

Eq. (16.1-3) separates into

$$\frac{d^2 P(r)}{dr^2} + \frac{2m}{\hbar^2} [E - V(r)] P(r) = \frac{\lambda}{r^2} P(r), \quad (16.1-6)$$

$$L^2 Y(\theta, \varphi) = \lambda Y(\theta, \varphi), \quad (16.1-7)$$

with λ as a separation constant. Further progress requires that boundary conditions be specified. On physical grounds it is assumed that ψ and its first derivatives are everywhere continuous, single-valued, and finite. The consequences of imposing these conditions are that

$$\lambda = l(l+1) \quad (l = 0, 1, 2, \dots) \quad (16.1-8)$$

and that the functions $Y(\theta, \varphi)$ are the spherical harmonics $Y_{lm}(\theta, \varphi)$ with*

$$m = l, l-1, \dots, -l. \quad (16.1-9)$$

Substituting (16.1-8) into (16.1-6),

$$\left\{ \frac{d^2}{dr^2} + \frac{2m}{\hbar^2} [E - V(r)] - \frac{l(l+1)}{r^2} \right\} P(r) = 0 \quad (16.1-10)$$

on which we impose the requirement

$$V(r) \rightarrow 0 \quad \text{as } r \rightarrow \infty. \quad (16.1-11)$$

Solutions to (16.1-10) may be obtained by first considering the behavior at large r . In the asymptotic region $r \rightarrow \infty$,

$$\frac{d^2 P(r)}{dr^2} + \frac{2m}{\hbar^2} EP(r) = 0 \quad (16.1-12)$$

has solutions

$$P(r) = e^{\pm ar} \quad (16.1-13)$$

where

$$a = \sqrt{-(2m/\hbar^2)E}. \quad (16.1-14)$$

If $E < 0$, $e^{ar} \rightarrow \infty$ as $r \rightarrow \infty$. Since this violates the conditions that the wave function must be finite everywhere, it is not an acceptable solution. On the other hand $e^{-ar} \rightarrow 0$ as $r \rightarrow \infty$; it is therefore a possible solution. If $E > 0$,

* Note that m appears both as a symbol to represent the mass of the electron and as a label for the spherical harmonics. Such confusion and others like it are unavoidable if we are not to depart too drastically from conventional notation.

CHAPTER 16

HYDROGEN ATOM

16.1 Schrödinger Equation

For an electron in a static field whose potential is φ , the Schrödinger equation (15.2-32), without the higher-order relativistic corrections, simplifies to

$$(E' + e\varphi)\psi = \frac{p^2}{2m} \psi. \quad (16.1-1)$$

Replacing E' by E (nonrelativistic energy), $e\varphi$ by $-V$, and \mathbf{p} by $-i\hbar\nabla$, Eq. (16.1-1) becomes

$$\mathcal{H}\psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = E\psi \quad (16.1-2)$$

or, in spherical coordinates,

$$r^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \psi + \frac{2mr^2}{\hbar^2} (E - V)\psi = L^2 \psi \quad (16.1-3)$$

in which

$$L^2 = - \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]. \quad (16.1-4)$$

Assuming $V = V(r)$ and

$$\psi(r, \theta, \varphi) = \frac{1}{r} P(r) Y(\theta, \varphi) = R(r) Y(\theta, \varphi), \quad (16.1-5)$$

either sign in the exponent will satisfy the boundary conditions. We concentrate on the case $E < 0$, that is, the bound states of the atom. The asymptotic behavior suggests that solutions to (16.1-10) be sought in the form

$$P(r) = e^{-\alpha r} f(r) \quad (16.1-15)$$

where $f(r)$ is a function to be determined by the radial equation (16.1-10) and the boundary conditions.

To proceed further it is necessary to specify the form of the potential $V(r)$. Let us now assume that the physical system consists of an electron of mass m interacting with a nucleus of charge Ze via the Coulomb interaction

$$V = -Ze^2/r. \quad (16.1-16)$$

With $Z = 1$ we have hydrogen, while hydrogen-like atoms or ions are represented by assigning an appropriate value to Z . The radial equation (16.1-10) now becomes

$$\frac{d^2 P(r)}{dr^2} + \left[\frac{2m}{\hbar^2} \left(E + \frac{Ze^2}{r} \right) - \frac{l(l+1)}{r^2} \right] P(r) = 0 \quad (16.1-17a)$$

or, in Rydberg units (Table 16.1),

$$\frac{d^2 P(r)}{dr^2} + \left[E + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] P(r) = 0. \quad (16.1-17b)$$

The substitution of (16.1-15) into (16.1-17b) yields

$$\frac{d^2 f}{dr^2} - 2a \frac{df}{dr} + \left[\frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] f = 0 \quad (16.1-18)$$

whose solution may be expressed as a power series

$$f = r^s [A_0 + A_1 r + A_2 r^2 + \dots]. \quad (16.1-19)$$

To ensure that f remains finite as $r \rightarrow 0$ it is necessary for s to be positive. When (16.1-19) is substituted into (16.1-18), it is found that

$$s = l + 1 > 0 \quad (16.1-20)$$

and that the coefficients obey the recursion relation

$$A_n/A_{n-1} = 2[(l+k)a - Z]/[k^2 + (2l+1)k]. \quad (16.1-21)$$

As $k \rightarrow \infty$,

$$A_n/A_{n-1} = 2a/k. \quad (16.1-22)$$

* To take into account the finite mass of the nucleus, m would be replaced by the reduced mass $\mu = mM/(m+M)$ where M is the mass of the nucleus (see also Section 23.8).

TABLE 16.1

Relations among Atomic Units^a

	Rydberg	Hartree ^b
Length r	$r_R = \frac{r}{a_0}$	$r_H = \frac{r}{a_0}$
Energy E	$E_R = \frac{E}{R_\infty}$	$E_H = \frac{E}{2R_\infty}$
∇^2	$\nabla_R^2 = a_0^2 \nabla^2$	$\nabla_H^2 = a_0^2 \nabla^2$
$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right) \psi = E\psi$	$\left(-\nabla_R^2 - \frac{2Z}{r_R} \right) \psi = E_R \psi$	$\left(-\frac{1}{2} \nabla_H^2 - \frac{Z}{r_H} \right) \psi = E_H \psi$

^a a_0 = Bohr radius = $\hbar^2/m_e^2 = 0.5292 \text{ \AA}$.

R_∞ = Rydberg constant = $\frac{1}{2} m c^2 (e^2/\hbar c)^2 = 13.605 \text{ eV} = 109,737.311 \text{ cm}^{-1}$.

^b Hartree units correspond to setting $e = \hbar = m = 1$.

We note that

$$e^{2\alpha r} = 1 + 2\alpha r + \frac{(2\alpha r)^2}{2!} + \dots \quad (16.1-23)$$

and

$$\frac{(2\alpha)^k/k!}{(2\alpha)^{k-1}/(k-1)!} = \frac{2\alpha}{k} \quad (16.1-24)$$

which indicates that f behaves like $e^{2\alpha r}$ for large k . Therefore

$$P(r) = e^{-\alpha r} f \approx e^{\alpha r} \quad (16.1-25)$$

for large k . Since this would mean that $P(r) \rightarrow \infty$ as $r \rightarrow \infty$, it is necessary that the series (16.1-19) be terminated at some finite value of k . We therefore set

$$(l+k)a - Z = (l+k)\sqrt{-E} - Z = 0 \quad (16.1-26)$$

or

$$E = -Z^2/(l+k)^2 \equiv -Z^2/n^2 \quad (\text{Ry}). \quad (16.1-27)$$

It is seen that the boundary conditions have forced the bound states to be discrete.

The series solution for $P(r)$ may be expressed in terms of Laguerre polynomials (Appendix 6)

$$L_{n-l-1}^{2l+1}(x) = B_0 + B_1 x + B_2 x^2 + \dots + B_{n-l-1} x^{n-l-1} \quad (16.1-28)$$

in which

$$B_{n-l-1} = (-1)^{l-1} [(n+l)! / (n-1-1)!] \quad (16.1-29)$$

In order that B_{n-l-1} remain finite, $n-l-1$ must be zero or a positive integer. Hence

$$n = l + 1, l + 2, \dots \quad (16.1-30)$$

The complete solution for the bound states of hydrogen may now be written as

$$|nlm\rangle \equiv \psi_{nlm}(r, \theta, \varphi) = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi) \quad (16.1-31)$$

TABLE 16.2

Radial Wave Functions in Hydrogen

n	l	$P_{nl}(r)$
1	0	$\left(\frac{Z}{a_0}\right)^{3/2} 2re^{-Zr/a_0}$
2	0	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{\sqrt{2}} r \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$
2	1	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{2\sqrt{6}} a_0 Zr^2 e^{-Zr/2a_0}$
3	0	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{2}{3\sqrt{3}} r \left[1 - \frac{2Zr}{3a_0} + \frac{2}{27} \left(\frac{Zr}{a_0}\right)^2\right] e^{-Zr/3a_0}$
3	1	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{8}{27\sqrt{6}} a_0 Zr^2 \left(1 - \frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$
3	2	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{4}{81\sqrt{30}} a_0^2 Zr^3 e^{-Zr/3a_0}$
4	0	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{r}{4} \left[1 - \frac{3Zr}{4a_0} + \frac{1}{8} \left(\frac{Zr}{a_0}\right)^2 - \frac{1}{192} \left(\frac{Zr}{a_0}\right)^3\right] e^{-Zr/4a_0}$
4	1	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{16\sqrt{3}} a_0 Zr^2 \left[1 - \frac{Zr}{4a_0} + \frac{1}{80} \left(\frac{Zr}{a_0}\right)^2\right] e^{-Zr/4a_0}$
4	2	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{64\sqrt{5}} a_0^2 Zr^3 \left(1 - \frac{Zr}{12a_0}\right) e^{-Zr/4a_0}$
4	3	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{768\sqrt{35}} a_0^3 Zr^4 e^{-Zr/4a_0}$

with

$$P_{nl}(r) = \sqrt{\frac{(n-l-1)! Z}{n^2 [(n+l)!]^3 a_0}} \left(\frac{2Zr}{na_0}\right)^{l+1} e^{-Zr/na_0} L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0}\right) \quad (16.1-32)$$

and

$$\int_0^\infty P_{nl}(r) P_{n'l'}(r) dr = \delta_{nn'} \quad (16.1-33)$$

Explicit forms of $P_{nl}(r)$ for several values of n and l are given in Table 16.2. In view of the orthogonality properties of $P_{nl}(r)$ and $Y_{lm}(\theta, \varphi)$ the eigenfunctions (16.1-31) must also obey orthogonality relations

$$\begin{aligned} \langle nlm|n'l'm'\rangle &= \int \psi_{nlm}^*(r, \theta, \varphi) \psi_{n'l'm'}(r, \theta, \varphi) dr \\ &= \delta_{nn'} \delta_{ll'} \delta_{mm'} \end{aligned} \quad (16.1-34)$$

To summarize, we have three quantum numbers $n, l,$ and m , where n is the principal quantum number with possible values $1, 2, 3, \dots$; l the orbital angular momentum quantum number (orbital quantum number, for short) with possible values $0, 1, 2, \dots, n-1$; and m the magnetic (or projection) quantum number whose values are restricted to $l, l-1, \dots, -l$. In spectroscopic notation, s, p, d, f, \dots correspond to $l = 0, 1, 2, 3, 4, \dots$, respectively. The bound states of hydrogen may now be described. Table 16.3 lists the quantum numbers, spectroscopic notation, wave functions, energy, and the degeneracy (not including spin). The latter gives the number of eigenfunctions associated with a particular energy and is equal to n^2 . This is somewhat unexpected because the Hamiltonian in (16.1-2) with $V = V(r)$ is invariant under all three-dimensional rotations. Based on the discussion in Section 8.1 we expect the eigenfunctions of the Hamiltonian to be of the form $R(r)Y_{lm}(\theta, \varphi)$ as indeed was shown by the detailed calculation culminating in (16.1-31). In that case the degeneracy ought to be $2l+1$ with $l = 0, 1, 2, \dots$. The fact that in hydrogen the degeneracy is actually n^2 is due to the special property of the Coulomb field. It has been shown (Fock, 1935) that the Schrödinger equation for the motion of an electron in a Coulomb field, is invariant under transformations of the four-dimensional rotation group of which $O^+(3)$ is a subgroup. The classification of states with respect to the irreducible representations of the four-dimensional group then leads to the n^2 degeneracy.[†]

The eigenfunctions in Table 16.3 are written with the phase factors all equal to $+1$ despite the fact that the phase factors depend on the quantum numbers in accordance with the definitions of $P_{nl}(r)$ [Eq. (16.1-32)] and

[†] The n^2 degeneracy in hydrogen is often said to be accidental.

* All the wave functions are written with a positive phase factor.

n	l	m	Notation	Wave function	Degeneracy (n^2)	Energy (Ry)
4	0	0	4s	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{1} \left[\frac{1536\sqrt{\pi}}{1} - 144 \frac{a_0}{Zr} + 24 \left(\frac{a_0}{Zr}\right)^2 - \left(\frac{a_0}{Zr}\right)^3 \right] e^{-Zr/4a_0}$	16	$-\frac{16}{Z^2}$
	1	0	4p ₀	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{\sqrt{5}} \left[\frac{2560\sqrt{\pi}}{80} - 20 \frac{a_0}{Zr} - 20 \left(\frac{a_0}{Zr}\right)^2 + \left(\frac{a_0}{Zr}\right)^3 \right] e^{-Zr/4a_0} \cos \theta$		
	1	± 1	4p _{± 1}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{\sqrt{5}} \left[\frac{2560\sqrt{\pi}}{80} - 20 \frac{a_0}{Zr} - 20 \left(\frac{a_0}{Zr}\right)^2 + \left(\frac{a_0}{Zr}\right)^3 \right] e^{-Zr/4a_0} \sin \theta e^{\pm i\phi}$		
	2	0	4d ₀	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{3062\sqrt{\pi}} \left[12 \left(\frac{a_0}{Zr}\right)^2 - \left(\frac{a_0}{Zr}\right)^3 \right] e^{-Zr/4a_0} (3 \cos^2 \theta - 1)$		
	2	± 1	4d _{± 1}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{1536\sqrt{\pi}} \left[12 \left(\frac{a_0}{Zr}\right)^2 - \left(\frac{a_0}{Zr}\right)^3 \right] e^{-Zr/4a_0} \sin \theta \cos \theta e^{\pm i\phi}$		
	2	± 2	4d _{± 2}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{3072\sqrt{\pi}} \left[12 \left(\frac{a_0}{Zr}\right)^2 - \left(\frac{a_0}{Zr}\right)^3 \right] e^{-Zr/4a_0} \sin^2 \theta e^{\pm 2i\phi}$		
	3	0	4f ₀	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{3072\sqrt{5\pi}} \left(\frac{a_0}{Zr}\right)^3 e^{-Zr/4a_0} (5 \cos^3 \theta - 3 \cos \theta)$		
	3	± 1	4f _{± 1}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{6144\sqrt{3\pi}} \left(\frac{a_0}{Zr}\right)^3 e^{-Zr/4a_0} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$		
	3	± 2	4f _{± 2}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{3072\sqrt{3\pi}} \left(\frac{a_0}{Zr}\right)^3 e^{-Zr/4a_0} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$		
	3	± 3	4f _{± 3}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{6144\sqrt{\pi}} \left(\frac{a_0}{Zr}\right)^3 e^{-Zr/4a_0} \sin^3 \theta e^{\pm 3i\phi}$		

Hydrogen Atom Wave Functions*

TABLE 16.3

n	l	m	Notation	Wave function	Degeneracy (n^2)	Energy (Ry)
1	0	0	1s	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{1} e^{-Zr/a_0}$	1	$-Z^2$
2	0	0	2s	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{\sqrt{32\pi}} \left(2 - \frac{a_0}{Zr} \right) e^{-Zr/2a_0}$	4	$-\frac{4}{Z^2}$
	1	0	2p ₀	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{\sqrt{32\pi}} \frac{a_0}{Zr} e^{-Zr/2a_0} \cos \theta$		
	1	± 1	2p _{± 1}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{\sqrt{64\pi}} \frac{a_0}{Zr} e^{-Zr/2a_0} \sin \theta e^{\pm i\phi}$		
3	0	0	3s	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{81\sqrt{3\pi}} \left[27 - 18 \frac{a_0}{Zr} + 2 \left(\frac{a_0}{Zr}\right)^2 \right] e^{-Zr/3a_0}$	9	$-\frac{9}{Z^2}$
	1	0	3p ₀	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{6\sqrt{2}} \left[\frac{81\sqrt{\pi}}{2} - \frac{a_0}{Zr} \right] e^{-Zr/3a_0} \cos \theta$		
	1	± 1	3p _{± 1}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{6\sqrt{\pi}} \left[\frac{81\sqrt{\pi}}{2} - \frac{a_0}{Zr} \right] e^{-Zr/3a_0} \sin \theta e^{\pm i\phi}$		
	2	0	3d ₀	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{81\sqrt{6\pi}} \left(\frac{a_0}{Zr}\right)^2 e^{-Zr/3a_0} (3 \cos^2 \theta - 1)$		
	2	± 1	3d _{± 1}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{81\sqrt{\pi}} \left(\frac{a_0}{Zr}\right)^2 e^{-Zr/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$		
	2	± 2	3d _{± 2}	$\left(\frac{a_0}{Z}\right)^{3/2} \frac{1}{162\sqrt{\pi}} \left(\frac{a_0}{Zr}\right)^2 e^{-Zr/3a_0} \sin^2 \theta e^{\pm 2i\phi}$		

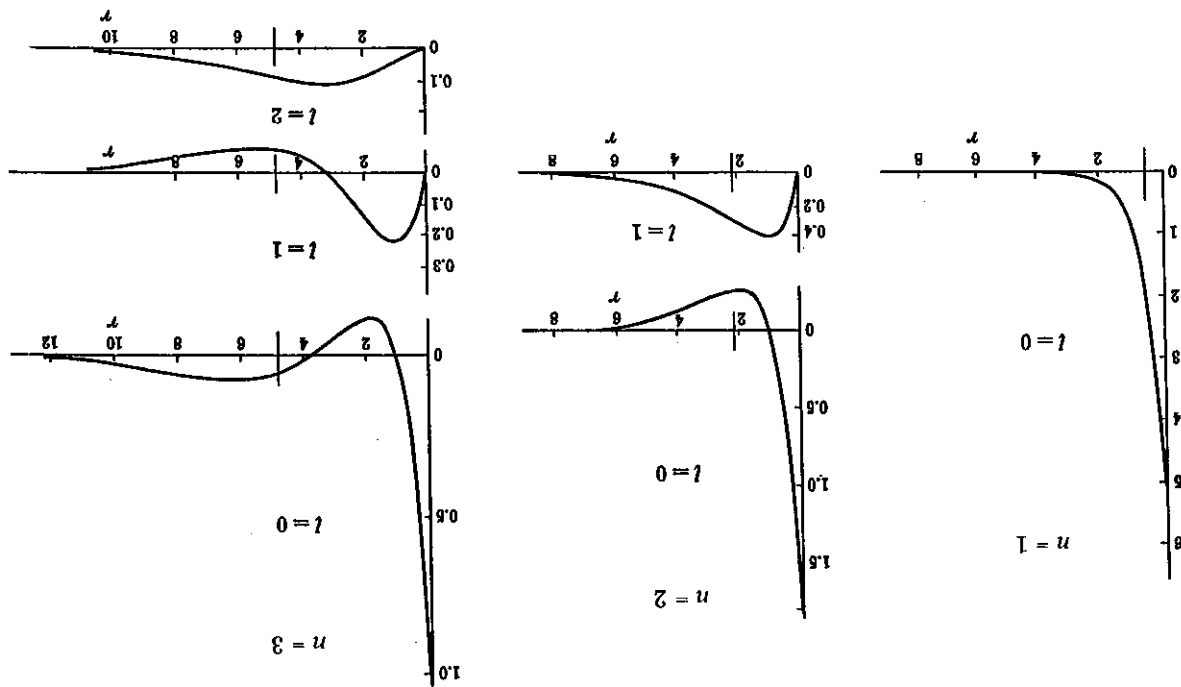


FIG. 16.1 Relative magnitude of the radial part $R_n(r)$ of the hydrogen wave function $\psi_{nlm}(r, \theta, \varphi) = R_n(r)Y_{lm}(\theta, \varphi)$ as a function of r (in angstroms). The vertical line on the horizontal axis is the radius of the corresponding Bohr orbit. (a) $n = 2$; (b) $n = 1$; (c) $n = 3$. (From Gerhard Herzberg "Atomic Spectra and Atomic Structure," Dover Publications, Inc., New York, 1944. Adapted through the permission of the publisher.)

$Y_{lm}(\theta, \varphi)$ [Eq. (1.2-1)]. Plots of $R_{nl}(r) [= (1/r)P_{nl}(r)]$ are shown in Fig. 16.1. Note that the higher the value of n and therefore the energy, the greater is the number of nodes in $R_{nl}(r)$ for a given value of l . Energies are plotted in Fig. 16.2.

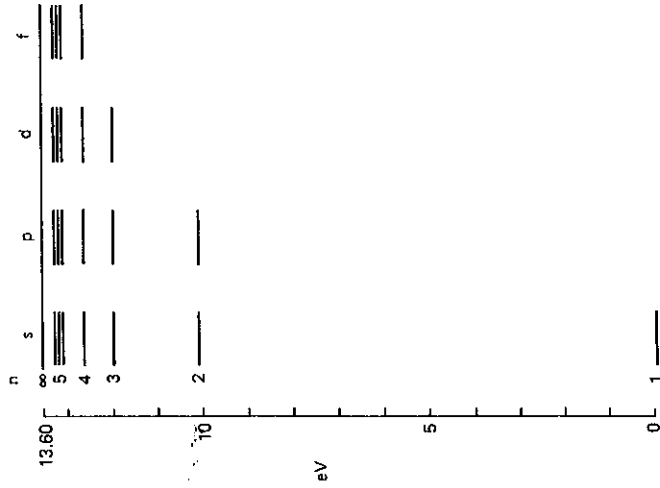


FIG. 16.2 Energy levels of the hydrogen atom, without fine structure.

The probability of finding an electron in an element of volume $d\tau$ is

$$\psi^* \psi d\tau = \frac{1}{r^2} P_{nl}^2(r) Y_{lm}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) d\tau. \quad (16.1-35)$$

If (16.1-35) is integrated over the surface of a sphere, we obtain the probability of finding an electron in a shell between two spheres of radii r and $r + dr$. Since the spherical harmonics are normalized to unity, the result is simply $P_{nl}^2(r) dr$. In the sense that $\psi^* \psi$ is a charge density, $P_{nl}^2(r)$ is a radial charge density; a plot is shown in Fig. 16.3. The probability of finding an electron between θ and $\theta + d\theta$ is proportional to

$$Y_{lm}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) \sin \theta d\theta = [P_l^m(\cos \theta)]^2 \sin \theta d\theta. \quad (16.1-36)$$

$[P_l^m(\cos \theta)]^2$ is shown in Fig. 16.4. Finally, the probability of finding an electron between φ and $\varphi + d\varphi$ is simply proportional to $d\varphi$.

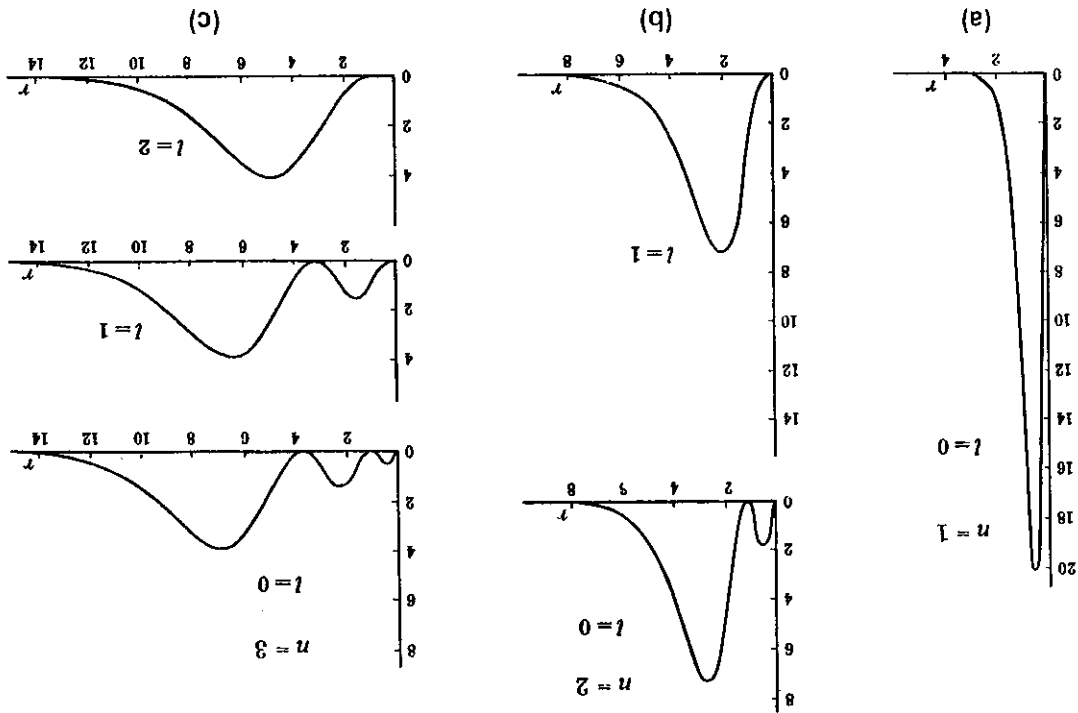


FIG. 16.3 Radial charge density $[P_{nl}(r)]^2$ for the hydrogen wave function $\psi_{nlm}(r, \theta, \varphi) = (1/r) P_{nl}(r) Y_{lm}(\theta, \varphi)$. (a) $n = 1$; (b) $n = 2$; (c) $n = 3$. (From Gerhard Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, Inc., New York, 1944. Adapted through the permission of the publisher.)

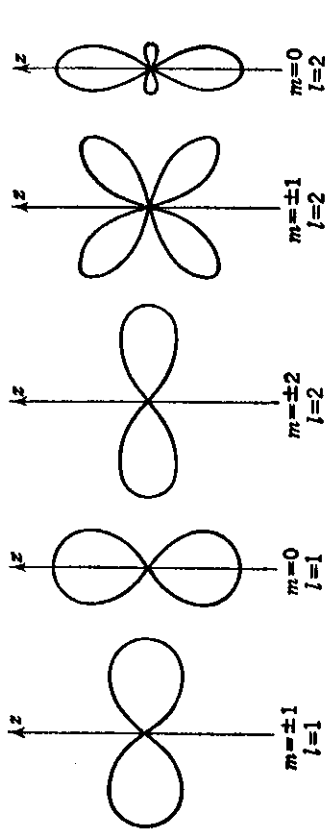


FIG. 16.4 Polar plots of $[P_{lm}(\cos \theta)]^2$. (Slater, 1960)

Average values of various powers of r are often needed in a computation; these are defined by

$$\langle r^k \rangle = \int_0^\infty r^k P_{nl}^2(r) dr. \quad (16.1-37)$$

The results for several values of k are given in Table 16.4.

TABLE 16.4

Expectation Values of r^k ^a

k	$\langle r^k \rangle$
1	$\frac{a_0}{2Z} [3n^2 - l(l+1)]$
2	$\frac{a_0^2 n^2}{Z^2} [5n^2 + 1 - 3l(l+1)]$
3	$\frac{a_0^3 n^2}{Z^3} [35n^2(n^2 - 1) - 30n^2(l - 1) + 3(l + 2)(l + 1)(l - 1)]$
4	$\frac{a_0^4 n^4}{Z^4} [63n^4 - 35n^2(2l^2 + 2l - 3) + 5(l + 1)(3l^2 + 3l - 10) + 12]$
-1	$\frac{Z}{a_0 n^2}$
-2	$\frac{Z^2}{a_0^2 n^3(l + \frac{1}{2})}$
-3	$\frac{Z^3}{a_0^3 n^3(l + 1)(l + \frac{3}{2})}$
-4	$\frac{Z^4}{a_0^4} \frac{3n^2 - l(l+1)}{2n^3(l + \frac{3}{2})(l + \frac{1}{2})(l - \frac{1}{2})}$

^a $\langle r^k \rangle = \int_0^\infty R_{nl}^2(r) r^{k+2} dr = \int_0^\infty P_{nl}^2(r) r^k dr.$

The states corresponding to $E > 0$, in contrast to those with $E < 0$, are not quantized; instead they form a continuum. This is evident from (16.1-13) which shows that, asymptotically, $P(r)$ has a sinusoidal behavior; it is therefore not necessary to terminate the series in (16.1-19). A more detailed development of the continuum states (Bethe and Salpeter, 1957) indicates that the radial solution is expressible in terms of the regular Coulomb function $F_l(\eta, kr)$ whose properties and numerical values are given by Abramowitz and Stegun (1965). It should be emphasized that, although the bound states of the hydrogen atom (16.1-31) form an infinite, discrete set, the set is not complete. If we wish to expand a function in terms of hydrogen atom solutions, it is necessary to include the continuum states as well as the bound states.

Previously it was shown (7.4-12) that $[\mathbf{L}, V^2] = 0$. It then follows that the Hamiltonian

$$\mathcal{H} = -(\hbar^2/2m)\nabla^2 + V(r) \quad (16.1-38)$$

also commutes with \mathbf{L} and L^2 . However, the components of \mathbf{L} do not commute with one another. We are therefore restricted to one component of \mathbf{L} which will commute both with L^2 and \mathcal{H} . The usual choice is to pick L_z . Thus

$$[L_z, \mathcal{H}] = 0. \quad (16.1-39)$$

Since \mathcal{H} does not contain any spin operators,

$$[S^2, \mathcal{H}] = [S_z, \mathcal{H}] = 0. \quad (16.1-40)$$

16.2 One-Electron Wave Functions

For the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} - \frac{Ze^2}{r} \quad (16.2-1)$$

the complete solution to the Schrödinger equation $\mathcal{H}\psi = E\psi$ for the bound states consists of the orbitals $\psi_{nlm}(r, \theta, \varphi)$ [Eq. (16.1-31)] together with the energy eigenvalues E_n [Eq. (16.1-27)]. However, the Schrödinger equation (15.2-32) contains additional terms which will have an effect on the eigenfunctions and eigenvalues of the system. To deal with these effects we must inquire, in the first place, whether the $\psi_{nlm}(r, \theta, \varphi)$ are suitable as a starting point for a perturbation treatment, i.e., whether the $\psi_{nlm}(r, \theta, \varphi)$ can serve as a zero-order basis set.

Examination of (15.2-32) reveals the presence of terms containing the operator σ whose components are the Pauli matrices. According to the

discussion in Section 1.4,

$$\sigma = 2\mathbf{S}$$

where the rectangular components of \mathbf{S} are angular momentum operators and

$$S_z\alpha = \frac{1}{2}\alpha, \quad S_z\beta = -\frac{1}{2}\beta \quad (16.2-2a)$$

$$S^2\alpha = \frac{1}{2}(\frac{1}{2} + 1)\alpha = \frac{3}{4}\alpha, \quad S^2\beta = \frac{1}{2}(\frac{1}{2} + 1)\beta = \frac{3}{4}\beta. \quad (16.2-2b)$$

Equations (16.2-2) identify the system as a particle with spin $s = \frac{1}{2}$. Thus the appearance of σ in the Hamiltonian indicates that the wave function of the system must include a spin eigenfunction. We adopt the notation:

$$\varphi(\mathbf{r}) \equiv \varphi_{nlm}(r, \theta, \varphi)$$

is a one-electron spatial orbital characterized by the quantum numbers n, l, m_l . This is identical to the function which had previously been written as $\psi_{nlm}(r, \theta, \varphi)$ as in (16.1-31).

$$\xi_{m_s} \equiv \xi(m_s) = \begin{cases} \alpha & \text{for } m_s = \frac{1}{2} \\ \beta & \text{for } m_s = -\frac{1}{2} \end{cases} \\ = \text{one-electron spin function,} \quad (16.2-3)$$

$$\psi(\lambda) = \psi(r, \theta, \varphi, m_s) = \varphi(\mathbf{r})\xi(m_s) \\ = \text{(one-electron) spin orbital.} \quad (16.2-4)$$

It shall be understood that an integral involving spin orbitals implies a spatial integration as well as a summation over spin coordinates.

In many instances the radial part of the wave function remains fixed so that the principal quantum number n may be suppressed without loss of information. Also, the Dirac notation is often the most convenient one. Thus $|sm_l m_s\rangle$ identifies the angular and spin parts of the wave function. The subscript in m_l has been added to emphasize that m_l is the projection quantum number associated with l in distinction to m_s which is the projection quantum number associated with s . For one-electron wave functions it is customary to use lower case letters to denote the quantum numbers, although we continue to write the operators in upper case letters (for the present).

The spin orbitals (16.2-4) are, of course, eigenfunctions of \mathcal{H} given by (16.2-1) and as long as we do not add any more terms to \mathcal{H} , the energy eigenvalues are the same as those associated with $\varphi_{nlm}(r, \theta, \varphi)$. The only difference is that we have an additional twofold spin degeneracy. As was shown in the previous section, the degeneracy of $\varphi_{nlm}(r, \theta, \varphi)$ is n^2 . We now

have a degeneracy of $2n^2$ associated with $\psi(\lambda) = \psi(r, \theta, \varphi, m_s)$. In summary, $|lsm_l m_s\rangle$ satisfies the relations:

$$\begin{aligned} L^2 |lsm_l m_s\rangle &= l(l+1) |lsm_l m_s\rangle, \\ S^2 |lsm_l m_s\rangle &= s(s+1) |lsm_l m_s\rangle = \frac{3}{4} |lsm_l m_s\rangle, \\ L_z |lsm_l m_s\rangle &= m_l |lsm_l m_s\rangle, \\ S_z |lsm_l m_s\rangle &= m_s |lsm_l m_s\rangle = \pm \frac{1}{2} |lsm_l m_s\rangle. \end{aligned} \quad (16.2-5)$$

Degenerate eigenfunctions may be combined linearly to form other sets of degenerate eigenfunctions. Consider, for example, the linear combination

$$|lsjm\rangle = \sum_{m_l m_s} |lsm_l m_s\rangle \langle lsm_l m_s | lsjm\rangle \quad (16.2-6)$$

where $\langle lsm_l m_s | lsjm\rangle$ is a coupling coefficient of the kind discussed in Section 1.5. As shown there, the $|lsjm\rangle$ have the properties:

$$\begin{aligned} L^2 |lsjm\rangle &= l(l+1) |lsjm\rangle, \\ S^2 |lsjm\rangle &= s(s+1) |lsjm\rangle = \frac{3}{4} |lsjm\rangle, \\ J^2 |lsjm\rangle &= j(j+1) |lsjm\rangle, \\ J_z |lsjm\rangle &= m |lsjm\rangle, \end{aligned} \quad (16.2-7)$$

in which

$$\begin{aligned} J^2 &= J_x^2 + J_y^2 + J_z^2, & (16.2-8) \\ \mathbf{J} &= \mathbf{L} + \mathbf{S}, & (16.2-9) \\ j &= l + s, l + s - 1, \dots, |l - s| = l + \frac{1}{2}, l - \frac{1}{2}, \quad m = m_l + m_s, & (16.2-10) \end{aligned}$$

It should further be noted that the $|lsjm\rangle$ are not eigenfunctions of L_z or S_z . The eigenfunctions $|lsm_l m_s\rangle$ are said to be in the *uncoupled representation* while the $|lsjm\rangle$, in view of (16.2-9), are said to be in the *coupled representation*.

We present a summary of notations including those commonly employed in spectroscopy:

$$\begin{aligned} \alpha &= (l) = |\frac{1}{2} \frac{1}{2}\rangle = \zeta(\frac{1}{2}) = \text{spin function with } s = \frac{1}{2}, \quad m_s = \frac{1}{2}, \\ \beta &= (l) = |\frac{1}{2} -\frac{1}{2}\rangle = \zeta(-\frac{1}{2}) = \text{spin function with } s = \frac{1}{2}, \quad m_s = -\frac{1}{2}. \end{aligned}$$

In $|lsm_l m_s\rangle$ (uncoupled representation), s, p, d, f, ... stand for $l = 0, 1, 2, 3, \dots$ with m_l written as a subscript. Example: $|\frac{1}{2} -1 \frac{1}{2}\rangle = |p -1 \alpha\rangle$ (with or without the ket). If it is necessary to specify the principal quantum number, we write $|nlsm_l m_s\rangle$. Thus, $|2l \frac{1}{2} -1 \frac{1}{2}\rangle = 2p_{-1\alpha}$. In $|lsjm\rangle$ (coupled representation—also called *terms*), S, P, D, F, ... stand for $l = 0, 1, 2, 3, \dots$. The spin s is indicated by writing $2s + 1$ as a superscript to the left. Thus 2D means $l = 2, 2s + 1 = 2$ or $s = \frac{1}{2}$, j is written as a subscript and m is indicated

separately. Example: $|\frac{1}{2} \frac{3}{2} -\frac{1}{2}\rangle = |{}^2D_{3/2} -\frac{1}{2}\rangle$ (with or without the ket). It should be emphasized that the choice of representation is basically a matter of convenience in carrying out the computation and the same physics must emerge from any representation. Nevertheless, depending on the specific interactions contained in the Hamiltonian, it is often possible to choose a representation in which physical results are obtained in the most efficient manner.

It is also instructive to consider the two representations from the standpoint of group theory. The eigenfunctions $\varphi_{nlm}(r, \theta, \varphi)$ are basis functions for the irreducible representation $D^{(l)}$ of the three-dimensional rotation group $O^+(3)$. The two spin functions α, β are basis functions for the irreducible representation $D^{(1/2)}$ of $O^+(3)$. When we construct $|lsm_l m_s\rangle$, which are products of the angular part of $\varphi_{nlm}(r, \theta, \varphi)$ and the spin functions, we obtain basis functions for the product representation $D^{(l)} \times D^{(1/2)}$. But the product representation is reducible:

$$D^{(l)} \times D^{(1/2)} = D^{(l+1/2)} + D^{(l-1/2)} = \sum_{l-1/2}^{l+1/2} D^{(j)}. \quad (16.2-11)$$

The functions $|lsjm\rangle$ in the coupled representation constructed according to (16.2-6) are basis functions for the irreducible representations $D^{(j)}$.

16.3 Spin-Orbit Coupling

We turn next to the spin-orbit coupling term in the Schrödinger equation (15.2-32). The Hamiltonian, denoted by \mathcal{H}_{so} , is given by

$$\mathcal{H}_{so} = -\frac{e\hbar}{4m^2 c^2} \boldsymbol{\sigma} \cdot \nabla \varphi \times \mathbf{p} \quad (16.3-1)$$

where φ is the electrostatic potential. If φ depends only on r ,

$$\nabla \varphi = \frac{d\varphi}{dr} \frac{\mathbf{r}}{r}$$

and

$$\nabla \varphi \times \mathbf{p} = \frac{d\varphi}{dr} \frac{1}{r} \mathbf{r} \times \mathbf{p} = \frac{d\varphi}{dr} \frac{\hbar}{r} \mathbf{L} \quad (16.3-2)$$

in which \mathbf{L} is the orbital angular momentum operator with components as in (1.1-3). When (16.3-2) is substituted in (16.3-1) and $\boldsymbol{\sigma}$ is replaced by $2\mathbf{S}$, we obtain

$$\mathcal{H}_{so} = -\frac{e\hbar^2}{2m^2 c^2} \frac{1}{r} \frac{d\varphi}{dr} \mathbf{L} \cdot \mathbf{S} = \zeta(r) \mathbf{L} \cdot \mathbf{S} \quad (16.3-3)$$

For hydrogen

$$\varphi = Ze/r$$

so that

$$\zeta(r) = Ze^2\hbar^2/2m^2c^2r^3. \quad (16.3-4)$$

The one-electron Hamiltonian with spin-orbit coupling now becomes

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{so} \quad (16.3-5)$$

with

$$\mathcal{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}, \quad \mathcal{H}_{so} = \zeta(r)\mathbf{L} \cdot \mathbf{S}.$$

We regard \mathcal{H}_{so} as a perturbation, although the justification for this may not be apparent until a calculation of the magnitude of the effect has been carried out. This will be done at a later stage. Since \mathcal{H}_0 has degenerate eigenvalues, the first-order corrections to the energy will be obtained from the solutions of the secular equation

$$|H_{ij}^{so} - E_n^{(1)}\delta_{ij}| = 0 \quad (16.3-6)$$

where

$$H_{ij}^{so} = \langle \psi_{ni}^{(0)} | \mathcal{H}_{so} | \psi_{nj}^{(0)} \rangle \quad (16.3-7)$$

and $\psi_{ni}^{(0)}, \psi_{nj}^{(0)}$ are degenerate eigenfunctions of \mathcal{H}_0 . Remembering that linear combinations of the $\psi_{ni}^{(0)}$ are also eigenfunctions of \mathcal{H}_0 , there is a certain latitude in the construction of basis functions with which to calculate the matrix elements. Examination of the commutators provides useful guidance.

Thus

$$[\mathcal{H}_0, L^2] = [\mathcal{H}_0, S^2] = [\mathcal{H}_0, J^2] = [\mathcal{H}_0, L_\mu] = [\mathcal{H}_0, S_\mu] = [\mathcal{H}_0, J_\mu] = 0 \quad (16.3-8)$$

in which L_μ, S_μ , and J_μ refer to any component—rectangular or spherical—of \mathbf{L}, \mathbf{S} , and \mathbf{J} , respectively. Also

$$[\mathbf{L} \cdot \mathbf{S}, L^2] = [\mathbf{L} \cdot \mathbf{S}, S^2] = [\mathbf{L} \cdot \mathbf{S}, J^2] = [\mathbf{L} \cdot \mathbf{S}, J_z] = 0 \quad (16.3-9)$$

but

$$[\mathbf{L} \cdot \mathbf{S}, L_z] \neq 0, \quad [\mathbf{L} \cdot \mathbf{S}, S_z] \neq 0. \quad (16.3-10)$$

On the basis of (16.3-8)–(16.3-10) we may draw the following conclusions: Both $|lsm_l m_s\rangle$ and $|lsm\rangle$ are eigenfunctions of \mathcal{H}_0 and it is immaterial which representation is used. However, $\mathbf{L} \cdot \mathbf{S}$ does not commute with L_z and S_z ; this means that $|lsm_l m_s\rangle$ will not necessarily be an eigenfunction of $\mathbf{L} \cdot \mathbf{S}$. On

the other hand, because of (16.3-9), $|lsm\rangle$ is a simultaneous eigenfunction of $L^2 \cdot S^2, J^2, J_z$, and $\mathbf{L} \cdot \mathbf{S}$. We therefore expect the coupled representation to be the most convenient since only diagonal matrix elements will appear in the secular determinant.

To see how this works out, let

$$\mathbf{J} = \mathbf{L} + \mathbf{S}, \quad J^2 = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S},$$

or

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2). \quad (16.3-11)$$

Using the coupled representation

$$\begin{aligned} \langle l's_j'm' | \mathbf{L} \cdot \mathbf{S} | l'sjm \rangle &= \frac{1}{2} \langle l's_j'm' | J^2 - L^2 - S^2 | l'sjm \rangle \\ &= \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)] \delta_{j,j'} \delta_{l,l'} \delta_{m,m'}. \end{aligned} \quad (16.3-12)$$

The Hamiltonian \mathcal{H}_{so} in (16.3-3) also contains the radial function $\zeta(r)$. To obtain the energy corrections it is also necessary to evaluate the expectation value of $\zeta(r)$:

$$\begin{aligned} \langle \zeta(r) \rangle &= \xi_{nl} = \langle nl | \zeta(r) | nl \rangle = \int_0^\infty \zeta(r) R_{nl}^2(r) r^2 dr \\ &= \int_0^\infty \zeta(r) P_{nl}^2(r) dr. \end{aligned} \quad (16.3-13)$$

In hydrogen $\zeta(r)$ is given by (16.3-4) in which case

$$\xi_{nl} = \frac{Ze^2\hbar^2}{2m^2c^2} \left\langle nl \left| \frac{1}{r^3} \right| nl \right\rangle = \frac{Ze^2\hbar^2}{2m^2c^2} \left\langle \frac{1}{r^3} \right\rangle. \quad (16.3-14)$$

From Table 16.4,

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_0^3} \frac{1}{n^3(l+1)(l+\frac{1}{2})l}. \quad (16.3-15)$$

On combining (16.3-12), (16.3-14), and (16.3-15), the spin-orbit interaction energy is

$$E_{so} = \frac{Z^4 e^2 \hbar^2}{4a_0^3 m^2 c^2} \frac{j(j+1) - l(l+1) - s(s+1)}{n^3(l+1)(l+\frac{1}{2})l} \quad (16.3-16a)$$

or, in Rydberg units,

$$E_{so} = \frac{Z^4 \alpha^2}{n^3} \frac{j(j+1) - l(l+1) - s(s+1)}{2l(l+1)(l+\frac{1}{2})} \text{ Ry} \quad (16.3-16b)$$

with

$$\alpha = e^2/\hbar c, \quad a_0 = \hbar^2/m_e e^2.$$

E_{so} becomes indeterminate when $l=0$ (and $j=s=\frac{1}{2}$). The difficulty stems from the apparent singularity of $\langle 1/r^3 \rangle$ for $l=0$. However, expression (16.3-15) for $\langle 1/r^3 \rangle$ contains the implicit assumption of the nonrelativistic Hamiltonian in (15.2-32) that $e\phi \ll mc^2$. But in the present case the potential energy $e\phi$ is the Coulomb energy Ze^2/r which becomes infinite at the origin where the wave function, for $l=0$, is finite. As pointed out in Section 15.2, a separate treatment of such cases is required. The mechanics of carrying out a computation with a potential that becomes singular at the origin will be demonstrated in connection with the magnetic hyperfine interaction (Section 18.1). Here we simply quote the result, as shown, for example, by Bethe and Salpeter (1957), that $\langle 1/r^3 \rangle$ is indeed finite for $l=0$. Since the matrix element of $\mathbf{L} \cdot \mathbf{S}$ vanishes for $l=0$ we have $E_{so} = 0$ for s states.

It is possible to rewrite (16.3-16) entirely in terms of l since j is confined to the values $l \pm \frac{1}{2}$ and $s = \frac{1}{2}$. We then have ($l \neq 0$)

$$E_{so} = E_{l \pm 1/2} = \frac{Z^4 e^2 \hbar^2}{2m^2 c^2 a_0^3} \frac{1}{n^3 (l+1)(l+\frac{1}{2})l} \left\{ \frac{l}{2} \right\} \quad (16.3-17)$$

$$\Delta E_{so} = 5.84 \frac{Z^4}{n^3 l(l+1)} \text{ cm}^{-1} \quad (16.3-18)$$

and in Rydberg units

$$E_{so} = E_{l \pm 1/2} = \frac{Z^4 \alpha^2}{n^3} \frac{1}{2l(l+1)(l+\frac{1}{2})} \left\{ -l(l+1) \right\} \text{ Ry} \quad (16.3-19)$$

$$\Delta E_{so} = \frac{Z^4 \alpha^2}{n^3} \frac{1}{l(l+1)} \text{ Ry} \quad (16.3-20)$$

For $Z=1$ and $l=1$, the splitting due to spin-orbit coupling is 0.36, 0.12, and 0.044 cm^{-1} for $n=2, 3$, and 4, respectively. Since these energies are much smaller than the energies which separate states with different values of the principal quantum number n —about 10^4 cm^{-1} —the use of perturbation theory to first order is certainly appropriate. Nevertheless, one should observe the Z^4 -dependence in E_{so} which causes spin-orbit interaction energies to increase rapidly with atomic number.

From (16.3-12) it is seen that the matrix element vanishes unless

$$\Delta j = \Delta l = 0; \quad \Delta m = \Delta(m_l + m_s) = 0. \quad (16.3-21)$$

These are the selection rules for spin-orbit coupling. It is also instructive to inquire whether there are any restrictions on m_l and m_s individually. For this purpose we must return to the $|sm_l m_s\rangle$ basis set and examine the matrix element of $\mathbf{L} \cdot \mathbf{S}$ in this basis set with respect to dependence on m_l and m_s .

If \mathbf{L} and \mathbf{S} are expressed in terms of their spherical components,

$$\mathbf{L} \cdot \mathbf{S} = -L_{+1}S_{-1} + L_0S_0 - L_{-1}S_{+1} \quad (16.3-22)$$

the matrix element

$$\langle sm_l m_s | -L_{+1}S_{-1} + L_0S_0 - L_{-1}S_{+1} | sm_l m_s \rangle$$

will vanish unless

$$\Delta m_l = 0, \quad \pm 1, \quad \Delta m_s = 0, \quad \pm 1. \quad (16.3-23)$$

These selection rules are a direct consequence of the properties of the raising and lowering operators as expressed by (1.7-11) and (1.7-12). In view of (16.3-21) it is seen that if m_l increases by one unit, m_s must decrease by one unit and vice versa. Values of $\langle 1/2 m_l m_s | \mathbf{L} \cdot \mathbf{S} | 1/2 m_l m_s \rangle$ are shown in Table 16.5.

TABLE 16.5

Matrix Elements of $\mathbf{L} \cdot \mathbf{S}$ for p States in Units of $\xi_{nl} = \langle nl | \xi(r) | nl \rangle^a$

$\left \frac{1}{2} \right\rangle$	$\left 1 \frac{1}{2} \right\rangle$	$\left 0 \frac{1}{2} \right\rangle$	$\left 0 -\frac{1}{2} \right\rangle$	$\left -1 \frac{1}{2} \right\rangle$	$\left -1 -\frac{1}{2} \right\rangle$
$\frac{1}{2}$	$\frac{1}{2}$	0	0	$-\frac{1}{2}$	$-\frac{1}{2}$
$\left\langle \frac{1}{2} \right $	$-\frac{1}{2}$	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0
$\left\langle 1 -\frac{1}{2} \right $	$\frac{1}{\sqrt{2}}$	0	0	0	0
$\left\langle 0 \frac{1}{2} \right $	$\frac{1}{\sqrt{2}}$	0	0	0	0
$\left\langle 0 -\frac{1}{2} \right $	0	0	0	0	0
$\left\langle -1 \frac{1}{2} \right $	0	0	0	0	0
$\left\langle -1 -\frac{1}{2} \right $	0	0	0	0	0

^a The notation for the states has been shortened to $|m_l m_s\rangle$ since $l=1, s=\frac{1}{2}$ for all states.

16.4 Other Interactions

The term in the Schrödinger equation (15.2-32) that corresponds to the relativistic correction to the kinetic energy is

$$\mathcal{K}_r = -\frac{p^4}{8m^3c^2} = -\frac{1}{2mc^2} \left(\frac{p^2}{2m} \right)^2 \quad (16.4-1)$$

or, with

$$\mathcal{H}_0 = \frac{p^2}{2m} - \frac{Ze^2}{r}, \quad (16.4-2)$$

\mathcal{H}_r can be written as

$$\begin{aligned} \mathcal{H}_r &= -\frac{1}{2mc^2} \left[\mathcal{H}_0 + \frac{Ze^2}{r} \right]^2 & (16.4-3) \\ &= -\frac{1}{2mc^2} \left[\mathcal{H}_0^2 + Ze^2 \left(\mathcal{H}_0 \frac{1}{r} + \frac{1}{r} \mathcal{H}_0 \right) + \frac{(Ze^2)^2}{r^2} \right]. & (16.4-4) \end{aligned}$$

We shall be interested in the effects produced by \mathcal{H}_r within a manifold of states specified by particular values of n, l, s, j as for example the $^2S_{1/2}$ or $^2P_{3/2}$ eigenstates of \mathcal{H}_0 belonging to a particular value of n . Therefore, treating \mathcal{H}_r as a perturbation, the basis set is $|nlsjm\rangle$ and the relevant matrix elements are

$$\begin{aligned} \langle nlsjm' | \mathcal{H}_r | nlsjm \rangle &= \frac{1}{2mc^2} \left[\langle nlsjm' | \mathcal{H}_0^2 | nlsjm \rangle + Ze^2 \left(\langle nlsjm' | \mathcal{H}_0 \frac{1}{r} | nlsjm \rangle \right. \right. \\ &\quad \left. \left. + \langle nlsjm' | \frac{1}{r} \mathcal{H}_0 | nlsjm \rangle \right) + (Ze^2)^2 \langle nlsjm' | \frac{1}{r^2} | nlsjm \rangle \right]. \end{aligned} \quad (16.4-5)$$

Equation (16.4-5) may be simplified. For the first term on the right we have

$$\langle nlsjm' | \mathcal{H}_0^2 | nlsjm \rangle = (E_n^{(0)})^2 \delta_{m'm} \quad (16.4-6)$$

where $E_n^{(0)}$ is an eigenvalue of \mathcal{H}_0 . In view of the noncommutativity of \mathbf{r} and \mathbf{p} , \mathcal{H}_0 and $1/r$ do not commute; nevertheless, the Hermitian property of \mathcal{H}_0 leads to the equality of the matrix elements

$$\begin{aligned} \left\langle nlsjm' \left| \frac{1}{r} \right| nlsjm \right\rangle &= \left\langle nlsjm' \left| \frac{1}{r} \mathcal{H}_0 \right| nlsjm \right\rangle \\ &= E_n^{(0)} \left\langle nlsjm' \left| \frac{1}{r} \right| nlsjm \right\rangle = E_n^{(0)} \left\langle \frac{1}{r} \right\rangle \delta_{m'm} \end{aligned} \quad (16.4-7)$$

in which $\langle 1/r \rangle$ depends only on the radial part of the wave function and is independent of m . Similarly

$$\left\langle nlsjm' \left| \frac{1}{r^2} \right| nlsjm \right\rangle = \left\langle \frac{1}{r^2} \right\rangle \delta_{m'm}. \quad (16.4-8)$$

The net result is that \mathcal{H}_r has only diagonal matrix elements:

$$\langle \mathcal{H}_r \rangle = -\frac{(E_n^{(0)})^2}{2mc^2} - \frac{Ze^2}{mc^2} E_n^{(0)} \left\langle \frac{1}{r} \right\rangle - \frac{(Ze^2)^2}{2mc^2} \left\langle \frac{1}{r^2} \right\rangle. \quad (16.4-9)$$

For hydrogen, from (16.1-27)

$$E_n^{(0)} = -\frac{Z^2 e^2}{n^2} \frac{1}{2a_0} = -\frac{Z^2 me^4}{n^2} \frac{1}{2\hbar^2} \quad (16.4-10a)$$

$$= -\frac{Z^2}{n^2} \text{ Ry}. \quad (16.4-10b)$$

Also, from Table 16.4

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0} \frac{1}{n^2}, \quad (16.4-11)$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{a_0^2} \frac{1}{n^3(l + \frac{1}{2})}. \quad (16.4-12)$$

Therefore

$$\langle \mathcal{H}_r \rangle = \frac{Z^2 e^2 E_n^{(0)}}{mc^2 a_0} \left[\frac{1}{4n^2} - \frac{1}{n^2} + \frac{1}{n(l + \frac{1}{2})} \right] \quad (16.4-13a)$$

$$= E_n^{(0)} Z^2 \alpha^2 \left[-\frac{3}{4n^2} + \frac{1}{n(l + \frac{1}{2})} \right] \quad (16.4-13b)$$

with

$$\alpha^2 = \left(\frac{e^2}{\hbar c} \right)^2 = \frac{e^2}{mc^2 a_0}, \quad a_0 = \frac{\hbar^2}{me^2}.$$

In Rydberg units,

$$\langle \mathcal{H}_r \rangle = E_r = -\frac{Z^4}{n^3} \alpha^2 \left[-\frac{3}{4n} + \frac{1}{l + \frac{1}{2}} \right] \text{ Ry}. \quad (16.4-14)$$

This expression holds for all values of l including $l = 0$. Next we consider the Darwin term in (15.2-32):

$$\mathcal{H}_D = \frac{e\hbar^2}{8m^2 c^2} \nabla \cdot \mathbf{E} \quad (16.4-15)$$

which is of the same order as \mathcal{H}_r . With $\mathbf{E} = -\nabla\phi$ and $\phi = Ze/r$,

$$\mathcal{H}_D = -\frac{Ze^2 \hbar^2}{8m^2 c^2} \nabla^2 \left(\frac{1}{r} \right) = \frac{4\pi Ze^2 \hbar^2}{8m^2 c^2} \delta(\mathbf{r}) \quad (16.4-16)$$

where we have used the relationship

$$\nabla^2(1/r) = -4\pi\delta(\mathbf{r}). \quad (16.4-17)$$

Since only the radial part of the wave function will influence the matrix element of \mathcal{H}_D

$$\langle n|\delta(\mathbf{r})|n'l\rangle = |\psi(0)|^2, \quad (16.4-18)$$

and

$$\langle \mathcal{H}_D \rangle = \frac{\pi Z e^2 \hbar^2}{2m^2 c^2} |\psi(0)|^2 = E_D. \quad (16.4-19)$$

Thus the matrix elements of \mathcal{H}_D are nonzero only for s states. In hydrogen

$$|\psi(0)|^2 = Z^3/\pi n^3 a_0^3. \quad (16.4-20)$$

Therefore

$$\begin{aligned} \langle \mathcal{H}_D \rangle &= E_D = Z^4 e^2 \hbar^2 / 2n^3 m^2 c^2 a_0^3 \quad (l = 0 \text{ only}) & (16.4-21) \\ &= Z^4 \alpha^2 / n^3 \text{ Ry}. & (16.4-22) \end{aligned}$$

It is now possible to combine the expressions for E_{so} [Eq. (16.3-19)], E_r [Eq. (16.4-14)], and E_D [Eq. (16.4-22)] into a single expression which depends on n and j but not on l (or m):

$$E_{so} + E_r + E_D = -\frac{Z^4 \alpha^2}{n^3} \left[1 + \frac{3}{j + \frac{1}{2}} - \frac{3}{4n} \right] \text{ Ry} \quad (16.4-23)$$

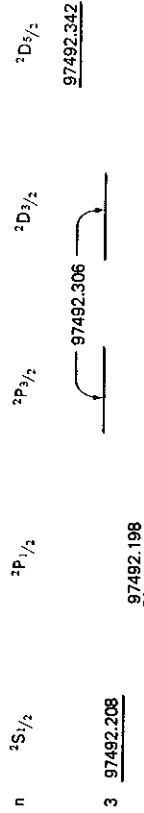
with $j = l \pm \frac{1}{2}$. When $l = 0$, $E_{so} = 0$, and

$$E_r + E_D = -\frac{Z^4 \alpha^2}{n^3} \left[1 - \frac{3}{4n} \right] \text{ Ry}. \quad (16.4-24)$$

When $l \neq 0$, $E_D = 0$ and

$$E_{so} + E_r = -\frac{Z^4 \alpha^2}{n^3} \left[1 + \frac{3}{j + \frac{1}{2}} - \frac{3}{4n} \right] \text{ Ry}. \quad (16.4-25)$$

Therefore the combined effects of the spin-orbit coupling, the relativistic energy correction, and the Darwin term are all included in (16.4-23). It is of interest to note that on the basis of (16.4-23) the energies of $^2S_{1/2}$ and $^2P_{1/2}$ are identical for a given n . The same result is obtained from the exact solution of the Dirac equation for hydrogen. Experimentally, a small difference (0.035 cm^{-1} for $Z = 1$) between the energies of $^2S_{1/2}$ and $^2P_{1/2}$ has been observed. This is known as the *Lamb shift* and its explanation is based on higher-order radiative corrections.



82259.272

2 82258.907

82258.907

1 0

FIG. 16.5 Energy levels of the hydrogen atom for $n = 1, 2$, and 3 . The energies are in reciprocal centimeters; the drawing is not to scale.

A partial energy level diagram of hydrogen is shown in Fig. 16.5. The splitting that arises within a manifold of states belonging to the same value of n is known as *fine structure* (see also Section 23.8).