

The Hydrogen Atom

PROBLEMS AND SOLUTIONS

6-1. Show that both  $\hbar^2 \nabla^2 / 2m_e$  and  $e^2 / 4\pi \epsilon_0 r$  have the units of energy (joules).

Recall that  $\nabla^2$  has units of  $m^{-2}$  (Section 5-8), so

$$\frac{\hbar^2 \nabla^2}{2m_e} \sim J^2 \cdot s^2 \cdot m^{-2} \cdot kg^{-1} = J$$

$$\frac{e^2}{4\pi \epsilon_0 r} \sim \frac{C^2}{C^2 \cdot s^2 \cdot kg^{-1} \cdot m^{-3} \cdot m} = kg \cdot m^2 \cdot s^{-2} = J$$

6-2. In terms of the variable  $\theta$ , Legendre's equation is

$$\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + (\beta^2 \sin^2 \theta - m^2) \Theta(\theta) = 0$$

Let  $x = \cos \theta$  and  $P(x) = \Theta(\theta)$  and show that

$$(1-x^2) \frac{d^2 P(x)}{dx^2} - 2x \frac{dP(x)}{dx} + \left[ \beta - \frac{m^2}{1-x^2} \right] P(x) = 0$$

Begin with Legendre's equation,

$$\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + (\beta^2 \sin^2 \theta - m^2) \Theta(\theta) = 0$$

Expanding the first term in  $\theta$  gives

$$\sin^2 \theta \frac{d^2 \Theta}{d\theta^2} + \sin \theta \cos \theta \frac{d\Theta}{d\theta} + (\beta^2 \sin^2 \theta - m^2) \Theta(\theta) = 0 \quad (1)$$

Let  $x = \cos \theta$  and  $P(x) = \Theta(\theta)$ . Then

$$\begin{aligned} \frac{d\Theta}{d\theta} &= \frac{dP}{dx} \frac{dx}{d\theta} = -\sin \theta \frac{dP}{dx} = -(1-x^2)^{1/2} \frac{dP}{dx} \\ \frac{d^2 \Theta}{d\theta^2} &= \frac{d}{d\theta} \left( \frac{d\Theta}{d\theta} \right) = \frac{dx}{d\theta} \frac{d}{dx} \left[ -(1-x^2)^{1/2} \frac{dP}{dx} \right] \\ &= -\sin \theta \left[ \frac{x}{(1-x^2)^{1/2}} \frac{dP}{dx} - (1-x^2)^{1/2} \frac{d^2 P}{dx^2} \right] \\ &= -x \frac{dP}{dx} + (1-x^2) \frac{d^2 P}{dx^2} \end{aligned}$$

Substituting these expressions into Equation 1 gives

$$(1-x^2)^2 \frac{d^2 P}{dx^2} - 2x(1-x^2) \frac{dP}{dx} + [\beta(1-x^2) - m^2] P = 0$$

$$(1-x^2) \frac{d^2 P(x)}{dx^2} - 2x \frac{dP(x)}{dx} + \left( \beta - \frac{m^2}{1-x^2} \right) P(x) = 0$$

6-3. Show that the Legendre polynomials given in Table 6.1 satisfy Equation 6.23 with  $m = 0$ .

Letting  $m = 0$ , Equation 6.23 becomes

$$(1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + l(l+1)P = 0$$

For  $l = 0$ ,  $P_0(x) = 1$  and the equation is satisfied. For  $l = 1$ ,  $P_1(x) = x$  and Equation 6.23 becomes

$$-2x + 1(2)x = 0$$

For  $l = 2$ ,  $P_2(x) = \frac{1}{2}(3x^2 - 1)$  and Equation 6.23 becomes

$$(1-x^2)(3) - 2x(3x) + 2(3) \left[ \frac{1}{2}(3x^2 - 1) \right] = 3 - 3x^2 - 6x^2 + 9x^2 - 3 = 0$$

For  $l = 3$ ,  $P_3(x) = \frac{1}{2}(5x^3 - 3x)$  and Equation 6.23 becomes

$$(1-x^2)15x - 2x \left[ \frac{1}{2}(15x^2 - 3) \right] + 3(4) \left[ \frac{1}{2}(5x^3 - 3x) \right] = 15x - 15x^3 - 15x^3 + 3x + 30x^3 - 18x = 0$$

For  $l = 4$ ,  $P_4(x) = \frac{1}{2}(35x^4 - 30x^2 + 3)$  and Equation 6.23 becomes

$$(1-x^2) \left[ \frac{1}{2}(420x^2 - 60) \right] - 2x \left[ \frac{1}{2}(140x^3 - 60x) \right] + 4(5) \left[ \frac{1}{2}(35x^4 - 30x^2 + 3) \right]$$

$$= 210x^2 - 210x^4 - 30 + 30x^2 - 140x^4 + 60x^2 + 350x^4 - 300x^2 + 30 = 0$$

6-4. Show that the orthogonality integral for the Legendre polynomials, Equation 6.24, is equivalent to

$$\int_0^\pi P_l(\cos \theta) P_n(\cos \theta) \sin \theta d\theta = 0 \quad l \neq n$$

Begin with

$$\int_{-1}^1 P_l(x) P_n(x) dx = 0 \quad l \neq n \quad (6.24)$$

Let  $x = \cos \theta$  and  $dx = -\sin \theta d\theta$  and write Equation 6.24 as an integral over  $\theta$ , where  $\theta$  ranges from  $\pi$  to 0:

$$\int_\pi^0 P_l(\cos \theta) P_n(\cos \theta) (-\sin \theta) d\theta = 0$$

Integrating from 0 to  $\pi$  and evaluating the result at the limits of integration yields

$$\int_0^\pi P_l(\cos \theta) P_n(\cos \theta) \sin \theta d\theta = 0$$

where  $l \neq n$ .

6-5. Show that the Legendre polynomials given in Table 6.1 satisfy the orthogonality and normalization conditions given by Equations 6.24 and 6.25.

We can write Equations 6.24 and 6.25 together as

$$\int_{-1}^1 P_l(x) P_n(x) dx = \frac{2\delta_{ln}}{2l+1}$$

Some examples of Legendre polynomials satisfying this condition are (for  $l = 0, 1$  and 2)

$$\int_{-1}^1 P_0^2(x) dx = \int_{-1}^1 dx = 2$$

$$\int_{-1}^1 P_1^2(x) dx = \int_{-1}^1 x^2 dx = \frac{2}{3}$$

$$\int_{-1}^1 P_2^2(x) dx = \frac{1}{4} \int_{-1}^1 (3x^2 - 1)^2 dx = \frac{1}{4} \left( \frac{18}{5} - \frac{12}{3} + 2 \right) = \frac{2}{5}$$

$$\int_{-1}^1 P_0(x) P_1(x) dx = \int_{-1}^1 x dx = 0$$

$$\int_{-1}^1 P_0(x) P_2(x) dx = \frac{1}{2} \int_{-1}^1 (3x^2 - 1) dx = 1 - 1 = 0$$

$$\int_{-1}^1 P_1(x) P_2(x) dx = \frac{1}{2} \int_{-1}^1 (3x^3 - x) dx = 0$$

6-6. Use Equation 6.26 to generate the associated Legendre functions in Table 6.2.

$$P_l^{lm}(x) = (1-x^2)^{|m|/2} \frac{d^m}{dx^m} P_l(x) \quad (6.26)$$

$$P_0^0(x) = (1-x^2)^0 \frac{d^0}{dx^0} P_0(x) = P_0(x) = 1$$

$$P_1^0(x) = (1-x^2)^0 \frac{d^0}{dx^0} P_1(x) = P_1(x) = x$$

$$P_1^1(x) = (1-x^2)^{1/2} \frac{d}{dx} P_1(x) = (1-x^2)^{1/2}$$

$$P_2^0(x) = (1-x^2)^0 \frac{d^0}{dx^0} P_2(x) = P_2(x) = \frac{1}{2}(3x^2 - 1)$$

$$P_2^1(x) = (1-x^2)^{1/2} \frac{d}{dx} P_2(x) = 3x(1-x^2)^{1/2}$$

$$P_2^2(x) = (1-x^2) \frac{d^2}{dx^2} P_2(x) = 3(1-x^2)$$

$$P_3^0(x) = (1-x^2)^0 \frac{d^0}{dx^0} P_3(x) = P_3(x) = \frac{1}{2}(5x^3 - 3x)$$

$$P_3^1(x) = (1-x^2)^{1/2} \frac{d}{dx} P_3(x) = \frac{3}{2}(5x^2-1)(1-x^2)^{1/2}$$

$$P_3^2(x) = (1-x^2) \frac{d^2}{dx^2} P_3(x) = 15x(1-x^2)$$

$$P_3^3(x) = (1-x^2)^{3/2} \frac{d^3}{dx^3} P_3(x) = 15(1-x^2)^{3/2}$$

6-7. Show that the first few associated Legendre functions given in Table 6.2 are solutions to Equation 6.23 and that they satisfy the orthonormality condition, Equation 6.28.

$$(1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left[ l(l+1) - \frac{m^2}{1-x^2} \right] P = 0 \quad (6.23)$$

When  $l = m = 0$ ,  $P_0^0(x) = 1$  and Equation 6.23 is clearly satisfied. When  $l = 1$  and  $m = 0$ ,  $P_1^0(x) = x$  and Equation 6.23 becomes

$$0 - 2x(1) + (2-0)x = 0$$

When  $l = m = 1$ ,  $P_1^1(x) = (1-x^2)^{1/2}$  and Equation 6.23 becomes

$$\begin{aligned} 0 &= (1-x^2) \left[ -\frac{1}{(1-x^2)^{1/2}} - \frac{x^2}{(1-x^2)^{3/2}} \right] - 2x \left[ -\frac{x}{(1-x^2)^{1/2}} \right] \\ &\quad + \left[ 2 - \frac{1}{(1-x^2)} \right] (1-x^2)^{1/2} \\ &= -(1-x^2)^{1/2} - \frac{x^2}{(1-x^2)^{1/2}} + \frac{2x^2}{(1-x^2)^{1/2}} \\ &\quad + 2(1-x^2)^{1/2} - \frac{1}{(1-x^2)^{1/2}} \\ &= \frac{x^2-1}{(1-x^2)^{1/2}} + (1-x^2)^{1/2} = 0 \end{aligned}$$

The orthonormality condition is

$$\int_{-1}^1 P_l^{m_l}(x) P_n^{m_n}(x) dx = \frac{2}{(2l+1)} \frac{(l+|m_l|)!}{(l-|m_l|)!} \delta_{ln} \quad (6.28)$$

Examples of associated Legendre functions satisfying this condition are

$$\int_{-1}^1 [P_1^1(x)]^2 dx = \int_{-1}^1 dx(1-x^2) = \frac{4}{3} = \frac{2}{3} \left( \frac{2!}{0!} \right)$$

$$\int_{-1}^1 [P_2^1(x)]^2 dx = \int_{-1}^1 dx(9x^2 - 9x^4) = \frac{12}{5} = \frac{2}{5} \left( \frac{3!}{1!} \right)$$

$$\int_{-1}^1 P_1^1(x) P_2^1(x) dx = \int_{-1}^1 dx [3x(1-x^2)] = 0$$

6-8. There are a number of recursion formulas for the associated Legendre functions. One that we will have occasion to use in Section 13-12 is

$$(2l+1)xP_l^{m_l}(x) = (l-|m_l|+1)P_{l+1}^{m_l}(x) + (l+|m_l|)P_{l-1}^{m_l}(x)$$

Show that the first few associated Legendre functions in Table 6.2 satisfy this recursion formula.

Let  $l = 1$  and  $m = 0$ :

$$\begin{aligned} 3xP_1^0(x) &\stackrel{?}{=} 2P_2^0(x) + P_0^0(x) \\ 3x^2 &= (3x^2-1) + 1 \end{aligned}$$

Let  $l = m = 1$ :

$$\begin{aligned} 3xP_1^1(x) &\stackrel{?}{=} P_2^1(x) + 2P_0^1(x) \\ 3x(1-x^2)^{1/2} &= 3x(1-x^2)^{1/2} + 0 \end{aligned}$$

$P_0^1(x) = 0$  because  $m$  cannot be greater than  $l$ . Let  $l = 2$  and  $m = 0$ :

$$\begin{aligned} 5xP_2^0(x) &\stackrel{?}{=} 3P_3^0(x) + 2P_1^0(x) \\ \frac{5}{2}(3x^3-x) &\stackrel{?}{=} \frac{3}{2}(5x^3-3x) + 2x \\ \frac{15}{2}x^3 - \frac{5}{2}x &= \frac{15}{2}x^3 - \frac{5}{2}x \end{aligned}$$

Let  $l = 2$  and  $m = 1$ :

$$\begin{aligned} 5xP_2^1(x) &\stackrel{?}{=} 2P_3^1(x) + 3P_1^1(x) \\ 15x^2(1-x^2)^{1/2} &\stackrel{?}{=} (15x^2-3)(1-x^2)^{1/2} + 3(1-x^2)^{1/2} \\ 15x^2(1-x^2)^{1/2} &= 15x^2(1-x^2)^{1/2} \end{aligned}$$

Let  $l = 2$  and  $m = 2$ :

$$\begin{aligned} 5xP_2^2(x) &\stackrel{?}{=} P_3^2(x) + 4P_1^2(x) \\ 15x(1-x^2) &= 15x(1-x^2) + 0 \end{aligned}$$

$P_1^2(x) = 0$ , because  $m$  cannot be greater than  $l$ .

6-9. Show that the first few spherical harmonics in Table 6.3 satisfy the orthonormality condition, Equation 6.31.

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi Y_l^m(\theta, \phi) Y_n^k(\theta, \phi) = \delta_{nl} \delta_{mk} \quad (6.31)$$

The normalization condition is

$$\begin{aligned} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta |Y_0^0(\theta, \phi)|^2 &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta (4\pi)^{-1} \\ &= 2\pi \left( \frac{2}{4\pi} \right) = 1 \end{aligned}$$

$$\begin{aligned} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta |Y_1^0(\theta, \phi)|^2 &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \left( \frac{3 \cos^2 \theta}{4\pi} \right) \\ &= 2\pi \left( \frac{3}{4\pi} \right) \int_{-1}^1 dx x^2 = 1 \end{aligned}$$

$$\begin{aligned} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta |Y_1^1(\theta, \phi)|^2 &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \left( \frac{3 \sin^2 \theta}{8\pi} \right) \\ &= 2\pi \left( \frac{3}{8\pi} \right) \int_{-1}^1 dx (1-x^2) = 1 \end{aligned}$$

The orthogonality condition is

$$\begin{aligned} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta Y_0^0(\theta, \phi)^* Y_1^0(\theta, \phi) &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \left(\frac{3^{1/2} \cos\theta}{4\pi}\right) \\ &= 2\pi \left(\frac{3^{1/2}}{4\pi}\right) \int_{-1}^1 dx x = 0 \\ \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta Y_0^0(\theta, \phi)^* Y_1^{\pm 1}(\theta, \phi) &= \int_0^{2\pi} e^{\pm i\phi} d\phi \int_0^\pi d\theta \sin\theta \left(\frac{3^{1/2} \cos\theta}{2^{5/2}\pi}\right) = 0 \\ \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta Y_1^0(\theta, \phi)^* Y_1^{\pm 1}(\theta, \phi) &= \int_0^{2\pi} e^{\pm i\phi} d\phi \int_0^\pi d\theta \sin\theta \left(\frac{3^{1/2} \sin\theta \cos\theta}{2^{5/2}\pi}\right) = 0 \end{aligned}$$

because we know that  $\int_0^{2\pi} d\phi e^{\pm i\phi} = 0$ .

6-10. Using explicit expressions for  $Y_l^m(\theta, \phi)$ , show that

$$|Y_1^1(\theta, \phi)|^2 + |Y_1^0(\theta, \phi)|^2 + |Y_1^{-1}(\theta, \phi)|^2 = \text{constant}$$

This is a special case of the general theorem

$$\sum_{m=-l}^{+l} |Y_l^m(\theta, \phi)|^2 = \text{constant}$$

known as Unsöld's theorem. What is the physical significance of this result?

$$|Y_1^1(\theta, \phi)|^2 + |Y_1^0(\theta, \phi)|^2 + |Y_1^{-1}(\theta, \phi)|^2 = \frac{3 \sin^2\theta}{8\pi} + \frac{3 \cos^2\theta}{4\pi} + \frac{3 \sin^2\theta}{8\pi} = \frac{3}{4\pi}$$

Unsöld's theorem states that the electron density in a filled subshell is spherically symmetric.

#### Converting Cartesian coordinates to spherical coordinates

In the following problems, we will often need to use the following equations relating Cartesian and spherical coordinates:

$$\begin{aligned} x &= r \sin\theta \cos\phi & r &= (x^2 + y^2 + z^2)^{1/2} \\ y &= r \sin\theta \sin\phi & \phi &= \tan^{-1}\left(\frac{y}{x}\right) \\ z &= r \cos\theta & \theta &= \cos^{-1}\left[\frac{z}{(x^2 + y^2 + z^2)^{1/2}}\right] \end{aligned}$$

From these expressions, we can derive the following relationships:

$$\begin{aligned} \left(\frac{\partial r}{\partial x}\right) &= \sin\theta \cos\phi & \left(\frac{\partial\theta}{\partial x}\right) &= \frac{\cos\theta \cos\phi}{r} & \left(\frac{\partial r}{\partial z}\right) &= \cos\theta \\ \left(\frac{\partial\phi}{\partial x}\right) &= -\frac{\sin\phi}{r \sin\theta} & \left(\frac{\partial r}{\partial y}\right) &= \sin\theta \sin\phi & \left(\frac{\partial\phi}{\partial z}\right) &= -\frac{\sin\theta}{r} \\ \left(\frac{\partial\theta}{\partial y}\right) &= \frac{\cos\theta \sin\phi}{r} & \left(\frac{\partial\phi}{\partial y}\right) &= -\frac{\cos\phi}{r \sin\theta} & \left(\frac{\partial\theta}{\partial z}\right) &= 0 \end{aligned}$$

6-11. In Cartesian coordinates,

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right)$$

Convert this equation to spherical coordinates, showing that

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi}$$

As in Problem 5-30, the chain rule of partial differentiation states that

$$\left(\frac{\partial f}{\partial x}\right) = \left(\frac{\partial f}{\partial r}\right) \left(\frac{\partial r}{\partial x}\right) + \left(\frac{\partial f}{\partial\phi}\right) \left(\frac{\partial\phi}{\partial x}\right) + \left(\frac{\partial f}{\partial\theta}\right) \left(\frac{\partial\theta}{\partial x}\right)$$

and that

$$\left(\frac{\partial f}{\partial y}\right) = \left(\frac{\partial f}{\partial r}\right) \left(\frac{\partial r}{\partial y}\right) + \left(\frac{\partial f}{\partial\phi}\right) \left(\frac{\partial\phi}{\partial y}\right) + \left(\frac{\partial f}{\partial\theta}\right) \left(\frac{\partial\theta}{\partial y}\right)$$

Using the relations between Cartesian and spherical coordinates, we find

$$\begin{aligned} \left(\frac{\partial f}{\partial x}\right) &= \sin\theta \cos\phi \left(\frac{\partial f}{\partial r}\right) + \frac{\cos\theta \cos\phi}{r} \left(\frac{\partial f}{\partial\theta}\right) - \frac{\sin\phi}{r \sin\theta} \left(\frac{\partial f}{\partial\phi}\right) \\ \left(\frac{\partial f}{\partial y}\right) &= \sin\theta \sin\phi \left(\frac{\partial f}{\partial r}\right) + \frac{\cos\theta \sin\phi}{r} \left(\frac{\partial f}{\partial\theta}\right) - \frac{\cos\phi}{r \sin\theta} \left(\frac{\partial f}{\partial\phi}\right) \end{aligned}$$

Now,

$$\begin{aligned} \left(x \frac{\partial f}{\partial y} - y \frac{\partial f}{\partial x}\right) &= r \sin\theta \cos\phi \left(\frac{\partial f}{\partial y}\right) - r \sin\theta \sin\phi \left(\frac{\partial f}{\partial x}\right) \\ &= (r \sin^2\theta \cos\phi \sin\phi - r \sin^2\theta \cos\phi \sin\phi) \left(\frac{\partial f}{\partial r}\right) \\ &\quad + (\sin\theta \cos\theta \cos\phi \sin\phi - \sin\theta \cos\theta \sin\phi \cos\phi) \left(\frac{\partial f}{\partial\theta}\right) \\ &\quad + (\cos^2\phi + \sin^2\phi) \left(\frac{\partial f}{\partial\phi}\right) \\ &= \frac{\partial f}{\partial\phi} \end{aligned}$$

Therefore

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right) = -i\hbar \frac{\partial}{\partial\phi}$$

6-12. Convert  $\hat{L}_x$  and  $\hat{L}_y$  from Cartesian coordinates to spherical coordinates.

We can use our expressions for  $(\partial f/\partial x)$  and  $(\partial f/\partial y)$  from the previous problem. The only new quantity needed is

$$\begin{aligned}\left(\frac{\partial f}{\partial z}\right) &= \left(\frac{\partial f}{\partial r}\right)\left(\frac{\partial r}{\partial z}\right) + \left(\frac{\partial f}{\partial \phi}\right)\left(\frac{\partial \phi}{\partial z}\right) + \left(\frac{\partial f}{\partial \theta}\right)\left(\frac{\partial \theta}{\partial z}\right) \\ \left(\frac{\partial f}{\partial z}\right) &= \cos\theta\left(\frac{\partial f}{\partial r}\right) - \frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \phi}\right)\end{aligned}$$

Then

$$\begin{aligned}\hat{L}_x &= -i\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right] \\ &= -i\hbar\left[(r\sin\theta\cos\theta\sin\phi - r\sin\theta\cos\theta\sin\phi)\frac{\partial}{\partial r} + (-\sin^2\theta\sin\phi - \cos^2\theta\sin\phi)\frac{\partial}{\partial \theta}\right. \\ &\quad \left. - \cot\theta\cos\phi\frac{\partial}{\partial \phi}\right] \\ &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial \theta} - \cot\theta\cos\phi\frac{\partial}{\partial \phi}\right)\end{aligned}$$

and

$$\begin{aligned}\hat{L}_y &= -i\hbar\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right] \\ &= -i\hbar\left[(r\cos\theta\sin\theta\cos\phi - r\cos\theta\sin\theta\cos\phi)\frac{\partial}{\partial r} + (\cos^2\theta\cos\phi - \sin^2\theta\cos\phi)\frac{\partial}{\partial \theta}\right. \\ &\quad \left. - \cot\theta\sin\phi\frac{\partial}{\partial \phi}\right] \\ &= -i\hbar\left(\cos\phi\frac{\partial}{\partial \theta} - \cot\theta\sin\phi\frac{\partial}{\partial \phi}\right)\end{aligned}$$

6-13. Prove that  $\hat{L}^2$  commutes with  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$  but that

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

(Hint: Use Cartesian coordinates.) Do you see a pattern in these formulas?

In Example 6-7, we showed that  $\hat{L}^2$  commutes with  $\hat{L}_z$ . Because the labelling of  $x$ ,  $y$  and  $z$  is arbitrary,  $\hat{L}^2$  must also commute with  $\hat{L}_y$  and  $\hat{L}_x$ . Recall that

$$\begin{aligned}\hat{L}_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) & \hat{L}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{L}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\end{aligned}$$

and now find

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x \\ &= -\hbar^2\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right] \\ &= -\hbar^2\left[y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial x\partial z} - xy\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial x\partial y} + xz\frac{\partial^2}{\partial y\partial z}\right. \\ &\quad \left. - yz\frac{\partial^2}{\partial x\partial z} + z^2\frac{\partial^2}{\partial x\partial y} + xy\frac{\partial^2}{\partial z^2} - x\frac{\partial}{\partial y} - xz\frac{\partial^2}{\partial y\partial z}\right] \\ &= -\hbar^2\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right) = i\hbar\hat{L}_z\end{aligned}$$

$$\begin{aligned}[\hat{L}_y, \hat{L}_z] &= \hat{L}_y\hat{L}_z - \hat{L}_z\hat{L}_y \\ &= -\hbar^2\left[\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) - \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right] \\ &= -\hbar^2\left[z\frac{\partial}{\partial y} + xz\frac{\partial^2}{\partial x\partial y} - yz\frac{\partial^2}{\partial x^2} - x^2\frac{\partial^2}{\partial y\partial z} + xy\frac{\partial^2}{\partial x\partial z}\right. \\ &\quad \left. - xz\frac{\partial^2}{\partial x\partial y} + x^2\frac{\partial^2}{\partial y\partial z} + yz\frac{\partial^2}{\partial x^2} - y\frac{\partial}{\partial z} - xy\frac{\partial^2}{\partial x\partial z}\right] \\ &= -\hbar^2\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right) = i\hbar\hat{L}_x\end{aligned}$$

$$\begin{aligned}[\hat{L}_z, \hat{L}_x] &= \hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z \\ &= -\hbar^2\left[\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) - \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \\ &= -\hbar^2\left[x\frac{\partial}{\partial z} + xy\frac{\partial^2}{\partial y\partial z} - xz\frac{\partial^2}{\partial y^2} - y^2\frac{\partial^2}{\partial x\partial z} + yz\frac{\partial^2}{\partial x\partial y}\right. \\ &\quad \left. - xy\frac{\partial^2}{\partial y\partial z} + y^2\frac{\partial^2}{\partial x\partial z} + xz\frac{\partial^2}{\partial y^2} - z\frac{\partial}{\partial x} - yz\frac{\partial^2}{\partial x\partial y}\right] \\ &= -\hbar^2\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right) = i\hbar\hat{L}_y\end{aligned}$$

These formulas involve a cyclic permutation of  $x$ ,  $y$ , and  $z$ .

6-14. It is a somewhat advanced exercise to prove generally that  $\langle L_x \rangle = \langle L_y \rangle = 0$  (see, however, Problem 6-58), but prove that they are zero at least for the first few  $l$ ,  $m$  states by using the spherical harmonics given in Table 6.3.

Because the labelling of  $x$  and  $y$  is arbitrary, if we can show that  $\langle L_x \rangle = 0$  we will have also shown that  $\langle L_y \rangle$  must equal zero.

$$\langle L_x \rangle = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta Y_l^m(\theta, \phi)^* \hat{L}_x Y_l^m(\theta, \phi)$$

Recall from Problem 6-12 that in spherical coordinates

$$\hat{L}_x = -i\hbar \left( -\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right)$$

For  $l = m = 0$ ,  $Y_0^0$  is a constant and so  $\langle L_x \rangle = 0$ . For  $l = 1$  and  $m = 0$ ,

$$\begin{aligned} \hat{L}_x Y_1^0(\theta, \phi) &= -i\hbar \left( \frac{3}{4\pi} \right)^{1/2} \sin\phi \sin\theta \\ \langle L_x \rangle &= -i\hbar \left( \frac{3}{4\pi} \right) \int_0^{2\pi} d\phi \sin\phi \int_0^\pi d\theta \sin^2\theta \cos\theta \\ &= -i\hbar \left( \frac{3}{4\pi} \right) (0) \int_0^\pi d\theta \sin^2\theta \cos\theta = 0 \end{aligned}$$

For  $l = 1$  and  $m = \pm 1$ ,

$$\begin{aligned} \hat{L}_x Y_1^{\pm 1}(\theta, \phi) &= -i\hbar \left( \frac{3}{8\pi} \right)^{1/2} \left( -\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) e^{\pm i\phi} \sin\theta \\ &= i\hbar \left( \frac{3}{8\pi} \right)^{1/2} (e^{\pm i\phi} \sin\phi \cos\theta \pm i e^{\pm i\phi} \cos\theta \cos\phi) \\ \langle L_x \rangle &= i\hbar \left( \frac{3}{8\pi} \right) \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta (\sin\phi \cos\theta \pm i \cos\theta \cos\phi) \\ &= i\hbar \left( \frac{3}{8\pi} \right) \left[ \int_0^{2\pi} \sin\phi d\phi \int_0^\pi d\theta \sin\theta \cos\theta \pm \int_0^{2\pi} d\phi \cos\phi \int_0^\pi i \sin\theta \cos\theta \right] \\ &= i\hbar \left( \frac{3}{8\pi} \right) \left[ (0) \int_0^\pi d\theta \sin\theta \cos\theta \pm (0) \int_0^\pi i \sin\theta \cos\theta \right] = 0 \end{aligned}$$

**6-15.** For an isolated hydrogen atom, why must the angular momentum vector  $\mathbf{L}$  lie on a cone that is symmetric about the  $z$ -axis? Can the angular momentum operator ever point exactly along the  $z$ -axis?

The uncertainty principle prohibits  $\mathbf{L}$  from lying along the  $z$ -axis. If we observe precise values of  $L^2$  and  $L_z$  we cannot observe precise values of  $L_x$  and  $L_y$ ; therefore (as discussed in Section 6-3) the angular momentum vector must lie on a cone that is symmetric about the  $z$ -axis. If it pointed exactly along the  $z$ -axis, we would know the precise values of  $L_x$  and  $L_y$  (both would be zero) as well as the exact values of  $L^2$  and  $L_z$ , so this can never occur.

**6-16.** Referring to Table 6.5, show that the first few hydrogen atomic wave functions are orthonormal.

The orthonormality condition for hydrogen atomic wave functions is

$$\int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \psi_{n'l'm'}^*(r, \theta, \phi) \psi_{n'l'm}(r, \theta, \phi) = \delta_{nn'} \delta_{ll'} \delta_{mm'} \quad (6.51)$$

We first show that the first few hydrogen atomic wave functions are normalized. For  $\psi_{100}$ ,

$$\int d\tau \psi_{100}^* \psi_{100} = \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \psi_{100}^* \psi_{100}$$

$$\begin{aligned} &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr r^2 \left[ \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-2\sigma} \right] \\ &= 4 \left( \frac{Z}{a_0} \right)^3 \int_0^\infty dr e^{-2\sigma} r^2 \\ &= 4 \int_0^\infty e^{-2\sigma} \sigma^2 d\sigma = 1 \end{aligned}$$

For  $\psi_{200}$ ,

$$\begin{aligned} \int d\tau \psi_{200}^* \psi_{200} &= \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \psi_{200}^* \psi_{200} \\ &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr r^2 \left[ \frac{1}{32\pi} \left( \frac{Z}{a_0} \right)^3 (4 - 4\sigma + \sigma^2) e^{-\sigma} \right] \\ &= \frac{1}{8} \left( \frac{Z}{a_0} \right)^3 \int_0^\infty dr r^2 (4 - 4\sigma + \sigma^2) e^{-\sigma} \\ &= \frac{1}{8} \int_0^\infty d\sigma (4\sigma^2 - 4\sigma^3 + \sigma^4) e^{-\sigma} \\ &= \frac{1}{8} (4 \cdot 2! - 4 \cdot 3! + 4!) = 1 \end{aligned}$$

For  $\psi_{210}$ ,

$$\begin{aligned} \int d\tau \psi_{210}^* \psi_{210} &= \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \psi_{210}^* \psi_{210} \\ &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr r^2 \left[ \frac{1}{32\pi} \left( \frac{Z}{a_0} \right)^3 \sigma^2 \cos^2\theta e^{-\sigma} \right] \\ &= \frac{1}{16} \left( \frac{Z}{a_0} \right)^3 \int_0^\pi d\theta \sin\theta \cos^2\theta \int_0^\infty dr r^2 \sigma^2 e^{-\sigma} \\ &= \frac{1}{16} \int_{-1}^1 dx x^2 \int_0^\infty d\sigma \sigma^4 e^{-\sigma} = \frac{1}{16} \left( \frac{2}{3} \right) (4!) = 1 \end{aligned}$$

For  $\psi_{211}$  or  $\psi_{21-1}$ ,

$$\begin{aligned} \int d\tau \psi_{21\pm 1}^* \psi_{21\pm 1} &= \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \psi_{21\pm 1}^* \psi_{21\pm 1} \\ &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr r^2 \left[ \frac{1}{64\pi} \left( \frac{Z}{a_0} \right)^3 \sigma^2 \sin^2\theta e^{-\sigma} \right] \\ &= \frac{1}{32} \int_0^\pi d\theta \sin^3\theta \int_0^\infty dr r^2 \sigma^2 e^{-\sigma} \\ &= \frac{1}{32} \int_{-1}^1 dx (1 - x^2) \int_0^\infty d\sigma \sigma^4 e^{-\sigma} = \frac{1}{32} \left( \frac{4}{3} \right) (4!) = 1 \end{aligned}$$

We now show that the first few hydrogen atomic wave functions are orthogonal:

$$\begin{aligned} \int d\tau \psi_{100}^* \psi_{200} &= \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \psi_{100}^* \psi_{200} \\ &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr r^2 \left[ \frac{1}{\pi^{1/2}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-\sigma} \right] \left[ \frac{1}{(32\pi)^{1/2}} \left( \frac{Z}{a_0} \right)^{3/2} (2 - \sigma) e^{-\sigma/2} \right] \end{aligned}$$

$$\begin{aligned}
 &= \frac{1}{\sqrt{2}} \left(\frac{Z}{a_0}\right)^3 \int_0^\infty dr r^2 (2 - \sigma) e^{-3\sigma/2} \\
 &= \frac{1}{\sqrt{2}} \int_0^\infty d\sigma (2\sigma^2 - \sigma^3) e^{-3\sigma/2} \\
 &= \frac{1}{\sqrt{2}} \left[ 2 \cdot 2! \left(\frac{2}{3}\right)^3 - 3! \left(\frac{2}{3}\right)^4 \right] = 0
 \end{aligned}$$

In showing that either  $\psi_{100}$  or  $\psi_{200}$  is orthogonal to  $\psi_{210}$ , we find that the integral over  $\theta$  is

$$\int_0^\pi d\theta \sin\theta \cos\theta = \int_{-1}^1 dx x = 0$$

and so these orbitals are orthogonal. Likewise, in showing that either  $\psi_{100}$ ,  $\psi_{200}$  or  $\psi_{210}$  is orthogonal to  $\psi_{211}$  or  $\psi_{21-1}$ , the integral over  $\phi$  is

$$\int_0^{2\pi} d\phi e^{\pm i\phi} = 0$$

and so these orbitals are orthogonal.

6-17. Show explicitly that

$$\hat{H}\psi = -\frac{m_e e^4}{8\varepsilon_0^2 \hbar^2} \psi$$

for the ground state of a hydrogen atom.

The Hamiltonian operator for a hydrogen atom is (Equations 6.2 and 6.3)

$$-\frac{\hbar^2}{2m_e} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] + \frac{e^2}{4\pi\varepsilon_0 r}$$

and from Table 6.5 the ground state wave function of a hydrogen atom is

$$\psi_0 = \frac{1}{\pi^{1/2} a_0^{3/2}} e^{-r/a_0} \quad a_0 = \frac{\varepsilon_0 \hbar^2}{\pi m_e e^2}$$

We can therefore write

$$\begin{aligned}
 \hat{H}\psi_0 &= -\frac{\hbar^2}{2m_e r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi_0}{\partial r} \right) + \frac{e^2 \psi_0}{4\pi\varepsilon_0 r} \\
 &= -\frac{\hbar^2}{(4\pi^2) 2m_e r^2 \pi^{1/2} a_0^{3/2}} \left( -\frac{2r}{a_0} e^{-r/a_0} + \frac{r^2}{a_0^2} e^{-r/a_0} \right) - \frac{e^2}{4\pi\varepsilon_0 r} \frac{1}{\pi^{1/2} a_0^{3/2}} e^{-r/a_0} \\
 &= \left[ \frac{e^2}{4\pi\varepsilon_0 r} - \frac{m_e e^4}{8\varepsilon_0^2 \hbar^2} - \frac{e^2}{4\pi\varepsilon_0 r} \right] \psi_0 \\
 &= -\frac{m_e e^4}{8\varepsilon_0^2 \hbar^2} \psi_0
 \end{aligned}$$

6-18. Show explicitly that

$$\hat{H}\psi = -\frac{m_e e^4}{32\varepsilon_0^2 \hbar^2} \psi$$

for a  $2p_0$  state of a hydrogen atom.

The Hamiltonian operator of a hydrogen atom is the same as in Problem 6-17, and the wave function of the  $2p_0$  state is

$$\psi_{2p_0} = \frac{1}{(32\pi)^{1/2} a_0^{5/2}} r e^{-r/2a_0} \cos\theta \quad a_0 = \frac{\varepsilon_0 \hbar^2}{\pi m_e e^2}$$

We can now write

$$\begin{aligned}
 \hat{H}\psi_{2p_0} &= -\frac{\hbar^2}{2m_e} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi_{2p_0}}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial \psi_{2p_0}}{\partial \theta} \right) \right] + \frac{e^2}{4\pi\varepsilon_0 r} \psi_{2p_0} \\
 &= -\frac{\hbar^2}{2m_e r^2} \frac{1}{(32\pi)^{1/2} a_0^{5/2}} \left[ e^{-r/2a_0} \cos\theta \left( 2r - \frac{r^2}{2a_0} - \frac{3r^2}{2a_0} + \frac{r^3}{4a_0^2} \right) \right. \\
 &\quad \left. + \frac{\hbar^2}{2m_e r^2} \frac{2r \cos\theta}{(32\pi)^{1/2} a_0^{5/2}} e^{-r/2a_0} + \frac{e^2}{4\pi\varepsilon_0 r} \frac{r e^{-r/2a_0}}{(32\pi)^{1/2} a_0^{5/2}} \cos\theta \right] \\
 &= -\frac{\hbar^2}{2m_e} \frac{1}{(32\pi)^{1/2} a_0^{5/2}} \left( \frac{r}{4a_0^2} e^{-r/2a_0} \cos\theta \right) - \frac{1}{(32\pi)^{1/2} a_0^{5/2}} \left( \frac{\hbar^2}{2m_e a_0} - \frac{e^2}{4\pi\varepsilon_0} \right) e^{-r/2a_0} \cos\theta \\
 &= -\frac{\hbar^2}{8m_e a_0^2} \psi_{2p_0} = -\frac{m_e e^4}{32\varepsilon_0^2 \hbar^2} \psi_{2p_0}
 \end{aligned}$$

6-19. Given the first equality, show that the ground-state energy of a hydrogen atom can be written as

$$E_0 = -\frac{\hbar^2}{2m_e a_0^2} = -\frac{e^2}{8\pi\varepsilon_0 a_0} = -\frac{m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} = -\frac{m_e e^4}{8\varepsilon_0^2 \hbar^2}$$

Recall that we can write  $a_0$  as

$$a_0 = \frac{\varepsilon_0 \hbar^2}{\pi m_e e^2} = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}$$

We showed in Problem 6-17 that

$$\hat{H}\psi = -\frac{m_e e^4}{8\varepsilon_0^2 \hbar^2} \psi$$

so we can write

$$\begin{aligned}
 E_0 &= -\frac{m_e e^4}{8\varepsilon_0^2 \hbar^2} = -\frac{m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} = -\frac{e^2}{8\pi\varepsilon_0} \frac{m_e e^2}{4\pi\varepsilon_0 \hbar^2} = -\frac{e^2}{8\pi\varepsilon_0 a_0} \\
 &= -\frac{\hbar^2}{2m_e a_0} \frac{m_e e^2}{4\pi\varepsilon_0 \hbar^2} = -\frac{\hbar^2}{2m_e a_0^2}
 \end{aligned}$$

6-20. Calculate the probability that a hydrogen 1s electron will be found within a distance  $2a_0$  from the nucleus.

This problem is similar to Example 6-10. The wave function for the 1s orbital of hydrogen is

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-\sigma}$$

where  $\sigma = r/a_0$ , and the probability that the electron will be found within a distance  $2a_0$  from the nucleus is

$$\begin{aligned} \text{prob} &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^{2a_0} dr r^2 \frac{1}{\pi} \left( \frac{1}{a_0} \right)^3 e^{-2\sigma} \\ &= 4 \left( \frac{1}{a_0} \right)^3 \int_0^{2a_0} dr r^2 e^{-2\sigma} = 4 \int_0^2 d\sigma \sigma^2 e^{-2\sigma} \\ &= 4 \left( \frac{1}{4} - \frac{13}{4} e^{-4} \right) = 1 - 13e^{-4} = 0.762 \end{aligned}$$

6-21. Calculate the radius of the sphere that encloses a 50% probability of finding a hydrogen 1s electron. Repeat the calculation for a 90% probability.

The probability that a 1s electron will be found within a distance  $Da_0$  of the nucleus is given by

$$\begin{aligned} \text{prob}(D) &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^{Da_0} dr r^2 \frac{1}{\pi} \left( \frac{1}{a_0} \right)^3 e^{-2\sigma} \\ &= 4 \int_0^D d\sigma \sigma^2 e^{-2\sigma} = 1 - e^{-2D}(2D^2 + 2D + 1) \end{aligned}$$

We find that  $D = 1.3$  for  $\text{prob}(D) = 0.50$  and  $D = 2.7$  for  $\text{prob}(D) = 0.90$ , so the 50% and 90% probability spheres have radii of  $1.3a_0$  and  $2.7a_0$ , respectively.

6-22. Many problems involving the calculation of average values for the hydrogen atom require evaluating integrals of the form

$$I_n = \int_0^\infty r^n e^{-\beta r} dr$$

This integral can be evaluated readily by starting with the elementary integral

$$I_0(\beta) = \int_0^\infty e^{-\beta r} dr = \frac{1}{\beta}$$

Show that the derivatives of  $I(\beta)$  are

$$\frac{dI_0}{d\beta} = - \int_0^\infty r e^{-\beta r} dr = -I_1$$

$$\frac{d^2 I_0}{d\beta^2} = \int_0^\infty r^2 e^{-\beta r} dr = I_2$$

and so on. Using the fact that  $I_0(\beta) = 1/\beta$ , show that the values of these two integrals are  $-1/\beta^2$  and  $2/\beta^3$ , respectively. Show that, in general

$$\begin{aligned} \frac{d^n I_0}{d\beta^n} &= (-1)^n \int_0^\infty r^n e^{-\beta r} dr = (-1)^n I_n \\ &= (-1)^n \frac{n!}{\beta^{n+1}} \end{aligned}$$

and that

$$I_n = \frac{n!}{\beta^{n+1}}$$

$$\begin{aligned} I_0(\beta) &= \int_0^\infty e^{-\beta r} dr \\ \frac{dI_0}{d\beta} &= \int_0^\infty \frac{\partial}{\partial \beta} (e^{-\beta r}) dr = - \int_0^\infty r e^{-\beta r} dr = -I_1 \\ \frac{d^2 I_0}{d\beta^2} &= \int_0^\infty \frac{\partial}{\partial \beta} (-r e^{-\beta r}) dr = \int_0^\infty r^2 e^{-\beta r} dr = I_2 \end{aligned}$$

Alternatively, since  $I_0(\beta) = 1/\beta$ ,

$$\begin{aligned} \frac{dI_0}{d\beta} &= \frac{\partial}{\partial \beta} \left( \frac{1}{\beta} \right) = -\frac{1}{\beta^2} \\ \frac{d^2 I_0}{d\beta^2} &= \frac{\partial}{\partial \beta} \left( -\frac{1}{\beta^2} \right) = \frac{2}{\beta^3} \end{aligned}$$

Generally,

$$\begin{aligned} \frac{d^n I_0}{d\beta^n} &= (-1)^n \int_0^\infty r^n e^{-\beta r} dr \\ &= (-1)^n \frac{n!}{\beta^{n+1}} \end{aligned}$$

and so

$$I_n = \frac{n!}{\beta^{n+1}}$$

6-23. Prove that the average value of  $r$  in the 1s and 2s states is  $3a_0/2Z$  and  $6a_0/Z$ , respectively.

The average value of  $r$ ,  $\langle r \rangle$ , is given by

$$\langle r \rangle = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^\infty dr r^2 \psi_{nlm}^*(r, \theta, \phi) \psi_{nlm}(r, \theta, \phi)$$

The wave functions for the 1s and 2s states are (Table 6.5)

$$\begin{aligned} \psi_{100} &= \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-\sigma} \\ \psi_{200} &= \frac{1}{\sqrt{32\pi}} \left( \frac{Z}{a_0} \right)^{3/2} (2 - \sigma) e^{-\sigma/2} \end{aligned}$$



so

$$\begin{aligned}\langle r \rangle_{1s} &= 4 \left( \frac{Z}{a_0} \right)^3 \int_0^\infty r^3 e^{-2\sigma} dr \\ &= \frac{4a_0}{Z} \int_0^\infty d\sigma \sigma^3 e^{-2\sigma} = \frac{4a_0}{Z} \left( \frac{3!}{16} \right) = \frac{3}{2} \left( \frac{a_0}{Z} \right)\end{aligned}$$

and

$$\begin{aligned}\langle r \rangle_{2s} &= \frac{1}{8} \left( \frac{Z}{a_0} \right)^3 \int_0^\infty r^3 (4 - 4\sigma + \sigma^2) e^{-\sigma} dr \\ &= \frac{a_0}{8Z} \int_0^\infty d\sigma (4\sigma^3 - 4\sigma^4 + \sigma^5) e^{-\sigma} \\ &= \frac{a_0}{8Z} (4 \cdot 3! - 4 \cdot 4! + 5!) = \frac{6a_0}{Z}\end{aligned}$$

6-24. Prove that  $\langle V \rangle = 2\langle E \rangle$  and, consequently, that  $\langle \hat{K} \rangle = -\langle E \rangle$ , for a 2s electron.

The average potential energy of a hydrogen-like 2s electron is (Equation 6.1)

$$\begin{aligned}\langle V \rangle &= \left\langle -\frac{e^2}{4\pi\epsilon_0 r} \right\rangle \\ &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr r^2 \psi_{2s}^* \left( -\frac{e^2}{4\pi\epsilon_0 r} \right) \psi_{2s} \\ &= -\frac{e^2}{32\pi\epsilon_0} \left( \frac{Z}{a_0} \right)^3 \int_0^\infty dr r (2 - \sigma)^2 e^{-\sigma} \\ &= -\frac{e^2}{32\pi\epsilon_0} \left( \frac{Z}{a_0} \right)^3 \int_0^\infty d\sigma (4\sigma - 4\sigma^2 + \sigma^3) e^{-\sigma} \\ &= -\frac{Ze^2}{16\pi\epsilon_0 a_0}\end{aligned}$$

The total energies of a hydrogenlike atom are (Problem 6-34)

$$E_n = -\frac{Ze^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{Ze^2}{32\pi\epsilon_0 a_0}$$

for  $n = 2$ , so  $\langle V \rangle = 2\langle E \rangle$ . Because  $\langle \hat{K} \rangle + \langle V \rangle = E$ ,  $\langle \hat{K} \rangle = -\langle E \rangle$ .

6-25. By evaluating the appropriate integrals, compute  $\langle r \rangle$  in the 2s, 2p, and 3s states of the hydrogen atom; compare your results with the general formula

$$\langle r_{nl} \rangle = \frac{a_0}{2} [3n^2 - l(l+1)]$$

In Problem 6-23 we found the average value of  $r$  in a hydrogen 2s orbital to be  $\langle r \rangle = 6a_0$ . The wave functions for the 2p and 3s states are (Table 6.5)

$$\begin{aligned}\psi_{210} &= \frac{1}{\sqrt{32\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \sigma e^{-\sigma/2} \cos\theta \\ \psi_{300} &= \frac{1}{81\sqrt{3\pi}} \left( \frac{Z}{a_0} \right)^{3/2} (27 - 18\sigma + 2\sigma^2) e^{-\sigma/3}\end{aligned}$$

So for  $Z = 1$ , we have

$$\begin{aligned}\langle r_{2p} \rangle &= \frac{1}{32\pi} \left( \frac{1}{a_0} \right)^3 \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \cos^2\theta \int_0^\infty dr r^3 \sigma^2 e^{-\sigma} \\ &= \frac{a_0}{16} \int_{-1}^1 dx x^2 \int_0^\infty d\sigma \sigma^5 e^{-\sigma} = \frac{a_0}{16} \left( \frac{2}{3} \right) (5!) = 5a_0\end{aligned}$$

and

$$\begin{aligned}\langle r_{3s} \rangle &= \frac{1}{3^9 \pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr r^3 (27 - 18\sigma + 2\sigma^2)^2 e^{-2\sigma/3} \\ &= \frac{4a_0}{3^9} \int_0^\infty d\sigma \sigma^3 [3^6 + 4(3^4 \sigma^2) + 4\sigma^4 - 4(3^5 \sigma) + 4(3^3 \sigma^2) - 8(3^2 \sigma^3)] e^{-2\sigma/3} \\ &= \frac{4a_0}{3^9} \left[ 3^6 \cdot 3! \left( \frac{3}{2} \right)^4 + 4 \cdot 3^4 \cdot 5! \left( \frac{5}{2} \right)^6 + 4 \cdot 7! \left( \frac{3}{2} \right)^8 \right. \\ &\quad \left. - 4 \cdot 3^5 \cdot 4! \left( \frac{3}{2} \right)^5 + 4 \cdot 3^3 \cdot 5! \left( \frac{3}{2} \right)^6 - 8 \cdot 3^2 \cdot 6! \left( \frac{3}{2} \right)^7 \right] \\ &= \frac{27a_0}{2}\end{aligned}$$

Using the general formula

$$\langle r_{nl} \rangle = \frac{a_0}{2} [3n^2 - l(l+1)]$$

we obtain  $6a_0$ ,  $5a_0$  and  $27a_0/2$  for the values of  $\langle r_{nl} \rangle$  for the 2s, 2p and 3s orbitals, in agreement with the above calculations.

6-26. Show that the first few hydrogen atomic orbitals in Table 6.6 are orthonormal.

See the solution to Problem 6-16.

6-27. Show that the two maxima in the plot of  $r^2 \psi_{2s}^2(r)$  against  $r$  occur at  $(3 \pm \sqrt{5})a_0$ . (See Figure 6.3.)

We can write  $r^2 \psi_{2s}^2(r)$  as

$$\begin{aligned}f(r) &= r^2 \psi_{2s}^2(r) \\ &= r^2 \frac{1}{32\pi} \left( \frac{1}{a_0} \right)^3 \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} \\ &= \frac{r^2}{32\pi a_0^3} \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0}\end{aligned}$$

To determine the maxima of  $f(r)$ , we find the values of  $r$  for which  $df(r)/dr = 0$ :

$$\begin{aligned}\frac{df(r)}{dr} &= \frac{1}{32\pi a_0^3} \left[ 2r \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} - \frac{2r^2}{a_0} \left( 2 - \frac{r}{a_0} \right) e^{-r/a_0} - \frac{r^2}{a_0} \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} \right] \\ 0 &= 2 \left( 2 - \frac{r_{\max}}{a_0} \right) - \frac{2r_{\max}}{a_0} - \frac{r_{\max}}{a_0} \left( 2 - \frac{r_{\max}}{a_0} \right) \\ &= 4a_0^2 - 2a_0 r_{\max} - 2a_0 r_{\max} - 2a_0 r_{\max} + r_{\max}^2 \\ &= r_{\max}^2 - 6a_0 r_{\max} + 4a_0^2 \\ r_{\max} &= (3 \pm \sqrt{5})a_0\end{aligned}$$

- 6-28. Calculate the value of  $\langle r \rangle$  for the  $n = 2, l = 1$  state and the  $n = 2, l = 0$  state of the hydrogen atom. Are you surprised by the answers? Explain.

The average value of  $r$ ,  $\langle r \rangle$ , is given by

$$\langle r \rangle = \int d\tau \psi_{nl}^*(r, \theta, \phi) r \psi_{nl}(r, \theta, \phi)$$

We use the wave functions in Table 6.6 to find

$$\begin{aligned} \langle r \rangle_{20} &= \frac{4\pi}{32\pi a_0^3} \int_0^\infty dr r^3 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} \\ &= \frac{a_0}{8} \int_0^\infty dx x^3 (2-x)^2 e^{-x} = \frac{a_0}{8} (4 \cdot 3! - 4 \cdot 4! + 5!) \\ &= 6a_0 \end{aligned}$$

and

$$\begin{aligned} \langle r \rangle_{21} &= \frac{2\pi}{32\pi a_0^3} \int_0^\infty d\theta \sin \theta \cos^2 \theta \int_0^\infty dr r^3 \left(\frac{r}{a_0}\right)^2 e^{-r/a_0} \\ &= \frac{a_0}{16} \left(\frac{2}{3}\right) \int_0^\infty dx x^5 e^{-x} \\ &= \frac{a_0}{16} \left(\frac{2}{3}\right) (5!) = 5a_0 \end{aligned}$$

These results show that an electron in the  $2s$  orbital is farther from the nucleus (on average) than an electron in the  $2p$  orbital. This is surprising, as we might expect the reverse to be true from our studies of multi-electron systems in general chemistry; note, however, that a one-electron hydrogen-like wave function differs from multi-electron wave functions (Chapter 8).

- 6-29. In Chapter 4, we learned that if  $\psi_1$  and  $\psi_2$  are solutions of the Schrödinger equation that have the same energy  $E_n$ , then  $c_1\psi_1 + c_2\psi_2$  is also a solution. Let  $\psi_1 = \psi_{210}$  and  $\psi_2 = \psi_{211}$  (see Table 6.5). What is the energy corresponding to  $\psi = c_1\psi_1 + c_2\psi_2$  where  $c_1^2 + c_2^2 = 1$ ? What does this result tell you about the uniqueness of the three  $p$  orbitals,  $p_x$ ,  $p_y$ , and  $p_z$ ?

Recall that the energy of the hydrogen atom depends only on the value of  $n$ . Therefore,  $\psi_{211}$  and  $\psi_{210}$  have the same energy,  $E_2$ , and so (Chapter 4) the energy corresponding to  $\psi = c_1\psi_1 + c_2\psi_2$  where  $c_1^2 + c_2^2 = 1$  is also  $E_2$ . The three  $p$  orbitals ( $p_x$ ,  $p_y$ , and  $p_z$ ), therefore, are not a unique representation of the three degenerate orbitals for  $n = 2$  and  $l = 1$ .

- 6-30. Show that the total probability density of the  $2p$  orbitals is spherically symmetric by evaluating  $\sum_{m=-1}^1 \psi_{21m}^2$ . (Use the wave functions in Table 6.6.)

$$\begin{aligned} \sum_{m=-1}^1 \psi_{21m}^2 &= \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^3 \sigma^2 e^{-\sigma} (\cos^2 \theta + \sin^2 \theta \cos^2 \phi + \sin^2 \theta \sin^2 \phi) \\ &= \frac{Z^3 \sigma^2 e^{-\sigma}}{32\pi a_0^3} [\cos^2 \theta + \sin^2 \theta (\cos^2 \phi + \sin^2 \phi)] \\ &= \frac{Z^3 \sigma^2 e^{-\sigma}}{32\pi a_0^3} (\cos^2 \theta + \sin^2 \theta) \\ &= \frac{Z^3 \sigma^2 e^{-\sigma}}{32\pi a_0^3} \end{aligned}$$

The sum depends only on the variable  $r$  (through  $\sigma$ ), so the total probability density of the  $2p$  orbitals is spherically symmetric.

- 6-31. Show that the total probability density of the  $3d$  orbitals is spherically symmetric by evaluating  $\sum_{m=-2}^2 \psi_{32m}^2$ . (Use the wave functions in Table 6.6.)

$$\begin{aligned} \sum_{m=-2}^2 \psi_{32m}^2 &= \frac{1}{81^2 \pi} \left(\frac{Z}{a_0}\right)^3 \sigma^4 e^{-2\sigma/3} \left[ \frac{(3 \cos^2 \theta - 1)^2}{6} + 2 \sin^2 \theta \cos^2 \theta \cos^2 \phi \right. \\ &\quad \left. + 2 \sin^2 \theta \cos^2 \theta \sin^2 \phi + \frac{\sin^4 \theta \cos^2 2\phi}{2} + \frac{\sin^4 \theta \sin^2 2\phi}{2} \right] \\ &= \frac{Z^3 \sigma^4 e^{-2\sigma/3}}{81^2 \pi a_0^3} \left[ \frac{(3 \cos^2 \theta - 1)^2}{6} + 2 \sin^2 \theta \cos^2 \theta (\sin^2 \phi + \cos^2 \phi) \right. \\ &\quad \left. + \frac{\sin^4 \theta (\cos^2 2\phi + \sin^2 2\phi)}{2} \right] \\ &= \frac{Z^3 \sigma^4 e^{-2\sigma/3}}{(81)^2 6\pi a_0^3} [(3 \cos^2 \theta - 1)^2 + 12 \sin^2 \theta \cos^2 \theta + 3 \sin^4 \theta] \end{aligned}$$

Now substitute  $\sin^2 \theta = 1 - \cos^2 \theta$  into the above expression to get

$$\begin{aligned} \sum_{m=-2}^2 \psi_{32m}^2 &= \frac{Z^3 \sigma^4 e^{-2\sigma/3}}{(81)^2 6\pi a_0^3} [9 \cos^4 \theta - 6 \cos^2 \theta + 1 \\ &\quad + 12(1 - \cos^2 \theta) \cos^2 \theta + 3(1 - \cos^2 \theta)^2] \\ &= \frac{Z^3 \sigma^4 e^{-2\sigma/3}}{(81)^2 6\pi a_0^3} [9 \cos^4 \theta - 6 \cos^2 \theta + 1 + 12 \cos^2 \theta - 12 \cos^4 \theta \\ &\quad + 3 - 6 \cos^2 \theta + 3 \cos^4 \theta] \\ &= \frac{4Z^3 \sigma^4 e^{-2\sigma/3}}{(81)^2 6\pi a_0^3} = \frac{2Z^3 \sigma^4 e^{-2\sigma/3}}{(81)^2 3\pi a_0^3} \end{aligned}$$

The sum depends only on the variable  $r$  (through  $\sigma$ ), so the total probability density of the  $3d$  orbitals is spherically symmetric.

- 6-32. Show that the sum of the probability densities for the  $n = 3$  states of the hydrogen atom is spherically symmetric. Do you expect this to be true for all values of  $n$ ? Explain.

In Problem 6-31 we showed that the sum of the probability densities of the  $3d$  orbitals is spherically symmetric. The probability density of the  $3s$  orbital is also spherically symmetric, and so we need only show that the sum of the probability densities of the  $3p$  orbitals is spherically symmetric. The

angular dependence of the  $3p$  orbitals is the same as that of the  $2p$  orbitals. In Problem 6–30 we showed that the sum of the squares of the  $2p$  orbitals is spherically symmetric, and therefore the same must be true for the  $3p$  orbitals. Thus, the sum of the probability densities for the  $n = 3$  states of the hydrogen atom is spherically symmetric. We expect this to be the case for all values of  $n$ . Recall from Problem 6–10 that

$$\sum_{m=-l}^{+l} |Y_l^m(\theta, \phi)|^2 = \text{constant} \quad (1)$$

When we sum all of the probability densities corresponding to any given  $n$ , we evaluate a sum similar to that in Equation 1. Because the sum is equal to a constant, it cannot have any angular dependence and will depend only on  $r$ . Such a sum is spherically symmetric.

6–33. Determine the degeneracy of each of the hydrogen atomic energy levels.

The energy depends only on the quantum number  $n$ :

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \quad n = 1, 2, \dots \quad (6.45)$$

For a given value of  $n$ , there are  $n - 1$  allowed values of  $l$ . For each  $l$  there are  $2l + 1$  allowed values of  $m$ . All of these combinations of  $l$  and  $m$  are degenerate, and so the total number of energy sublevels for one value of  $n$  is

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

6–34. Set up the Hamiltonian operator for the system of an electron interacting with a fixed nucleus of atomic number  $Z$ . The simplest such system is singly ionized helium, where  $Z = 2$ . We will call this a hydrogenlike system. Observe that the only difference between this Hamiltonian operator and the hydrogen Hamiltonian operator is the correspondance that  $e^2$  for the hydrogen atom becomes  $Ze^2$  for the hydrogenlike ion. Consequently, show that the energy becomes (cf. Equation 6.44)

$$E_n = -\frac{m_e Z^2 e^4}{8\epsilon_0^2 h^2 n^2} \quad n = 1, 2, \dots$$

Furthermore, now show that the solutions to the radial equation, Equation 6.47, are

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

Show that the  $1s$  orbital for this system is

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

and show that it is normalized. Show that

$$\langle r \rangle = \frac{3a_0}{2Z}$$

and that

$$r_{\text{mp}} = \frac{a_0}{Z}$$

Last, calculate the ionization energy of a hydrogen atom and a singly ionized helium atom. Express your answer in kilojoules per mole.

The Hamiltonian operator for a hydrogenlike system is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The only difference between this Hamiltonian and that of a hydrogen atom is that  $e^2$  is replaced by  $Ze^2$ . Because  $e$  appears nowhere else, we can obtain the results of this problem by replacing  $e^2$  by  $Ze^2$  in the hydrogen atom results. For example, the expression for the energy of a hydrogen atom is

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} \quad n = 1, 2, \dots \quad (6.44)$$

and so the energy of a hydrogenlike atom is given by

$$E_n = -\frac{m_e (Ze^2)^2}{8\epsilon_0^2 h^2 n^2} = -\frac{m_e Z^2 e^4}{8\epsilon_0^2 h^2 n^2} \quad n = 1, 2, \dots \quad (1)$$

The Bohr radius ( $\epsilon_0 \hbar^2 / \pi \mu e^2$  for hydrogen) for a hydrogenlike atom is

$$a_0 = \frac{\epsilon_0 \hbar^2}{\pi \mu Z e^2}$$

Consequently, we can replace  $a_0$  by  $a_0/Z$  in Equation 6.47 to find

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

The hydrogen atomic  $1s$  orbital for a hydrogen atom is

$$\psi_{1s} = \frac{1}{\pi^{1/2} a_0^{3/2}} e^{-r/a_0}$$

and becomes, for a hydrogenlike atom of atomic number  $Z$ ,

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \quad (2)$$

To see whether this function is normalized, we evaluate

$$\begin{aligned} \int d\tau \psi_{1s}^* \psi_{1s} &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr r^2 \frac{Z^3}{\pi a_0^3} e^{-2Zr/a_0} \\ &= \frac{4Z^3}{a_0^3} \int_0^\infty dr r^2 e^{-2Zr/a_0} \\ &= \frac{4Z^3}{a_0^3} \frac{2! a_0^3}{8Z^3} = 1 \end{aligned}$$

We now evaluate  $\langle r \rangle_{1s}$  using Equation 2.

$$\begin{aligned} \langle r \rangle_{1s} &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr r^3 \left( \frac{Z^3}{\pi a_0^3} \right) e^{-2Zr/a_0} \\ &= \frac{4Z^3}{a_0^3} \int_0^\infty dr r^3 e^{-2Zr/a_0} = \frac{4a_0}{Z} \int_0^\infty d\sigma \sigma^3 e^{-2\sigma} \\ &= \frac{4a_0}{Z} \frac{3!}{16} = \frac{3a_0}{2Z} \end{aligned}$$

The value of  $r_{\text{mp}}$  is given by

$$\begin{aligned} \frac{d}{dr} \psi_{1s}^* \psi_{1s} r_{\text{mp}}^2 &= 0 \\ \frac{d}{dr} r_{\text{mp}}^2 \frac{Z^3}{\pi a_0^3} e^{-2Zr_{\text{mp}}/a_0} &= 0 \\ 2r_{\text{mp}} e^{-2Zr_{\text{mp}}/a_0} + \frac{-2Zr_{\text{mp}}^2}{a_0} e^{-2Zr_{\text{mp}}/a_0} &= 0 \\ a_0 - Zr_{\text{mp}} &= 0 \\ r_{\text{mp}} &= \frac{a_0}{Z} \end{aligned}$$

The ionization energy is given by  $-E_1$ , and so we find from Equation 1

$$\text{IE} = \frac{m_e Z^2 e^4}{8\epsilon_0^2 h^2} = (1312 \text{ kJ}\cdot\text{mol}^{-1}) Z^2$$

Therefore,

$$\text{IE}_{\text{H}} = 1312 \text{ kJ}\cdot\text{mol}^{-1} = 13.60 \text{ eV} \quad \text{and} \quad \text{IE}_{\text{He}^+} = 5248 \text{ kJ}\cdot\text{mol}^{-1} = 54.39 \text{ eV}$$

6-35. How does  $E_n$  for a hydrogen atom differ from Equation 6.44 if the nucleus is not considered to be fixed at the origin?

See the solution to Problem 5-44.

6-36. Determine the ratio of the ground-state energy of atomic hydrogen to that of atomic deuterium.

The energy of the ground state of a hydrogen atom is given by (Problem 6-35)

$$E = -\frac{\mu e^4}{8\epsilon_0^2 h^2}$$

where  $\mu$  is the reduced mass of the atom. The ratio of the ground-state energy of a hydrogen atom to a deuterium atom,  $E_{\text{H}}/E_{\text{D}}$ , is then

$$\frac{E_{\text{H}}}{E_{\text{D}}} = \frac{\mu_{\text{H}}}{\mu_{\text{D}}}$$

In Problems 5-7 and 5-46 we calculated that  $\mu_{\text{H}} = 9.104431 \times 10^{-31} \text{ kg}$  and that  $\mu_{\text{D}} = 9.106909 \times 10^{-31} \text{ kg}$ , so the ratio of the energies is

$$\frac{E_{\text{H}}}{E_{\text{D}}} = \frac{9.104431 \times 10^{-31} \text{ kg}}{9.106909 \times 10^{-31} \text{ kg}} = 0.999728$$

6-37. In this problem, we will prove the so-called *quantum-mechanical virial theorem*. Start with

$$\hat{H}\psi = E\psi$$

where

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$$

Using the fact that  $\hat{H}$  is a Hermitian operator (Problem 4-28), show that

$$\int \psi^* [\hat{H}, \hat{A}] \psi d\tau = 0 \quad (1)$$

where  $\hat{A}$  is any linear operator. Choose  $\hat{A}$  to be

$$\hat{A} = -i\hbar \left( x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} \right) \quad (2)$$

and show that

$$\begin{aligned} [\hat{H}, \hat{A}] &= i\hbar \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right) - \frac{i\hbar}{m} (\hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2) \\ &= i\hbar \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right) - 2i\hbar \hat{K} \end{aligned}$$

where  $\hat{K}$  is the kinetic energy operator. Now use Equation 1 and show that

$$\left\langle x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right\rangle = 2\langle \hat{K} \rangle \quad (3)$$

Equation 3 is the quantum-mechanical virial theorem. Now show that if  $V(x, y, z)$  is a Coulombic potential

$$V(x, y, z) = -\frac{Ze^2}{4\pi\epsilon_0(x^2 + y^2 + z^2)^{1/2}}$$

then

$$\langle V \rangle = -2\langle \hat{K} \rangle = 2\langle E \rangle \quad (4)$$

where

$$\langle E \rangle = \langle \hat{K} \rangle + \langle V \rangle$$

In Problem 6-24 we proved that this result is valid for a  $2s$  electron. Although we proved Equation 4 only for the case of one electron in the field of one nucleus, Equation 4 is valid for many-electron atoms and molecules. The proof is a straightforward extension of the proof developed in this problem.

We first show that

$$\int \psi^* [\hat{H}, \hat{A}] \psi d\tau = 0 \quad (1)$$

Writing out the commutator, we have

$$\int \psi^* \hat{H} \hat{A} \psi d\tau - \int \psi^* \hat{A} \hat{H} \psi d\tau \stackrel{?}{=} 0$$

Using the Hermitian property of  $\hat{H}$ , we can write this difference as

$$\int (\psi \hat{H})^* \psi d\tau - \int \psi^* \hat{A} (\hat{H} \psi) d\tau \stackrel{?}{=} 0$$

We know that  $\hat{H}\psi = E\psi$ , so

$$\int \psi^* [\hat{H}, \hat{A}] \psi d\tau = E \int \psi^* \hat{A} \psi d\tau - E \int \psi^* \hat{A} \psi d\tau = 0$$

Now let

$$\hat{A} = -i\hbar \left( x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} \right) \quad (2)$$

We are given

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$$

Then

$$\begin{aligned} \hat{H}\hat{A}f &= -i\hbar \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z) \right] \left[ x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + z \frac{\partial f}{\partial z} \right] \\ &= \frac{i\hbar^3}{2m} \left( 2 \frac{\partial^2 f}{\partial x^2} + x \frac{\partial^3 f}{\partial x^3} + y \frac{\partial^3 f}{\partial x^2 \partial y} + z \frac{\partial^3 f}{\partial x^2 \partial z} + x \frac{\partial^3 f}{\partial x \partial y^2} \right. \\ &\quad \left. + 2 \frac{\partial^2 f}{\partial y^2} + y \frac{\partial^3 f}{\partial y^3} + z \frac{\partial^3 f}{\partial y^2 \partial z} + x \frac{\partial^3 f}{\partial x \partial z^2} + y \frac{\partial^3 f}{\partial y \partial z^2} + 2 \frac{\partial^2 f}{\partial z^2} + z \frac{\partial^3 f}{\partial z^3} \right) \\ &\quad - i\hbar \left[ V \left( x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + z \frac{\partial f}{\partial z} \right) \right] \end{aligned}$$

and

$$\begin{aligned} \hat{A}\hat{H}f &= \frac{i\hbar^3}{2m} \left( x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} \right) \left( \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \right) - i\hbar \left( x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} \right) V f \\ &= \frac{i\hbar^3}{2m} \left( x \frac{\partial^3 f}{\partial x^3} + x \frac{\partial^3 f}{\partial x \partial y^2} + x \frac{\partial^3 f}{\partial x \partial z^2} + y \frac{\partial^3 f}{\partial x^2 \partial y} + y \frac{\partial^3 f}{\partial y^3} + y \frac{\partial^3 f}{\partial y \partial z^2} + z \frac{\partial^3 f}{\partial x^2 \partial z} + z \frac{\partial^3 f}{\partial z^3} \right) \\ &\quad - i\hbar \left[ \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right) f + \left( x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + z \frac{\partial f}{\partial z} \right) V \right] \end{aligned}$$

Therefore,

$$\begin{aligned} [\hat{H}, \hat{A}] &= \frac{i\hbar^3}{2m} \left( 2 \frac{\partial^2}{\partial x^2} + 2 \frac{\partial^2}{\partial y^2} + 2 \frac{\partial^2}{\partial z^2} \right) + i\hbar \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right) \\ &= i\hbar \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right) - \frac{i\hbar}{m} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) \\ &= i\hbar \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right) - 2i\hbar \hat{K} \end{aligned}$$

where we know  $\hat{P}$  and  $\hat{K}$  from Table 4.1. Now, substituting this result into Equation 1 gives

$$\begin{aligned} \int \psi^* \left[ i\hbar \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right) - 2i\hbar \hat{K} \right] \psi d\tau &= 0 \\ i\hbar \int \psi^* \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right) \psi d\tau &= i\hbar \int \psi^* 2\hat{K} \psi d\tau \\ \left\langle x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \right\rangle &= 2\langle \hat{K} \rangle \quad (3) \end{aligned}$$

Now consider the Coulombic potential

$$V(x, y, z) = \frac{Ze^2}{4\pi\epsilon_0(x^2 + y^2 + z^2)^{1/2}}$$

This gives

$$\begin{aligned} x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} &= -\frac{Ze^2}{4\pi\epsilon_0} \left( \frac{x^2}{r^3} + \frac{y^2}{r^3} + \frac{z^2}{r^3} \right) \\ &= -\frac{Ze^2}{4\pi\epsilon_0 r} = -V \end{aligned}$$

and so substituting into Equation 3 gives  $\langle V \rangle = -2\langle \hat{K} \rangle$ . Because  $\langle \hat{K} \rangle + \langle V \rangle = E$ , we can write

$$E - \langle \hat{K} \rangle = -2\langle \hat{K} \rangle$$

or  $E = -\langle \hat{K} \rangle$  for a Coulombic potential.

**6-38.** Use the virial theorem (Problem 6-37) to prove that  $\langle \hat{K} \rangle = \langle V \rangle = E/2$  for a harmonic oscillator (cf. Problem 5-23).

For a three-dimensional harmonic oscillator,

$$V(x, y, z) = \frac{k_x x^2}{2} + \frac{k_y y^2}{2} + \frac{k_z z^2}{2}$$

Therefore,

$$x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} = k_x x^2 + k_y y^2 + k_z z^2 = 2V$$

and substituting into Equation 3 of Problem 6-37 gives  $2\langle V \rangle = 2\langle \hat{K} \rangle$ . Because  $\langle \hat{K} \rangle + \langle V \rangle = E$ , we can also write

$$\langle \hat{K} \rangle = \langle V \rangle = \frac{1}{2}E$$

**6-39.** The average value of  $r$  for a hydrogenlike atom can be evaluated in general and is given by

$$\langle r \rangle_{nl} = \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left[ 1 - \frac{l(l+1)}{n^2} \right] \right\}$$

Verify this formula explicitly for the  $\psi_{211}$  orbital.

We first determine  $\langle r \rangle_{21}$  directly:

$$\begin{aligned} \langle r \rangle_{21} &= \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 dr \phi_{211}^* r \phi_{211} \\ &= \frac{Z^3}{32\pi a_0^3} \int_0^{2\pi} d\phi \cos^2\phi \int_0^\pi d\theta \sin^3\theta \int_0^\infty dr r^3 \left( \frac{Zr}{a_0} \right)^2 e^{-Zr/a_0} \\ &= \frac{a_0}{32\pi Z} \cdot \pi \cdot \frac{4}{3} \int_0^\infty dx x^5 e^{-x} \\ &= \frac{a_0}{24Z} (5!) = \frac{5a_0}{Z} \end{aligned}$$

Using the equation given in the problem,

$$\begin{aligned}\langle r \rangle_{21} &= \frac{2^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left[ 1 - \frac{1(1+1)}{2^2} \right] \right\} \\ &= \frac{4a_0}{Z} \frac{5}{4} = \frac{5a_0}{Z}\end{aligned}$$

6-40. The average value of  $r^2$  for a hydrogenlike atom can be evaluated in general and is given by

$$\langle r^2 \rangle_{nl} = \frac{n^4 a_0^2}{Z^2} \left\{ 1 + \frac{3}{2} \left[ 1 - \frac{l(l+1) - \frac{1}{3}}{n^2} \right] \right\}$$

Verify this formula explicitly for the  $\psi_{210}$  orbital.

We first determine  $\langle r^2 \rangle_{21}$  directly:

$$\begin{aligned}\langle r^2 \rangle_{21} &= \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 dr \phi_{210}^* r^2 \phi_{210} \\ &= \frac{Z^3}{32\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \cos^2\theta \int_0^\infty \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0} r^4 dr \\ &= \frac{2\pi Z^3}{32\pi a_0^3} \frac{2}{3} \int_0^\infty \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0} r^4 dr \\ &= \frac{a_0^2}{24Z^2} \int_0^\infty dx x^6 e^{-x} \\ &= \frac{a_0^2}{24Z^2} (6!) = \frac{30a_0^2}{Z^2}\end{aligned}$$

Using the equation given in the problem,

$$\begin{aligned}\langle r^2 \rangle_{21} &= \frac{2^4 a_0^2}{Z^2} \left\{ 1 + \frac{3}{2} \left[ 1 - \frac{1(1+1) - \frac{1}{3}}{2^2} \right] \right\} \\ &= \frac{16a_0^2}{Z^2} \left[ 1 + \frac{3}{2} \left( \frac{7}{12} \right) \right] \\ &= \frac{16a_0^2}{Z^2} \left( \frac{15}{8} \right) = \frac{30a_0^2}{Z^2}\end{aligned}$$

6-41. The average values of  $1/r$ ,  $1/r^2$ , and  $1/r^3$  for a hydrogenlike atom can be evaluated in general and are given by

$$\left\langle \frac{1}{r} \right\rangle_{nl} = \frac{Z}{a_0 n^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{nl} = \frac{Z^2}{a_0^2 n^3 (l + \frac{1}{2})}$$

and

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{Z^3}{a_0^3 n^3 l (l + \frac{1}{2}) (l + 1)}$$

Verify these formulas explicitly for the  $\psi_{210}$  orbital.

We first evaluate these quantities directly:

$$\begin{aligned}\left\langle \frac{1}{r} \right\rangle_{21} &= \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 dr \psi_{210}^* \frac{1}{r} \psi_{210} \\ &= \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \cos^2\theta \int_0^\infty dr r^2 \frac{1}{r} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0} \\ &= \frac{Z^5}{16a_0^5} \frac{2}{3} \int_0^\infty dr r^3 e^{-Zr/a_0} = \frac{Z}{24a_0} \int_0^\infty dx x^3 e^{-x} \\ &= \frac{Z}{24a_0} (3!) = \frac{Z}{4a_0}\end{aligned}$$

$$\begin{aligned}\left\langle \frac{1}{r^2} \right\rangle_{21} &= \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 dr \psi_{210}^* \frac{1}{r^2} \psi_{210} \\ &= \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \cos^2\theta \int_0^\infty dr r^2 \frac{1}{r^2} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0} \\ &= \frac{Z^5}{16a_0^5} \frac{2}{3} \int_0^\infty dr r^2 e^{-Zr/a_0} = \frac{Z^2}{24a_0^2} \int_0^\infty dx x^2 e^{-x} \\ &= \frac{Z^2}{24a_0^2} (2!) = \frac{Z^2}{12a_0^2}\end{aligned}$$

$$\begin{aligned}\left\langle \frac{1}{r^3} \right\rangle_{21} &= \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 dr \psi_{210}^* \frac{1}{r^3} \psi_{210} \\ &= \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \cos^2\theta \int_0^\infty dr r^2 \frac{1}{r^3} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0} \\ &= \frac{Z^5}{16a_0^5} \frac{2}{3} \int_0^\infty dr r e^{-Zr/a_0} = \frac{Z^3}{24a_0^3} \int_0^\infty dx x e^{-x} \\ &= \frac{Z^3}{24a_0^3}\end{aligned}$$

Using the equation given in the problem,

$$\left\langle \frac{1}{r} \right\rangle_{21} = \frac{Z}{a_0 (2)^2} = \frac{Z}{4a_0}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{21} = \frac{Z^2}{a_0^2 (2)^3 (1 + \frac{1}{2})} = \frac{Z^2}{12a_0^2}$$

$$\left\langle \frac{1}{r^3} \right\rangle_{21} = \frac{Z^3}{a_0^3 (2)^3 [1 + \frac{1}{2}(2)]} = \frac{Z^3}{24a_0^3}$$

6-42. The designations of the  $d$  orbitals can be rationalized in the following way. Equation 6.63 shows that  $d_{xz}$  goes as  $\sin\theta \cos\theta \cos\phi$ . Using the relation between Cartesian and spherical coordinates, show that  $\sin\theta \cos\theta \cos\phi$  is proportional to  $xz$ . Similarly, show that  $\sin\theta \cos\theta \sin\phi$  ( $d_{yz}$ ) is proportional to  $yz$ ; that  $\sin^2\theta \cos 2\phi$  ( $d_{x^2-y^2}$ ) is proportional to  $x^2 - y^2$ ; and that  $\sin^2\theta \sin 2\phi$  ( $d_{xy}$ ) is proportional to  $xy$ .

The relations between Cartesian and spherical coordinates are

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

Thus, for the  $d_{xz}$  and  $d_{yz}$  orbitals, we see that

$$\begin{aligned} r^2 \sin^2 \theta \cos^2 \phi &= xz \\ \sin^2 \theta \cos^2 \phi &\propto xz \\ r^2 \sin^2 \theta \cos \theta \sin \phi &= yz \\ \sin^2 \theta \cos \theta \sin \phi &\propto yz \end{aligned}$$

Likewise, for the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals,

$$\begin{aligned} r^2 \sin^2 \theta \cos^2 \phi - r^2 \sin^2 \theta \sin^2 \phi &= x^2 - y^2 \\ r^2 \sin^2 \theta \cos 2\phi &= x^2 - y^2 \\ \sin^2 \theta \cos 2\phi &\propto x^2 - y^2 \\ r^2 \sin^2 \theta \cos \phi \sin \phi &= xy \\ \frac{1}{2} r^2 \sin^2 \theta \sin 2\phi &= xy \\ \sin^2 \theta \sin 2\phi &\propto xy \end{aligned}$$

Problems 6-43 through 6-47 examine the energy levels for a hydrogen atom in an external magnetic field.

6-43. Recall from your course in physics that the motion of an electric charge around a closed loop produces a magnetic dipole,  $\mu$ , whose direction is perpendicular to the loop and whose magnitude is given by

$$\mu = iA$$

where  $i$  is the current in amperes ( $\text{C}\cdot\text{s}^{-1}$ ) and  $A$  is the area of the loop ( $\text{m}^2$ ). Notice that the units of a magnetic dipole are coulombs·meters<sup>2</sup>·seconds<sup>-1</sup> ( $\text{C}\cdot\text{m}^2\cdot\text{s}^{-1}$ ), or amperes·meters<sup>2</sup> ( $\text{A}\cdot\text{m}^2$ ). Show that

$$i = \frac{qv}{2\pi r}$$

for a circular loop, where  $v$  is the velocity of the charge  $q$  and  $r$  is the radius of the loop. Show that

$$\mu = \frac{qrv}{2}$$

for a circular loop. If the loop is not circular, then we must use vector calculus and the magnetic dipole is given by

$$\mu = \frac{q(\mathbf{r} \times \mathbf{v})}{2}$$

Show that this formula reduces to the preceding one for a circular loop. Last, using the relationship  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ , show that

$$\mu = \frac{q}{2m} \mathbf{L}$$

Thus, the orbital motion of an electron in an atom imparts a magnetic moment to the atom. For an electron,  $q = -|e|$  and so

$$\mu = -\frac{|e|\hbar}{2m_e} \mathbf{L}$$

For a circular loop, the frequency with which a charge  $q$  will pass a given point is  $v/2\pi r$  (the speed of the charge divided by the circumference of the circle). Then

$$i = qv = \frac{qv}{2\pi r}$$

The area  $A$  of the loop is  $\pi r^2$ , so

$$\mu = iA = \frac{qv\pi r^2}{2\pi r} = \frac{qrv}{2}$$

Using vector calculus, we find

$$\mu = \frac{q(\mathbf{r} \times \mathbf{v})}{2} = \frac{qrv \sin \theta}{2} = \frac{qrv}{2}$$

because  $\theta = \pi/2$  for a circular loop. Finally, to show the last relationship, recall that  $\mathbf{p} = m\mathbf{v}$ , so

$$\begin{aligned} \mu &= \frac{q(\mathbf{r} \times \mathbf{v})}{2} = \frac{qm(\mathbf{r} \times \mathbf{v})}{2m} \\ &= \frac{q(\mathbf{r} \times \mathbf{p})}{2m} = \frac{q}{2m} \mathbf{L} \end{aligned}$$

6-44. In Problem 6-43, we derived an expression for the magnetic moment of a hydrogen atom imparted by the orbital motion of its electron. Using the result that  $L^2 = \hbar^2 l(l+1)$ , show that the magnitude of the magnetic moment is

$$\mu = -\beta_e [l(l+1)]^{1/2}$$

where  $\beta_e = \hbar|e|/2m_e$  is called the *Bohr magneton*. What are the units of  $\beta_e$ ? What is its numerical value? A magnetic dipole in a magnetic field ( $\mathbf{B}$ ) has a potential energy

$$V = -\mu \cdot \mathbf{B}$$

(We will discuss magnetic fields when we study nuclear magnetic resonance, NMR, in Chapter 14.) Show that the units of the intensity of a magnetic field are  $\text{J}\cdot\text{A}^{-1}\cdot\text{m}^{-2}$ . This set of units is called a *tesla* (T), so that we have  $1 \text{ T} = 1 \text{ J}\cdot\text{A}^{-1}\cdot\text{m}^{-2}$ . In terms of teslas, the units of the Bohr magneton,  $\beta_e$ , are  $\text{J}\cdot\text{T}^{-1}$ .

Taking the square root of both sides of the equation  $L^2 = \hbar^2 l(l+1)$  gives  $|\mathbf{L}| = \hbar [l(l+1)]^{1/2}$ . Recall from Problem 6-43 that

$$\mu = -\frac{|e|\hbar}{2m_e} \mathbf{L}$$

Substituting in  $|\mathbf{L}| = \hbar [l(l+1)]^{1/2}$  gives

$$|\mu| = -\frac{|e|\hbar}{2m_e} [l(l+1)]^{1/2} = -\beta_e [l(l+1)]^{1/2}$$

Because the quantity  $[l(l+1)]^{1/2}$  is unitless, the units of  $\beta_e$  are the same as the units of  $\mu$  ( $\text{C}\cdot\text{m}^2\cdot\text{s}^{-1}$ ). The numerical value of  $\beta_e$  is

$$\begin{aligned}\beta_e &= -\frac{(1.602\,177 \times 10^{-19} \text{ C})(1.054\,572 \times 10^{-34} \text{ J}\cdot\text{s})}{2(9.109\,390 \times 10^{-31} \text{ kg})} \\ &= 9.274\,007 \times 10^{-24} \text{ C}\cdot\text{m}^2\cdot\text{s}^{-1} = 9.274\,007 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}\end{aligned}$$

The units of  $\mathbf{B}$  are the units of  $V$  divided by the units of  $\mu$ , or

$$\frac{\text{J}}{\text{C}\cdot\text{m}^2\cdot\text{s}^{-1}} = \text{J}\cdot\text{A}^{-1}\cdot\text{m}^{-2} = 1 \text{ T}$$

6-45. Using the results of Problems 6-43 and 6-44, show that the Hamiltonian operator for a hydrogen atom in an external magnetic field where the field is in the  $z$  direction is given by

$$\hat{H} = \hat{H}_0 + \frac{\beta_e B_z}{\hbar} \hat{L}_z$$

where  $\hat{H}_0$  is the Hamiltonian operator of a hydrogen atom in the absence of the magnetic field. Show that the wave functions of the Schrödinger equation for a hydrogen atom in a magnetic field are the same as those for the hydrogen atom in the absence of the field. Finally, show that the energy associated with the wave function  $\psi_{nlm}$  is

$$E = E_n^{(0)} + \beta_e B_z m \quad (1)$$

where  $E_n^{(0)}$  is the energy in the absence of the magnetic field and  $m$  is the magnetic quantum number.

The Hamiltonian operator for a hydrogen atom in an electromagnetic field can be expressed as

$$\hat{H} = \hat{H}_0 + V$$

where  $\hat{H}_0$  is the Hamiltonian operator of an isolated hydrogen atom and  $V = -\boldsymbol{\mu}\cdot\mathbf{B}$  is the potential energy associated with the external magnetic field. If the external magnetic field is in the  $z$  direction, then only the  $z$  components of the vectors  $\boldsymbol{\mu}$  and  $\mathbf{B}$  effect the potential energy of the atom, and we find

$$\begin{aligned}\hat{H} &= \hat{H}_0 - \mu_z B_z = \hat{H}_0 + \frac{|e|\hbar}{2m_e} \hat{L}_z B_z \\ &= \hat{H}_0 + \frac{\beta_e B_z}{\hbar} \hat{L}_z\end{aligned}$$

The hydrogen atomic orbitals which satisfy the equation  $\hat{H}_0\psi_n = E_n^{(0)}\psi_n$  are eigenfunctions of  $\hat{L}_z$ , and so they are also eigenfunctions of  $\hat{H}$ . Because  $\hat{L}_z\psi_{nlm} = m\hbar\psi_{nlm}$ ,

$$\begin{aligned}\hat{H}\psi_{nlm} &= \hat{H}_0\psi_{nlm} + \frac{\beta_e B_z}{\hbar} \hat{L}_z\psi_{nlm} \\ E\psi_{nlm} &= E_n^{(0)}\psi_{nlm} + \beta_e B_z m\psi_{nlm}\end{aligned}$$

giving

$$E = E_n^{(0)} + \beta_e B_z m$$

6-46. Equation 1 of Problem 6-45 shows that a state with given values of  $n$  and  $l$  is split into  $2l+1$  levels by an external magnetic field. For example, Figure 6.8 shows the results for the  $1s$  and  $2p$  states of atomic hydrogen. The  $1s$  state is not split ( $2l+1=1$ ), but the  $2p$  state is split into three levels ( $2l+1=3$ ). Figure 6.8 also shows that the  $2p$  to  $1s$  transition in atomic hydrogen could (see Problem 6-47) be split into three distinct transitions instead of just one. Superconducting magnets have magnetic field strengths of the order of 15 T. Calculate the magnitude of the splitting shown in Figure 6.8 for a magnetic field of 15 T. Compare your result with the energy difference between the unperturbed  $1s$  and  $2p$  levels. Show that the three distinct transitions shown in Figure 6.8 lie very close together. We say that the  $2p$  to  $1s$  transition that occurs in the absence of a magnetic field becomes a *triplet* in the presence of the field. The occurrence of such multiplets when atoms are placed in magnetic fields is known as the *Zeeman effect*.

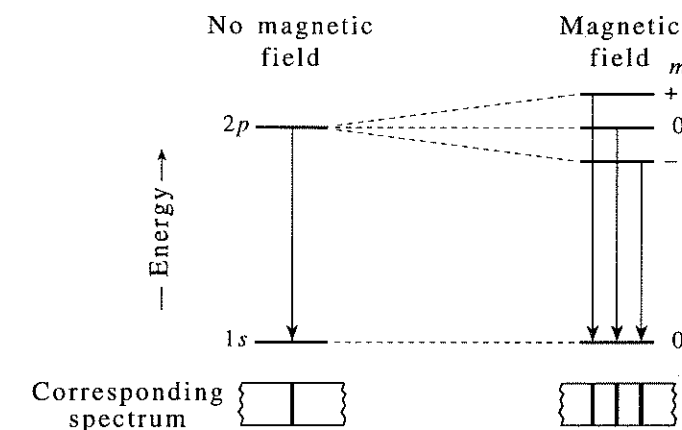


FIGURE 6.8

The splitting of the  $2p$  state of the hydrogen atom in a magnetic field. The  $2p$  state is split into three closely spaced levels. In a magnetic field, the  $2p$  to  $1s$  transition is split into three distinct transition frequencies.

In Problem 6-45 we derived the equation  $E = E_n^{(0)} + \beta_e B_z m$ . Thus

$$\Delta E = E_2 - E_1 = \beta_e B_z (m_2 - m_1)$$

For the  $1s$  state  $m = 0$  and for the  $2p$  state  $m = 0, \pm 1$ . Thus  $(m_2 - m_1) = 0, \pm 1$  and so the magnitude of the splitting shown for a magnetic field of 15 T is either 0 or

$$\begin{aligned}\Delta E &= (9.274 \times 10^{-24} \text{ J}\cdot\text{T}^{-1})(15 \text{ T})(1) \\ &= 1.391 \times 10^{-22} \text{ J}\end{aligned}$$

The energy difference between the unperturbed  $2p$  and  $1s$  energy levels is (Equation 1.11)

$$\Delta\tilde{\nu} = (109\,737 \text{ cm}^{-1}) \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = 82\,303 \text{ cm}^{-1}$$

$$E_{2p} - E_{1s} = 1.635 \times 10^{-18} \text{ J}$$

The magnitude of the splitting caused by the magnetic field is on the order of 0.01% of the energy difference between the unperturbed energy levels.



6-47. Consider a transition between the  $l = 2$  and the  $l = 3$  states of atomic hydrogen. What is the total number of conceivable transitions between these two states in an external magnetic field? For light whose electric field vector is parallel to the direction of the external magnetic field, the selection rule is  $\Delta m = 0$ . For light whose electric field vector is perpendicular to the direction of the external magnetic field, the selection rule is  $\Delta m = \pm 1$ . In each case, how many of the possible transitions are allowed?

Recall from Problem 6-46 that a state with given values of  $n$  and  $l$  is split into  $2l + 1$  levels by an external magnetic field. The  $l = 2$  state will therefore be split into 5 states ( $m = 0, \pm 1, \pm 2$ ) and the  $l = 3$  state will be split into 7 states ( $m = 0, \pm 1, \pm 2, \pm 3$ ), making a total of 35 possible transitions. Using the selection rule  $\Delta m = 0$ , five transitions are possible (when  $m = 0, m = 1, m = -1, m = 2$ , or  $m = -2$  for both states). Using the selection rule  $\Delta m = \pm 1$ , the following ten transitions are allowed:

$l = 2$	$\rightarrow$	$l = 3$
$m = 0$		$m = 1$
$m = 0$		$m = -1$
$m = 1$		$m = 2$
$m = -1$		$m = -2$
$m = 1$		$m = 0$
$m = -1$		$m = 0$
$m = 2$		$m = 3$
$m = 2$		$m = 1$
$m = -2$		$m = -3$
$m = -2$		$m = -1$

Problems 6-48 through 6-57 develop the quantum-mechanical properties of angular momentum using operator notation, without solving the Schrödinger equation.

6-48. Define the two (not necessarily Hermitian) operators

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad \text{and} \quad \hat{L}_- = \hat{L}_x - i\hat{L}_y$$

Using the results of Problem 6-13, show that

$$\begin{aligned} [\hat{L}_z, \hat{L}_+] &= \hat{L}_z \hat{L}_+ - \hat{L}_+ \hat{L}_z = \hbar \hat{L}_+ \\ [\hat{L}_z, \hat{L}_-] &= \hat{L}_z \hat{L}_- - \hat{L}_- \hat{L}_z = -\hbar \hat{L}_- \end{aligned}$$

and

$$[\hat{L}^2, \hat{L}_+] = [\hat{L}^2, \hat{L}_-] = 0$$

In Problem 6-13, we showed that

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \quad [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \quad [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

Now

$$\begin{aligned} [\hat{L}_z, \hat{L}_+] &= \hat{L}_z \hat{L}_+ - \hat{L}_+ \hat{L}_z \\ &= \hat{L}_z (\hat{L}_x + i\hat{L}_y) - \hat{L}_x \hat{L}_z - i\hat{L}_y \hat{L}_z \\ &= \hat{L}_z \hat{L}_x + i\hat{L}_z \hat{L}_y - \hat{L}_x \hat{L}_z - i\hat{L}_y \hat{L}_z \\ &= (\hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z) - i(\hat{L}_y \hat{L}_z - \hat{L}_z \hat{L}_y) \\ &= [\hat{L}_z, \hat{L}_x] - i[\hat{L}_y, \hat{L}_z] \\ &= i\hbar \hat{L}_y - i(i\hbar \hat{L}_x) = \hbar(\hat{L}_x + i\hat{L}_y) = \hbar \hat{L}_+ \end{aligned}$$

$$\begin{aligned} [\hat{L}_z, \hat{L}_-] &= \hat{L}_z \hat{L}_- - \hat{L}_- \hat{L}_z \\ &= \hat{L}_z (\hat{L}_x - i\hat{L}_y) - \hat{L}_x \hat{L}_z + i\hat{L}_y \hat{L}_z \\ &= \hat{L}_z \hat{L}_x - i\hat{L}_z \hat{L}_y - \hat{L}_x \hat{L}_z + i\hat{L}_y \hat{L}_z \\ &= (\hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z) + i(\hat{L}_y \hat{L}_z - \hat{L}_z \hat{L}_y) \\ &= [\hat{L}_z, \hat{L}_x] + i[\hat{L}_y, \hat{L}_z] \\ &= i\hbar \hat{L}_y + i(i\hbar \hat{L}_x) = \hbar(-\hat{L}_x + i\hat{L}_y) = -\hbar \hat{L}_- \end{aligned}$$

We also showed in Problem 6-13 that  $\hat{L}^2$  commutes with  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$ . Using this result, we find

$$\begin{aligned} [\hat{L}^2, \hat{L}_+] &= \hat{L}^2 \hat{L}_+ - \hat{L}_+ \hat{L}^2 \\ &= \hat{L}^2 (\hat{L}_x + i\hat{L}_y) - \hat{L}_x \hat{L}^2 - i\hat{L}_y \hat{L}^2 \\ &= \hat{L}^2 \hat{L}_x + i\hat{L}^2 \hat{L}_y - \hat{L}_x \hat{L}^2 - i\hat{L}_y \hat{L}^2 \\ &= (\hat{L}^2 \hat{L}_x - \hat{L}_x \hat{L}^2) - i(\hat{L}_y \hat{L}^2 - \hat{L}^2 \hat{L}_y) \\ &= [\hat{L}^2, \hat{L}_x] - i[\hat{L}_y, \hat{L}^2] = 0 \end{aligned}$$

$$\begin{aligned} [\hat{L}^2, \hat{L}_-] &= \hat{L}^2 \hat{L}_- - \hat{L}_- \hat{L}^2 \\ &= \hat{L}^2 (\hat{L}_x - i\hat{L}_y) - \hat{L}_x \hat{L}^2 + i\hat{L}_y \hat{L}^2 \\ &= \hat{L}^2 \hat{L}_x - i\hat{L}^2 \hat{L}_y - \hat{L}_x \hat{L}^2 + i\hat{L}_y \hat{L}^2 \\ &= (\hat{L}^2 \hat{L}_x - \hat{L}_x \hat{L}^2) + i(\hat{L}_y \hat{L}^2 - \hat{L}^2 \hat{L}_y) \\ &= [\hat{L}^2, \hat{L}_x] + i[\hat{L}_y, \hat{L}^2] = 0 \end{aligned}$$

6-49. Show that

$$\begin{aligned} \hat{L}_- \hat{L}_+ &= \hat{L}_x^2 + \hat{L}_y^2 + i\hat{L}_x \hat{L}_y - i\hat{L}_y \hat{L}_x \\ &= \hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z \end{aligned}$$

and

$$\hat{L}_+ \hat{L}_- = \hat{L}^2 - \hat{L}_z^2 + \hbar \hat{L}_z$$

$$\begin{aligned}
\hat{L}_- \hat{L}_+ &= (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) \\
&= \hat{L}_x^2 + \hat{L}_y^2 + i\hat{L}_x \hat{L}_y - i\hat{L}_y \hat{L}_x = \hat{L}^2 - \hat{L}_z^2 + i[\hat{L}_x, \hat{L}_y] \\
&= \hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z \\
\hat{L}_+ \hat{L}_- &= (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) \\
&= \hat{L}_x^2 + \hat{L}_y^2 + i[\hat{L}_y, \hat{L}_x] = \hat{L}^2 - \hat{L}_z^2 + \hbar \hat{L}_z
\end{aligned}$$

6-50. Because  $\hat{L}^2$  and  $\hat{L}_z$  commute, they have mutual eigenfunctions. We know from the chapter that these mutual eigenfunctions are the spherical harmonics,  $Y_l^m(\theta, \phi)$ , but we really don't need that information here. To emphasize this point, let  $\psi_{\alpha\beta}$  be the mutual eigenfunctions of  $\hat{L}^2$  and  $\hat{L}_z$  such that

$$\hat{L}^2 \psi_{\alpha\beta} = \beta^2 \psi_{\alpha\beta}$$

and

$$\hat{L}_z \psi_{\alpha\beta} = \alpha \psi_{\alpha\beta}$$

Now let

$$\psi_{\alpha\beta}^{+1} = \hat{L}_+ \psi_{\alpha\beta}$$

Show that

$$\hat{L}_z \psi_{\alpha\beta}^{+1} = (\alpha + \hbar) \psi_{\alpha\beta}^{+1}$$

and

$$\hat{L}^2 \psi_{\alpha\beta}^{+1} = \beta^2 \psi_{\alpha\beta}^{+1}$$

Therefore, if  $\alpha$  is an eigenvalue of  $\hat{L}_z$ , then  $\alpha + \hbar$  is also an eigenvalue (unless  $\psi_{\alpha\beta}^{+1}$  happens to be zero). In the notation for the spherical harmonics that we use in the chapter,  $\hat{L}_+ Y_l^m(\theta, \phi) \propto Y_l^{m+1}(\theta, \phi)$ .

We start with

$$\psi_{\alpha\beta}^{+1} = \hat{L}_+ \psi_{\alpha\beta}$$

Operating by  $\hat{L}_z$  from the left gives

$$\begin{aligned}
\hat{L}_z \psi_{\alpha\beta}^{+1} &= \hat{L}_z \hat{L}_+ \psi_{\alpha\beta} = (\hat{L}_z \hat{L}_x + i\hat{L}_z \hat{L}_y) \psi_{\alpha\beta} \\
&= \left( [\hat{L}_z, \hat{L}_x] + \hat{L}_x \hat{L}_z + i[\hat{L}_z, \hat{L}_y] + i\hat{L}_y \hat{L}_z \right) \psi_{\alpha\beta} \\
&= \left( i\hbar \hat{L}_y + \hat{L}_x \hat{L}_z + \hbar \hat{L}_x + i\hat{L}_y \hat{L}_z \right) \psi_{\alpha\beta} \\
&= \left( \hat{L}_+ \hat{L}_z + \hbar \hat{L}_+ \right) \psi_{\alpha\beta} = \hat{L}_+ (\alpha + \hbar) \psi_{\alpha\beta} \\
&= (\alpha + \hbar) \psi_{\alpha\beta}^{+1}
\end{aligned}$$

Finally,

$$\begin{aligned}
\hat{L}^2 \psi_{\alpha\beta}^{+1} &= \hat{L}^2 \hat{L}_+ \psi_{\alpha\beta} \\
&= \left( \hat{L}^2 \hat{L}_x + i\hat{L}^2 \hat{L}_y \right) \psi_{\alpha\beta} \\
&= \left( [\hat{L}^2, \hat{L}_x] + \hat{L}_x \hat{L}^2 + i[\hat{L}^2, \hat{L}_y] + i\hat{L}_y \hat{L}^2 \right) \psi_{\alpha\beta} \\
&= \left( \hat{L}_x \hat{L}^2 + i\hat{L}_y \hat{L}^2 \right) \psi_{\alpha\beta} = \hat{L}_+ \beta^2 \psi_{\alpha\beta} = \beta^2 \psi_{\alpha\beta}^{+1}
\end{aligned}$$

6-51. Using  $\hat{L}_-$  instead of  $\hat{L}_+$  in Problem 6-50, show that if  $\alpha$  is an eigenvalue of  $\hat{L}_z$ , then  $\alpha - \hbar$  is also an eigenvalue (unless  $\psi_{\alpha\beta}^{-1} = \hat{L}_- \psi_{\alpha\beta}$  happens to be zero). In the notation for the spherical harmonics that we use in the chapter,  $\hat{L}_- Y_l^m(\theta, \phi) \propto Y_l^{m-1}(\theta, \phi)$ .

We solve this problem by using the same approach as in Problem 6-50.

$$\begin{aligned}
\hat{L}_z \psi_{\alpha\beta}^{-1} &= \hat{L}_z \hat{L}_- \psi_{\alpha\beta} = \left( \hat{L}_z \hat{L}_x - i\hat{L}_z \hat{L}_y \right) \psi_{\alpha\beta} \\
&= \left( [\hat{L}_z, \hat{L}_x] + \hat{L}_x \hat{L}_z - i[\hat{L}_z, \hat{L}_y] - i\hat{L}_y \hat{L}_z \right) \psi_{\alpha\beta} \\
&= \left( i\hbar \hat{L}_y + \hat{L}_x \hat{L}_z - \hbar \hat{L}_x - i\hat{L}_y \hat{L}_z \right) \psi_{\alpha\beta} \\
&= \left( \hat{L}_- \hat{L}_z - \hbar \hat{L}_- \right) \psi_{\alpha\beta} = \hat{L}_- (\alpha - \hbar) \psi_{\alpha\beta} = (\alpha - \hbar) \psi_{\alpha\beta}^{-1}
\end{aligned}$$

6-52. Show that each application of  $\hat{L}_+$  to  $\psi_{\alpha\beta}$  raises the eigenvalue by  $\hbar$ , so long as the result is nonzero.

In Problem 6-50, we showed that if

$$\hat{L}_z \phi_{\alpha\beta} = \alpha \phi_{\alpha\beta}$$

then

$$\hat{L}_z \hat{L}_+ \psi_{\alpha\beta} = (\alpha + \hbar) \psi_{\alpha\beta}^{+1}$$

Now applying  $\hat{L}_+$  to  $\psi_{\alpha\beta}^{+1}$  and operating with  $\hat{L}_z$  gives

$$\hat{L}_z \hat{L}_+ \psi_{\alpha\beta}^{+1} = \hat{L}_+ (\hat{L}_z + \hbar) \psi_{\alpha\beta}^{+1}$$

where we have used the relation  $\hat{L}_z \hat{L}_+ = \hat{L}_+ \hat{L}_z + \hbar \hat{L}_+$ . Now  $\hat{L}_z \psi_{\alpha\beta}^{+1} = (\alpha + \hbar) \psi_{\alpha\beta}^{+1}$ , so

$$\hat{L}_z \hat{L}_+ \psi_{\alpha\beta}^{+1} = \hat{L}_+ (\alpha + 2\hbar) \psi_{\alpha\beta}^{+1} = (\alpha + 2\hbar) \psi_{\alpha\beta}^{+2}$$

which shows that the eigenvalue once again increases by  $\hbar$ . We can continue this process to show that  $\hat{L}_z \psi_{\alpha\beta}^{+2} = (\alpha + 3\hbar) \psi_{\alpha\beta}^{+3}$ , and so forth.

6-53. Show that each application of  $\hat{L}_-$  to  $\psi_{\alpha\beta}$  lowers the eigenvalue by  $\hbar$ , so long as the result is nonzero.

In Problem 6–51, we showed that if

$$\hat{L}_z \phi_{\alpha\beta} = \alpha \phi_{\alpha\beta}$$

then

$$\hat{L}_z \hat{L}_- \psi_{\alpha\beta} = (\alpha - \hbar) \psi_{\alpha\beta}^{-1}$$

Applying  $\hat{L}_-$  to  $\psi_{\alpha\beta}^{-1}$  and then operating by  $\hat{L}_z$  gives

$$\hat{L}_z \hat{L}_- \psi_{\alpha\beta}^{-1} = \hat{L}_- (\hat{L}_z - \hbar) \psi_{\alpha\beta}^{-1}$$

where we have used the relation  $\hat{L}_z \hat{L}_- = \hat{L}_- \hat{L}_z - \hbar \hat{L}_-$ . Now  $\hat{L}_z \psi_{\alpha\beta}^{-1} = (\alpha - \hbar) \psi_{\alpha\beta}^{-1}$ , so

$$\hat{L}_z \hat{L}_- \psi_{\alpha\beta}^{-1} = \hat{L}_- (\alpha - 2\hbar) \psi_{\alpha\beta}^{-1} = (\alpha - 2\hbar) \psi_{\alpha\beta}^{-2}$$

Just as in Problem 6–52, we can continue this process to show that  $\hat{L}_z \psi_{\alpha\beta}^{-2} = (\alpha - 3\hbar) \psi_{\alpha\beta}^{-3}$ , and so forth.

6–54. According to Problem 6–48,  $\hat{L}^2$  commutes with  $\hat{L}_+$  and  $\hat{L}_-$ . Now prove that  $\hat{L}^2$  commutes with  $\hat{L}_+^2$  and  $\hat{L}_-^2$ . Now prove that

$$[\hat{L}^2, \hat{L}_\pm^m] = 0 \quad m = 1, 2, 3, \dots$$

$$[\hat{L}^2, \hat{L}_+^2] = \hat{L}^2 \hat{L}_+^2 - \hat{L}_+^2 \hat{L}^2 = (\hat{L}^2 \hat{L}_+) (\hat{L}_+) - \hat{L}_+ (\hat{L}_+ \hat{L}^2)$$

Using the fact that  $\hat{L}^2$  and  $\hat{L}_+$  commute, we can rewrite this as

$$[\hat{L}^2, \hat{L}_+^2] = \hat{L}_+ \hat{L}^2 \hat{L}_+ - \hat{L}_+ \hat{L}^2 \hat{L}_+ = 0$$

We can show that  $\hat{L}^2$  commutes with  $\hat{L}_-^2$  by replacing  $\hat{L}_+$  with  $\hat{L}_-$  in the above proof. We can show that the general statement is true using a stepwise approach. For example, consider the case of  $m = 3$ . We have already shown that  $\hat{L}^2$  commutes with  $\hat{L}_+^2$  and  $\hat{L}_-^2$ . Then

$$[\hat{L}^2, \hat{L}_+^3] = \hat{L}^2 \hat{L}_+^3 - \hat{L}_+^3 \hat{L}^2 = (\hat{L}^2 \hat{L}_+) (\hat{L}_+^2) - \hat{L}_+^2 (\hat{L}_+ \hat{L}^2)$$

Using the fact that  $[\hat{L}^2, \hat{L}_+^2] = 0$ , we can rewrite this as

$$[\hat{L}^2, \hat{L}_+^3] = \hat{L}_+ (\hat{L}^2 \hat{L}_+) \hat{L}_+ - \hat{L}_+^2 \hat{L}^2 \hat{L}_+ = \hat{L}_+ \hat{L}^2 \hat{L}_+ - \hat{L}_+^2 \hat{L}^2 \hat{L}_+ = 0$$

We can show the general statement is true for any  $m = n$  as long as we have proved it for  $m = n - 1$ . Again, the case with  $\hat{L}_-$  is proved in the same way, substituting  $\hat{L}_-$  for  $\hat{L}_+$ .

6–55. In Problems 6–50 through 6–53, we proved that if  $\psi_{\alpha\beta}^{\pm m} = \hat{L}_\pm^m \psi_{\alpha\beta}$ , then

$$\hat{L}_z \psi_{\alpha\beta}^{\pm m} = (\alpha \pm m\hbar) \psi_{\alpha\beta}^{\pm m} \quad m = 0, 1, 2, \dots$$

so long as the result is non-zero. The operators  $\hat{L}_\pm$  are called raising ( $\hat{L}_+$ ) or lowering ( $\hat{L}_-$ ) operators because they raise or lower the eigenvalues of  $\hat{L}_z$ . They are also called ladder operators because the set of eigenvalues  $\alpha \pm m\hbar$  form a ladder of eigenvalues. Use the result of Problem 6–54 to show that

$$\hat{L}^2 \psi_{\alpha\beta}^{\pm m} = \beta^2 \psi_{\alpha\beta}^{\pm m}$$

$$\begin{aligned} \hat{L}^2 \psi_{\alpha\beta}^{\pm m} &= \hat{L}^2 \hat{L}_\pm^m \psi_{\alpha\beta} \\ &= \hat{L}_\pm^m \hat{L}^2 \psi_{\alpha\beta} \\ &= \hat{L}_\pm^m \beta^2 \psi_{\alpha\beta} \\ &= \beta^2 \psi_{\alpha\beta}^{\pm m} \end{aligned}$$

6–56. Start with

$$\hat{L}_z \psi_{\alpha\beta}^{\pm m} = (\alpha \pm m\hbar) \psi_{\alpha\beta}^{\pm m}$$

Operate on both sides with  $\hat{L}_z$  and subtract the result from (Problem 6–55)

$$\hat{L}^2 \psi_{\alpha\beta}^{\pm m} = \beta^2 \psi_{\alpha\beta}^{\pm m}$$

to get

$$(\hat{L}^2 - \hat{L}_z^2) \psi_{\alpha\beta}^{\pm m} = (\hat{L}_x^2 + \hat{L}_y^2) \psi_{\alpha\beta}^{\pm m} = [\beta^2 - (\alpha \pm m\hbar)^2] \psi_{\alpha\beta}^{\pm m}$$

Because the operator  $\hat{L}_x^2 + \hat{L}_y^2$  corresponds to a nonnegative physical quantity, show that

$$\beta^2 - (\alpha \pm m\hbar)^2 \geq 0$$

or that

$$-\beta \leq \alpha \pm m\hbar \leq \beta \quad m = 0, 1, 2, \dots$$

Because  $\beta$  is fixed, the possible values of  $m$  must be finite in number.

The steps outlined in the problem lead easily to the result

$$(\hat{L}^2 - \hat{L}_z^2) \psi_{\alpha\beta}^{\pm m} = (\hat{L}_x^2 + \hat{L}_y^2) \psi_{\alpha\beta}^{\pm m} = [\beta^2 - (\alpha \pm m\hbar)^2] \psi_{\alpha\beta}^{\pm m}$$

Because the operator  $\hat{L}_x^2 + \hat{L}_y^2$  corresponds to a nonnegative physical quantity, we know that

$$\begin{aligned} \int d\tau (\psi_{\alpha\beta}^{\pm m})^* (\hat{L}_x^2 + \hat{L}_y^2) \psi_{\alpha\beta}^{\pm m} &\geq 0 \\ [\beta^2 - (\alpha \pm m\hbar)^2] \int d\tau (\psi_{\alpha\beta}^{\pm m})^* \psi_{\alpha\beta}^{\pm m} &\geq 0 \\ \beta^2 - (\alpha \pm m\hbar)^2 &\geq 0 \end{aligned}$$

Then

$$-\beta \leq \alpha \pm m\hbar \leq \beta \quad m = 0, 1, 2, \dots$$

6–57. Let  $\alpha_{\max}$  be the largest possible value of  $\alpha \pm m\hbar$ . By definition then, we have that

$$\hat{L}_z \psi_{\alpha_{\max}\beta} = \alpha_{\max} \psi_{\alpha_{\max}\beta}$$

$$\hat{L}^2 \psi_{\alpha_{\max}\beta} = \beta^2 \psi_{\alpha_{\max}\beta}$$

and

$$\hat{L}_+ \psi_{\alpha_{\max}\beta} = 0$$

Operate on the last equation with  $\hat{L}_-$  to obtain

$$\begin{aligned} \hat{L}_- \hat{L}_+ \psi_{\alpha_{\max}\beta} &= 0 \\ &= (\hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z) \psi_{\alpha_{\max}\beta} \end{aligned}$$

and

$$\beta^2 = \alpha_{\max}^2 + \hbar \alpha_{\max}$$

Use a parallel procedure on  $\psi_{\alpha_{\min}\beta}$  to obtain

$$\beta^2 = \alpha_{\min}^2 - \hbar \alpha_{\min}$$

Now show that  $\alpha_{\max} = -\alpha_{\min}$ , and then argue that the possible values of the eigenvalues  $\alpha$  of  $\hat{L}_z$  extend from  $+\alpha_{\max}$  to  $-\alpha_{\max}$  in steps of magnitude  $\hbar$ . This is possible only if  $\alpha_{\max}$  is itself an integer (or perhaps a half-integer) times  $\hbar$ . Finally, show that this last result leads to

$$\beta^2 = l(l+1)\hbar^2 \quad l = 0, 1, 2, \dots$$

and

$$\alpha = m\hbar \quad m = 0, \pm 1, \pm 2, \dots, \pm l$$

Recall from Problem 6-49 that  $\hat{L}_- \hat{L}_+ = \hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z$ . Then

$$\begin{aligned} \hat{L}_- \hat{L}_+ \psi_{\alpha_{\max}\beta} &= \hat{L}_-(0) = 0 = (\hat{L}_- \hat{L}_+) \psi_{\alpha_{\max}\beta} \\ &= (\hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z) \psi_{\alpha_{\max}\beta} \end{aligned}$$

Using our definitions in the beginning of this problem, we can evaluate the result for the operation of each operator on  $\psi_{\alpha_{\max}\beta}$  to get

$$0 = [\beta^2 - \alpha_{\max}^2 - \hbar \alpha_{\max}] \psi_{\alpha_{\max}\beta}$$

This result implies that

$$\beta^2 - (\alpha_{\max}^2 + \hbar \alpha_{\max}) = 0$$

or, equivalently,

$$\beta^2 = \alpha_{\max}^2 + \hbar \alpha_{\max} \quad (1)$$

Similarly, for  $\alpha_{\min}$ , recall that  $\hat{L}_+ \hat{L}_- = \hat{L}^2 - \hat{L}_z^2 + \hbar \hat{L}_z$ . Then

$$\begin{aligned} \hat{L}_+ \hat{L}_- \psi_{\alpha_{\min}\beta} &= \hat{L}_+(0) = 0 = (\hat{L}_+ \hat{L}_-) \psi_{\alpha_{\min}\beta} \\ &= (\hat{L}^2 - \hat{L}_z^2 + \hbar \hat{L}_z) \psi_{\alpha_{\min}\beta} \end{aligned}$$

Using the definitions at the beginning of this problem (replacing  $\alpha_{\max}$  with  $\alpha_{\min}$ ), we can substitute the result in for each operation and write

$$0 = [\beta^2 - \alpha_{\min}^2 - \hbar \alpha_{\min}] \psi_{\alpha_{\min}\beta}$$

This result implies that

$$\beta^2 - (\alpha_{\min}^2 - \hbar \alpha_{\min}) = 0$$

or, equivalently,

$$\beta^2 = \alpha_{\min}^2 - \hbar \alpha_{\min}$$

Now we have two equations for  $\beta^2$ , one in terms of  $\alpha_{\max}$  and one in terms of  $\alpha_{\min}$ . Setting these equal to one another, we find

$$\begin{aligned} \alpha_{\max}^2 + \hbar \alpha_{\max} &= \alpha_{\min}^2 - \hbar \alpha_{\min} \\ \alpha_{\max} &= \frac{-\hbar \pm \sqrt{\hbar^2 - 4(\hbar \alpha_{\min} - \alpha_{\min}^2)}}{2} \\ &= -\frac{\hbar}{2} \pm \frac{2\alpha_{\min} - \hbar}{2} \\ \alpha_{\max} &= -\alpha_{\min} \quad \text{or} \quad \alpha_{\min} - \hbar \end{aligned}$$

However,  $\alpha_{\min}$  is the minimum value of  $\alpha$ , so  $\alpha_{\max} \neq \alpha_{\min} - \hbar$  and we can conclude that  $\alpha_{\max} = -\alpha_{\min}$ . According to Problem 6-55,  $\alpha$  varies in integral steps of  $\hbar$ , so  $\alpha$  must vary from  $\alpha_{\min}$  to  $\alpha_{\max}$  in steps of  $\hbar$ . This is only true if  $\alpha_{\max}$  is an integer or half-integer times  $\hbar$ . We call this multiplicative constant  $l$  and so

$$\alpha_{\max} = l\hbar \quad \alpha_{\min} = -l\hbar$$

Because  $\alpha$  varies in integral steps of  $\hbar$ , we can describe any value of  $\alpha$  by

$$\alpha = m\hbar \quad m = 0, \pm 1, \pm 2, \dots, \pm l$$

(If  $\alpha = 0$ , then  $l$  must be an integer.) We can also write (from Equation 1)

$$\beta^2 = (l\hbar)^2 + \hbar(l\hbar) = \hbar^2(l^2 + l) = l(l+1)\hbar^2$$

where  $l$  is, of course, an integer.

6-58. According to Problems 6-50 and 6-51,

$$\hat{L}_+ Y_l^m(\theta, \phi) = \hbar c_{lm}^+ Y_l^{m+1}(\theta, \phi)$$

and

$$\hat{L}_- Y_l^m(\theta, \phi) = \hbar c_{lm}^- Y_l^{m-1}(\theta, \phi)$$

where we are using the notation  $Y_l^m(\theta, \phi)$  instead of  $\psi_{\alpha,\beta}$ . Show that

$$\hat{L}_x Y_l^m(\theta, \phi) = \frac{\hbar c_{lm}^+}{2} Y_l^{m+1}(\theta, \phi) + \frac{\hbar c_{lm}^-}{2} Y_l^{m-1}(\theta, \phi)$$

and

$$\hat{L}_y Y_l^m(\theta, \phi) = \frac{\hbar c_{lm}^+}{2i} Y_l^{m+1}(\theta, \phi) - \frac{\hbar c_{lm}^-}{2i} Y_l^{m-1}(\theta, \phi)$$

Use this result to show that

$$\langle L_x \rangle = \langle L_y \rangle = 0$$

for any rotational state (see Problem 6-14).

Add the first two equations given in the problem to obtain

$$\begin{aligned}(\hat{L}_+ + \hat{L}_-)Y_l^m(\theta, \phi) &= \hbar c_{lm}^+ Y_l^{m+1}(\theta, \phi) + \hbar c_{lm}^- Y_l^{m-1}(\theta, \phi) \\ 2\hat{L}_x Y_l^m(\theta, \phi) &= \hbar c_{lm}^+ Y_l^{m+1}(\theta, \phi) + \hbar c_{lm}^- Y_l^{m-1}(\theta, \phi) \\ \hat{L}_x Y_l^m(\theta, \phi) &= \frac{\hbar c_{lm}^+}{2} Y_l^{m+1}(\theta, \phi) + \frac{\hbar c_{lm}^-}{2} Y_l^{m-1}(\theta, \phi)\end{aligned}\quad (1)$$

Subtract the first two equations given in the problem to obtain

$$\begin{aligned}(\hat{L}_+ - \hat{L}_-)Y_l^m(\theta, \phi) &= \hbar c_{lm}^+ Y_l^{m+1}(\theta, \phi) - \hbar c_{lm}^- Y_l^{m-1}(\theta, \phi) \\ 2i\hat{L}_y Y_l^m(\theta, \phi) &= \hbar c_{lm}^+ Y_l^{m+1}(\theta, \phi) - \hbar c_{lm}^- Y_l^{m-1}(\theta, \phi) \\ \hat{L}_y Y_l^m(\theta, \phi) &= \frac{\hbar c_{lm}^+}{2i} Y_l^{m+1}(\theta, \phi) - \frac{\hbar c_{lm}^-}{2i} Y_l^{m-1}(\theta, \phi)\end{aligned}\quad (2)$$

We will now use these results to show that  $\langle L_x \rangle = \langle L_y \rangle = 0$  for any rotational state.

$$\langle L_x \rangle = \int Y_l^m(\theta, \phi)^* \hat{L}_x Y_l^m(\theta, \phi) \sin\theta d\theta d\phi$$

Substituting in from Equation 1 gives

$$\begin{aligned}\langle L_x \rangle &= \frac{\hbar c_{lm}^+}{2} \int Y_l^m(\theta, \phi)^* Y_l^{m+1}(\theta, \phi) \sin\theta d\theta d\phi \\ &\quad + \frac{\hbar c_{lm}^-}{2} \int Y_l^m(\theta, \phi)^* Y_l^{m-1}(\theta, \phi) \sin\theta d\theta d\phi \\ &= 0\end{aligned}$$

because the functions  $Y_l^m(\theta, \phi)$  are orthogonal. Likewise,

$$\langle L_y \rangle = \int Y_l^m(\theta, \phi)^* \hat{L}_y Y_l^m(\theta, \phi) \sin\theta d\theta d\phi$$

Substituting in from Equation 2 gives

$$\begin{aligned}\langle L_y \rangle &= \frac{\hbar c_{lm}^+}{2i} \int Y_l^m(\theta, \phi)^* Y_l^{m+1}(\theta, \phi) \sin\theta d\theta d\phi \\ &\quad - \frac{\hbar c_{lm}^-}{2i} \int Y_l^m(\theta, \phi)^* Y_l^{m-1}(\theta, \phi) \sin\theta d\theta d\phi \\ &= 0\end{aligned}$$

because the functions  $Y_l^m(\theta, \phi)$  are orthogonal.

6-59. Show that

$$\hat{L}_+ = \hbar e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right]$$

and

$$\hat{L}_- = \hbar e^{-i\phi} \left[ -\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right]$$

From Equations 6.37 and the definitions of  $\hat{L}_+$  and  $\hat{L}_-$  (Problem 6-48),

$$\begin{aligned}\hat{L}_+ &= \hat{L}_x + i\hat{L}_y \\ &= -i\hbar \left( -\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) + \hbar \left( \cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right) \\ &= \hbar \left[ (\cos\phi + i \sin\phi) \frac{\partial}{\partial\theta} + i (\cos\phi + i \sin\phi) \cot\theta \frac{\partial}{\partial\phi} \right] \\ &= \hbar e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] \\ \hat{L}_- &= \hat{L}_x - i\hat{L}_y \\ &= -i\hbar \left( -\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) - \hbar \left( \cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right) \\ &= \hbar \left[ -(\cos\phi - i \sin\phi) \frac{\partial}{\partial\theta} + i (\cos\phi - i \sin\phi) \cot\theta \frac{\partial}{\partial\phi} \right] \\ &= \hbar e^{-i\phi} \left[ -\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right]\end{aligned}$$