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Hydrogen-Like Ion: An Atom (Ion) With One Electron

The atom can be viewed in a variety of ways. From a macroscopic point of view, the atom is the smallest entity of significance and the building blocks of matter. From a microscopic point of view, the atom is a perplexing composite of more basic particles of which only the electron appears to be fundamental or elementary; the proton and neutron are composed of more bizarre constituents. Our focus will not be at the subatomic level where the strong and weak forces must be considered along with the electromagnetic force nor the macroscopic and mesoscopic levels involving clusters of particles. Rather, we will concentrate on the atomic level where the Coulomb interaction between the electrons and the nucleus as well as between electrons (and between different nuclear centers in molecules) is the dominant interparticle force of concern, at least in the absence of an applied strong field. We will assume the nucleus (composed of protons and neutrons) and the electron to be the basic constituents of concern. Our primary goal is to model atoms and molecules both in the absence and presence of weak and strong external electromagnetic fields. We will treat the motion of the electrons and nuclei quantum mechanically, for the most part, and the external field classically. Consequently, we will seek solutions to Schrödinger's equation,

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = \hat{H} \Psi(\vec{r}, t), \quad (1.1)$$

for specific Hamiltonians, \hat{H} .

We begin our discussion by considering the hydrogen-like, one-electron atom, in the absence of an external field. This atom will be described by a family of stationary states of well-defined energies, that can be ascertained from the time-independent Schrödinger equation

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}). \quad (1.2)$$

Equation (1.2) is obtained from Eq. (1.1) by letting $\Psi(\vec{r}, t) \rightarrow e^{-iEt/\hbar}\psi(\vec{r})$. The Hamiltonian is taken as the quantum mechanical analog of the classical Hamiltonian given by $T + V$, where $T = p^2/2m_e$ and the potential, $V(r)$, is just the Coulomb potential, $-Ze^2/4\pi\epsilon_0 r$, with Z being the charge on the

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nucleus ($Z = 1$ for neutral atoms). Since $p \rightarrow -i\hbar\nabla$ (see Appendix B.8), the quantum mechanical Hamiltonian for this single-particle nonrelativistic case takes the simple form

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}, \quad (1.3)$$

where m_e is the mass of the electron, e is the elementary charge (which we take to be positive in this book), \hbar is Planck's constant divided by 2π and ϵ_0 is the vacuum permittivity. We will refer to this as our one-electron, field-free Hamiltonian.

1.1

Bohr Model of the Atom

Before solving Eq. (1.2) with the Hamiltonian given in Eq. (1.3), it is interesting to see that it is possible to determine the energy spectrum classically by assuming the existence of stationary states – Bohr's hypothesis that the electron does not radiate when circling the nucleus. For stationary states to exist, the Coulomb force ($-Ze^2/4\pi\epsilon_0 r^2$) must equal the centripetal force ($-m_e v^2/r$, where v is the tangential velocity). This leads to a kinetic energy of

$$T = \frac{1}{2}m_e v^2 = \frac{1}{2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} \right) \quad (1.4a)$$

and a total energy of

$$E = T + V = -\frac{1}{2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} \right). \quad (1.4b)$$

Here, we adopt the usual convention that negative energy means that the system is bound. Prior to the development of quantum mechanics, it was known that atoms emitted light at specific wavelengths. In the late 19th century it was determined that the energy of the light, in wavenumbers (see Eq. (A.4) of Appendix A), associated with a transition between energy levels n and n' was found to obey¹

$$\tilde{\nu}_{n'n} = C \left(\frac{1}{n^2} - \frac{1}{n'^2} \right), \quad (1.5)$$

where C is a constant that is related to the Rydberg constant. If one further postulates that the energy levels are quantized such that $r \rightarrow n^2 r_1$, where r_1 is

1) This general formula was proposed by Rydberg in 1889. Prior to this date, Balmer used the empirical formula $(4/B)(1/2^2 - 1/n^2)$ to fit the visible hydrogen spectral lines he observed. With $n = 3, 4, 5, 6, \dots$, he extracted a value of 3645.6 \AA for B .

the minimum stable radius, Eq. (1.4b) becomes

$$E_n = -\frac{1}{2} \left(\frac{Ze^2}{4\pi\epsilon_0 n^2 r_1} \right). \quad (1.6)$$

It follows that

$$hc\tilde{\nu}_{n'n} = E_{n'} - E_n = \frac{1}{2} \left(\frac{Ze^2}{4\pi\epsilon_0 r_1} \right) \left(\frac{1}{n^2} - \frac{1}{n'^2} \right). \quad (1.7)$$

If we identify the constant as

$$C = \frac{1}{2hc} \left(\frac{Ze^2}{4\pi\epsilon_0 r_1} \right), \quad (1.8)$$

the energy spectrum for hydrogen and hydrogen-like ions² takes this simple form:

$$E_n = -hcC \frac{1}{n^2}. \quad (1.9)$$

Since the potential is not harmonic, the energy levels are not equally spaced. Figure 1.1 shows that the second level, the first excited state, is three-quarters of the way to the ionization limit while subsequent levels become more closely spaced.

It is possible to determine C by fitting the spectrum to Eq. (1.5), from which we can estimate r_1 . Furthermore, it is possible to predict C and r_1 theoretically from the correspondence principle.³ When the radius of the electron orbit becomes large, n becomes large and the circulating electron will radiate, as any charged particle must classically, with a frequency given by

$$\nu = \frac{v}{2\pi n^2 r_1}. \quad (1.10)$$

When a classical particle radiates, it loses energy. Quantum mechanically, radiation is accompanied by transitions between quantum levels, as implied by Eq. (1.5). To remain classical, radiation must be between levels with large n . Consider a transition between two adjacent levels where $n' = n + 1$. Equation (1.5) then becomes

$$\tilde{\nu}_{n'n} = C \left(\frac{1}{n^2} - \frac{1}{(n+1)^2} \right) \simeq \frac{2C}{n^3}. \quad (1.11)$$

- 2) Hydrogen-like ions are ions with a single electron plus the nucleus. These include H, He⁺, as well as all multiply-charged ions that have all but one electron removed; Ca¹⁹⁺ would be an example.
- 3) The correspondence principle states that in the limit of large sizes the quantum description must approach the classical description.

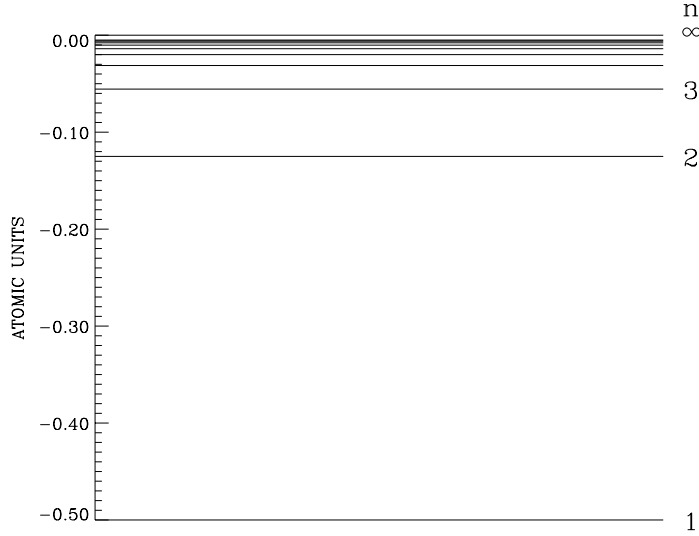


Fig. 1.1 Bound energy levels of the traditional Bohr hydrogen atom.

Multiplying Eq. (1.11) by c , the speed of light, and equating it with Eq. (1.10), using Eq. (1.4a) to express v and Eq. (1.8) to express \mathcal{C} , we can show that

$$r_1 \simeq \left(\frac{4\pi\epsilon_0}{e^2} \right) \frac{\hbar^2}{Zm_e}, \quad (1.12)$$

from which we identify the minimum radius for $Z = 1$,

$$a_0 \equiv \left(\frac{4\pi\epsilon_0}{e^2} \right) \frac{\hbar^2}{m_e}, \quad (1.13)$$

called the Bohr radius.⁴ The Rydberg constant, for an infinitely massive nucleus,⁵ is then defined as

$$\mathcal{R}_\infty \equiv \frac{1}{4\pi} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{\hbar c a_0} = \frac{\mathcal{C}}{Z^2}. \quad (1.14)$$

The energy spectrum can then be expressed as

$$E_n = -\frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{Z^2}{n^2 a_0} = -hc\mathcal{R}_\infty \frac{Z^2}{n^2} = -\frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{Z^2 m_e}{n^2 \hbar^2}, \quad (1.15)$$

which depends only on the integers, Z and n , and fundamental constants.

4) We note that $r_1 = a_0/Z$.

5) An atom with an infinite nuclear mass is sometimes called a *fixed nucleus* or *stationary nucleus* atom.

For an infinite nuclear mass, we identify $n^2 a_0$ as the radius of the orbit of the n th state for hydrogen. This is not exact because the nucleus has finite mass m_N . To account for this, we can let $m_e \rightarrow \mu$, the reduced mass. The n th radius then becomes

$$r_n = \frac{m_e}{\mu} \frac{n^2 a_0}{Z} \simeq \frac{n^2 a_0}{Z}, \quad (1.16)$$

assuming that the nucleus has charge Z , where the reduced mass is given by

$$\mu \equiv \left(\frac{1}{m_e} + \frac{1}{m_N} \right)^{-1}. \quad (1.17)$$

If we let $m_e \rightarrow \mu$ in Eq. (1.15), however, we shift the energy levels, requiring the *finite-mass* Rydberg constant to be defined as

$$\mathcal{R}_M = \mathcal{R}_\infty \left(1 + \frac{m_e}{M_N} \right)^{-1}. \quad (1.18)$$

1.2

Hydrogen-Like Ions, Quantum Approach: Bound States

Although we were able to determine the spectrum for the simple hydrogen-like ions from our classical approach, to study any of the details of the structure (energy levels) requires the time-independent Schrödinger equation (Eq. (1.2)) to be solved. In this section we will look at exact solutions in the nonrelativistic approximation for hydrogen-like ions.

1.2.1

Angular Wavefunctions

When we generalize the field-free Hamiltonian (Eq. (1.3)) by letting $m_e \rightarrow \mu$, the reduced mass (Eq. (1.17)), the Schrödinger equation takes the form

$$\nabla^2 \psi(\vec{r}) + \frac{2\mu}{\hbar^2} \left(E + \frac{Ze^2}{4\pi\epsilon_0 r} \right) \psi(\vec{r}) = 0. \quad (1.19)$$

Again, Z is the residual charge on the nucleus. That is, $Z = 1$ for H, $Z = 2$ for He^+ , etc. The Coulomb potential only depends on $|\vec{r}|$ and, thus, falls into the class of centrally symmetric potentials. It is natural to seek solutions to Eq. (1.19) in spherical coordinates in this case. If we write the Laplacian in spherical coordinates,

$$\nabla^2 \rightarrow \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2}, \quad (1.20)$$

the radial and angular variables separate and the solutions to Eq. (1.19) take the form

$$\psi(\vec{r}) = R_{nl}(r)Y_{lm}(\vartheta, \varphi), \quad (1.21)$$

where $R_{nl}(r)$ is known as the radial wavefunction and $Y_{lm}(\vartheta, \varphi)$ the spherical harmonics (see Appendix B.7). Such wavefunctions describe stationary states with definite energy E and angular momentum l . For centrally symmetric potentials, the angular momentum is conserved.⁶ The $Y_{lm}(\vartheta, \varphi)$ s describe the angular part of the electron distribution and are given by

$$Y_{lm}(\vartheta, \varphi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos\vartheta) e^{im\varphi}, \quad (1.22)$$

with $P_l^m(\cos\vartheta)$ being the associated Legendre polynomial (see Appendix B.6) given by

$$P_l^m(x) = \frac{1}{2^l l!} (1-x^2)^{m/2} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l, \quad (1.23)$$

where $m = -l, -(l-1), \dots, 0, \dots, l-1, l$.⁷ The spherical harmonics are orthogonal, normalized and obey

$$\int_0^{2\pi} d\varphi \int_0^\pi Y_{l'm'}^*(\vartheta, \varphi) Y_{lm}(\vartheta, \varphi) \sin\vartheta d\vartheta = \delta_{l'l} \delta_{m'm}, \quad (1.24)$$

where δ_{ij} is the Kronecker delta (see Appendix B.1). The first six spherical harmonics are

$$\left. \begin{aligned} Y_{00}(\vartheta, \varphi) &= \sqrt{1/4\pi} \\ Y_{10}(\vartheta, \varphi) &= \sqrt{3/4\pi} \cos\vartheta \\ Y_{1\pm 1}(\vartheta, \varphi) &= \mp \sqrt{3/8\pi} \sin\vartheta e^{\pm i\varphi} \\ Y_{20}(\vartheta, \varphi) &= \sqrt{5/4\pi} \left(\frac{3}{2} \cos^2\vartheta - \frac{1}{2} \right) \\ Y_{2\pm 1}(\vartheta, \varphi) &= \mp \sqrt{15/8\pi} \sin\vartheta \cos\vartheta e^{\pm i\varphi} \\ Y_{2\pm 2}(\vartheta, \varphi) &= \sqrt{15/32\pi} \sin^2\vartheta e^{\pm 2i\varphi} \end{aligned} \right\}. \quad (1.25)$$

Figure 1.2 shows spherical polar representations of the first few Y_{lm} s.

⁶ We will find that when the spherical symmetry is broken, there will be a preferred direction in space and l will not be conserved in gen-

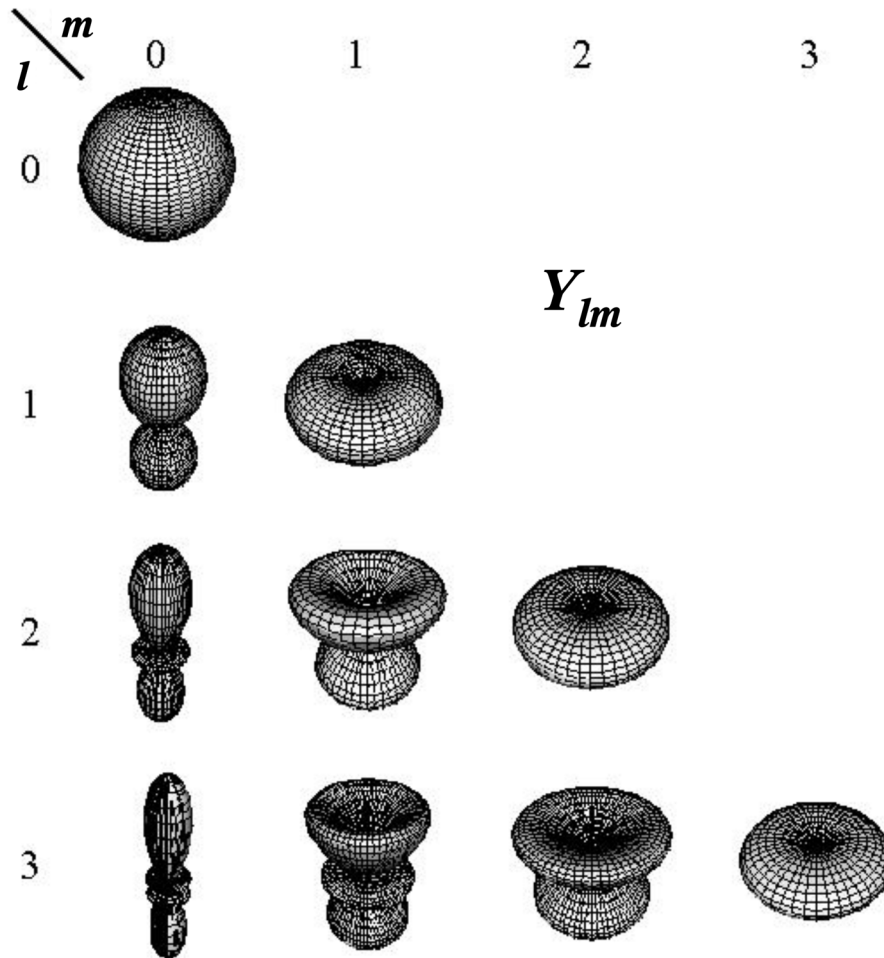


Fig. 1.2 Spherical polar plots of the spherical harmonics, $|Y_{lm}(\vartheta, \varphi)|^2$, for $l = 0, \dots, 3$ and $m = -l, \dots, l$. The z -axis is vertical in these 3D images. Note that only Y_{00} has a nonzero contribution at the origin. The Y_{l0} and Y_{l1} harmonics are oriented along and perpendicular to the z -axis, respectively.

The radial wave function is a solution to the equation

$$\left\{ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + \frac{2\mu}{\hbar^2} [E - V_{eff}(r; l)] \right\} R_{nl}(r) = 0, \quad (1.26)$$

eral. This occurs in diatomic molecules, for example, or when an atom is placed in an external field. However, in both cases the projection of l along the axis of symmetry often will remain conserved.

- 7) The phases for the spherical harmonics are consistent with *Mathematical Methods for Physicists* by Arfken and Weber [1], *The Theory of Atomic Structure and Spectra* by Cowan [2] and MATHEMATICA®.

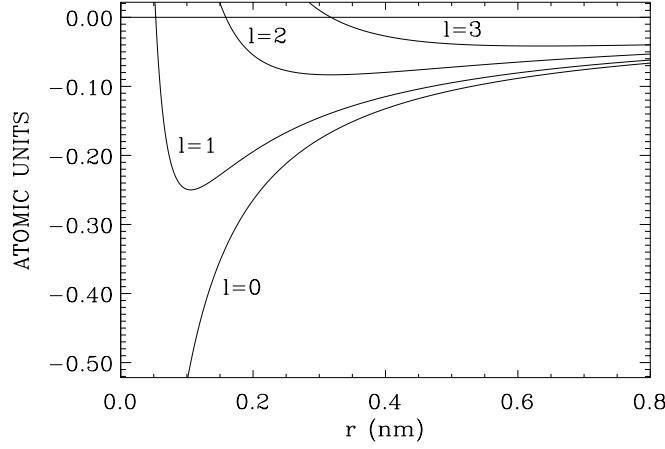


Fig. 1.3 Effective single-electron potential for $l = 0, 1, 2, 3$.

where

$$V_{eff}(r; l) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{r^2} \frac{1}{2\mu} \quad (1.27)$$

is the effective potential. Figure 1.3 shows that the potentials for $l \neq 0$ become repulsive at the origin. As we will see below, this causes the wavefunction for states with $l \neq 0$ to vanish at the origin. For $l = 0$ the wavefunctions do not have to vanish at the origin.

1.2.2

Radial Wavefunction and Energy States

It is straightforward to show that the radial wavefunction leads to the same energy spectrum predicted by the Bohr model.⁸ To see this, consider the asymptotic behavior of Eq. (1.26). As $r \rightarrow \infty$, $V_{eff} \rightarrow 0$ and Eq. (1.26) reduces to

$$\left[\frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2} E \right] R(r) = 0 \quad (1.28)$$

and has solutions of the form

$$R(r) = e^{\pm ir\sqrt{2\mu E/\hbar^2}}. \quad (1.29)$$

For positive energy, $E > 0$, the exponent is imaginary and the electron is described by unbounded plane waves. These correspond to continuum states.

⁸ Our treatment follows that found in Bethe and Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* [3] and Messiah, *Quantum Mechanics* [4].

For bound states we want $R \rightarrow 0$ as $r \rightarrow \infty$. This requires $E < 0$ and the minus sign in the exponent. The solution to Eq. (1.26) must then take the form

$$R(r) = f(r) e^{-r\sqrt{-2\mu E/\hbar^2}}, \quad (1.30)$$

where $f(r)$ is a function that must be finite at the origin and blows up slower than $\exp\left[r\sqrt{-2\mu E/\hbar^2}\right]$ as $r \rightarrow \infty$. The minus sign was inserted under the radical to take care of the fact that $E < 0$. Substituting this expression for $R(r)$ into Eq. (1.26) produces

$$f''(r) + 2 \left[\frac{1}{r} - \sqrt{-\frac{2\mu}{\hbar^2} E} \right] f'(r) + \left[\frac{2}{r} \left(\frac{Ze^2}{4\pi\epsilon_0} \frac{\mu}{\hbar^2} - \sqrt{-\frac{2\mu}{\hbar^2} E} \right) - \frac{l(l+1)}{r^2} \right] f(r) = 0. \quad (1.31)$$

The general solution for $f(r)$ will be polynomials,

$$f(r) = r^\beta \sum_{\nu=0}^{\infty} b_\nu r^\nu. \quad (1.32)$$

Equation (1.32) can be written in the form of Laplace's equation with a regular solution of confluent hypergeometric series that will be introduced in the next section. Substituting this back into Eq. (1.31) gives

$$\sum_{\nu=0}^{\infty} b_\nu \left\{ [(\beta + \nu)(\beta + \nu + 1) - l(l+1)] r^{\beta+\nu-2} - \frac{2}{\hbar^2} \left[\hbar\sqrt{-2\mu E}(\beta + \nu + 1) - \frac{Ze^2}{4\pi\epsilon_0} \mu \right] r^{\beta+\nu-1} \right\} = 0. \quad (1.33)$$

In order for Eq. (1.33) to hold for all r , the coefficient of each term must vanish. For the lowest-order term, the $r^{\beta-2}$ term, we must demand that

$$\beta(\beta + 1) = l(l+1) \rightarrow \beta = \begin{cases} l \\ -(l+1) \end{cases} \quad (1.34)$$

if b_0 is nonzero. In order that $R(r)$ be finite as $r \rightarrow 0$, we must choose $\beta = l$. Setting the coefficient of the second term in Eq. (1.33), the $r^{\beta-1}$ term, to zero with $\beta = l$ yields

$$b_1 = 2b_0 \frac{\sqrt{-2\mu E/\hbar^2}(l+1) - (Ze^2/4\pi\epsilon_0)\mu/\hbar^2}{(l+1)(l+2) - l(l+1)},$$

from which the recursion relation,

$$b_\nu = 2b_{\nu-1} \frac{\sqrt{-2\mu E/\hbar^2} (l + \nu) - (Ze^2/4\pi\epsilon_0) \mu/\hbar^2}{(l + \nu)(l + \nu + 1) - l(l + 1)}, \quad (1.35)$$

follows. It is convenient to write b_ν as

$$b_\nu = b_{\nu-1} \frac{2\zeta}{\nu} \frac{\nu + l - \lambda}{\nu + 2l + 1}, \quad (1.36)$$

where

$$\zeta = \sqrt{\frac{-2\mu E}{\hbar^2}} \text{ and} \quad (1.37)$$

$$\lambda = \frac{Ze^2/4\pi\epsilon_0}{\sqrt{-2\mu E/\hbar^2}} \frac{\mu}{\hbar^2}.$$

Using Eq. (1.36), we can write b_ν in terms of b_0 as

$$b_\nu = \left(\frac{2\zeta}{\nu} \frac{\nu + l - \lambda}{\nu + 2l + 1} \right) \cdot \left(b_{\nu-2} \frac{2\zeta}{\nu-1} \frac{\nu-1+l-\lambda}{\nu-1+2l+1} \right) \quad (1.38)$$

$$= \left(\frac{2\zeta}{\nu} \frac{\nu + l - \lambda}{\nu + 2l + 1} \right) \cdot \left(\frac{2\zeta}{\nu-1} \frac{\nu-1+l-\lambda}{\nu-1+2l+1} \right) \cdots \left(b_0 \frac{2\zeta}{1} \frac{1+l-\lambda}{1+2l+1} \right) \quad (1.39)$$

$$= b_0 \frac{(2\zeta)^\nu (\nu + l - \lambda)!(2l + 1)!}{\nu! (l - \lambda)!(\nu + 2l + 1)!}, \quad (1.40)$$

and $f(r)$ becomes

$$f(r) = r^l b_0 \sum_{\nu=0}^{\infty} \frac{(2r\zeta)^\nu (\nu + l - \lambda)!(2l + 1)!}{\nu! (l - \lambda)!(\nu + 2l + 1)!}. \quad (1.41)$$

We need to consider again the behavior as $r \rightarrow \infty$. This can be done by looking at the asymptotic form of $f(r)$ as ν becomes large. From Eq. (1.41) we write

$$f(r) \xrightarrow{\nu \rightarrow \infty} r^l b_0 \sum_{\nu=\text{large}}^{\infty} \frac{(2r\zeta)^\nu}{\nu!} = b_0 r^l e^{2r\sqrt{-2\mu E/\hbar^2}},$$

from which it follows that

$$R(r) = e^{-r\sqrt{-2\mu E/\hbar^2}} f(r) \rightarrow r^l e^{r\sqrt{-2\mu E/\hbar^2}}.$$

This exponential divergence at large r can be avoided if we truncate the power series with a judicious choice for the value of λ , namely an integer. The integer

must be chosen to make $b_{v=n-l} = 0$. Thus, $\lambda = l + 1 + k$ where $k = 0, 1, 2, 3, 4$ and we find that

$$E_{lk} = -\frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{Z^2\mu}{(l+1+k)^2\hbar^2}, \quad (1.42)$$

from Eq. (1.35), which we see is the energy spectrum for bound states. This energy spectrum is identical to Eq. (1.15) when we recognize $n \equiv \lambda = l + 1 + k$, the principal quantum number, and we let $m_e \rightarrow \mu$.

1.2.3

Exact Radial Solution, Hydrogen-Like Ions

The exact solutions to the radial equation, Eq. (1.26), can be determined from Eq. (1.41) by recognizing that

$$\sum_{v=0}^{\infty} \frac{(2r\zeta)^v}{v!} \frac{(v+l-\lambda)!(2l+1)!}{(l-\lambda)!(v+2l+1)!} = F(l+1-\lambda; 2l+2; 2r\zeta), \quad (1.43)$$

where $F(l+1-\lambda; 2l+2; 2r\zeta)$ is the confluent hypergeometric function (see Appendix B.4). Truncating the series at $n-l-1$ as discussed in the previous section leads to the normalized wavefunction expressed as

$$R_{nl}(r) = \frac{1}{(2l+1)!} \sqrt{\frac{(n+l)!}{2n(n-l-1)!}} \left(\frac{2Z}{na_0} \right)^{3/2} e^{-\frac{Zr}{na_0}} \left(\frac{2Zr}{na_0} \right)^l \times F\left(l+1-n, 2l+2; \frac{2Zr}{na_0}\right), \quad (1.44a)$$

which can also be expressed as an associated Laguerre polynomial (see Appendix B.5)

$$R_{nl}(r) = -\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2Z}{na_0} \right)^{3/2} e^{-\frac{Zr}{na_0}} \left(\frac{2Zr}{na_0} \right)^l \times L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right). \quad (1.44b)$$

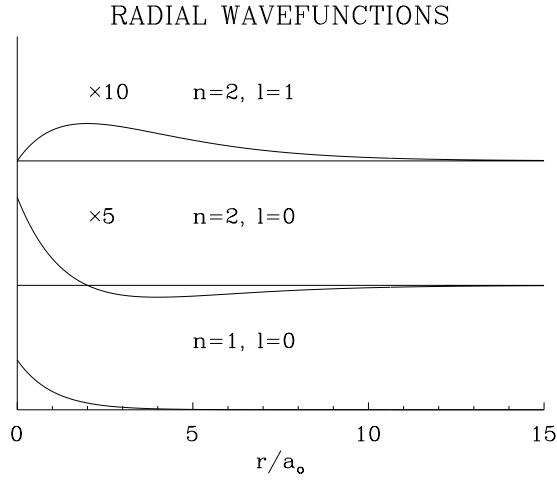


Fig. 1.4 First three radial wavefunctions, R_{nl} , for hydrogen-like ions.

Explicit expressions for the first four functions are

$$\left. \begin{aligned} R_{10}(r) &= 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \\ R_{20}(r) &= 2 \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0} \\ R_{21}(r) &= \frac{2}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \left(\frac{Zr}{2a_0} \right) e^{-Zr/2a_0} \\ R_{30}(r) &= 2 \left(\frac{Z}{3a_0} \right)^{3/2} \left[1 - 2 \left(\frac{Zr}{3a_0} \right) + \frac{2}{3} \left(\frac{Zr}{3a_0} \right)^2 \right] e^{-Zr/3a_0} \end{aligned} \right\} . \quad (1.45)$$

Additional radial functions can be generated from one of the two expressions using a symbolic manipulation program.

The radial wavefunctions are normalized and orthogonal and thus satisfy

$$\int R_{nl}(r) R_{n'l'}(r) r^2 dr = \delta_{n'n'} \quad (1.46)$$

where $\delta_{n'n'}$ is the Kronecker delta (see Appendix B). The first three solutions are shown graphically in Fig. 1.4. We note that (1) R_{nl} is finite at $r = 0$ for $l = 0$, while $R_{nl} \rightarrow 0$ as $r \rightarrow 0$ for $l \neq 0$, and (2) the number of times the wavefunction crosses the axis (number of zeros) is given by $n - l - 1$.

The probability density, $r^2 R_{nl}^2$,⁹ for finding the electron at radius r in an effective potential (given by Eq. (1.27)) is displayed in Fig. 1.5 for a few wavefunctions. It is clear from this figure that we are more likely to find the electron

⁹ We will discuss this probability density at the end of this chapter.

at larger r as the principal quantum number increases. Specifically, the mean value of r is given by $\langle r \rangle = (a_0/2Z) [3n^2 - l(l+1)]$. This and other moments of r can be determined from

$$\langle r^\gamma \rangle = \int r^{2+\gamma} R_{nl}^2(r) dr. \quad (1.47)$$

A few common moments are¹⁰

$$\left. \begin{aligned} \langle r^2 \rangle &= \frac{a_0^2 n^2}{2Z^2} [5n^2 + 1 - 3l(l+1)] \\ \langle r^3 \rangle &= \frac{a_0^3 n^2}{8Z^3} [35n^2(n^2 - 1) - 30n^2(l+2)(l-1) \\ &\quad + 3(l+2)(l+1)(l-1)] \\ \langle r^4 \rangle &= \frac{a_0^4 n^4}{8Z^4} [63n^4 - 35n^2(2l^2 + 2l - 3) + 5l(l+1) \\ &\quad \times (3l^2 + 3l - 10) + 12] \\ \langle r^{-1} \rangle &= \frac{Z}{a_0 n^2} \\ \langle r^{-2} \rangle &= \frac{Z^2}{a_0^2 n^3 (l + \frac{1}{2})} \\ \langle r^{-3} \rangle &= \frac{Z^3}{a_0^3 n^3 (l+1)(l + \frac{1}{2})l} \\ \langle r^{-4} \rangle &= \frac{Z^4 [3n^2 - l(l+1)]}{a_0^4 2n^5 (l+3/2)(l+1)(l + \frac{1}{2})l(l - \frac{1}{2})} \end{aligned} \right\}. \quad (1.48)$$

Combining our radial and angular solutions, the three-dimensional nonrelativistic wavefunction for a one-electron atom can be written as

$$\Psi_{nlm}(r, \vartheta, \varphi) = R_{nl}(r) Y_{lm}(\vartheta, \varphi), \quad (1.49)$$

which is the same as Eq. (1.21). With this definition Ψ is normalized according to¹¹

$$\int |\Psi_{nlm}(r, \vartheta, \varphi)|^2 r^2 \sin \theta dr d\vartheta d\varphi = 1. \quad (1.50)$$

We must remember, however, that even though Ψ depends on n , l and m , the energy,

$$E_n = -\frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{Z^2 \mu}{n^2 \hbar^2} = -hc \frac{Z^2}{n^2} \mathcal{R}_M, \quad (1.51)$$

10 These expressions are taken from Bockasten [5].

11 *Caution!* Some authors define the radial wavefunction as $rR_{nl}(r)$, leading to a different normalization from that in Eq. (1.50).

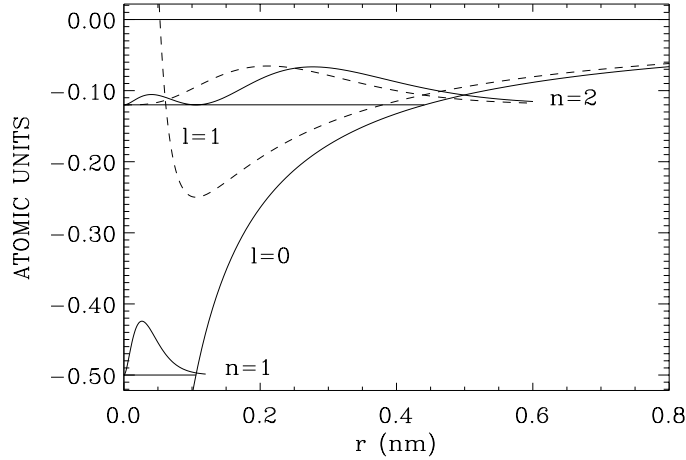


Fig. 1.5 Radial probability densities, $r^2 R_{nl}^2$, for the first three radial wavefunctions, $n, l = 1, 0; 2, 0$ and $2, 1$, respectively, for hydrogen-like ions displayed in conjunction with the associated effective potentials of Fig. 1.3. The solid curve corresponds to $l = 0$ and the dashed curve to $l = 1$.

only depends on n , nonrelativistically. The reader will note that the difference between Eqs. (1.15) and (1.51) is that the former describes the energy spectrum for an infinitely massive nucleus while the latter accounts for the finite mass of a particular nucleus; \mathcal{R}_M and \mathcal{R}_∞ are given respectively by Eqs. (1.18) and (1.14). This one-electron wavefunction is often called an *atomic orbital*. We will use the atomic orbitals to create states for more complex multielectron atoms and molecules in Chapters 2 and 5, respectively.

Probability Density. We are now in a position to put everything together and talk about how to visualize the electron in an atom. To that end, we recall that one of the main tenets of quantum mechanics, due to Max Born, is that $|\Psi_{nlm}(r, \vartheta, \varphi)|^2$ represents the probability per unit volume or the probability density for measuring the electron with a specific set of physical coordinates. One should not think of the electron, however, as a corpuscular particle actually whizzing about the nucleus as planets do the Sun so that at time t_1 it is at position \vec{r}_1 and at time t_2 it is at position \vec{r}_2 as one would classically. Rather, Ψ describes the electron as a wave – the electron’s wavefunction – that exists in an abstract space. We can picture this density as a cloud with the electron everywhere within the cloud simultaneously. Figure 1.6 shows a few representations of the density for the first few states for the case of $Z = 1$. While Ψ contains all the information we can know about the electron, according to quantum mechanics, what we measure in the laboratory is related to $|\Psi|^2$. For physical coordinates where $|\Psi|^2$ is large, there is a large probability for find-

ing the electron. The probability density should be understood in a statistical sense. When we make a measurement, we project the electron into a physical space with classical parameters, position and momentum, but subject to the uncertainty principle.^{12,13}

Several comments can be made concerning Fig. 1.6, which can be deduced from Figs. 1.2 and 1.5 as well. In fact, the images in Fig. 1.6 were generated by mapping R_{nl}^2 onto the distributions in Fig. 1.2. The first observation we can make is that the atom increases in size as n increases ($\langle r \rangle$ scales as n^2) and the electron cloud becomes more diffuse. Only $l = 0$, s states that are spherically symmetric contribute to the electron density near the origin. Finally, we notice that the contribution to the density from the $np, m = \pm 1$ state is about half that of the $np, m = 0$ state. This is because each $m = \pm 1$ state is actually spread between two orientations. This is more easily seen in rectangular coordinates. To show this, we first recognize that $\Psi_{n,l=1,m}$ represents a spherical vector as discussed in Appendix E. From the general conversion between spherical and Cartesian vectors, Eq. (E.8), it is straightforward to show that

$$\psi_{np_z} = \Psi_{n10}, \quad (1.52)$$

$$\psi_{np_x} = \frac{1}{\sqrt{2}} (\Psi_{n11} + \Psi_{n1,-1}), \quad (1.53)$$

$$\psi_{np_y} = \frac{1}{i\sqrt{2}} (\Psi_{n11} - \Psi_{n1,-1}), \quad (1.54)$$

where $\psi_{np_x,y,z}$ are the Cartesian vectors – the wavefunctions in rectangular coordinates. Whereas $\psi_{np_z} = \Psi_{n10}$, ψ_{np_x} and ψ_{np_y} are reduced by $1/\sqrt{2}$ while being linear combinations of Ψ_{n11} and $\Psi_{n1,-1}$ and vice versa. In Cartesian coordinates, we would view the electron distribution as being double-lobed clouds along the x -, y - and z -axes, each similar to that of the $2p_{m=0}$ distribution in Fig. 1.6 (see also Y_{10} in Fig. 1.2). The Cartesian representation is the one usually presented in chemistry text books.

1.2.4

Energy Units and Atomic States

Generally, there are two conventions for energy levels and several energy units (see Appendix A) in use. Theorists tend to prefer atomic units (Hartree, see Appendix A) and to set the zero of the energy at the ionization threshold.

- 12) The wave nature of quantum mechanics leads quite naturally to an uncertainty in our knowledge of the position, Δx , and momentum, Δp , of the electron or any particle and a limit on the determination of both simultaneously, $\Delta x \Delta p \geq \hbar/2$.
- 13) It is interesting to note that Schrödinger actually misinterpreted Ψ as the density distribution of matter, with some regions of space richer in matter than others.

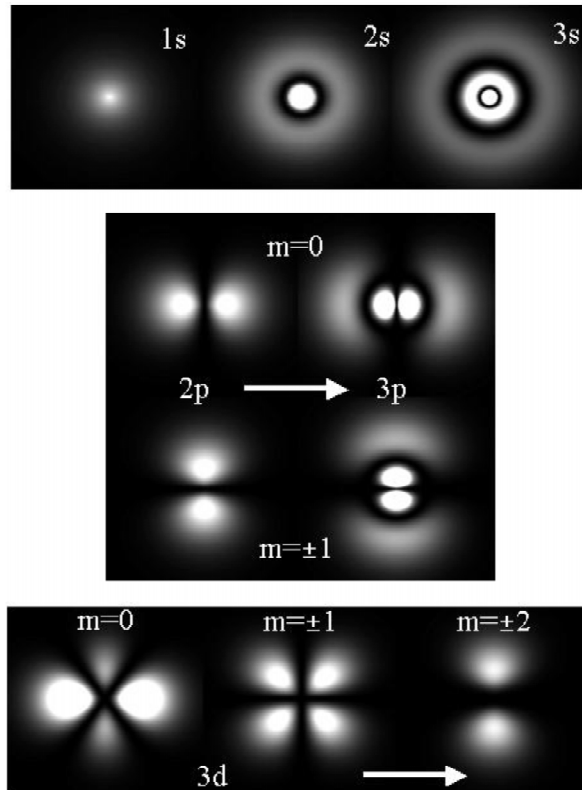


Fig. 1.6 The probability per unit volume, the probability density $|\Psi_{nlm}(r, \vartheta, \varphi)|^2$, for several states of the hydrogen atom. These are cross-sectional images of the densities with the symmetry axis – the z -axis – in the plane of the paper as indicated by the arrows. The top row represents the probability densities for the first three s states, the middle block all m values for the $2p$ and $3p$ states and the bottom row all m values for the $3d$ state. The spatial and intensity scales vary from image to image. Relative to the $1s$ image, the ratios between the spa-

tial scales are 1:5:10:5:5:10:10:10:10:10, respectively, for $1s:2s:3s:2p, m=0:2p, m=\pm 1:3p, m=0:3p, m=\pm 1:3d, m=0:3d, m=\pm 1:3d, m=\pm 2$. That is, the $1s$ distribution extends over about 0.1 nm while the $2s$ distribution extends over about 0.5 nm. To make it visible, each image is multiplied by 1:200:2000:67:133:1000:2000:1000:1333:1000 respectively from top left to bottom right. We note that to make the weaker components visible, the stronger contributions are saturated in several of the images.

Bound states then will have negative values and continuum states will have positive values. When energy levels are determined experimentally, they are often expressed as wavenumbers,¹⁴ as in the energy-level tables provided by

14) It is interesting to note that wavenumbers originated at a time before computers. While we think nothing of multiplying by hc today, it was very time consuming in the past. Wavenumbers were invented to aid calculations.

the National Institute for Standards and Technology (NIST).¹⁵ Typically, the energies of both bound and continuum states have positive values when expressed as wavenumbers. This is due simply to shifting the zero of the scale down from the ionization threshold to the ground state. To see this, we write the energy of level n relative to level n' as

$$E_n = E_{n'} - hcZ^2\mathcal{R}_M \left(\frac{1}{n^2} - \frac{1}{n'^2} \right). \quad (1.55)$$

If we let $n' \rightarrow \infty$, then we have

$$E_n = E_\infty - hc\frac{Z^2}{n^2}\mathcal{R}_M, \quad (1.56)$$

the energy of level n relative to the ionization energy I_P . That is, we let $E_\infty = I_P$ instead of 0. Thus, in wavenumbers the energy of level n becomes

$$\bar{\nu}_n = I_P - \frac{Z^2}{n^2}\mathcal{R}_M. \quad (1.57)$$

We point out that the fact that such a shift is possible illustrates the important point that only the relative energy is important. Furthermore, it would be possible to use atomic units with the zero set to the ground state or wavenumbers with the zero set at the ionization threshold.

The energies of the first three states of hydrogen and the ionization threshold in wavenumbers and atomic units are

	n			
	1	2	3	∞
cm ⁻¹	0	82 259.07	97 492.23	109 678.8
Energy				
a.u.	-0.50	-0.12	-0.06	0

1.3

Classification of Nonrelativistic States

The full nonrelativistic hydrogen (one-electron atom or ion) wavefunction, $\psi_{nlm}(r, \vartheta, \varphi)$, has three quantum numbers:

n = the principal quantum number, integers ranging from 1 to ∞ in steps of 1

l = the (orbital) angular momentum, integers ranging from 0 to $n - 1$ in steps of 1

¹⁵ Other possible units in use are eV (electron volt), Hz (s⁻¹) and kcal/mol (kilocalorie per mole, a unit often used by chemists). The conversion between these units is given in Appendix A.

m = the magnetic quantum number, integers ranging from $-l$ to l in steps of 1.

The states are named according to their angular momentum,

$$l = \begin{array}{cccccc} 0 & 1 & 2 & 3 & 4 & 5 \\ & s & p & d & f & g & h \end{array}$$

The state with $n = 3$ and $l = 2$ is called the $3d$ state. An electron in the $3d$ state is also said to be in the $3d$ subshell, where a shell is designated by nl .¹⁶

1.3.1

Parity

The wavefunction is said to have positive parity if $\psi(-\vec{r}) = \psi(\vec{r})$ (i.e., inversion $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$) and negative parity if $\psi(-\vec{r}) = -\psi(\vec{r})$. In spherical coordinates this translates into $r \rightarrow r$, $\vartheta \rightarrow \pi - \vartheta$ and $\varphi \rightarrow \varphi + \pi$. The parity is thus determined by the angular part of the wavefunction, $Y_{lm}(\vartheta, \varphi) \propto P_l^m(\cos \vartheta)e^{im\varphi}$. Since

$$\left. \begin{array}{l} \vartheta \rightarrow \pi - \vartheta \rightarrow P_l^m(\cos[\pi - \vartheta]) = (-1)^{l-m} P_l^m(\cos \vartheta) \\ \varphi \rightarrow \varphi + \pi \rightarrow e^{im(\varphi + \pi)} = (-1)^m e^{im\varphi} \end{array} \right\}, \quad (1.58)$$

$$Y_{lm}(\pi - \vartheta, \varphi + \pi) = (-1)^l Y_{lm}(\vartheta, \varphi).$$

Consequently, $\psi(-\vec{r}) = (-1)^l \psi(\vec{r})$ implies that

$$\begin{array}{ll} s, d, \dots & \text{even parity,} \\ p, f, \dots & \text{odd parity.} \end{array}$$

Neither n nor m participate in the determination of parity.

1.3.2

Degeneracy

Each energy state in Eq. (1.42) is n^2 degenerate, with n^2 unique combinations of values for l and m . The energy, however, does not depend on l nor m . This is because the potential is spherically symmetric so that all the forces are isotropic. As we mentioned before, if an external field were applied to the atom the symmetry could be broken and part of the degeneracy would be lifted. It should be understood that the l -independent Hamiltonian of Eq. (1.3) is a result of ignoring the spin of the electron. When spin is included, we will see that part of the l degeneracy will be lifted.

¹⁶ Shell and subshell are often used interchangeably. We will reserve shell for states with the same n regardless of l . As we will discuss in the next chapter, the $3d$ designation also refers to an atomic orbital.

1.4 Corrections to the Energy Levels

Thus far, we have examined idealized hydrogen-like ions in the absence of external fields. These ions were composed of a nonrelativistic spinless electron and a nucleus that we have treated as a spinless point charge. In reality, of course, the nucleus has a finite size (see Problem 1.3), the electron and nucleus have spin and the electron can move with relativistic velocities when near the nucleus. These lead to shifts of the energy levels (Eq. (1.42)) and symmetry breaking. In this section we will examine three corrections to the energy levels for hydrogen-like ions: (1) relativistic motion, (2) the spin of the electron and (3) the spin of the nucleus. The first two will give rise to what is called the fine structure and partially splits the l degeneracy, while the latter gives rise to one form of the hyperfine structure. In addition, we will set up the framework for looking at atoms in applied electric and magnetic fields.

1.4.1

Relativistic Motion

The relativistic energy of the electron is given by

$$\begin{aligned}
 E_R &= V + \sqrt{p^2 c^2 + m_e^2 c^4} \\
 &\simeq V + m_e c^2 + \underbrace{\left[\frac{p^2}{2m_e} - \frac{p^4}{8m_e^3 c^2} + \dots \right]}_{\text{kinetic energy}}.
 \end{aligned} \tag{1.59}$$

The first term is the usual Coulomb potential, the second is the rest mass, the third is the nonrelativistic kinetic energy while the fourth is the first-order relativistic correction term to the kinetic energy. If we define

$$\hat{H}_0 = \frac{p^2}{2m_e} + V \tag{1.60}$$

$$\hat{\zeta}_R = -\frac{p^4}{8m_e^3 c^2} \tag{1.61}$$

$$= -\frac{1}{2m_e c^2} [\hat{H}_0 - V]^2, \tag{1.62}$$

we can apply first-order perturbation theory to $\hat{\zeta}_R$ (i.e., find the expectation value of $\hat{\zeta}_R$ with the state vectors of \hat{H}_0) to determine the energy shift, ΔE_R . Doing this gives

$$\begin{aligned}
 \Delta E_R &= \langle \psi_n | \hat{\zeta}_R | \psi_n \rangle \\
 &= -\frac{1}{2m_e c^2} \langle \psi_n | \hat{H}_0^2 - 2\hat{H}_0 V + V^2 | \psi_n \rangle.
 \end{aligned} \tag{1.63a}$$

But,¹⁷

$$\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle \rightarrow \langle \hat{H}_0^2 \rangle = E_n^2, \quad (1.63b)$$

while

$$\langle \hat{H}_0 V \rangle = -E_n \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle = - \left(\frac{Z^2 e^2}{4\pi\epsilon_0} \right) \frac{E_n}{n^2 a_0} \quad (1.63c)$$

and

$$\langle |V^2| \rangle = \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle = \left(\frac{Z^2 e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^3 a_0^2 (l + \frac{1}{2})}. \quad (1.63d)$$

The expressions in Eq. (1.48) were used to evaluate the expectation values for $1/r$ and $1/r^2$. Collecting the terms leads to

$$\Delta E_R = -\frac{E_n^2}{2m_e c^2} \left[1 + 2 \frac{Z^2 e^2}{4\pi\epsilon_0 n^2 a_0} \frac{1}{E_n} + \left(\frac{Z^2 e^2}{4\pi\epsilon_0 n^2 a_0} \right)^2 \frac{n}{E_n^2 (l + \frac{1}{2})} \right]. \quad (1.64)$$

Finally, with the help of Eq. (1.42) the shift can be written as

$$\Delta E_R = -\frac{E_n^2}{2m_e c^2} \left(\frac{4n}{l + \frac{1}{2}} - 3 \right) \quad (1.65a)$$

$$= -\frac{\alpha^2 E_n}{4} \left(\frac{4n}{l + \frac{1}{2}} - 3 \right) \frac{Z^2}{n^2} \quad (1.65b)$$

$$= -\frac{\alpha^2 \mathcal{R}_M}{4} \left(\frac{4n}{l + \frac{1}{2}} - 3 \right) \frac{Z^4}{n^4}, \quad (1.65c)$$

where α is the fine-structure constant (see Appendix A). We see that the shift depends on both n and l ; thus, the degeneracy between states with the same n but different l is broken.

1.4.1.1 Electron Spin and the Dirac Equation

The electron, a fermion, has half-integer spin and thus obeys Fermi–Dirac statistics. Spin, which plays a major role in atomic and molecular physics, is not included in the nonrelativistic Hamiltonian or its correction term (Eq. (1.61)). Instead of inserting a series of terms to account for spin and its interaction with other angular momenta, we will endeavor to understand the origin of

¹⁷ Here, $|\psi_n\rangle$ is an eigenstate of \hat{H}_0 with eigenvalue E_n . See Appendix B.8 for further discussion of the mathematical formalism of $\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle$.

the spin terms in this section. Spin, as it turns out, is relativistic in origin. To derive the terms we need, we must start with an equation that is relativistically invariant. We will use the free-particle Dirac equation,

$$[c\underline{\alpha} \cdot \vec{p} + \underline{\beta}m_e c^2] \psi = E\psi, \quad (1.66)$$

where $\underline{\alpha}$ and $\underline{\beta}$ are 4×4 matrices given by¹⁸

$$\underline{\alpha} = \begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} \quad \underline{\beta} = \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix}, \quad (1.67)$$

$\underline{\sigma}$ are the 2×2 Pauli spin matrices and \mathbb{I} is the identity matrix.¹⁹

As before, \vec{p} is our momentum operator ($-i\hbar \vec{\nabla}$) and the wavefunction, ψ , is now a four-component column vector,

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}, \quad (1.68)$$

where we can define ψ_u and ψ_v as

$$\psi_u = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \quad \psi_v = \begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix}, \quad (1.69)$$

which correspond to the positive and negative energies, respectively. Inserting this wavefunction into the Dirac equation leads to two equations that must be solved simultaneously,

$$\begin{aligned} c\underline{\sigma} \cdot \vec{p} \psi_v + (m_e c^2 - E) \psi_u &= 0, \\ c\underline{\sigma} \cdot \vec{p} \psi_u - (m_e c^2 + E) \psi_v &= 0, \end{aligned} \quad (1.70)$$

In the nonrelativistic limit, $v \ll c$, these reduce to the Schrödinger equation. From the second equation in Eq. (1.70), we have

$$\psi_v = \frac{c\underline{\sigma} \cdot \vec{p}}{m_e c^2 + E} \psi_u. \quad (1.71)$$

18) We will use a tilde under a symbol to indicate a matrix.

19) The Pauli spin matrices (see, for example, Eq. (4.73) of Ref. [6]) can be represented as

$$\underline{\sigma}(x) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \underline{\sigma}(y) = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \underline{\sigma}(z) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \mathbb{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

When the velocities are small $|\vec{p}| \rightarrow m_e v$ and $E \rightarrow mc^2$, which implies

$$|\psi_v| \approx \frac{v}{2c} |\psi_u| \ll |\psi_u|. \quad (1.72)$$

Thus, most of the physics will be represented by the positive-energy wavefunctions at nonrelativistic velocities. Substituting Eq. (1.71) into the upper expression in Eq. (1.70) to eliminate ψ_v gives

$$c^2 (\underline{\sigma} \cdot \vec{p})^2 \psi_u = (m_e c^2 + E) (E - m_e c^2) \psi_u \quad (1.73a)$$

$$= E^2 - m_e^2 c^4 \psi_u \quad (1.73b)$$

$$\approx 2m_e c^2 E^{nr} \psi_u, \quad (1.73c)$$

where $E^{nr} = E - m_e c^2$. Using the spinor identity

$$(\underline{\sigma} \cdot \vec{A}) (\underline{\sigma} \cdot \vec{B}) = \vec{A} \cdot \vec{B} + i \underline{\sigma} \cdot (\vec{A} \times \vec{B}), \quad (1.74)$$

we can write

$$c^2 p^2 \psi_u = 2m_e c^2 E^{nr} \psi_u, \quad (1.75)$$

which is just the free-particle Schrödinger equation.

To account for interactions with the Coulomb potential of the nucleus and external magnetic and time-varying electric fields, we introduce two additional terms into the free-particle equation (Eq. (1.70)). We incorporate the external fields with the vector potential, \vec{A} , by letting

$$\vec{p} \rightarrow \vec{p} - \frac{e}{c} \vec{A} \equiv \vec{\pi}, \quad (1.76)$$

where the electric and magnetic fields are given by

$$\vec{E} = -\vec{\nabla} \phi - \frac{\partial \vec{A}}{\partial t}, \quad (1.77a)$$

$$\vec{B} = \vec{\nabla} \times \vec{A}. \quad (1.77b)$$

A static potential, $-e\phi$, was added to Eq. (1.77a) to account for the nuclear charge. In Chapter 4, $\vec{\pi}$ will lead to the radiation Hamiltonian used in photoexcitation. The modified Dirac equation takes the form

$$c \underline{\sigma} \cdot \left(\vec{p} - \frac{e}{c} \vec{A} \right) \psi_v = (E - m_e c^2 - e\phi) \psi_u, \quad (1.78)$$

$$c \underline{\sigma} \cdot \left(\vec{p} - \frac{e}{c} \vec{A} \right) \psi_u = (E + m_e c^2 - e\phi) \psi_v.$$

Following steps similar to those taken above, the lower expression in Eq. (1.71) becomes

$$\psi_v = \frac{c\boldsymbol{\alpha} \cdot \left(\vec{p} - \frac{e}{c}\vec{A} \right)}{E + m_e c^2 - e\phi} \psi_u. \quad (1.79)$$

Substituting this into the upper expression and expanding the denominator,

$$\frac{1}{E + m_e c^2 - e\phi} \approx \frac{1}{2m_e c^2} \left[1 - \frac{E^{nr} - e\phi}{2m_e c^2} + \dots \right] \quad (1.80)$$

(where terms of order v^2/c^2 have been kept), gives

$$\frac{1}{2m_e} \left[(\boldsymbol{\alpha} \cdot \vec{\pi})^2 - (\boldsymbol{\alpha} \cdot \vec{\pi}) \frac{E^{nr} - e\phi}{2m_e c^2} (\boldsymbol{\alpha} \cdot \vec{\pi}) \right] \psi_u = (E^{nr} - e\phi) \psi_u. \quad (1.81)$$

We will solve this equation by allowing $\psi = \zeta \psi_u$, where

$$\zeta = 1 + \frac{(\boldsymbol{\alpha} \cdot \vec{\pi})^2}{8m_e^2 c^2}. \quad (1.82)$$

To first order in v^2/c^2 ,

$$\zeta^{-1} \approx 1 - \frac{(\boldsymbol{\alpha} \cdot \vec{\pi})^2}{8m_e^2 c^2}. \quad (1.83)$$

Making this substitution for ψ_u and multiplying the resulting equation on the left by ζ^{-1} gives

$$\begin{aligned} & \left[\frac{1}{2m_e} (\boldsymbol{\alpha} \cdot \vec{\pi})^2 - \frac{(\boldsymbol{\alpha} \cdot \vec{\pi})^4}{8m_e^2 c^2} + \frac{(\boldsymbol{\alpha} \cdot \vec{\pi})^2}{8m_e^2 c^2} (E^{nr} - e\phi) \right. \\ & \left. - \frac{1}{4m_e^2 c^2} (\boldsymbol{\alpha} \cdot \vec{\pi}) (E^{nr} - e\phi) (\boldsymbol{\alpha} \cdot \vec{\pi}) + (E^{nr} - e\phi) \frac{(\boldsymbol{\alpha} \cdot \vec{\pi})^2}{8m_e^2 c^2} \right] \psi \\ & = (E^{nr} - e\phi) \psi. \end{aligned} \quad (1.84)$$

Recognizing that

$$\begin{aligned} (\boldsymbol{\alpha} \cdot \vec{\pi})^2 &= \left(\vec{p} - \frac{e}{c}\vec{A} \right)^2 - \frac{e\hbar}{c} \boldsymbol{\alpha} \cdot \vec{\nabla} \times \vec{A}, \\ (\boldsymbol{\alpha} \cdot \vec{\pi}) (E^{nr} - e\phi) - (E^{nr} - e\phi) (\boldsymbol{\alpha} \cdot \vec{\pi}) &= ie\hbar (\boldsymbol{\alpha} \cdot \vec{\nabla} \phi), \\ (\boldsymbol{\alpha} \cdot \vec{\pi}) (\boldsymbol{\alpha} \cdot \vec{\nabla} \phi) \\ - (\boldsymbol{\alpha} \cdot \vec{\nabla} \phi) (\boldsymbol{\alpha} \cdot \vec{\pi}) &= -i\hbar \vec{\nabla} \cdot \vec{\nabla} \phi + 2i\boldsymbol{\alpha} \cdot \vec{\pi} \times \vec{\nabla} \phi, \end{aligned} \quad (1.85)$$

we can rewrite Eq. (1.84) as

$$\left[\frac{1}{2m_e} \left(\vec{p} - \frac{e}{c} \vec{A} \right)^2 - \frac{e\hbar}{2m_e c} \vec{\sigma} \cdot \vec{\nabla} \times \vec{A} - \frac{\vec{p}^4}{8m_e^3 c^3} + \frac{e\hbar^2}{8m_e^2 c^2} \vec{\nabla} \cdot \vec{\nabla} \phi - \frac{e\hbar}{4m_e^2 c^2} \vec{\sigma} \cdot \vec{\nabla} \phi \times \vec{p} \right] \psi = (E^{nr} - e\phi) \psi. \quad (1.86)$$

Again, only terms of order v^2/c^2 have been kept. The quantity in parentheses on the left- and the right-hand sides comprises the nonrelativistic Schrödinger equation with an interaction term represented by $-e\vec{A}/c$. The rest of the terms all have a relativistic origin and are responsible for spin-1/2 particle interaction with magnetic fields as well as spin-orbit interaction. A brief description of each term along with its approximate magnitude is given in Table 1.1.

The second perturbation in Table 1.1 allows us to define the Bohr magneton, $\mu_B = e\hbar/2m_e c$ while the fifth, the spin-orbit interaction, further splits the degeneracy between states of different l . Before we calculate the magnitude of this splitting, we will say a few words about spin.

1.4.1.2 Classification of Relativistic Hydrogen States

The spin quantum number, \vec{s} , assumes only one value, $1/2$. Similar to the orbital angular momentum, the eigenvalues of \vec{s}^2 will be $s(s+1) = 3/4$. There is also a magnetic or z component of \vec{s} , \vec{s}_z , that will have eigenvalues $m_s = \pm 1/2$. We will define a new operator called the total angular momentum,

$$\vec{j} = \vec{l} + \vec{s}, \quad (1.87)$$

with eigenvalues (of \vec{j}^2) $j(j+1)$. The sum in Eq. (1.87) is a vector sum. The values that \vec{j} can assume are

$$j = \begin{cases} l \pm \frac{1}{2}, & l \neq 0, \\ \frac{1}{2}, & l = 0. \end{cases} \quad (1.88)$$

The magnetic quantum number or the eigenvalue of the z component of \vec{j} is m_j , with $2j+1$ values, $m_j = -j, -j+1, \dots, j$.

In Section 1.3 we introduced the concept of a shell, designated by nl . Each l will have two values of j associated with it when $l > 0$. For example, an electron in a state of $n = 4$ and $l = 2$ will have $j = 3/2, 5/2$. Thus, we introduce the concept of a subshell designated by nl_j . This electron is said to be in the $4d$ shell and will be in either the $4d_{3/2}$ or $4d_{5/2}$ subshell. Note that now we have two angular momenta about which to be concerned, l and j . To

Tab. 1.1 Summary of relativistic and spin-dependent interaction terms.

Perturbation	Description	Magnitude
$\frac{1}{2m_e} \left(\vec{p} - \frac{e}{c} \vec{A} \right)^2$	The nonrelativistic motion, $p^2/2m_e$, and the interaction terms $\frac{e}{2m_e c} \vec{A} \cdot \vec{\nabla} + \frac{e^2}{2m_e c^2} \vec{A} \cdot \vec{A}$. The latter terms are responsible for absorption and emission; they can be written as $-e \vec{r} \cdot \vec{E}$ (see Section 4.1.1).	$\gtrsim 10^5 \text{ cm}^{-1}$
$\frac{e\hbar}{2m_e c} \boldsymbol{\sigma} \cdot \vec{\nabla} \times \vec{A}$	The spin-1/2 ($\vec{s} = \boldsymbol{\sigma}/2$) interaction with a magnetic field ($\vec{B} \equiv \vec{\nabla} \times \vec{A}$). This term gives the correct g-factor, $g = 2$, and magnetic moment of the electron, $\mu = \frac{e\hbar}{2m_e c} g \vec{s}$.	$\approx 1 \text{ cm}^{-1}$
$\frac{\vec{p}^4}{8m_e^3 c^3}$	Relativistic mass correction term.	$\approx 0.1 \text{ cm}^{-1}$
$\frac{e\hbar^2}{8m_e^2 c^2} \vec{\nabla} \cdot \vec{\nabla} \phi$	The ‘‘Darwin’’ term responsible for s -state shifts. It represents the relativistic nonlocalizability of the electron and is related to both the negative-energy sea and its rapid motion.	$< 0.1 \text{ cm}^{-1}$
$\frac{e\hbar}{4m_e^2 c^2} \boldsymbol{\sigma} \cdot \vec{\nabla} \phi \times \vec{p}$	Spin-orbit interaction. As shown in Problem 1.4, this term can be written as $\frac{e\hbar^2}{2m_e^2 c^2} \frac{1}{r} \frac{d\phi}{dr} (\vec{l} \cdot \vec{s})$, where \vec{l} is the orbital angular momentum. In contrast to the previous term, this does not affect s states.	$10\text{--}10^3 \text{ cm}^{-1}$

distinguish their magnetic quantum numbers, we will add subscripts l and j to the orbital, m_l , and total, m_j , quantum numbers.

1.4.1.3 Hydrogen-Like Ion Wavefunction Including Spin

We are now in a position to write down the three-dimensional wavefunction for a one-electron atom including the spin of the electron. This wavefunction takes the form

$$\Psi_{nlm_l m_s} = R_{nl}(r) Y_{lm_l}(\vartheta, \varphi) \phi_{m_s}(s_z), \quad (1.89)$$

where we have placed the subscripts l and s on the magnetic quantum numbers to distinguish orbital from spin. Since this wavefunction describes the state of a single electron, we only need to specify the direction of the spin.

1.4.2

Fine Structure and Spin–Orbit Interaction

In general, subshells have different energies. The splitting between the states is determined in part by the spin–orbit interaction

$$\hat{H}_{so} = \frac{e\hbar^2}{2m_e^2c^2} \frac{1}{r} \frac{d\phi}{dr} (\vec{l} \cdot \vec{s}). \quad (1.90)$$

This interaction causes a level to shift by $\Delta E_{so} = \langle \hat{H}_{so} \rangle$.²⁰ To calculate $\langle \hat{H}_{so} \rangle$, it is convenient to write $\vec{l} \cdot \vec{s}$ as²¹

$$\vec{l} \cdot \vec{s} = \frac{j^2 - l^2 - s^2}{2}. \quad (1.91)$$

The energy shift then becomes

$$\Delta E_{so} = \frac{e\hbar^2}{2m_e^2c^2} \left[\frac{j(j+1) - l(l+1) - s(s+1)}{2} \right] \left\langle \frac{1}{r} \frac{d\phi}{dr} \right\rangle. \quad (1.92)$$

But,

$$\frac{1}{r} \frac{d\phi}{dr} = \frac{Ze}{4\pi\epsilon_0 r^3}. \quad (1.93)$$

Using the expressions in Eq. (1.48), it is possible to write

$$\Delta E_{so} = \frac{Z^4 e^2 \hbar^2}{4\pi\epsilon_0} \frac{\hbar^2}{2m^2 c^2 a_0^3 n^3} \frac{j(j+1) - l(l+1) - s(s+1)}{2l(l + \frac{1}{2})(l+1)}. \quad (1.94)$$

Combining this with the relativistic energy correction (Eq. (1.65a)), we obtain

$$\Delta E_{nlj} = \Delta E_R + \Delta E_{so} = \alpha^2 \mathcal{R}_M \left(\frac{3}{4n} - \frac{1}{j + \frac{1}{2}} \right) \frac{Z^4}{n^3}. \quad (1.95)$$

At the maximum value of $j + 1/2 = n$, ΔE_{nlj} is always < 0 , which means that the combination of the relativistic and spin–orbit interactions binds the system more tightly as shown for a few levels in Fig. 1.7. The figure shows as well that the degeneracy has not been lifted completely. States of different l

20 We saw in Eq. (1.65a) that the relativistic correction shifted levels of different l by different amounts. Below, we will combine the spin–orbit with the relativistic correction to remove the degeneracy of a shell partially.

21 This can be shown using the algebra developed in Appendix E; see Eq. (E.29) and surrounding discussion.

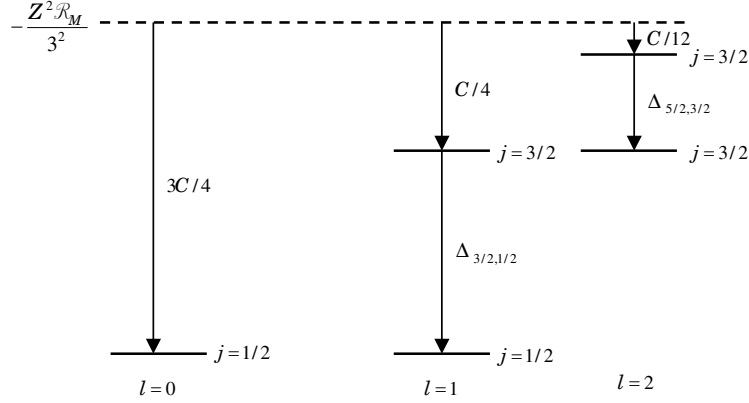


Fig. 1.7 Fine structure of hydrogen-like ions in wavenumbers for $n = 3$ where $C = \alpha^2 Z^4 \mathcal{R}_M / n^3$ and $\Delta_{j+1,j} = \Delta E_{nlj+1} - \Delta E_{nlj} = C/l(l+1)$. The levels are all shifted below $-Z^2 \mathcal{R}_M / n^2$, the nonrelativistic energy.

but with the same j have the same energy. The splitting between $j = l \pm 1/2$ levels will be given by

$$\Delta_{j+1,j} = \frac{\alpha^2 Z^4 \mathcal{R}_M}{n^3} \frac{1}{l(l+1)}. \quad (1.96)$$

Example. For $j = 1/2$ and $3/2$ in hydrogen, Eq. (1.95) gives $\Delta_{j+1,j} = 0.36, 0.12, 0.044 \text{ cm}^{-1}$, respectively, for $n = 2, 3, 4$.

1.4.3

Rydberg Series

Figure 1.1 shows a progression of energy levels to the ionization limit as $n \rightarrow \infty$. To lowest order, the energy of each level in the series is given by Eq. (1.56). For each level n , there are n nearly degenerate l sublevels. For all but s ($l = 0$) states, there are two possible j ($= l \pm s$) values for each l and thus two series for each l . Consequently, there are an infinite number of series of levels marching their way toward the ionization limit. Each series, nl_j for fixed l and j , is called a *Rydberg series*. For hydrogen-like systems (ions with just one electron) these series have a simple behavior. Systems with two or more electrons behave very differently because the members of the series can interact in very profound ways leading to a variety of interesting phenomena such as autoionization. We will look at Rydberg series for multielectron atoms in Chapter 2.

1.5

Continuum States

Thus far, we have focused on bound states, which correspond to solutions to the radial equation (Eq. (1.26)) when $E < 0$. However, when $E > 0$ the electron energy lies above the $n = \infty$ level in Fig. 1.1. The asymptotic ($r \rightarrow \infty$) solutions for the positive-energy states take the form $R(r) = e^{\pm ir\sqrt{2\mu E/\hbar^2}}$ (Eq. (1.29)), which oscillates sinusoidally and does not tend to zero. The radial solution for these states can be obtained by following the steps we took for the negative-energy states up to the recursion relation in Eq. (1.35), which become complex when $E > 0$. Since the wavefunctions are finite at $r = \infty$ (Eq. (1.29) is bounded by 1), there is now no need to truncate the series. As a result, the state of the electron can assume all positive energies; hence, the name *continuum state*. Since Eq. (1.35) is still valid, the wavefunctions can be written in terms of hypergeometric functions; however, the principal quantum number, n , becomes imaginary in Eq. (1.37),

$$n \equiv \lambda = -i \frac{Ze^2/4\pi\epsilon_0 \mu}{\sqrt{2\mu E/\hbar^2} \hbar^2}. \quad (1.97)$$

The solution, Eq. (4.23) of Bethe and Salpeter, can be written as

$$R_{\epsilon l}(r) = (-1)^{l+1} \frac{2\sqrt{\frac{Ze^2}{4\pi\epsilon_0}}}{\sqrt{1 - e^{-2\pi n'}}} \times \prod_{v=1}^l \sqrt{v^2 - n'^2} \frac{(2kr)^l}{(2l+1)!} e^{-ikr} F(in' + l + 1, 2l + 2, 2ikr), \quad (1.98)$$

where $n' = in$ is real, and $k = \sqrt{2\mu E/\hbar^2}$ also real with dimensions of $1/r$.

In general, each nl Rydberg series in the bound region is associated with a series of the same-parity energy states in the continuum region. The continuum states are designated by the label ϵl . An nl Rydberg series plus its ϵl continuum is called a *channel*. The channel is said to be *closed* when $E < 0$ (the electron is bound to the nucleus) and *open* when $E > 0$ (the electron is free).

Further Reading

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- 5 J. Mathews and R. L. Walker, *Mathematical Methods of Physics*, Benjamin Cummings, San Francisco, CA, 1970. ISBN 0-8053-7002-1, Second edition.B
- 6 N. N. Lebedev, *Special Functions and Their Applications*, translated and edited by R. A. Silverman, Dover, New York, NY, 1972.
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- 9 F. Yang and J. H. Hamilton, *Modern Atomic and Nuclear Physics*, McGraw-Hill, San Francisco, CA, 1996.
- 10 J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics*, McGraw-Hill, San Francisco, CA, 1964.
- 11 For additional problems with worked solutions see D. Budker, D. F. Kimball and D. P. DeMille, *Atomic Physics: An Exploration Through Problems and Solutions*, Oxford University Press, New York, NY, 2004.

Problems

1.1 Find the lowest-energy state of the one-dimensional hydrogen atom where the Schrödinger equation takes the form

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} \psi(x) - \left(\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{|x|} - E \right) \psi(x) = 0 \quad (-\infty < x < \infty). \quad (1.99)$$

1.2 Calculate

$$\langle r^\gamma \rangle = \int r^{2+\gamma} R_{nl}^2(r) dr \quad (1.100)$$

for $\gamma = -3, -2, -1, 1, 2, 3$.

1.3 Since the wavefunctions of the s levels are finite at the origin, the potential for s electrons changes when the electron penetrates the nucleus and gives rise to a shift in the energy levels relative to Eq. (1.42). If the radius of the nucleus is r_0 , the potential will be given by

$$\begin{aligned} & \frac{Q}{|r|} && \text{when } r > r_0, \\ & \int_N \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' && \text{when } r < r_0, \end{aligned} \quad (1.101)$$

where ρ is the charge density of the nucleus. Use first-order perturbation theory to show that the s states are shifted by

$$(\Delta E_s)_{\text{finite size}} = \frac{2}{3} \frac{e^2}{4\pi\epsilon_0} \frac{\langle r^2 \rangle_N}{a_0^3}, \quad (1.102)$$

where

$$\langle r^2 \rangle_N = \int_N r'^2 \rho(\vec{r}') d^3 r'. \quad (1.103)$$

If you take the size of the nucleus to be about 8 fm, estimate the magnitude of this shift for the ground state, i.e., calculate $(\Delta E_s)_{\text{finite size}} / E_{1s}$.

1.4 Show that

$$\frac{e\hbar}{4m_e^2 c^2} \vec{\sigma} \cdot \vec{\nabla} \phi \times \vec{p} \quad (1.104)$$

in Table 1.1 can be rewritten as

$$\frac{e\hbar^2}{2m_e^2 c^2} \frac{1}{r} \frac{d\phi}{dr} (\vec{L} \cdot \vec{S}). \quad (1.105)$$

1.5 It is possible to derive the spin-orbit interaction by going to the rest frame of the electron and allowing the nucleus to orbit the electron. The electron then feels a magnetic field due to the circular current. Determine the expression for the Hamiltonian, $-\vec{\mu} \cdot \vec{B}$, that describes the interaction.

1.6 Sketch the probability densities similar to Fig. 1.6 for the $1s$ through $3d$ states of hydrogen in Cartesian coordinates. You might find it helpful first to express the spherical harmonics in terms of Cartesian coordinates. That is, relate the spherical components (l, m) to combinations of x , y and z .