in the $n = 2, l = 1$ state is $4a_0$.

$n=2$ { From Table 6.1
 $l=1$ { Radial Probability Density

$$R_{21}(r) = \frac{1}{2\sqrt{6}a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \rightarrow P(r) = r^2 |R_{21}(r)|^2 = \frac{r^2}{24a_0^3} \frac{r^2}{a_0^2} e^{-r/a_0}$$

where this function $(P(r))$ is maximum: $\frac{dP(r)}{dr} = 0$

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

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

5. For the $n = 2$ states ($l = 0$ and $l = 1$), compare the probabilities of the electron being found inside the Bohr radius.

Compare the probabilities of the electron being found inside a_0 .

$n=2, l=0 \sim R_{20}(r) = \frac{1}{2\sqrt{2}a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \rightarrow P = \int_0^{a_0} r^2 |R_{20}(r)|^2 dr$

$n=2, l=1 \sim R_{21}(r) = \frac{1}{2\sqrt{6}a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \rightarrow P = \int_0^{a_0} r^2 |R_{21}(r)|^2 dr$

$\rightarrow P_{0,a_0} = \frac{1}{8a_0^3} \int_0^{a_0} r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-2r/2a_0} dr = \frac{1}{8a_0^3} \int_0^{a_0} \left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}\right) e^{-r/a_0} dr = \underline{\underline{0.034}}$

$\rightarrow P_{1,a_0} = \frac{1}{24a_0^3} \int_0^{a_0} \frac{r^4}{a_0^2} e^{-r/a_0} dr = \underline{\underline{0.0037}}$

6. What is the expectation value of the radius of an electron in hydrogen atom in a 3d state? Just write the expression without evaluating the integral.

$$\langle r \rangle = \int \psi^* r \psi dr = \int r \psi^* \psi dr = \int r P(r) dr \quad \left\{ \text{where } P(r) = r^2 R_{3,2}^2(r) \right.$$

$$\Rightarrow \langle r \rangle = \int_0^{\infty} r \left(r^2 \frac{16}{81^2 30 a_0^3} \frac{r^4}{a_0^4} e^{-2r/3a_0} \right) dr = \frac{16}{81^2 30 a_0^7} \int_0^{\infty} r^7 e^{-2r/3a_0} dr$$

From Table; $\int_0^{\infty} x^m e^{-bx} dx = m! / b^{m+1}$ where $m=7$ & $b=\frac{2}{3a_0}$

$$\Rightarrow \frac{16}{81^2 30 a_0^7} \left(\frac{7!}{\left(\frac{2}{3a_0}\right)^8} \right) = \frac{2^4}{3^8 (2 \times 3 \times 5) a_0^7} \left(\frac{3^8 a_0^8}{2^8} 1 \times 2 \times 3 \times 4 \times 5 \times 6 \times 7 \right)$$

$$\Rightarrow \frac{1}{1} \frac{a_0}{2^4} 4 \times 6 \times 7 = \langle r \rangle \Rightarrow \langle r \rangle = 10.5 a_0$$

8. Consider an atomic electron in the $l=3$ state. Calculate the magnitude $|\mathbf{L}|$ of the total angular momentum and the allowed values of L_z and θ .

$l=3$ & atomic electron

$$|\mathbf{L}| = \sqrt{l(l+1)}\hbar = \sqrt{12}\hbar = 2\sqrt{3}\hbar \quad \& \quad L_z = m_l\hbar \text{ with } m_l = 0, \pm 1, \dots, \pm l$$

$$\rightarrow m_l = 0, \pm 1, \pm 2, \pm 3 \rightarrow \underline{L_z = -3\hbar, -2\hbar, -\hbar, 0, \hbar, 2\hbar, 3\hbar}$$

for θ : $L_z = \cos\theta |\mathbf{L}| \rightarrow \cos\theta = \frac{m_l\hbar}{2\sqrt{3}\hbar} = \frac{m_l}{2\sqrt{3}}$

$$\Rightarrow \cos\theta = \pm 0.866, \pm 0.577, \pm 0.289, 0$$

$$\rightarrow \underline{\underline{\theta = \pm 30^\circ, \pm 54.8^\circ, \pm 73.2^\circ, 90^\circ}}$$

9. Compute the change in wavelength of the $2p \rightarrow 1s$ photon when a hydrogen atom is placed in a magnetic field of 2.00 T.

Transition $2p \rightarrow 1s$: in a magnetic field (2T). Hydrogen atom

$$\frac{1}{\lambda} = \frac{-E_1}{ch} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{13.6}{ch} \left(\frac{3}{4} \right) \rightarrow \lambda = \frac{(3 \times 10^8 \text{ m/s})(6.626 \times 10^{-34} \text{ J}\cdot\text{s})}{(13.6 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})} \frac{4}{3} = \underline{\underline{122 \text{ nm}}}$$

and Energy = $\frac{hc}{\lambda} = \underline{\underline{10.2 \text{ eV}}}$. The energy change since inside of a \vec{B}

$$\Delta E = \mu_B B = (9.27 \times 10^{-24} \text{ J/T})(2 \text{ T})$$

$$= 18.5 \times 10^{-24} \text{ J} = 11.6 \times 10^{-5} \text{ eV}$$

$$\rightarrow \Delta \lambda = \frac{\lambda^2}{hc} \Delta E = \frac{(122 \times 10^{-9} \text{ m})^2 (18.5 \times 10^{-24} \text{ J})}{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3 \times 10^8 \text{ m/s})} = \underline{\underline{0.00139 \text{ nm}}}$$

Additional Materials