The degeneracy in m at each l we understand in terms of rotational invariance. The degeneracy of the different l states (which are not related by rotation operators or the generators) appears mysterious. For this reason it is occasionally termed *accidental degeneracy*. This is, however, a misnomer, for the degeneracy in l can be attributed to additional invariance properties of H. Exactly what these extra invariances or symmetries of H are, and how they explain the degeneracy in l, we will see in Chapter 15.

*Exercise 12.6.11.** (i) By combining Eqs. (12.6.48) and (12.6.49) derive the two-term recursion relation. Argue that $C_0 \neq 0$ if U is to have the right properties near $y = 0$. Derive the quantizations condition, Eq. (12.6.50).

(ii) Calculate the degeneracy and parity at each n and compare with Exercise 10.2.3, where the problem was solved in Cartesian coordinates.

(iii) Construct the normalized eigenfunction ψ_{nlm} for $n = 0$ and 1. Write them as linear combinations of the $n = 0$ and $n = 1$ eigenfunctions obtained in Cartesian coordinates.

13

The Hydrogen Atom

13.1. The Eigenvalue Problem

We have here a two-body problem, of an electron of charge $-e$ and mass m, and a proton of charge $+e$ and mass M. By using CM and relative coordinates and working in the CM frame, we can reduce the problem to the dynamics of a single particle whose mass $\mu = mM/(m + M)$ is the reduced mass and whose coordinate $\mathbf{r}$ is the relative coordinate of the two particles. However, since $m/M \simeq 1/2000$, as a result of which the relative coordinate is essentially the electron's coordinate and the reduced mass is essentially m, let us first solve the problem in the limit $M \to \infty$. In this case we have just the electron moving in the field of the immobile proton. At a later stage, when we compare the theory with experiment, we will see how we can easily take into account the finiteness of the proton mass.

Since the potential energy of the electron in the Coulomb potential

$$\phi = e/r \tag{13.1.1}$$

due to the proton is $V = -e^2/r$, the Schrödinger equation

$$\left\{\frac{d^2}{dr^2} + \frac{2m}{\hbar^2}\left[E + \frac{e^2}{r} - \frac{l(l+1)\hbar^2}{2mr^2}\right]\right\}U_{El} = 0 \tag{13.1.2}$$

determines the energy levels in the rest frame of the atom, as well as the wave functions[‡]

$$\psi_{Elm}(r, \theta, \phi) = R_{El}(r)Y_l^m(\theta, \phi) = \frac{U_{El}(r)}{r}\, Y_l^m(\theta, \phi) \tag{13.1.3}$$

It is clear upon inspection of Eq. (13.1.2) that a power series *ansatz* will lead to a three-term recursion relation. So we try to factor out the

---

[‡] It should be clear from the context whether m stands for the electron mass or the z component of angular momentum.

asymptotic behavior. We already know from Section 12.6 that up to (possibly fractional) powers of r [Eq. (12.6.19)],

$$U_{El} \underset{r\to\infty}{\sim} \exp[-(2mW/\hbar^2)^{1/2}r] \tag{13.1.4}$$

where

$$W = -E$$

is the *binding energy* (which is the energy it would take to liberate the electron) and that

$$U_{El} \underset{r\to 0}{\sim} r^{l+1} \tag{13.1.5}$$

Equation (13.1.4) suggests the introduction of the dimensionless variable

$$\varrho = (2mW/\hbar^2)^{1/2}r \tag{13.1.6}$$

and the auxiliary function v_{El} defined by

$$U_{El} = e^{-\varrho}v_{El} \tag{13.1.7}$$

The equation for v is then

$$\frac{d^2v}{d\varrho^2} - 2\frac{dv}{d\varrho} + \left[\frac{e^2\lambda}{\varrho} - \frac{l(l+1)}{\varrho^2}\right]v = 0 \tag{13.1.8}$$

where

$$\lambda = (2m/\hbar^2 W)^{1/2} \tag{13.1.9}$$

and the subscripts on v are suppressed. You may verify that if we feed in a series into Eq. (13.1.8), a two-term recursion relation will obtain. Taking into account the behavior near $\varrho = 0$ [Eq. (13.1.5)] we try

$$v_{El} = \varrho^{l+1}\sum_{k=0}^{\infty} C_k\varrho^k \tag{13.1.10}$$

and obtain the following recursion relation between *successive* coefficients:

$$\frac{C_{k+1}}{C_k} = \frac{-e^2\lambda + 2(k+l+1)}{(k+l+2)(k+l+1) - l(l+1)} \tag{13.1.11}$$

The Energy Levels

Since

$$\frac{C_{k+1}}{C_k} \xrightarrow[k\to\infty]{} \frac{2}{k} \tag{13.1.12}$$

is the behavior of the series $\varrho^m e^{2\varrho}$, and would lead to $U \sim e^{-\varrho}v \sim \varrho^m e^{-\varrho}e^{2\varrho} \sim \varrho^m e^{\varrho}$ as $\varrho \to \infty$, we demand that the series terminate at some k. This will happen if

$$e^2\lambda = 2(k+l+1) \tag{13.1.13}$$

or [from Eq. (13.1.9)]

$$E = -W = \frac{-me^4}{2\hbar^2(k+l+1)^2}, \qquad k = 0, 1, 2, \ldots; \qquad l = 0, 1, 2, \ldots \tag{13.1.14}$$

In terms of the *principal quantum number*

$$n = k + l + 1 \tag{13.1.15}$$

the allowed energies are

$$E_n = \frac{-me^4}{2\hbar^2 n^2}, \qquad n = 1, 2, 3, \ldots \tag{13.1.16}$$

and at each n the allowed values of l are, according to Eq. (13.1.15),

$$l = n - k - 1 = n-1, n-2, \ldots, 1, 0 \tag{13.1.17}$$

That states of different l should be degenerate indicates that H contains more symmetries besides rotational invariance. We discuss these later. For the present, let us note that the degeneracy at each n is

$$\sum_{l=0}^{n-1}(2l+1) = n^2 \tag{13.1.18}$$

It is common to refer to the states with $l = 0, 1, 2, 3, 4, \ldots$ as $s, p, d, f, g, h, \ldots$ states. In this *spectroscopic notation*, 1s denotes the state ($n = 1$, $l = 0$); 2s and 2p the $l = 0$ and $l = 1$ states at $n = 2$; 3s, 3p, and 3d the $l = 0$, 1, and 2 states at $n = 3$, and so on. No attempt is made to keep track of m.

It is convenient to employ a natural unit of energy, called a *Rydberg* (Ry), for measuring the energy levels of hydrogen:

$$\text{Ry} = \frac{me^4}{2\hbar^2} \tag{13.1.19}$$

in terms of which

$$E_n = \frac{-\text{Ry}}{n^2} \tag{13.1.20}$$

Figure 13.1 shows some of the lowest-energy states of hydrogen.

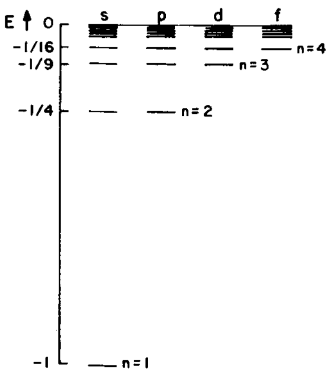

Fig. 13.1. The first few eigenstates of hydrogen. The energy is measured in Rydbergs and the states are labeled in the spectroscopic notation.

The Wave Functions

Given the recursion relations, it is a straightforward matter to determine the wave functions and to normalize them. Consider a given n and l. Since the series in Eq. (13.1.10) terminates at

$$k = n - l - 1 \tag{13.1.21}$$

the corresponding function v_l is ϱ^{l+1} times a polynomial of degree $n - l - 1$. This polynomial is called the *associated Laguerre polynomial*, $L^{2l+1}_{n-l-1}(2\varrho)$.[‡] The corresponding radial function is

$$R_{nl}(\varrho) \sim e^{-\varrho}\varrho^l L^{2l+1}_{n-l-1}(2\varrho) \tag{13.1.22}$$

Recall that

$$\begin{aligned}\varrho &= \left(\frac{2mW}{\hbar^2}\right)^{1/2} r = \left[\frac{2m}{\hbar^2}\cdot\left(\frac{me^4}{2\hbar^2 n^2}\right)\right]^{1/2} r \\ &= \frac{me^2}{\hbar^2 n} r \end{aligned} \tag{13.1.23}$$

In terms of the length

$$a_0 = \frac{\hbar^2}{me^2} \tag{13.1.24}$$

called the *Bohr radius*, which provides the natural distance scale for the hydrogen atom,

$$R_{nl}(r) \sim e^{-r/na_0}\left(\frac{r}{na_0}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{a_0}\right) \tag{13.1.25}$$

[‡] $L_p^k(x) = (-1)^k(d^k/dx^k)L^0_{p+k}$, $\quad L_p^0 = e^x(d^p/dx^p)(e^{-x}x^p)$.

As $r \to \infty$, L will be dominated by the highest power, r^{n-l-1}, and

$$R_{nl} \underset{r\to\infty}{\sim} (r)^{n-1}e^{-r/na_0} \qquad \text{(independent of } l\text{)} \tag{13.1.26}$$

(If $l = n - 1$, this form is valid at all r since L_0^{2l+1} is a constant.) Equation (13.1.26) was anticipated in the last chapter when we considered the behavior of U_{El} as $r \to \infty$, in a Coulomb potential (see Exercise 13.1.4).

The following are the first few normalized eigenfunctions, $\psi_{Elm} \equiv \psi_{nlm}$:

$$\begin{aligned}\psi_{1,0,0} &= \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0} \\ \psi_{2,0,0} &= \left(\frac{1}{32\pi a_0^3}\right)^{1/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0} \\ \psi_{2,1,0} &= \left(\frac{1}{32\pi a_0^3}\right)^{1/2}\frac{r}{a_0}e^{-r/2a_0}\cos\theta \\ \psi_{2,1,\pm1} &= \mp\left(\frac{1}{64\pi a_0^3}\right)^{1/2}\frac{r}{a_0}e^{-r/2a_0}\sin\theta e^{\pm i\phi}\end{aligned} \tag{13.1.27}$$

Exercise 13.1.1. Derive Eqs. (13.1.11) and (13.1.14) starting from Eqs. (13.1.8)–(13.1.10).

Exercise 13.1.2. Derive the degeneracy formula, Eq. (13.1.18).

Exercise 13.1.3. Starting from the recursion relation, obtain ψ_{210} (normalized).

Exercise 13.1.4. Recall from the last chapter [Eq. (12.6.19)] that as $r \to \infty$, $U_E \sim (r)^{me^2/\kappa\hbar^2}e^{-\kappa r}$ in a Coulomb potential $V = -e^2/r$ [$\kappa = (2mW/\hbar^2)^{1/2}$]. Show that this agrees with Eq. (13.1.26).

Let us explore the statement that a_0 provides a natural length scale for the hydrogen atom. Consider the state described by

$$\psi_{n,n-1,m} \propto e^{-r/na_0}r^{n-1}Y^m_{n-1}(\theta, \phi) \tag{13.1.28}$$

Let us ask for the probability of finding the electron in a spherical shell of radius r and thickness dr:

$$\int_\Omega P(\mathbf{r})r^2\,dr\,d\Omega \propto e^{-2r/na_0}r^{2n}\,dr \tag{13.1.29}$$

The probability density in r reaches a maximum when

$$\frac{d}{dr}\left(e^{-2r/na_0}r^{2n}\right) = 0$$

or

$$r = n^2 a_0 \tag{13.1.30}$$

When $n = 1$, this equals a_0. Thus the Bohr radius gives the most probable value of r in the ground state and this defines the "size" of the atom (to the extent one may speak of it in quantum theory). If $n > 1$ we see that the size grows as n^2, at least in the state of $l = n - 1$. If $l \neq n - 1$, the radial function has $n - l - 1$ zeros and the density in r has several bumps. In this case, we may define the size by $\langle r \rangle$.[‡] It can be shown, by using properties of L_{n-l-1}^{2l+1} that

$$\langle r \rangle_{nlm} = \frac{a_0}{2}\,[3n^2 - l(l+1)] \tag{13.1.31}$$

Rather than go through the lengthy derivation of this formula let us consider the following argument, which indicates that the size grows as $n^2 a_0$. In any eigenstate

$$\langle H \rangle = E = \langle T \rangle + \langle V \rangle = \langle P^2/2m \rangle - \langle e^2/r \rangle \tag{13.1.32}$$

It can be shown (Exercise 13.1.5) that

$$\langle T \rangle = -\tfrac{1}{2}\langle V \rangle \tag{13.1.33}$$

which is just the quantum version of the classical virial theorem, which states that if $V = cr^k$, then the averages $\bar{T}$ and $\bar{U}$ are related by

$$\bar{T} = \frac{k}{2}\,\bar{V}$$

It follows that

$$E = \tfrac{1}{2}\langle V \rangle = -\tfrac{1}{2}\langle e^2/r \rangle \tag{13.1.34}$$

Now, in the state labeled by n,

$$E_n = \frac{-me^4}{2\hbar^2 n^2} = \frac{-e^2}{2a_0 n^2} \tag{13.1.35}$$

from which it follows that

$$\left\langle \frac{1}{r} \right\rangle_n = \frac{1}{a_0 n^2} \tag{13.1.36}$$

[‡] Even though r represents the abstract operator $(X^2 + Y^2 + Z^2)^{1/2}$ only in the coordinate basis, we shall use the same symbol to refer to it in the abstract, so as to keep the notation simple.

Although

$$\frac{1}{\langle r \rangle} \neq \left\langle \frac{1}{r} \right\rangle$$

the two are of the same order of magnitude (see Exercise 9.4.2) and we infer that

$$\langle r \rangle_n \sim n^2 a_0 \tag{13.1.37}$$

which agrees with the result Eq. (13.1.31). (One must be somewhat cautious with statements like $\langle 1/r \rangle \simeq 1/\langle r \rangle$. For example it is not true in an s state that $\langle 1/r^4 \rangle \simeq 1/\langle r^4 \rangle$, since $\langle 1/r^4 \rangle$ is divergent while $1/\langle r^4 \rangle$ is not. In the present case, however, $\langle 1/r \rangle$ is well defined in all states and indeed $\langle 1/r \rangle$ and $1/\langle r \rangle$ are of the same order of magnitude.)

This completes our analysis of the hydrogen spectrum and wave functions. Several questions need to be answered, such as (i) What are the numerical values of E_n, a_0, etc.? (ii) How does one compare the energy levels and wave functions deduced here with experiment?

These questions will be taken up in Section 13.3. But first let us address a question raised earlier: What is the source of the degeneracy in l at each n?

*Exercise 13.1.5** (*Virial Theorem*). Since $|n, l, m\rangle$ is a stationary state, $\langle \dot{\Omega} \rangle = 0$ for any Ω. Consider $\Omega = \mathbf{R} \cdot \mathbf{P}$ and use Ehrenfest's theorem to show that $\langle T \rangle = (-1/2)\langle V \rangle$ in the state $|n, l, m\rangle$.

13.2. The Degeneracy of the Hydrogen Spectrum

The hydrogen atom, like the oscillator, exhibits "accidental degeneracy." Quotation marks are used once again, because, as in the case of the oscillator, the degeneracy can be explained in terms of other symmetries the Hamiltonian has besides rotational invariance. Now, we have seen that the symmetries of H imply the conservation of the generators of the symmetries. Consequently, if there is an extra symmetry (besides rotational invariance) there must be some extra conserved quantities (besides angular momentum). Now it is well known classically that the Coulomb[‡] potential is special (among rotationally invariant potentials) in that it conserves the *Runge–Lenz vector*

$$\mathbf{n} = \frac{\mathbf{p} \times \mathbf{l}}{m} - \frac{e^2}{r}\,\mathbf{r} \tag{13.2.1}$$

[‡] Or generally any $1/r$ potential, say, gravitational.

The conservation of $\mathbf{n}$ implies that not only is the orbit confined to a plane perpendicular to $\mathbf{l}$ (as in any rotationally invariant problem) it is also *closed* (Exercise 13.2.1).

In quantum theory then, there will be an operator $\mathbf{N}$ which commutes with H:

$$[\mathbf{N}, H] = 0 \tag{13.2.2}$$

and is given by[‡]

$$\mathbf{N} = \frac{1}{2m}[\mathbf{P}\times\mathbf{L} - \mathbf{L}\times\mathbf{P}] - \frac{e^2\mathbf{R}}{(X^2+Y^2+Z^2)^{1/2}} \tag{13.2.3}$$

We have seen that the conservation of $\mathbf{L}$ implies that $[L_\pm, H] = 0$, which means that we can raise and lower the m values at a given l without changing the energy. This is how the degeneracy in m is "explained" by rotational invariance.

So it must be that since $[\mathbf{N}, H] = 0$, we must be able to build some operator out of the components of $\mathbf{N}$, which commutes with H and which raises l by one unit. This would then explain the degeneracy in l at each n. Precisely what this operator is and how it manages to raise l by one unit will be explained in Section 15.4, devoted to the study of "accidental" degeneracy. You will also find therein the explanation of the degeneracy of the oscillator.

Exercise 13.2.1. Let us see why the conservation of the Runge–Lenz vector $\mathbf{n}$ implies closed orbits.

(i) Express $\mathbf{n}$ in terms of $\mathbf{r}$ and $\mathbf{p}$ alone (get rid of $\mathbf{l}$).

(ii) Since the particle is bound, it cannot escape to infinity. So, as we follow it from some arbitrary time onwards, it must reach a point $\mathbf{r}_{\max}$ where its distance from the origin stops growing. Show that

$$\mathbf{n} = \mathbf{r}_{\max}\left(2E + \frac{e^2}{r_{\max}}\right)$$

at this point. (Use the law of conservation of energy to eliminate p^2.) Show that, for similar reasons, if we wait some more, it will come to $\mathbf{r}_{\min}$, where

$$\mathbf{n} = \mathbf{r}_{\min}\left(2E + \frac{e^2}{r_{\min}}\right)$$

Thus $\mathbf{r}_{\max}$ and $\mathbf{r}_{\min}$ are parallel to each other and to $\mathbf{n}$. The conservation or constancy of $\mathbf{n}$ implies that the maximum (minimum) separation is always reached at the same point $\mathbf{r}_{\max}(\mathbf{r}_{\min})$, i.e., the orbit is closed. In fact, all three vectors $\mathbf{r}_{\max}$, $\mathbf{r}_{\min}$, and $\mathbf{n}$ are aligned with the major axis of the ellipse along which the particle moves; $\mathbf{n}$ and $\mathbf{r}_{\min}$ are parallel, while $\mathbf{n}$ and $\mathbf{r}_{\max}$ are antiparallel. (Why?) Convince yourself that for a circular orbit, $\mathbf{n}$ must and does vanish.

[‡] Since $[\mathbf{P}, \mathbf{L}] \neq 0$, we have used the symmetrization rule to construct $\mathbf{N}$ from $\mathbf{n}$, i.e., $\mathbf{p}\times\mathbf{l} \to \frac{1}{2}[(\mathbf{P}\times\mathbf{L}) + (\mathbf{P}\times\mathbf{L})^\dagger] = \frac{1}{2}[\mathbf{P}\times\mathbf{L} - \mathbf{L}\times\mathbf{P}]$ (verify this).

13.3. Numerical Estimates and Comparison with Experiment

In this section we (i) obtain numerical estimates for various quantities such as the Bohr radius, energy levels, etc.; (ii) ask how the predictions of the theory are actually compared with experiment.

Numerical Estimates

Consider first the particle masses. We will express the rest energies of the particles in million-electron volts or MeV:

$$mc^2 \simeq 0.5\text{ MeV} \qquad (0.511\text{ is a more exact value}) \tag{13.3.1}$$

$$Mc^2 = 1000\text{ MeV} \qquad (938.3)^{‡} \tag{13.3.2}$$

$$m/M \simeq 1/2000 \qquad (1/1836)^{‡} \tag{13.3.3}$$

Consequently the reduced mass μ and electron mass m are almost equal:

$$\mu = \frac{mM}{m+M} \simeq \frac{mM}{M} = m \tag{13.3.4}$$

as are the relative coordinate and the electron coordinate.

Consider now an estimate of the Bohr radius

$$a_0 = \hbar^2/me^2 \tag{13.3.5}$$

To find this we need the values of $\hbar$ and e. It was mentioned earlier that

$$\hbar = 1.054\times 10^{-27}\text{ erg sec}$$

A more useful thing to remember for performing quick estimates is[§]

$$\hbar c \simeq 2000\text{ eV Å} \qquad (1973.3) \tag{13.3.6}$$

where 1 angstrom (Å) $= 10^{-8}$ cm. The best way to remember e^2 is through

---

[‡] A more exact value.

[§] Many of the tricks used here were learned from Professor A. Rosenfeld at Berkeley.

the *fine-structure constant*:

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137} \quad \left(\frac{1}{137.04}\right) \tag{13.3.7}$$

This constant plays a fundamental role in quantum mechanical problems involving electrodynamics. Since it is dimensionless, its numerical value has an absolute significance: no matter what units we use for length, mass, and time, α will be 1/137. Thus, although no one tries to explain why $c = 3\times 10^{10}$ cm/sec, several attempts have been made to arrive at the magic figure of 1/137. Since it is a God-given number (independent of mortal choice of units) one tries to relate it to fundamental numbers such as π, e, e^{π}, π^{e}, the number of space–time dimensions, etc.

Anyway, returning to our main problem, we can now estimate a_0:

$$a_0 \simeq \frac{\hbar^2}{me^2} = \frac{\hbar c}{mc^2}\left(\frac{\hbar c}{e^2}\right) = \frac{(2000)(137)}{0.5\times 10^6}\ \text{Å} \simeq 0.55\ \text{Å}\ (0.53)$$

Consider next the energy levels

$$E_n = -\text{Ry}/n^2$$

We estimate

$$\begin{aligned}\text{Ry} &= \frac{me^4}{2\hbar^2} = \frac{mc^2}{2}\left(\frac{e^2}{\hbar c}\right)^2\\ &\simeq \frac{0.25\times 10^6}{(137)^2}\ \text{eV} \simeq 13.3\ \text{eV} \qquad (13.6)\end{aligned}$$

So, using the more accurate value of R_y,

$$E_n = \frac{-13.6}{n^2}\ \text{eV}$$

The electron in the ground state needs 13.6 eV to be liberated or ionized. One may imagine that it is 13.6 eV down the infinitely deep Coulomb potential.

Let us digress to consider two length scales related to a_0. The first

$$a_0\alpha = \frac{\hbar^2}{me^2}\cdot\frac{e^2}{\hbar c} = \frac{\hbar}{mc} \equiv \bar{\lambda}_e \tag{13.3.8}$$

is called the *Compton wavelength* of the electron and is 137 times smaller than the Bohr radius. What does $\bar{\lambda}_e$ represent? In discussing the nuclear force, it was pointed out that the Compton wavelength of the pion was the distance over which it could be exchanged. It can also be defined as the lower limit on how well a particle can be localized. In the nonrelativistic theory we are considering, the lower limit is zero, since we admit position eigenkets $|\,x\rangle$. But in reality, as we try to locate the particle better and better, we use more and more energetic probes, say photons to be specific. To locate it to some ΔX, we need a photon of momentum

$$\Delta P \sim \frac{\hbar}{\Delta X}$$

Since the photon is massless, the corresponding energy is

$$\Delta E \sim \frac{\hbar c}{\Delta X}$$

in view of Einstein's formula $E^2 = c^2p^2 + m^2c^4$.

If this energy exceeds twice the rest energy of the particle, relativity allows the production of a particle–antiparticle pair in the measurement process. So we demand

$$\Delta E \lesssim 2mc^2$$

$$\frac{\hbar c}{\Delta X} \lesssim 2mc^2$$

or

$$\Delta X \gtrsim \frac{\hbar}{2mc} \sim \frac{\hbar}{mc}$$

If we attempt to localize the particle any better, we will see pair creation and we will have three (or more) particles instead of the one we started to locate.

In our analysis of the hydrogen atom, we treated the electron as a localized point particle. The preceding analysis shows that this is not strictly correct, but it also shows that it is a fair approximation, since the "fuzziness" or "size" of the electron is α times smaller than the size of the atom, a_0

$$\frac{\hbar/mc}{a_0} = \alpha \simeq \frac{1}{137}$$

Had the electric charge been ten times as big, α would have been of order unity, and the size of the electron and the size of its orbit would have been of the same order and the point particle approximation would have been untenable. Let us note that

$$\bar{\lambda}_e = \alpha\cdot a_0 \simeq 0.5\times\frac{1}{137}\ \text{Å} \simeq \frac{1}{250}\ \text{Å} \simeq 4\times 10^{-3}\ \text{Å}$$

If we multiply $\bar{\lambda}_e$ by α we get another length, called the *classical radius of the electron*:

$$r_e = \alpha\bar{\lambda}_e = \frac{\hbar}{mc}\cdot\frac{e^2}{\hbar c} = \frac{e^2}{mc^2} \simeq 3\times 10^{-5}\ \text{Å} \tag{13.3.9}$$

If we imagine the electron to be a spherical charge distribution, the Coulomb energy of the distribution (the energy it takes to assemble it) will be of the order e^2/r_e, where r_e is the radius of the sphere. If we attribute the rest energy of the electron to this Coulomb energy, we arrive at the classical radius. In summary

$$\begin{array}{ccccc} a_0 & \underset{\alpha}{\rightarrow} & \bar{\lambda}_e & \underset{\alpha}{\rightarrow} & r_0 \\ \left(\frac{1}{2}\,\text{Å}\right) & & \left(\frac{\alpha}{2}\,\text{Å}\right) & & \left(\frac{\alpha^2}{2}\,\text{Å}\right) \end{array}$$

Let us now return to the hydrogen atom. The mnemonics discussed so far are concerned only with the numbers. Let us now consider mnemonics that help us remember the dynamics. These must be used with caution, for they are phrased in terms not allowed in quantum theory.

The source of these mnemonics is the *Bohr model* of the hydrogen atom. About a decade or so prior to the formulation of quantum mechanics as described in this text, Bohr proposed a model of the atom along the following lines. Consider a particle of mass m in $V(r) = -e^2/r$, moving in a circular orbit of radius r. The dynamical equation is

$$\frac{mv^2}{r} = \frac{e^2}{r^2} \tag{13.3.10}$$

or

$$mv^2 = \frac{e^2}{r} \tag{13.3.11}$$

Thus any radius is allowed if r satisfies this equation. It also follows that any energy is allowed since

$$E = \frac{1}{2}mv^2 - \frac{e^2}{r} = -\frac{e^2}{2r} = -\frac{1}{2}mv^2 \tag{13.3.12}$$

Bohr conjectured that the only allowed orbits were those that had integral angular momentum:

$$mvr = n\hbar \tag{13.3.13}$$

Feeding this into Eq. (13.3.11) we get

$$m\cdot\frac{n^2\hbar^2}{m^2r^2} = \frac{e^2}{r}$$

or

$$r = n^2\frac{\hbar^2}{me^2} = n^2a_0 \tag{13.3.14}$$

and

$$E_n = -\frac{e^2}{2r} = -\frac{e^2}{2a_0}\cdot\left(\frac{1}{n^2}\right) \tag{13.3.15}$$

Thus, if you ever forget the formula for a_0 or E_n, you can go back to this model for the formulas (though not for the physics, since it is perched on the fence between classical and quantum mechanics; it speaks of orbits, but quantizes angular momentum and so on). The most succinct way to remember the Bohr atom (i.e., a mnemonic for the mnemonic) is the equation

$$\alpha = \beta \tag{13.3.16}$$

where β is the velocity of the electron in the ground state of hydrogen measured in units of velocity of light ($\beta = v/c$). Given this, we get the ground state energy as

$$\begin{aligned} E_1 &= -\frac{1}{2}mv^2 = -\frac{1}{2}mc^2(v/c)^2 = -\frac{1}{2}mc^2\beta^2 = -\frac{1}{2}mc^2\alpha^2 \\ &= -\frac{1}{2}mc^2\left(\frac{e^2}{\hbar c}\right)^2 = -\frac{me^4}{2\hbar^2} \end{aligned} \tag{13.3.17}$$

Given this, how could one forget that the levels go as n^{-2}, i.e.,

$$E_n = -\frac{E_1}{n^2}?$$

If we rewrite E_1 as $-e^2/2a_0$, we can get the formula for a_0. The equation $\alpha = \beta$ also justifies the use of nonrelativistic quantum mechanics. An equivalent way (which avoids the use of velocity) is Eq. (13.3.17), which states that the binding energy is $\simeq (1/137)^2$ times the rest energy of the electron.

*Exercise 13.3.1.** The pion has a range of 1 Fermi $= 10^{-5}$ Å as a mediator of nuclear force. Estimate its rest energy.

*Exercise 13.3.2.** Estimate the deBroglie wavelength of an electron of kinetic energy 200 eV. (Recall $\lambda = 2\pi\hbar/p$.)

Comparison with Experiment

Quantum theory makes very detailed predictions for the hydrogen atom. Let us ask how these are to be compared with experiment. Let us consider first the energy levels and then the wave functions. In principle, one can measure the energy levels by simply weighing the atom. In practice, one measures the *differences in energy levels* as follows. If we start with the atom in an eigenstate $|nlm\rangle$, it will stay that way forever. However, if we perturb it for a time T, by turning on some external field (i.e., change the Hamiltonian from H^0, the Coulomb Hamiltonian, to $H^0 + H^1$) its state vector can start moving around in Hilbert space, since $|nlm\rangle$ isn't a stationary state of $H^0 + H^1$. If we measure the energy at time $t > T$, we may find it corresponds to another state with $n' \neq n$. One measures the energy by detecting the photon emitted by the atom. The frequency of the detected photon will be

$$\omega_{nn'} = \frac{E_n - E_{n'}}{\hbar} \tag{13.3.18}$$

Thus the frequency of light coming out of hydrogen will be

$$\begin{aligned}\omega_{nn'} &= \frac{\text{Ry}}{\hbar}\left(-\frac{1}{n^2} + \frac{1}{n'^2}\right)\\ &= \frac{\text{Ry}}{\hbar}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)\end{aligned} \tag{13.3.19}$$

For a fixed value $n' = 1, 2, 3, \ldots$, we obtain a family of lines as we vary n. These families have in fact been seen, at least for several values of n'. The $n' = 1$ family is called the *Lyman series* (it corresponds to transitions to the ground state from the upper ones):

$$\omega_{n1} = \frac{\text{Ry}}{\hbar}\left(\frac{1}{1} - \frac{1}{n^2}\right) \tag{13.3.20}$$

The $n' = 2$ family is called the *Balmer series* and corresponds to transitions to the states $|2lm\rangle$ from $n = 3, 4, \ldots$, etc. The $n' = 3$ family called the *Paschen* series, etc. Let us estimate the wavelength of a typical line in the Lyman series, say the one corresponding to the transition $n = 2 \rightarrow n' = 1$:

$$\begin{aligned}\omega_{21} &= \frac{13.5 \text{ eV}}{\hbar}\left(1 - \frac{1}{4}\right)\\ &\simeq \frac{10}{\hbar}\text{ eV}\end{aligned}$$

The wavelength is estimated to be

$$\lambda = \frac{2\pi c}{\omega} = \frac{2\pi}{10}(\hbar c) \simeq 1200 \text{ Å}$$

A more refined estimate gives a value of 1216 Å, in very good agreement with experiment. Equally good is the agreement for all other observed lines. However, there are, in all cases, small discrepancies. Much of these may be explained by corrections that are calculable in theory. First we must correct for the fact that the proton is not really immobile; that we have here a two-body problem. As explained in Chapter 10, this is done by writing Schrödinger's equation for the relative (and not electron) coordinate and working in the CM frame. This equation would differ from Eq. (13.1.2) only in that m would be replaced by μ. This in fact would be the only change in all the formulas that follow, in particular Eq. (13.1.16) for the energy levels. This would simply rescale the entire spectrum by a factor $\mu/m = M/(M + m)$, which differs from 1 by less than a tenth of a percent. This difference is, however, observable in practice: one sees it in the difference between the levels of hydrogen and deuterium (whose nucleus has a proton and a neutron).

Then there is the correction due to the fact that the kinetic energy of the electron is not $\frac{1}{2}mv^2 = p^2/2m$ in Einstein's theory, but instead $mc^2[(1 - v^2/c^2)^{-1/2} - 1]$, which is the difference between the energy at velocity v and the energy at rest. The $\frac{1}{2}mv^2$ term is just the first in the power series expansion of the above, in the variable v^2/c^2. In Chapter 17 we will take into account the effect of the next term, which is $-3mv^4/8c^2$, or in terms of the momentum, $-3p^4/8m^3c^2$. This is a correction of order v^2/c^2 relative to the $p^2/2m$ piece we included, or since $v/c \simeq \alpha$, a correction of order α^2 relative to main piece. There are other corrections of the same order, and these go by the name of *fine-structure corrections*. They will be included (in some approximation) in Chapter 17. The Dirac equation, which we will not solve in this book, takes into account the relativistic corrections to all orders in v/c. However, it too doesn't give the full story; there are tiny corrections due to quantum fluctuations of the electromagnetic field (which we have treated classically so far). These corrections are calculable in theory and measurable experimentally. The agreement between theory and experiment is spectacular. It is, however, important to bear in mind that all these corrections are icing on the cake; that the simple nonrelativistic Schrödinger equation by itself provides an excellent description of the hydrogen spectrum. (Much of the present speculation on what the correct theory of elementary particles is will be put to rest if one can come up with a description of these particles that is half as good as the description of the hydrogen atom by Schrödinger's equation.)

Consider next the wave functions. To test the predictions, one once again relies on perturbing the system. The following example should give you a feeling for how this is done. Suppose we apply an external perturbation H^1 for a short time ε. During this time, the system goes from $|nlm\rangle$ to

$$\begin{aligned}|\psi(\varepsilon)\rangle &= \left[I - \frac{i\varepsilon}{\hbar}(H^0 + H^1)\right]|nlm\rangle \\ &= |nlm\rangle - \left(\frac{i\varepsilon E_n}{\hbar} + \frac{i\varepsilon H^1}{\hbar}\right)|nlm\rangle\end{aligned}$$

The probability of it being in a state $|n'l'm'\rangle$ (assuming $|n'l'm'\rangle$ is different from $|nlm\rangle$) is

$$|\langle n'l'm'|\psi(\varepsilon)\rangle|^2 = \left|-\frac{i\varepsilon}{\hbar}\langle n'l'm'|H^1|nlm\rangle\right|^2$$

Thus quantum theory can also determine for us the rate of transition to the state $|n'l'm'\rangle$. This rate is controlled by the matrix element $\langle n'l'm'|H^1|nlm\rangle$, which in coordinate space, will be some integral over $\psi^*_{n'l'm'}$ and ψ_{nlm} with H^1 sandwiched between them. The evaluation of the integrals entails detailed knowledge of the wave functions, and conversely, agreement of the calculated rates with experiment is a check on the predicted wave functions. We shall see a concrete example of this when we discuss the interaction of radiation with matter in Chapter 18.

Exercise 13.3.3. Instead of looking at the emission spectrum, we can also look at the *absorption* spectrum of hydrogen. Say some hydrogen atoms are sitting at the surface of the sun. From the interior of the sun, white light tries to come out and the atoms at the surface absorb what they can. The atoms in the ground state will now *absorb* the Lyman series and this will lead to dark lines if we analyze the light coming from the sun. The presence of these lines will tell us that there is hydrogen at the surface of the sun. We can also estimate the surface temperature as follows. Let T be the surface temperature. The probabilities $P(n = 1)$ and $P(n = 2)$ of an atom being at $n = 1$ and $n = 2$, respectively, are related by Boltzmann's formula

$$\frac{P(n=2)}{P(n=1)} = 4e^{-(E_2-E_1)/kT}$$

where the factor 4 is due to the degeneracy of the $n = 2$ level. Now only atoms in $n = 2$ can produce the Balmer lines in the absorption spectrum. The relative strength of the Balmer and Lyman lines will tell us $P(n = 2)/P(n = 1)$, from which we may infer T. Show that for $T = 6000°\text{K}$, $P(n = 2)/P(n = 1)$ is negligible and that it becomes significant only for $T \simeq 10^5\,°\text{K}$. (The Boltzmann constant is $k \simeq 9\times10^{-5}$ eV/°K. A mnemonic is $kT \simeq \frac{1}{40}$ eV at room temperature, $T = 300°\text{K}$.)

13.4. Multielectron Atoms and the Periodic Table

It is not possible to treat multielectron atoms analytically even if we treat the nucleus as immobile. Although it is possible, in principle, to treat an arbitrarily complex atom by solving the exact Schrödinger equation numerically, a more practical method is to follow some approximation scheme. Consider the one due to Hartree. Here one assumes that each electron obeys a one-particle Schrödinger equation wherein the potential energy $V = -e\phi(r)$ is due to the nucleus and the other electrons. In computing the electronic contribution to $\phi(r)$, each electron is assigned a charge distribution which is $(-e)$ times the probability density associated with its wave function. And what are the wave functions? They are the eigenstates in the potential $\phi(r)$! To break the vicious circle, one begins with a reasonable guess for the potential, call it $\phi_0(r)$, and computes the allowed energy eigenstates. One then fills them up in the order of increasing energy, putting in just two electrons in each orbital state, with opposite spins (the Pauli principle will not allow any more)‡ till all the electrons have been used up. One then computes the potential $\phi_1(r)$ due to this electronic configuration.§ If it coincides with $\phi_0(r)$ (to some desired accuracy) one stops here and takes the configuration one got to be the ground state of the atom. If not, one goes through one more round, this time starting with $\phi_1(r)$. The fact that, in practice, one soon finds a potential that reproduces itself, signals the soundness of this scheme.

What do the eigenstates look like? They are still labeled by (nlm) as in hydrogen, with states of different m degenerate at a given n and l. [This is because $\phi(r)$ is rotationally invariant.] The degeneracy in l is, however, lost. Formally this is because the potential is no longer $1/r$ and physically this is because states with lower angular momentum have a larger amplitude to be near the origin and hence sample more of the nuclear charge, while states of high angular momentum, which are suppressed at the origin, see the nuclear charge shielded by the electrons in the inner orbits. *As a result,*

---

‡ In this discussion electron spin is viewed as a spectator variable whose only role is to double the states. This is a fairly good approximation.

§ If necessary, one averages over angles to get a spherically symmetric ϕ.

at each n the energy goes up with l. The "radius" of each state grows with n, with a slight dependence on l. States of a given n are thus said to form a *shell* (for, in a semiclassical sense, they may be viewed as moving on a sphere of radius equal to the most probable value of r). States of a given l and n are said to form a *subshell.*

Let us now consider the electronic configurations of some low Z (Z is the nuclear charge) atoms. Hydrogen (^{1}H) has just one electron, which is in the $1s$ state. This configuration is denoted by $1s^1$. Helium (^{2}He) has two electrons in the $1s$ state with opposite spins, a configuration denoted by $1s^2$. ^{2}He has its $n = 1$ shell filled. Lithium (^{3}Li) has its third electron in the $2s$ state, i.e., it is in the configuration $1s^2 2s^1$. (Recall that the s state is lower than the p state.) We keep going this way through beryllium (^{4}Be), boron (^{5}B), carbon (^{6}C), nitrogen (^{7}N), oxygen (^{8}O), fluorine (^{9}F), till neon (^{10}Ne). Neon is in the configuration $1s^2 2s^2 2p^6$, i.e., has its $n = 2$ shell filled. The next element, sodium (^{11}Na), has a solitary electron in the $3s$ state. The $3s$ and $3p$ subshells are filled when we get to argon (^{18}Ar). The next one, potassium (^{19}K) has its nineteenth electron in the $4s$ and not $3d$ state. This is because the growth in energy due to a change in n from 3 to 4 is less than the growth due to change in l from 2 to 3 at $n = 3$. This phenomenon occurs often as we move up in Z. For example, in the "rare earth" elements, the $6s$ shell is filled before the $4f$ shell.

Given the electronic configurations, one can anticipate many of the chemical properties of the elements. Consider an element such as ^{10}Ne, which has a closed outer shell. Since the total electronic charge is spherically symmetric ($|R_{nl}|^2 \sum_{m=-l}^{l} |Y_l^m|^2$ is independent of θ and ϕ), it shields the nuclear charge very effectively and the atom has no significant electrostatic affinity for electrons in other atoms. If one of the electrons in the outer shell could be excited to a higher level, this would change, but there is a large gap in energy to cross. Thus the atom is rarely excited and is chemically inert. On the other hand, consider an element like ^{11}Na, which has one more electron, which occupies the $3s$ state. This electron sees a charge of $+e$ when it looks inward (the nuclear charge of 11 shielded by the 10 electrons in the $n = 1$ and 2 shells) and is thus very loosely bound. Its binding energy is 5.1 eV compared to an $n = 2$ electron in Ne, which has a binding energy of 21.6 eV. If ^{11}Na could get rid of this electron, it could reach a stable configuration with a closed $n = 2$ shell. If we look one place to the left (in Z) of ^{10}Ne, we see a perfect acceptor for this electron: we have here ^{9}F, whose $n = 2$ shell is all full except for one electron. So when ^{11}Na and ^{9}F get together, Na passes on its electron to F and the system as a whole lowers its energy, since the binding energy in F is 17.4 eV.

Having carried out the transfer, the atoms cannot part company, for they have now become charged ions, Na$^+$ and F$^-$, which are held together by electrostatic attraction, called the *ionic bond* and form the NaF molecule.

Once we grasp that the chemical behavior is dictated by what is happening in the outermost shell, we can see that several elements will have similar chemical properties because they have similar outer shells. For example, we expect all elements with filled outer shells to be chemically inert. This is true. It is also true that some elements with filled *sub*shells are also inert, such as ^{18}Ar, in which just the $3s$ and $3p$ subshells are filled. The origin of this inertness is the same as in the case with filled shells: a spherically symmetric electronic charge distribution and a large excitation energy. If we move one place to the right of the inert elements, we meet those that behave like Na, i.e., eager to give up an electron, while if we move one place to the left, we meet the likes of F, eager to accept an electron. If we move two places to the left, we see the likes of oxygen, which want two electrons, while two places to the right we have elements like magnesium, which want to get rid of two electrons. It follows that as we move in Z, we see a certain chemical tendency over and over again. This quasiperiodic behavior was emphasized in 1869 by Mendeleev, who organized the elements into a *periodic table*, in which the elements are arranged into a matrix, with all similar elements in the same column. As we go down the first column, for example, we see H, Li, Na, etc., i.e., elements with one electron to spare. In the last column we see the inert elements, He, Ne, etc. Given the maxim that happiness is a filled outer shell, we can guess who will interact with whom. For instance, not only can Na give its electron to F, it can give to Cl, which is one shy of a filled $3p$ subshell. Likewise F can get its electron from K as well, which has a lone electron in the $4s$ state. More involved things can happen, such as the formation of H_2O when two H atoms get together with an oxygen atom, forming the *covalent bond*, in which each hydrogen atom shares an electron with the oxygen atom. This way all three atoms get to fill their outer shells at least part of the time.

There are many more properties of elements that follow from the configuration of the outer electrons. Consider the *rare earth* elements, ^{58}Ce through ^{71}Lu, which have very similar chemical properties. Why doesn't the chemical behavior change with Z in this range? The answer is that in these elements the $6s$ subshell *is* filled and the $4f$ subshell, deep in the interior (but of a higher energy), is *being* filled. Since what happens in the interior does not affect the chemical properties, they all behave alike. The same goes for the *actinides*, ^{90}Th to ^{103}Lw, which have a filled $7s$ subshell and a $5f$ subshell that is getting filled up.

Since we must stop somewhere, let us stop here. If you want to know more, you must consult books devoted to the subject.[‡]

*Exercise 13.4.1.** Show that if we ignore interelectron interactions, the energy levels of a multielectron atom go as Z^2. Since the Coulomb potential is Ze/r, why is the energy $\propto Z^2$?

*Exercise 13.4.2.** Compare (roughly) the sizes of the uranium atom and the hydrogen atom. Assume levels fill in the order of increasing n, and that the nonrelativistic description holds. Ignore interelectron effects.

*Exercise 13.4.3.** Visible light has a wavelength of approximately 5000 Å. Which of the series–Lyman, Balmer, Paschen—do you think was discovered first?

[‡] See, for a nice trip through the Periodic Table, Chapter 18 of *Basic Physics of Atoms and Molecules*, U. Fano and L. Fano, Wiley, New York (1959).

14

Spin

14.1. Introduction

In this chapter we consider a class of quantum phenomena that cannot be handled by a straightforward application of the four postulates. The reason is that these phenomena involve a quantum degree of freedom called *spin*, which has no classical counterpart. Consequently, neither can we obtain the spin operator by turning to Postulate II, nor can we immediately write down the quantum Hamiltonian that governs its time evolution. The problem is very important, for most particles—electrons, protons, neutrons, photons—have the spin degree of freedom. Fortunately the problem can be solved by a shrewd mixture of classical intuition and reasoning by analogy. In this chapter we study just electron spin. The treatment of the spins of other particles is quite similar, with the exception of the photon, which moves at speed c and can't be treated nonrelativistically. Photon spin will be discussed in Chapter 18.

In the next three sections we address the following questions:

(i) What is the nature of this new spin degree of freedom?

(ii) How is the Hilbert space modified to take this new degree of freedom into account? What do the spin operators look like in this space (kinematics of spin)?

(iii) How does spin evolve with time, i.e., how does it enter the Hamiltonian (dynamics of spin)?

14.2. What is the Nature of Spin?

The best way to characterize spin is as a form of angular momentum. It is, however, not the angular momentum associated with the operator **L**, as the following experiment shows. An electron is prepared in a state of zero linear momentum, i.e., in a state with a constant (space-independent)