

6.1 SCHRÖDINGER'S EQUATION FOR THE HYDROGEN ATOM

Symmetry suggests spherical polar coordinates

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

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

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

The potential energy U here is the electric potential energy

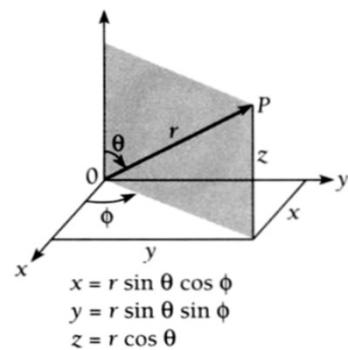
$$\text{Electric potential energy} \quad U = -\frac{e^2}{4\pi\epsilon_0 r} \quad (6.2)$$

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

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

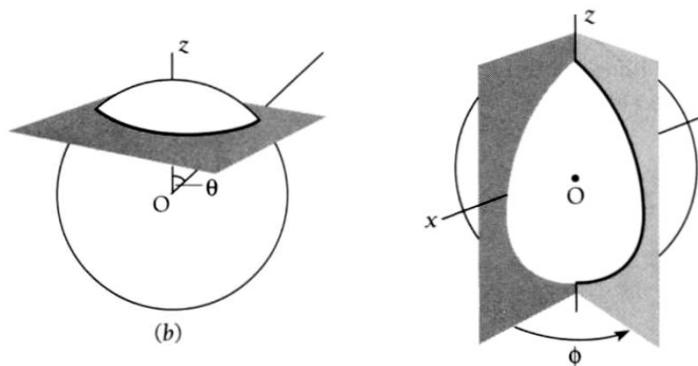
Spherical polar coordinates	r = length of radius vector from origin O to point P $= \sqrt{x^2 + y^2 + z^2}$
	θ = angle between radius vector and $+z$ axis $=$ zenith angle $= \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}}$
	ϕ = angle between the projection of the radius vector in the xy plane and the $+x$ axis, measured in the direction shown $=$ azimuth angle $= \tan^{-1} \frac{y}{x}$



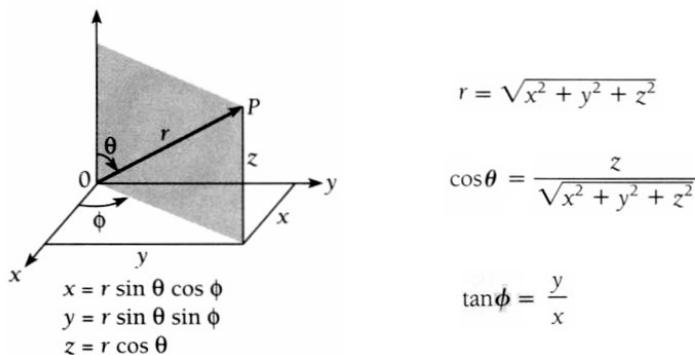
$$x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta$$

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



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

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

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

A particle in a three-dimensional box needs three quantum numbers for its description, since there are now three sets of boundary conditions that the particle's wave function ψ must obey: ψ must be 0 at the walls of the box in the x , y , and z directions independently. In a hydrogen atom the electron's motion is restricted by the inverse-square electric field of the nucleus instead of by the walls of a box, but the electron is nevertheless free to move in three dimensions, and it is accordingly not surprising that three quantum numbers govern its wave function also.

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6.2 SEPARATION OF VARIABLES

A differential equation for each variable

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

**Hydrogen-atom
wave function**

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

and then seeing if it leads to the desired separation.

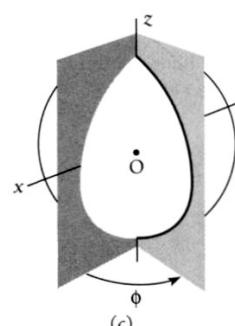
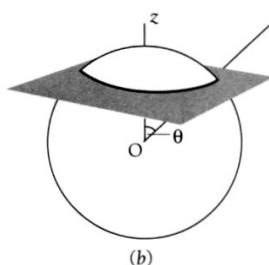
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The function $R(r)$ describes how the wave function ψ of the electron varies along a radius vector from the nucleus, with θ and ϕ constant.

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).

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



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

$$\frac{\partial \psi}{\partial r} = \Theta \Phi \frac{\partial R}{\partial r} = \Theta \Phi \frac{dR}{dr}$$

$$\frac{\partial \psi}{\partial \theta} = R \Phi \frac{\partial \Theta}{\partial \theta} = R \Phi \frac{d\Theta}{d\theta}$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = R \Theta \frac{\partial^2 \Phi}{\partial \phi^2} = R \Theta \frac{d^2 \Phi}{d\phi^2}$$

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

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

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

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.

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Let us rearrange Eq. (6.6) to read

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

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 ϕ is therefore

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

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

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

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

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

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

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

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

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

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

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

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

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

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6.3 QUANTUM NUMBERS

Three dimensions, three quantum numbers

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

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

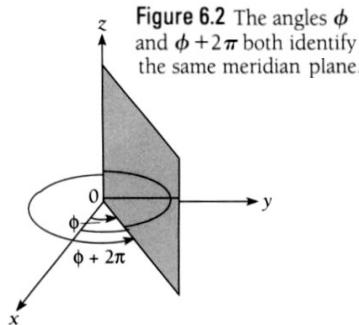


Figure 6.2 The angles ϕ and $\phi + 2\pi$ both identify the same meridian plane.

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

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

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

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

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

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

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

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

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

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

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

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

Principal quantum number $n = 1, 2, 3, \dots$

Orbital quantum number $l = 0, 1, 2, \dots, (n - 1)$ (6.17)

Magnetic quantum number $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

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

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

$$\psi = R_n \Theta_{lm} \Phi_{m_l} \quad (6.18)$$

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

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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	$\frac{1}{\sqrt{2\pi}} \cos \theta$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
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	$\frac{1}{\sqrt{2\pi}} \cos \theta$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
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 $a_0 = 4\pi\epsilon_0 k^2/mc^3 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

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

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

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

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

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

Each parenthesis must equal 0 for the entire equation to equal 0.

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

$$\text{For the second parenthesis this gives } \frac{me^2}{\pi\epsilon_0\hbar^2 a_0^{3/2}} - \frac{4}{a_0^{5/2}} = 0 \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

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,

$$\frac{2}{a_0^{7/2}} + \frac{4mE_1}{\hbar^2 a_0^{3/2}} = 0 \quad E_1 = -\frac{\hbar^2}{2ma_0^2} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}$$

which agrees with Eq. (6.16).

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6.4 PRINCIPAL QUANTUM NUMBER

Quantization of energy

It is interesting to consider what the hydrogen-atom quantum numbers signify in terms of the classical model of the atom. This model, as we saw in Chap. 4, corresponds exactly to planetary motion in the solar system except that the inverse-square force holding the electron to the nucleus is electrical rather than gravitational. Two quantities are conserved—that is, maintain a constant value at all times—in planetary motion; the scalar total energy and 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 .

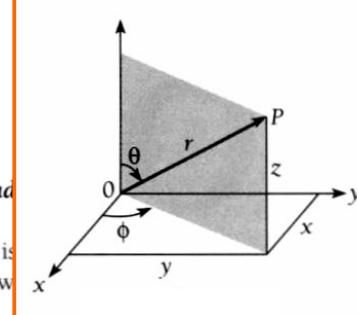
The theory of planetary motion can also be worked out from Schrödinger's equation, and it yields a similar energy restriction. However, the total quantum number n for any of the planets turns out to be so immense (see Exercise 11 of Chap. 4) that the separation of permitted levels is far too small to be observable. For this reason classical physics provides an adequate description of planetary motion but fails within the atom.

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6.5 ORBITAL QUANTUM NUMBER

Quantization of angular momentum magnitude

The interpretation of the orbital quantum number l is



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

This equation is solely concerned with the radial aspect of the electron's motion, that is, its motion toward or away from the nucleus. However, we notice the presence of E , the total electron energy, in the equation. The total energy E includes the electron's kinetic energy of orbital motion, which should have nothing to do with its radial motion.

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This contradiction may be removed by the following argument. 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

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

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

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

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

If the last two terms in the square brackets of this equation cancel each other out, 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

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

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

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

$$KE_{\text{orbital}} = \frac{1}{2} mv_{\text{orbital}}^2 \quad L = rmv_{\text{orbital}}$$

we may write for the orbital kinetic energy

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

$$\text{Hence, from Eq. (6.20), } \frac{L^2}{2mr^2} = \frac{\hbar^2 l(l+1)}{2mr^2}$$

$$\text{Electron angular momentum } L = \sqrt{l(l+1)}\hbar$$

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Electron angular momentum

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

Because the orbital quantum number l is restricted to the values

$$l = 0, 1, 2, \dots, (n-1) \quad (6.21)$$

the electron can have only those particular angular momenta L specified by Eq. (6.21). Like total energy E , angular momentum is both conserved and quantized. The quantity

$$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34} \text{ J} \cdot \text{s}$$

is thus the natural unit of angular momentum.

In macroscopic planetary motion, as in the case of energy, the quantum number describing angular momentum is so large that the separation into discrete angular-momentum states cannot be experimentally observed. For example, an electron (or, for that matter, any other body) whose orbital quantum number is 2 has the angular momentum

$$\begin{aligned} L &= \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar \\ &= 2.6 \times 10^{-34} \text{ J} \cdot \text{s} \end{aligned}$$

By contrast the orbital angular momentum of the earth is $2.7 \times 10^{40} \text{ J} \cdot \text{s}$!

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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:

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

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 $n = 6, l = 5$.

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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

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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. (The vector \mathbf{L} , we recall, is perpendicular to the plane in which the rotational motion takes place, and its sense is given by the right-hand rule: When the fingers of the right hand point in the direction of the motion, the thumb is in the direction of \mathbf{L} . This rule is illustrated in Fig. 6.3.)

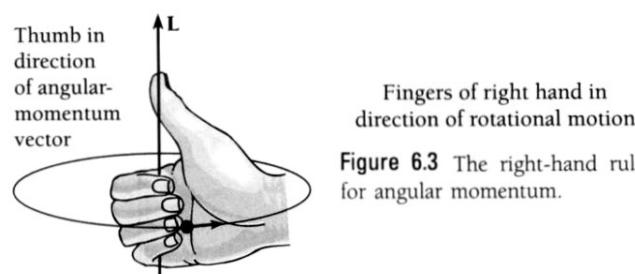


Figure 6.3 The right-hand rule for angular momentum.

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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.

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.

Link

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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. We note that \mathbf{L} can never be aligned exactly parallel or antiparallel to \mathbf{B} because L_z is always smaller than the magnitude $\sqrt{l(l+1)}\hbar$ of the total angular momentum.

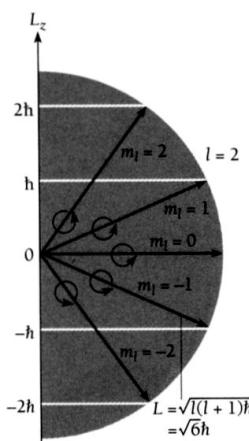


Figure 6.4 Space quantization of orbital angular momentum. Here the orbital quantum number is $l = 2$ and there are accordingly $2l + 1 = 5$ possible values of the magnetic quantum number m_l , with each value corresponding to a different orientation relative to the z axis.

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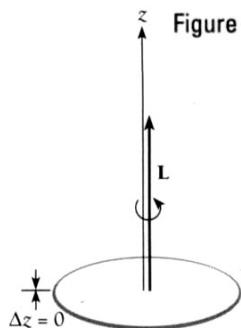
In the absence of an external magnetic field, the direction of the z axis is arbitrary. What must be true is that the component of \mathbf{L} in *any* direction we choose is $m_l\hbar$. What an external magnetic field does is to provide an experimentally meaningful reference direction. A magnetic field is not the only such reference direction possible. For example, the line between the two H atoms in the hydrogen molecule H_2 is just as experimentally meaningful as the direction of a magnetic field, and along this line the components of the angular momenta of the H atoms are determined by their m_l values.

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The Uncertainty Principle and Space Quantization

Why is only one component of \mathbf{L} quantized? The answer is related to the fact that \mathbf{L} can never point in any specific direction but instead is somewhere on a cone in space such that its projection L_z is $m_l\hbar$. Were this not so, the uncertainty principle would be violated. If \mathbf{L} were fixed in space, so that L_x and L_y as well as L_z had definite values, the electron would be confined to a definite plane. For instance, if L were in the z direction, the electron would have to be in the xy plane at all times (Fig. 6.5a). This can occur only if the electron's momentum component p_z in the z direction is infinitely uncertain, which of course is impossible if it is to be part of a hydrogen atom.

Figure 6.5 (a)



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However, since in reality only *one* component L_z of \mathbf{L} together with its magnitude L have definite values and $|L| > |L_z|$, the electron is not limited to a single plane (Fig. 6.5b). Thus there is a built-in uncertainty in the electron's z coordinate. The direction of \mathbf{L} is not fixed, as in Fig. 6.6, and so the average values of L_x and L_y are 0, although L_z always has the specific value $m_l\hbar$.

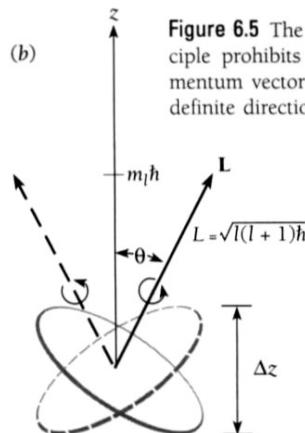


Figure 6.5 The uncertainty principle prohibits the angular momentum vector \mathbf{L} from having a definite direction in space.

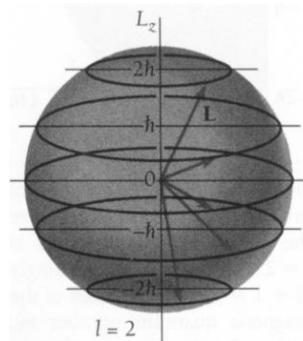


Figure 6.6 The angular-momentum vector \mathbf{L} precesses constantly about the z axis.

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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 $r = n^2 a_0$ (where n is the quantum number of the orbit and a_0 is the radius of the innermost orbit) from the nucleus and in the equatorial plane $\theta = 90^\circ$, while its azimuthal angle ϕ changes with time.

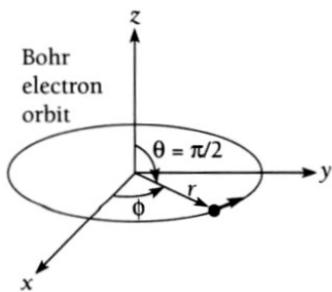


Figure 6.7 The Bohr model of the hydrogen atom in a spherical polar coordinate system.

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

- 1 No definite values for r , θ , or ϕ 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

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

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As usual the square of any function that is complex is to be replaced by the product of the function and its complex conjugate. (We recall that the complex conjugate of a function is formed by changing i to $-i$ whenever it appears.)

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

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

The likelihood of finding the electron at a particular azimuth angle ϕ is a constant that does not depend upon ϕ 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 ϕ as at another.

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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.

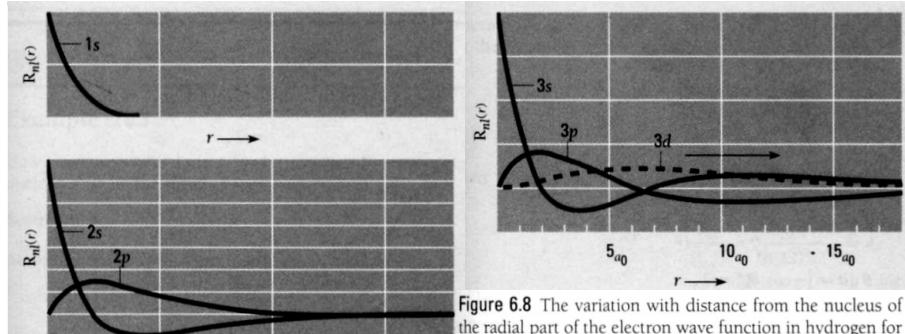


Figure 6.8 The variation with distance from the nucleus of the radial part of the electron wave function in hydrogen for various quantum states. The quantity $a_0 = 4\pi\epsilon_0\hbar^2/m e^2 = 0.053 \text{ nm}$ is the radius of the first Bohr orbit.

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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),

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

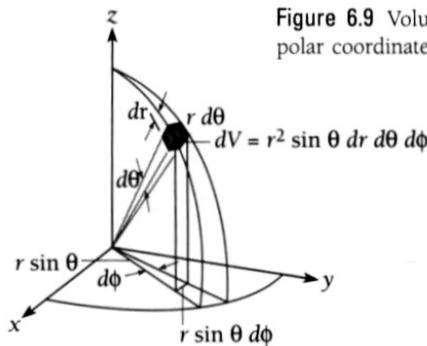


Figure 6.9 Volume element dV in spherical polar coordinates.

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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 (Fig. 6.10) is

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

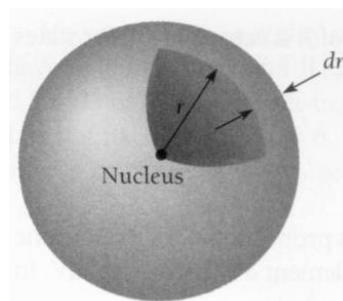


Figure 6.10 The probability of finding the electron in a hydrogen atom in the spherical shell between r and $r + dr$ from the nucleus is $P(r) dr$.

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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. We note immediately that P is not a maximum at the nucleus for s states, as R itself is, but has its maximum at a definite distance from it.

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. However, the average value of r for a 1s electron is $1.5a_0$, which is puzzling at first sight because the energy levels are the same in both the quantum-mechanical and Bohr atomic models. This apparent discrepancy is removed when we recall that the electron energy depends upon $1/r$ rather than upon r directly, and the average value of $1/r$ for a 1s electron is exactly $1/a_0$.

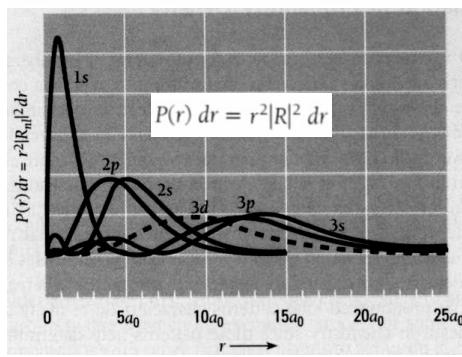


Figure 6.11 The probability of finding the electron in a hydrogen atom at a distance between r and $r + dr$ from the nucleus for the quantum states of Fig. 6.8.

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$$dV = r^2 \sin \theta dr d\theta d\phi \quad (6.24)$$

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 $1/r$

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

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The integrals have the respective values

$$\begin{aligned} \int_0^\infty r e^{-2r/a_0} dr &= \left[\frac{a_0^2}{4} e^{-2r/a_0} - \frac{ia_0}{2} e^{-2r/a_0} \right]_0^\infty = \frac{a_0^2}{4} \\ \int_0^\pi \sin \theta d\theta &= [-\cos \theta]_0^\pi = 2 \\ \int_0^{2\pi} d\phi &= [\phi]_0^{2\pi} = 2\pi \end{aligned}$$

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

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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).

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$$|\psi|^2 = |R|^2 |\Theta|^2 |\Phi|^2$$

Angular Variation of Probability Density

[<Link>](#)

The function Θ varies with zenith angle θ for all quantum numbers l and m_l except $l = m_l = 0$, which are s states. The value of $|\Theta|^2$ for an s state is a constant; $\frac{1}{2}$, in fact. This means that since $|\Phi|^2$ is also a constant, the electron probability density $|\psi|^2$ is spherically symmetric: it has the same value at a given r in all directions. Electrons in other states, however, do have angular preferences, sometimes quite complicated ones. This can be seen in Fig. 6.12, in which electron probability densities as functions of r and θ are shown for several atomic states. (The quantity plotted is $|\psi|^2$, not $|\psi|^2 dV$.) Since $|\psi|^2$ is independent of ϕ , we can obtain a three-dimensional picture of $|\psi|^2$ by rotating a particular representation about a vertical axis. When this is done, we see that the probability densities for s states are spherically symmetric whereas those for other states are not. The pronounced lobe patterns characteristic of many of the states turn out to be significant in chemistry since these patterns help determine the manner in which adjacent atoms in a molecule interact.

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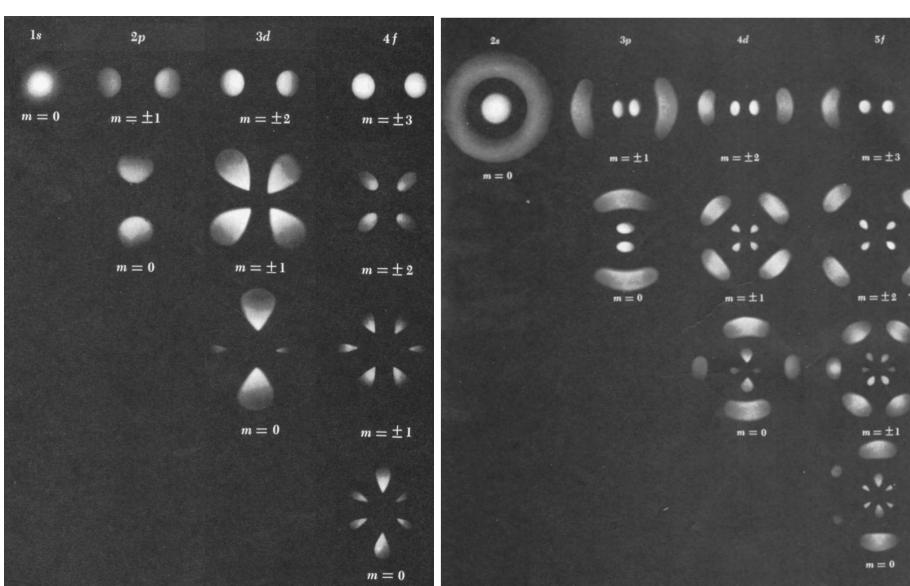


Figure 6.12 Photographic representation of the electron probability-density distribution $|\psi|^2$ for several energy states. These may be regarded as sectional views of the distribution in a plane containing the polar axis, which is vertical and in the plane of the paper. The scale varies from figure to figure.

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A look at Figure 6.12 also reveals quantum-mechanical states that resemble those of the Bohr model. The electron probability-density distribution for a $2p$ state with $m_l = \pm 1$, for instance, is like a doughnut in the equatorial plane centered at the nucleus. Calculation shows the most probable distance of such an electron from the nucleus to be $4a_0$ —precisely the radius of the Bohr orbit for the same principal quantum number $n = 2$. Similar correspondences exist for $3d$ states with $m_l = \pm 2$, $4f$ states with $m_l = \pm 3$, and so on. In each of these cases the angular momentum is the highest possible for that energy level, and the angular-momentum vector is as near the z axis as possible so that the probability density is close to the equatorial plane. Thus the Bohr model predicts the most probable location of the electron in one of the several possible states in each energy level.

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6.8 RADIATIVE TRANSITIONS

What happens when an electron goes from one state to another

In formulating his theory of the hydrogen atom, Bohr was obliged to postulate that the frequency ν of the radiation emitted by an atom dropping from an energy level E_m to a lower level E_n is

$$\nu = \frac{E_m - E_n}{h}$$

It is not hard to show that this relationship arises naturally in quantum mechanics. For simplicity we shall consider a system in which an electron moves only in the x direction.

From Sec. 5.5 we know that the time-dependent wave function Ψ_n of an electron in a state of quantum number n and energy E_n is the product of a time-independent wave function ψ_n and a time-varying function whose frequency is

$$\nu_n = \frac{E_n}{h}$$

Hence $\Psi_n = \psi_n e^{-(iE_n/\hbar)t} \quad \Psi_n^* = \psi_n^* e^{+(iE_n/\hbar)t}$ (6.26)

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The expectation value $\langle x \rangle$ of the position of such an electron is

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} x \Psi_n^* \Psi_n dx = \int_{-\infty}^{\infty} x \psi_n^* \psi_n e^{[(iE_n/\hbar) - (iE_n/\hbar)]t} dx \\ &= \int_{-\infty}^{\infty} x \psi_n^* \psi_n dx \end{aligned} \quad (6.27)$$

The expectation value $\langle x \rangle$ is constant in time since ψ_n and ψ_n^* are, by definition, functions of position only. The electron does not oscillate, and no radiation occurs. Thus quantum mechanics predicts that a system in a specific quantum state does not radiate, as observed.

We next consider an electron that shifts from one energy state to another. A system might be in its ground state n when an excitation process of some kind (a beam of radiation, say, or collisions with other particles) begins to act upon it. Subsequently we find that the system emits radiation corresponding to a transition from an excited state of energy E_m to the ground state. We conclude that at some time during the intervening period the system existed in the state m . What is the frequency of the radiation?

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The wave function Ψ of an electron that can exist in both states n and m is

$$\Psi = a\Psi_n + b\Psi_m \quad (6.28)$$

where a^*a is the probability that the electron is in state n and b^*b the probability that it is in state m . Of course, it must always be true that $a^*a + b^*b = 1$. Initially $a = 1$ and $b = 0$; when the electron is in the excited state, $a = 0$ and $b = 1$; and ultimately $a = 1$ and $b = 0$ once more. While the electron is in either state, there is no radiation, but when it is in the midst of the transition from m to n (that is, when both a and b have nonvanishing values), electromagnetic waves are produced.

The expectation value $\langle x \rangle$ that corresponds to the composite wave function of Eq. (6.28) is

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} x(a^*\Psi_n^* + b^*\Psi_m^*)(a\Psi_n + b\Psi_m) dx \\ &= \int_{-\infty}^{\infty} x(a^2\Psi_n^*\Psi_n + b^*a\Psi_m^*\Psi_n + a^*b\Psi_n^*\Psi_m + b^2\Psi_m^*\Psi_m) dx \end{aligned} \quad (6.29)$$

Here, as before, we let $a^*a = a^2$ and $b^*b = b^2$. The first and last integrals do not vary with time, so the second and third integrals are the only ones able to contribute to a time variation in $\langle x \rangle$.

$$\Psi_n = \psi_n e^{-(iE_n/\hbar)t} \quad \Psi_n^* = \psi_n^* e^{+(iE_n/\hbar)t} \quad (6.26)$$

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With the help of Eqs. (6.26) we expand Eq. (6.29) to give

$$\begin{aligned} \langle x \rangle &= a^2 \int_{-\infty}^{\infty} x\psi_n^*\psi_n dx + b^*a \int_{-\infty}^{\infty} x\psi_m^*e^{+(iE_m/\hbar)t}\psi_n e^{-(iE_n/\hbar)t} dx \rightarrow x\psi_m^*\psi_n e^{i\frac{E_m-E_n}{\hbar}t} \\ &\quad + a^*b \int_{-\infty}^{\infty} x\psi_n^*e^{+(iE_n/\hbar)t}\psi_m e^{-(iE_m/\hbar)t} dx + b^2 \int_{-\infty}^{\infty} x\psi_m^*\psi_m dx \end{aligned} \quad (6.30)$$

Because $e^{i\theta} = \cos \theta + i \sin \theta$ and $e^{-i\theta} = \cos \theta - i \sin \theta$ $x\psi_n^*\psi_m e^{-i\frac{E_m-E_n}{\hbar}t}$

the two middle terms of Eq. (6.30), which are functions of time, become

$$\begin{aligned} \cos\left(\frac{E_m - E_n}{\hbar}t\right) &\int_{-\infty}^{\infty} x[b^*a\psi_m^*\psi_n + a^*b\psi_n^*\psi_m] dx \\ &\quad + i \sin\left(\frac{E_m - E_n}{\hbar}t\right) \int_{-\infty}^{\infty} x[b^*a\psi_m^*\psi_n - a^*b\psi_n^*\psi_m] dx \end{aligned} \quad <\text{Back}> \quad (6.31)$$

The real part of this result varies with time as

$$\cos\left(\frac{E_m - E_n}{\hbar}t\right) = \cos 2\pi\left(\frac{E_m - E_n}{h}\right)t = \cos 2\pi\nu t \quad (6.32)$$

The electron's position therefore oscillates sinusoidally at the frequency

$$\nu = \frac{E_m - E_n}{h} \quad (6.33)$$

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$$\nu = \frac{E_m - E_n}{h} \quad (6.33)$$

When the electron is in state n or state m the expectation value of the electron's position is constant. When the electron is undergoing a transition between these states, its position oscillates with the frequency ν . Such an electron, of course, is like an electric dipole and radiates electromagnetic waves of the same frequency ν . This result is the same as that postulated by Bohr and verified by experiment. As we have seen, quantum mechanics gives Eq. (6.33) without the need for any special assumptions.

6.9 SELECTION RULES

Some transitions are more likely to occur than others

We did not have to know the values of the probabilities a and b as functions of time, nor the electron wave functions ψ_n and ψ_m , in order to find the frequency ν . We need these quantities, however, to calculate the chance a given transition will occur. The general condition necessary for an atom in an excited state to radiate is that the integral

$$\int_{-\infty}^{\infty} x \psi_n \psi_m^* dx \quad (6.34) \quad \text{<Link>}$$

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 the coordinate u represents either the x , y , or z coordinate, the condition for an allowed transition is

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

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.

Since the wave functions ψ_{n,l,m_l} for the hydrogen atom are known, Eq. (6.35) can be evaluated for $u = x$, $u = y$, and $u = z$ for all pairs of states differing in one or more quantum numbers. When this is done, 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 0 and the magnetic quantum number m_l does not change or changes by ± 1 or 0 . That is, the condition for an allowed transition is that

$$\Delta l = \pm 1 \quad (6.36)$$

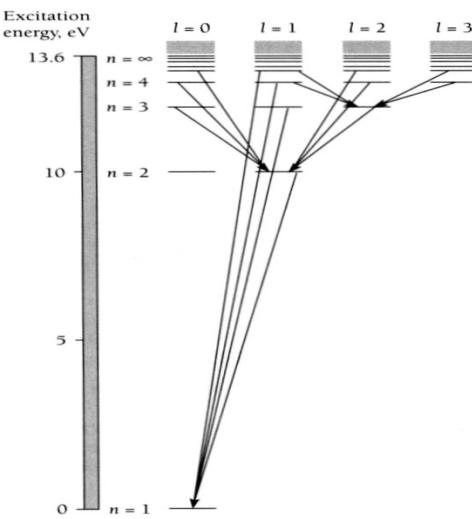
$$\text{Selection rules} \quad \Delta m_l = 0, \pm 1 \quad (6.37)$$

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).

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The selection rule requiring that l change by ± 1 if an atom is to radiate means that an emitted photon carries off the angular momentum $\pm \hbar$ equal to the difference between the angular momenta of the atom's initial and final states. The classical analog of a photon with angular momentum $\pm \hbar$ is a left or right circularly polarized electromagnetic wave, so this notion is not unique with quantum theory.

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.



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6.10 ZEEMAN EFFECT

What happens to an atom in 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 μ of its magnetic moment and the orientation of this moment with respect to the field (Fig. 6.15).

The torque τ on a magnetic dipole in a magnetic field of flux density \mathbf{B} is

$$\tau = \mu B \sin \theta$$

where θ is the angle between μ and \mathbf{B} . The torque is a maximum when the dipole is perpendicular to the field, and zero when it is parallel or antiparallel to it.

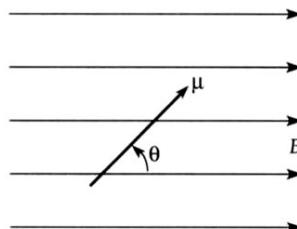


Figure 6.15 A magnetic dipole of moment μ at the angle θ relative to a magnetic field B .

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To calculate the potential energy U_m we must first establish a reference configuration in which U_m is zero by definition. (Since only changes in potential energy are ever experimentally observed, the choice of a reference configuration is arbitrary.) It is convenient to set $U_m = 0$ when $\theta = \pi/2 = 90^\circ$, that is, when μ is perpendicular to \mathbf{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

$$\begin{aligned} U_m &= \int_{\pi/2}^{\theta} \tau d\theta = \mu B \int_{\pi/2}^{\theta} \sin \theta d\theta \\ &= -\mu B \cos \theta \end{aligned} \quad \text{Back} \quad (6.38)$$

When μ points in the same direction as \mathbf{B} , then $U_m = -\mu B$, its minimum value. This follows from the fact that a magnetic dipole tends to align itself with an external magnetic field.

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The magnetic moment of the orbital electron in a hydrogen atom depends on its angular momentum \mathbf{L} . Hence both the magnitude of \mathbf{L} and its orientation with respect to the field determine the extent of the magnetic contribution to the total energy of the atom when it is in a magnetic field. The magnetic moment of a current loop is

$$\mu = IA$$

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

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

\uparrow
 $(v = 2\pi rf)$

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

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

for an orbital electron (Fig. 6.16).

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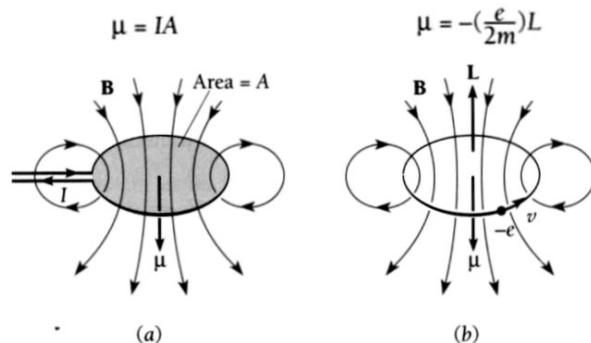


Figure 6.16 (a) Magnetic moment of a current loop enclosing area A . (b) Magnetic moment of an orbiting electron of angular momentum \mathbf{L} .

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The quantity $(-e/2m)$, which involves only the charge and mass of the electron, is called its **gyromagnetic ratio**. The minus sign means that μ is in the opposite direction to \mathbf{L} and is a consequence of the negative charge of the electron. While the above expression for the magnetic moment of an orbital electron has been obtained by a classical calculation, quantum mechanics yields the same result. The magnetic potential energy of an atom in a magnetic field is therefore

$$U_m = \left(\frac{e}{2m} \right) LB \cos \theta \quad (6.40) \quad <\text{Link}>$$

which depends on both B and θ .

From Fig. 6.4 we see that the angle θ between \mathbf{L} and the z direction can have only the values specified by

$$\cos \theta = \frac{m_l}{\sqrt{l(l+1)}}$$

with the permitted values of L specified by

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

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To find the magnetic energy that an atom of magnetic quantum number m_l has when it is in a magnetic field \mathbf{B} , we put the above expressions for $\cos \theta$ and L in Eq. (6.40) to give

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

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

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

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

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** after the Dutch physicist Pieter Zeeman, who first observed it in 1896. The Zeeman effect is a vivid confirmation of space quantization.

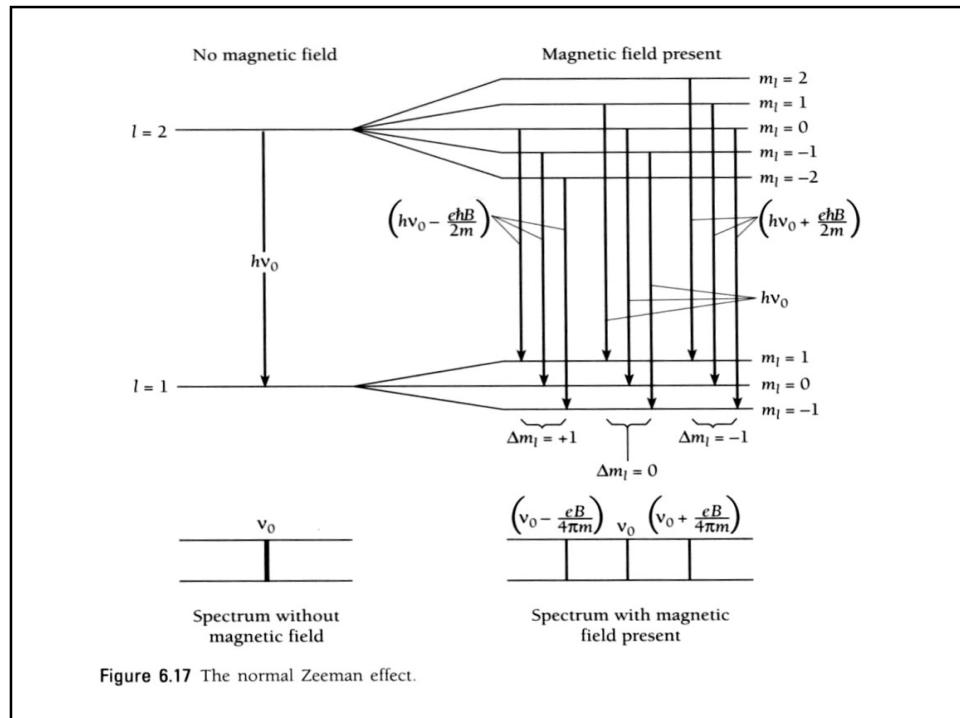
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Because m_l can have the $2l + 1$ values of $+l$ through 0 to $-l$, a state of given orbital quantum number l is split into $2l + 1$ substates that differ in energy by $\mu_B B$ when the atom is in a magnetic field. However, because changes in m_l 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 ν_0 into three components whose frequencies are

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

In Secs. 7.1 and 7.7 we will see that this is not the whole story of the Zeeman effect.

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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,

$$\Delta\lambda = \frac{\lambda^2 \Delta\nu}{c} = \frac{eB\lambda^2}{4\pi mc}$$

$$= \frac{(1.60 \times 10^{-19} \text{ C})(0.300 \text{ T})(4.50 \times 10^{-7} \text{ m})^2}{(4\pi)(9.11 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m/s})}$$

$$= 2.83 \times 10^{-12} \text{ m} = 0.00283 \text{ nm}$$

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$$\begin{aligned}
r &= (x^2 + y^2 + z^2)^{\frac{1}{2}} \quad \frac{\partial r}{\partial x} = \frac{1}{2} \frac{2x}{(x^2 + y^2 + z^2)^{\frac{1}{2}}} = \frac{x}{r} \\
\text{If } \psi &= \psi(r) \quad \frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial r} \frac{\partial r}{\partial x} = \frac{x}{r} \frac{\partial \psi}{\partial r} \\
\frac{\partial^2 \psi}{\partial x^2} &= \frac{1}{r} \frac{\partial \psi}{\partial r} - \frac{x^2}{r^3} \frac{\partial \psi}{\partial r} + \frac{x^2}{r^2} \frac{\partial^2 \psi}{\partial r^2} \\
\frac{\partial^2 \psi}{\partial y^2} &= \frac{1}{r} \frac{\partial \psi}{\partial r} - \frac{y^2}{r^3} \frac{\partial \psi}{\partial r} + \frac{y^2}{r^2} \frac{\partial^2 \psi}{\partial r^2} \\
\frac{\partial^2 \psi}{\partial z^2} &= \frac{1}{r} \frac{\partial \psi}{\partial r} - \frac{z^2}{r^3} \frac{\partial \psi}{\partial r} + \frac{z^2}{r^2} \frac{\partial^2 \psi}{\partial r^2}. \\
(x^2 + y^2 + z^2 &= r^2) \\
\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} &\stackrel{\downarrow}{=} \left(\frac{3}{r} - \frac{r^2}{r^3} \right) \frac{\partial \psi}{\partial r} + \frac{r^2}{r^2} \frac{\partial^2 \psi}{\partial r^2} \\
&= \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) \\
\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right)
\end{aligned}$$

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

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

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

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

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

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

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Electrical charges

Electric dipole moment: $p = q \cdot l$

Magnetic dipoles

Magnetic dipole moment

$$\mu = q_m \cdot l$$

Unlike electrical charge, there is no single magnetic pole discovered so far. If you cut a magnet into smaller pieces, each of them always has two poles! **Inside a magnet there really are no poles!**

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Equivalent magnetic dipole of an electric current loop

The field of a magnet of pole strength q_m and length l , at a distance r from the magnet, depends only on the moment $q_m \cdot l$ of the magnet and not on the separate values of q_m and l , provided r is large relative to l .

Thus the field is the same if we halve the length of the magnet and double its pole strength. Continuing this process, we obtain in the limit a **very short magnet of finite moment equal to that from a circular electrical loop**.

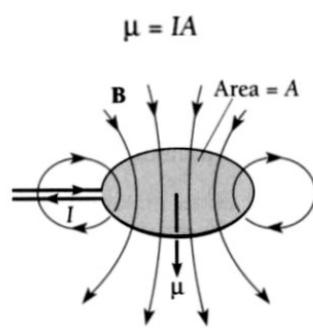
Any magnet, as far as its external field is concerned, may be thought as being made up of such dipoles.

$$\mu = IA$$

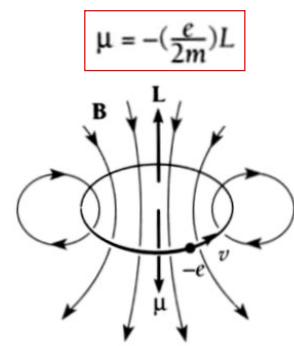
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Magnetic moment of a current loop enclosing area A



Magnetic moment of an orbiting electron of angular momentum L



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