

The energies of the ground and first excited states are

$$E_{110} = \frac{\pi^2 \hbar^2}{ma^2} + \frac{\hbar\omega}{2} - \frac{q^2 \epsilon^2}{2m\omega^2}, \quad E_{120} = E_{210} = \frac{5\pi^2 \hbar^2}{ma^2} + \frac{3\hbar\omega}{2} - \frac{q^2 \epsilon^2}{2m\omega^2}. \quad (6.209)$$

Problem 6.2

Show how one obtains the expressions of: (a) $\langle nl|r^{-2}|nl\rangle$ and (b) $\langle nl|r^{-1}|nl\rangle$; that is, prove (6.176) and (6.175).

Solution

The starting point is the radial equation (6.120),

$$-\frac{\hbar^2}{2\mu} \frac{d^2 U_{nl}(r)}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r} \right] U_{nl}(r) = E_n U_{nl}(r), \quad (6.210)$$

which can be rewritten as

$$\frac{U_{nl}''(r)}{U_{nl}(r)} = \frac{l(l+1)}{r^2} - \frac{2\mu e^2}{\hbar^2} \frac{1}{r} + \frac{\mu^2 e^4}{\hbar^4 n^2}, \quad (6.211)$$

where $U_{nl}(r) = r R_{nl}(r)$, $U_{nl}''(r) = d^2 U_{nl}(r)/dr^2$ and $E_n = \mu e^4/(2\hbar^2 n^2)$.

(a) To find $\langle r^{-2} \rangle_{nl}$, let us treat the orbital quantum number l as a continuous variable and take the first l derivative of (6.211):

$$\frac{\partial}{\partial l} \left[\frac{U_{nl}''(r)}{U_{nl}(r)} \right] = \frac{2l+1}{r^2} - \frac{2\mu^2 e^4}{\hbar^4 n^3}, \quad (6.212)$$

where we have the fact that n depends on l since, as shown in (6.138), $n = N + l + 1$; thus $\partial n/\partial l = 1$. Now since $\int_0^\infty U_{nl}^2(r) dr = \int_0^\infty r^2 R_{nl}^2(r) dr = 1$, multiplying both sides of (6.212) by $U_{nl}^2(r)$ and integrating over r we get

$$\int_0^\infty U_{nl}^2(r) \frac{\partial}{\partial l} \left[\frac{U_{nl}''(r)}{U_{nl}(r)} \right] dr = (2l+1) \int_0^\infty U_{nl}^2(r) \frac{1}{r^2} dr - \frac{2\mu^2 e^4}{\hbar^4 n^3} \int_0^\infty U_{nl}^2(r) dr, \quad (6.213)$$

or to

$$\int_0^\infty U_{nl}^2(r) \frac{\partial}{\partial l} \left[\frac{U_{nl}''(r)}{U_{nl}(r)} \right] dr = (2l+1) \left\langle nl \left| \frac{1}{r^2} \right| nl \right\rangle - \frac{2\mu^2 e^4}{\hbar^4 n^3}. \quad (6.214)$$

The left-hand side of this relation is equal to zero, since

$$\int_0^\infty U_{nl}^2(r) \frac{\partial}{\partial l} \left[\frac{U_{nl}''(r)}{U_{nl}(r)} \right] dr = \int_0^\infty U_{nl}(r) \frac{\partial U_{nl}''(r)}{\partial l} dr - \int_0^\infty U_{nl}''(r) \frac{\partial U_{nl}(r)}{\partial l} dr = 0. \quad (6.215)$$

We may therefore rewrite (6.214) as

$$(2l+1) \left\langle nl \left| \frac{1}{r^2} \right| nl \right\rangle = \frac{2\mu^2 e^4}{\hbar^4 n^3}, \quad (6.216)$$

hence

$$\left\langle nl \left| \frac{1}{r^2} \right| nl \right\rangle = \frac{2}{n^3 (2l+1) a_0^2}, \quad (6.217)$$

since $a_0 = \hbar^2/(\mu e^2)$.

(b) To find $\langle r^{-1} \rangle_{nl}$ we need now to treat the electron's charge e as a continuous variable in (6.211). The first e -derivative of (6.211) yields

$$\frac{\partial}{\partial e} \left[\frac{U''_{nl}(r)}{U_{nl}(r)} \right] = -\frac{4\mu e}{\hbar^2} \frac{1}{r} + \frac{4\mu^2 e^3}{\hbar^4 n^2}. \quad (6.218)$$

Again, since $\int_0^\infty U_{nl}^2(r) dr = 1$, multiplying both sides of (6.218) by $U_{nl}^2(r)$ and integrating over r we obtain

$$\int_0^\infty U_{nl}^2(r) \frac{\partial}{\partial e} \left[\frac{U''_{nl}(r)}{U_{nl}(r)} \right] dr = -\frac{4\mu e}{\hbar^2} \int_0^\infty U_{nl}^2(r) \frac{1}{r} dr + \frac{4\mu^2 e^3}{\hbar^4 n^2} \int_0^\infty U_{nl}^2(r) dr, \quad (6.219)$$

or to

$$\int_0^\infty U_{nl}^2(r) \frac{\partial}{\partial e} \left[\frac{U''_{nl}(r)}{U_{nl}(r)} \right] dr = -\frac{4\mu e}{\hbar^2} \left\langle nl \left| \frac{1}{r} \right| nl \right\rangle + \frac{4\mu^2 e^3}{\hbar^4 n^2}. \quad (6.220)$$

As shown in (6.215), the left-hand side of this is equal to zero. Thus, we have

$$\frac{4\mu e}{\hbar^2} \left\langle nl \left| \frac{1}{r} \right| nl \right\rangle = \frac{4\mu^2 e^3}{\hbar^4 n^2} \implies \left\langle nl \left| \frac{1}{r} \right| nl \right\rangle = \frac{1}{n^2 a_0}, \quad (6.221)$$

since $a_0 = \hbar^2/(\mu e^2)$.

Problem 6.3

(a) Use Kramer's recursion rule (6.177) to obtain (6.173) to (6.175) for $\langle nl|r^{-1}|nl\rangle$, $\langle nl|r|nl\rangle$ and $\langle nl|r^2|nl\rangle$.

(b) Using (6.217) for $\langle nl|r^{-2}|nl\rangle$ and combining it with Kramer's rule, obtain the expression for $\langle nl|r^{-3}|nl\rangle$.

(c) Repeat (b) to obtain the expression for $\langle nl|r^{-4}|nl\rangle$.

Solution

(a) First, to obtain $\langle nl|r^{-1}|nl\rangle$, we need simply to insert $k = 0$ into Kramer's recursion rule (6.177):

$$\frac{1}{n^2} \langle nl|r^0|nl\rangle - a_0 \langle nl|r^{-1}|nl\rangle = 0, \quad (6.222)$$

hence

$$\left\langle nl \left| \frac{1}{r} \right| nl \right\rangle = \frac{1}{n^2 a_0}. \quad (6.223)$$

Second, an insertion of $k = 1$ into (6.177) leads to the relation for $\langle nl|r|nl\rangle$:

$$\frac{2}{n^2} \langle nl|r|nl\rangle - 3a_0 \langle nl|r^0|nl\rangle + \frac{a_0^2}{4} [(2l+1)^2 - 1] \langle nl|r^{-1}|nl\rangle = 0, \quad (6.224)$$

and since $\langle nl|r^{-1}|nl\rangle = 1/(n^2 a_0)$, we have

$$\langle nl|r|nl\rangle = \frac{1}{2} [3n^2 - l(l+1)] a_0. \quad (6.225)$$

Third, substituting of $k = 2$ into (6.177) we get

$$\frac{3}{n^2} \langle nl | r^2 | nl \rangle - 5a_0 \langle nl | r | nl \rangle + \frac{a_0^2}{2} [(2l+1)^2 - k^2] \langle nl | r^0 | nl \rangle = 0, \quad (6.226)$$

which when combined with $\langle nl | r | nl \rangle = \frac{1}{2} [3n^2 - l(l+1)] a_0$ yields

$$\boxed{\langle nl | r^2 | nl \rangle = \frac{1}{2} n^2 [5n^2 + 1 - 3l(l+1)] a_0^2.} \quad (6.227)$$

We can continue in this way to obtain any positive power of r : $\langle nl | r^k | nl \rangle$.

(b) Inserting $k = -1$ into Kramer's rule,

$$0 + a_0 \langle nl | r^{-2} | nl \rangle - \frac{1}{4} [(2l+1)^2 - 1] a_0^2 \langle nl | r^{-3} | nl \rangle, \quad (6.228)$$

we obtain

$$\langle nl | \frac{1}{r^3} | nl \rangle = \frac{1}{l(l+1)a_0} \langle nl | \frac{1}{r^2} | nl \rangle, \quad (6.229)$$

where the expression for $\langle nl | r^{-2} | nl \rangle$ is given by (6.217); thus, we have

$$\boxed{\langle nl | \frac{1}{r^3} | nl \rangle = \frac{2}{n^3 l(l+1)(2l+1) a_0^3}.} \quad (6.230)$$

(c) To obtain the expression for $\langle nl | r^{-4} | nl \rangle$ we need to substitute $k = -2$ into Kramer's rule:

$$-\frac{1}{n^2} \langle nl | r^{-2} | nl \rangle + 3a_0 \langle nl | r^{-3} | nl \rangle - \frac{a_0^2}{2} [(2l+1)^2 - 4] \langle nl | r^{-4} | nl \rangle = 0. \quad (6.231)$$

Inserting (6.217) and (6.230) for $\langle nl | r^{-2} | nl \rangle$ and $\langle nl | r^{-3} | nl \rangle$, we obtain

$$\boxed{\langle nl | \frac{1}{r^4} | nl \rangle = \frac{4 [3n^2 - l(l+1)]}{n^5 l(l+1)(2l+1) [(2l+1)^2 - 4] a_0^4}.} \quad (6.232)$$

We can continue in this way to obtain any negative power of r : $\langle nl | r^{-k} | nl \rangle$.

Problem 6.4

An electron is trapped inside a infinite spherical well $V(r) = \begin{cases} 0, & r < a \\ +\infty, & r > a. \end{cases}$

(a) Using the radial Schrödinger equation, determine the bound eigenenergies and the corresponding normalized radial wave functions for the case where the orbital angular momentum of the electron is zero (i.e., $l = 0$).

(b) Show that the lowest energy state for $l = 7$ lies above the second lowest energy state for $l = 0$.

(c) Calculate the probability of finding the electron in a sphere of radius $a/2$, and then in a spherical shell of thickness $a/2$ situated between $r = a$ and $r = 3a/2$.

To obtain the total wave function $\psi_{nlm}(\vec{r})$, we need simply to divide the radial function by a factor $1/\sqrt{4\pi}$ factor, because in this case of $l = 0$ the wave function $\psi_{n00}(r)$ depends on no angular degrees of freedom, it depends only on the radius:

$$\psi_{n00}(r) = \frac{1}{\sqrt{4\pi}} R_{n0}(r) = \begin{cases} \sqrt{\frac{2}{4\pi(b-a)}} \frac{1}{r} \sin\left[\frac{n\pi(r-a)}{b-a}\right] & a < r < b \\ 0 & \text{elsewhere.} \end{cases} \quad (6.250)$$

Problem 6.6

(a) For the following cases, calculate the value of r at which the radial probability density of the hydrogen atom reaches its maximum: (i) $n = 1, l = 0, m = 0$ (ii) $n = 2, l = 1, m = 0$ (iii) $l = n - 1, m = 0$.

(b) Compare the values obtained with the Bohr radius for circular orbits.

Solution

(a) Since the radial wave function for $n = 1$ and $l = 0$ is $R_{10}(r) = 2a_0^{-3/2} e^{-r/a_0}$, the probability density is given by

$$P_{10}(r) = r^2 |R_{10}(r)|^2 = \frac{4}{a_0^3} r^2 e^{-2r/a_0}. \quad (6.251)$$

(i) The maximum of $P_{10}(r)$ occurs at r_1

$$\left. \frac{dP_{10}(r)}{dr} \right|_{r=r_1} = 0 \implies 2r_1 - \frac{2r_1^2}{a_0} = 0 \implies r_1 = a_0. \quad (6.252)$$

(ii) Similarly, since $R_{21}(r) = 1/(2\sqrt{6}a_0^{5/2}) r e^{-r/2a_0}$, we have

$$P_{21}(r) = r^2 |R_{21}(r)|^2 = \frac{1}{24a_0^5} r^4 e^{-r/a_0}. \quad (6.253)$$

The maximum of the probability density is given by

$$\left. \frac{dP_{21}(r)}{dr} \right|_{r=r_2} = 0 \implies 4r_2^3 - \frac{r_2^4}{a_0} = 0 \implies r_2 = 4a_0. \quad (6.254)$$

(iii) The radial function for $l = n - 1$ can be obtained from (6.163):

$$R_{n(n-1)}(r) = - \left(\frac{2}{na_0} \right)^{3/2} \frac{1}{\sqrt{2n[(2n-1)!]^3}} \left(\frac{2r}{na_0} \right)^{(n-1)} e^{-r/na_0} L_{2n-1}^{2n-1} \left(\frac{2r}{na_0} \right). \quad (6.255)$$

From (6.152) and (6.153) we can verify that the associated Laguerre polynomial L_{2n-1}^{2n-1} is a constant, $L_{2n-1}^{2n-1}(y) = -(2n-1)!$. We can thus write $R_{n(n-1)}(r)$ as $R_{n(n-1)}(r) = A_n r^{n-1} e^{-r/na_0}$, where A_n is a constant. Hence the probability density is given by

$$P_{n(n-1)}(r) = r^2 |R_{n(n-1)}(r)|^2 = A_n^2 r^{2n} e^{-2r/na_0}. \quad (6.256)$$

The maximum of the probability density is given by

$$\left. \frac{dP_{n(n-1)}(r)}{dr} \right|_{r=r_n} = 0 \implies 2nr_n^{2n-1} - \frac{2r_n^{2n}}{na_0} = 0 \implies r_n = n^2 a_0. \quad (6.257)$$

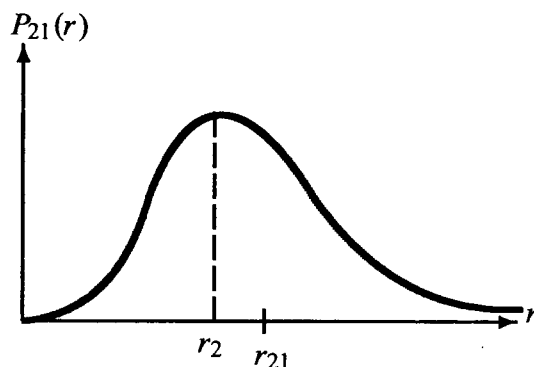


Figure 6.5 The probability density $P_{21}(r) = a_0^5 r^4 e^{-r/a_0} / 24$ is asymmetric about its maximum $r_2 = 4a_0$; the average of r is $r_{21} = 5a_0$ and the width of the probability density is $\Delta r_{21} = \sqrt{5}a_0$.

(b) The values of r_n displayed in (6.252), (6.254), and (6.257) are nothing but the Bohr radii for circular orbits, $r_n = n^2 a_0$. The Bohr radius $r_n = n^2 a_0$ gives the position of maximum probability density for an electron in a hydrogen atom.

Problem 6.7

(a) Calculate the expectation value $\langle r \rangle_{21}$ for the hydrogen atom and compare it with the value r at which the radial probability density reaches its maximum for the state $n = 2, l = 1$.

(b) Calculate the width of the probability density distribution for r .

Solution

(a) Since $R_{21}(r) = r e^{-r/2a_0} / \sqrt{24a_0^5}$ the average value of r in the state $R_{21}(r)$ is

$$\langle r \rangle_{21} = \frac{1}{24a_0^5} \int_0^\infty r^5 e^{-r/a_0} dr = \frac{a_0}{24} \int_0^\infty u^5 e^{-u} du = \frac{120a_0}{24} = 5a_0; \quad (6.258)$$

in deriving this relation we have made use of $\int_0^\infty x^n e^{-x} dx = n!$.

The value r at which the radial probability density reaches its maximum for the state $n = 2, l = 1$ is given by $r_2 = 4a_0$, as shown in (6.254).

What makes the results $r_2 = 4a_0$ and $\langle r \rangle_{21} = 5a_0$ different? The reason that $\langle r \rangle_{21}$ is different from r_2 can be attributed to the fact that the probability density $P_{21}(r)$ is asymmetric about its maximum, as shown in Figure 6.5. Although the most likely location of the electron is at $r_0 = 4a_0$, the average value of the measurement of its location is $\langle r \rangle_{21} = 5a_0$.

(b) The width of the probability distribution is given by $\Delta r = \sqrt{\langle r^2 \rangle_{21} - \langle r \rangle_{21}^2}$, where the expectation value of r^2 is

$$\langle r^2 \rangle_{21} = \int_0^\infty r^3 R_{21}^2(r) dr = \frac{1}{24a_0^5} \int_0^\infty r^6 \exp\left(-\frac{r}{a_0}\right) dr = \frac{6!a_0^7}{24a_0^5} = 30a_0^2. \quad (6.259)$$

Thus, the width of the probability distribution shown in Figure 6.5 is given by

$$\Delta r_{21} = \sqrt{\langle r^2 \rangle_{21} - \langle r \rangle_{21}^2} = \sqrt{30a_0^2 - (5a_0)^2} = \sqrt{5}a_0. \quad (6.260)$$

Table 6.7 Hydrogen energy levels and their degeneracies when the electron's spin is ignored.

n	l	orbitals	m	g_n	E_n
1	0	s	0	1	$-e^2/(2a_0)$
2	0	s	0	4	$-e^2/(8a_0)$
	1	p	-1, 0, 1		
3	0	s	0	9	$-e^2/(18a_0)$
	1	p	-1, 0, 1		
	2	d	-2, -1, 0, 1, 2		
4	0	s	0	16	$-e^2/(32a_0)$
	1	p	-1, 0, 1		
	2	d	-2, -1, 0, 1, 2		
	3	f	-3, -2, -1, 0, 1, 2, 3		
5	0	s	0	25	$-e^2/(50a_0)$
	1	p	-1, 0, 1		
	2	d	-2, -1, 0, 1, 2		
	3	f	-3, -2, -1, 0, 1, 2, 3		
	4	g	-4, -3, -2, -1, 0, 1, 2, 3, 4		

6.3.5.3 Degeneracy of the Bound States of Hydrogen

Besides being independent of m , which is a property of central potentials (see (6.55)), the energy levels (6.140) are also independent of l . This *additional degeneracy* in l is not a property of central potentials, but a *particular feature of the Coulomb potential*. In the case of central potentials, the energy E usually depends on two quantum numbers: one radial, n , and the other orbital, l , giving E_{nl} .

The total quantum number n takes only nonzero values $1, 2, 3, \dots$. As displayed in Table 6.7, for a given n , the quantum l number may vary from 0 to $n - 1$; and for each l , m can take $(2l + 1)$ values: $m = -l, -l + 1, \dots, l - 1, l$. The degeneracy of the state n , which is specified by the total number of different states associated with n , is then given by

$$g_n = \sum_{l=0}^{n-1} (2l + 1) = n^2. \quad (6.164)$$

Remarks

- The state of every hydrogenic electron is specified by three quantum numbers (n, l, m) , called sing-particle state or *orbital*, $|nlm\rangle$. According to the spectroscopic notation, the states corresponding to the respective numerical values $l = 0, 1, 2, 3, 4, 5, \dots$ are called the s, p, d, f, g, h, \dots states; the letters s, p, d, f refer to sharp, principal, diffuse, and fundamental labels, respectively (the letters g, h, \dots have yet to be assigned labels, the reader then is free to guess how to refer to them!). Hence, as shown in Table 6.7, for

a given n an s-state has 1 orbital $|n00\rangle$, a p-state has 3 orbitals $|n1m\rangle$ corresponding to $m = -1, 0, 1$, a d-state has 5 orbitals $|n2m\rangle$ corresponding to $m = -2, -1, 0, 1, 2$, and so on.

- If we take into account the spin of the electron, the state of every electron will be specified by four quantum numbers (n, l, m_l, m_s) , where $m_s = \pm \frac{1}{2}$ is the z-component of the spin of the electron. Hence the complete wave function of the hydrogen atom must be equal to the product of a space part or orbital $\psi_{nlm_l}(r, \theta, \varphi) = R_{nl}(r)Y_{lm_l}(\theta, \varphi)$, and a spin part $\left| \frac{1}{2}, m_s \right\rangle$:

$$\Psi_{nlm_l m_s}(\vec{r}) = \psi_{nlm_l}(r, \theta, \varphi) \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle = R_{nl}(r)Y_{lm_l}(\theta, \varphi) \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle. \quad (6.165)$$

Using the spinors from Chapter 5 we can write the spin-up wave function as

$$\Psi_{nlm_l \frac{1}{2}}(\vec{r}) = \psi_{nlm_l}(r, \theta, \varphi) \left| \frac{1}{2}, \frac{1}{2} \right\rangle = \psi_{nlm_l} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \psi_{nlm_l} \\ 0 \end{pmatrix}, \quad (6.166)$$

and the spin-down wave function as

$$\Psi_{nlm_l -\frac{1}{2}}(\vec{r}) = \psi_{nlm_l}(r, \theta, \varphi) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = \psi_{nlm_l} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ \psi_{nlm_l} \end{pmatrix}, \quad (6.167)$$

For instance, the spin-up and spin-down *ground state* wave functions of hydrogen are given by

$$\Psi_{100 \frac{1}{2}}(\vec{r}) = \begin{pmatrix} \psi_{100} \\ 0 \end{pmatrix} = \begin{pmatrix} (1/\sqrt{\pi})a_0^{-3/2}e^{-r/a_0} \\ 0 \end{pmatrix}, \quad (6.168)$$

$$\Psi_{100 -\frac{1}{2}}(\vec{r}) = \begin{pmatrix} 0 \\ \psi_{100} \end{pmatrix} = \begin{pmatrix} 0 \\ (1/\sqrt{\pi})a_0^{-3/2}e^{-r/a_0} \end{pmatrix}. \quad (6.169)$$

- When spin is included the degeneracy of the hydrogen's energy levels is given by

$$2 \sum_{l=0}^{n-1} (2l+1) = 2n^2, \quad (6.170)$$

since, in addition to the degeneracy (6.164), each level is doubly degenerate with respect to the spin degree of freedom. For instance, the ground state of hydrogen is doubly degenerate since $\Psi_{100 \frac{1}{2}}(\vec{r})$ and $\Psi_{100 -\frac{1}{2}}(\vec{r})$ correspond to the same energy -13.6 eV. Similarly, the first excited state is eightfold degenerate ($2(2)^2 = 8$) because the eight states $\Psi_{200 \pm \frac{1}{2}}(\vec{r})$, $\Psi_{211 \pm \frac{1}{2}}(\vec{r})$, $\Psi_{210 \pm \frac{1}{2}}(\vec{r})$ and $\Psi_{21-1 \pm \frac{1}{2}}(\vec{r})$ correspond to the same energy $-13.6 \text{ eV}/4 = -3.4$ eV.

6.3.5.4 Probabilities and Averages



When a hydrogen atom is in the stationary state $\psi_{nlm}(r, \theta, \varphi)$, the quantity $|\psi_{nlm}(r, \theta, \varphi)|^2 d^3r$ represents the probability of finding the electron in the volume element d^3r , where

$d^3r = r^2 \sin \theta dr d\theta d\varphi$. The probability of finding the electron in a spherical shell located between r and $r + dr$ (i.e., a shell of thickness dr) is given by

$$\begin{aligned} P_{nl}(r) dr &= \left(\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi |\psi_{nlm}(r, \theta, \varphi)|^2 \right) r^2 dr \\ &= |R_{nl}(r)|^2 r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} Y_{lm}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) d\varphi \\ &= |R_{nl}(r)|^2 r^2 dr. \end{aligned} \quad (6.171)$$

If we integrate this quantity between $r = 0$ and $r = a$, we obtain the probability of finding the electron in a sphere of radius a centered about the origin. Hence integrating between $r = 0$ and $r = \infty$, we would obtain 1, which is the probability of finding the electron somewhere in space.

Let us now specify the average values of the various powers of r . Since $\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi)$, we can see that the average of r^k is independent of the azimuthal quantum number m :

$$\begin{aligned} \langle nlm | r^k | nlm \rangle &= \int r^k |\psi_{nlm}(r, \theta, \varphi)|^2 r^2 \sin \theta dr d\theta d\varphi \\ &= \int_0^\infty r^{k+2} |R_{nl}(r)|^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} Y_{lm}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) d\varphi \\ &= \int_0^\infty r^{k+2} |R_{nl}(r)|^2 dr \\ &= \langle nl | r^k | nl \rangle. \end{aligned} \quad (6.172)$$

Using the properties of Laguerre polynomials, we can show that (Problem 6.2 page 353)

$$\langle nl | r | nl \rangle = \frac{1}{2} [3n^2 - l(l+1)] a_0, \quad (6.173)$$

$$\langle nl | r^2 | nl \rangle = \frac{1}{2} n^2 [5n^2 + 1 - 3l(l+1)] a_0^2, \quad (6.174)$$

$$\langle nl | r^{-1} | nl \rangle = \frac{1}{n^2 a_0}, \quad (6.175)$$

$$\langle nl | r^{-2} | nl \rangle = \frac{2}{n^3 (2l+1) a_0^2}, \quad (6.176)$$

where a_0 is the Bohr radius, $a_0 = \hbar^2/(\mu e^2)$. The averages (6.173) to (6.176) can be easily found from Kramer's recursion relation (Problem 6.3 page 354):

$$\frac{k+1}{n^2} \langle nl | r^k | nl \rangle - (2k+1) a_0 \langle nl | r^{k-1} | nl \rangle + \frac{k a_0^2}{4} [(2l+1)^2 - k^2] \langle nl | r^{k-2} | nl \rangle = 0. \quad (6.177)$$

Equations (6.173) and (6.175) reveal that $1/\langle r \rangle$ and $\langle 1/r \rangle$ are not equal, but are of the same order of magnitude:

$$\langle r \rangle \sim n^2 a_0, \quad (6.178)$$

This relation is in agreement with the expression obtained from the Bohr theory of hydrogen: the quantized radii of circular orbits for the hydrogen atom are given by $r_n = n^2 a_0$. We will

show in Problem 6.6 page 358 that the Bohr radii for circular orbits give the locations where the probability density of finding the electron reaches its maximum.

Next, using the expression (6.175) for $\langle r^{-1} \rangle$, we can obtain the average value of the Coulomb potential

$$\langle V(r) \rangle = -e^2 \left\langle \frac{1}{r} \right\rangle = -\frac{e^2}{a_0} \frac{1}{n^2}, \quad (6.179)$$

which, as specified by (6.140), is equal to twice the total energy:

$$E_n = \frac{1}{2} \langle V(r) \rangle = -\frac{e^2}{2a_0} \frac{1}{n^2}. \quad (6.180)$$

This is known as the virial theorem, which states that if $V(ar) = \alpha^n V(r)$, the average expressions of the kinetic and potential energies are related by

$$\langle T \rangle = \frac{n}{2} \langle V(r) \rangle. \quad (6.181)$$

For instance, in the case of a Coulomb potential $V(ar) = \alpha^{-1} V(r)$, we have $\langle T \rangle = -\frac{1}{2} \langle V \rangle$, hence $E = -\frac{1}{2} \langle V \rangle + \langle V \rangle = \frac{1}{2} \langle V \rangle$.

Example 6.3 (Degeneracy relation for the hydrogen atom)

Prove the degeneracy relation (6.164) for the hydrogen atom.

Solution

The energy $E_n = -e^2/(2a_0n^2)$ of the hydrogen atom (6.140) does not depend on the orbital quantum number l or on the azimuthal number m , it depends only on the principal quantum number n . For a given n , the orbital number l can take $n-1$ values: $l = 0, 1, 2, 3, \dots, n-1$; while for each l , the azimuthal number m takes $2l+1$ values: $m = -l, -l+1, \dots, l-1, l$. Thus, for each n , there exist g_n different wave functions $\psi_{nlm}(\vec{r})$, which correspond to the same energy E_n , with

$$g_n = \sum_{l=0}^{n-1} (2l+1) = \sum_{l=0}^{n-1} 1 + 2 \sum_{l=0}^{n-1} l = n + 2n(n-1) = n^2. \quad (6.182)$$

Another way of finding this result consists of writing $\sum_{l=0}^{n-1} (2l+1)$ in the following two equivalent forms:

$$g_n = 1 + 3 + 5 + 7 + \dots + (2n-7) + (2n-5) + (2n-3) + (2n-1), \quad (6.183)$$

$$g_n = (2n-1) + (2n-3) + (2n-5) + (2n-7) + \dots + 7 + 5 + 3 + 1, \quad (6.184)$$

and then add them, term by term:

$$2g_n = (2n) + (2n) + (2n) + (2n) + \dots + (2n) + (2n) + (2n) + (2n). \quad (6.185)$$

Since there are n terms (because l can take n values: $l = 0, 1, 2, 3, \dots, n-1$), we have $2g_n = n(2n)$ hence $g_n = n^2$.