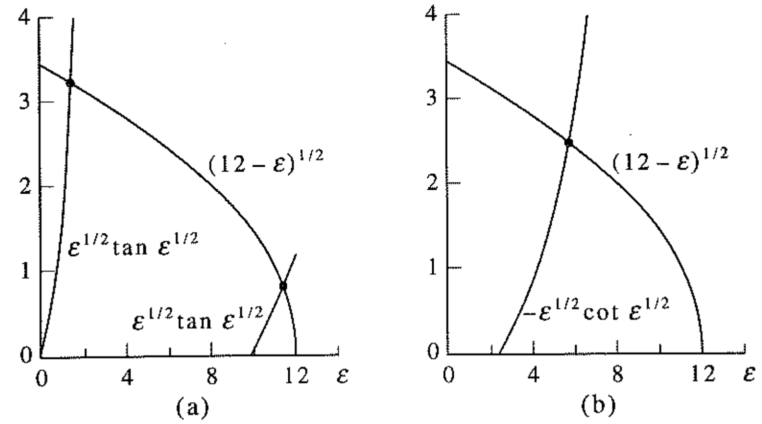

FIGURE 4.4
(a) Plots of both $\varepsilon^{1/2}\tan\varepsilon^{1/2}$ and $(12-\varepsilon)^{1/2}$ versus ε. The intersections of the curves give the allowed values of ε for a one-dimensional potential well of depth $V_0 = 12\hbar^2/2ma^2$. (b) Plots of both $-\varepsilon^{1/2}\cot\varepsilon^{1/2}$ and $(12-\varepsilon)^{1/2}$ plotted against ε. The intersection gives an allowed value of ε for a one-dimensional potential well of depth $V_0 = 12\hbar^2/2ma^2$.

MATHCHAPTER D

Spherical Coordinates

PROBLEMS AND SOLUTIONS

D–1. Derive Equation D.2 from D.1.

Equations D.1 are

$$x = r\sin\theta\cos\phi \qquad y = r\sin\theta\sin\phi \qquad z = r\cos\theta \tag{D.1}$$

We use these equations to write $\tan\phi$ as

$$\tan\phi = \frac{\sin\phi}{\cos\phi} = \frac{r\sin\theta}{r\sin\theta}\left(\frac{\sin\phi}{\cos\phi}\right) = \frac{y}{x} \tag{1}$$

Likewise, we can write (using trigonometric identities)

$$\begin{aligned} r^2 &= r^2(\sin^2\theta + \cos^2\theta)(\sin^2\phi + \cos^2\phi) \\ &= r^2\sin^2\theta\sin^2\phi + r^2\cos^2\theta\sin^2\phi + r^2\sin^2\theta\cos^2\phi + r^2\cos^2\theta\cos^2\phi \\ &= (r\sin\theta\sin\phi)^2 + (r\sin\theta\sin\phi)^2 + (r\cos\theta)^2(\sin^2\phi + \cos^2\phi) \\ &= x^2 + y^2 + z^2 \\ r &= (x^2 + y^2 + z^2)^{1/2} \end{aligned} \tag{2}$$

and

$$\begin{aligned} z &= r\cos\theta \\ \cos\theta &= \frac{z}{(x^2 + y^2 + z^2)^{1/2}} \end{aligned} \tag{3}$$

Equations 1, 2, and 3 are Equations D.2.

D–2. Express the following points given in Cartesian coordinates in terms of spherical coordinates.

$$(x, y, z): \quad (1, 0, 0); \quad (0, 1, 0); \quad (0, 0, 1); \quad (0, 0, -1)$$

Use the equations derived in the previous problem (Equations D.2).

a. $(1, 0, 0)$

$$\begin{aligned} r &= (x^2 + y^2 + z^2)^{1/2} = 1 \\ \theta &= \cos^{-1}\left(\frac{z}{r}\right) = \cos^{-1} 0 = \frac{\pi}{2} \\ \phi &= \tan^{-1}\left(\frac{y}{x}\right) = \tan^{-1} 0 = 0 \end{aligned}$$

Spherical coordinates: $(1, \frac{\pi}{2}, 0)$

b. (0, 1, 0)

$$r = (x^2 + y^2 + z^2)^{1/2} = 1$$
$$\theta = \cos^{-1}\left(\frac{z}{r}\right) = \cos^{-1} 0 = \frac{\pi}{2}$$
$$\phi = \tan^{-1}\left(\frac{y}{x}\right) = \tan^{-1}\left(\frac{1}{0}\right) = \frac{\pi}{2}$$

Spherical coordinates: $(1, \frac{\pi}{2}, \frac{\pi}{2})$

c. (0, 0, 1)

$$r = (x^2 + y^2 + z^2)^{1/2} = 1$$
$$\theta = \cos^{-1}\left(\frac{z}{r}\right) = \cos^{-1}(1) = 0$$
$$\phi = \tan^{-1}\left(\frac{y}{x}\right) = \tan^{-1}\frac{0}{0}$$

(This means that ϕ can take on any value.) Spherical coordinates: $(1, 0, \phi)$

d. (0, 0, −1)

$$r = (x^2 + y^2 + z^2)^{1/2} = 1$$
$$\theta = \cos^{-1}\left(\frac{z}{r}\right) = \cos^{-1}(-1) = \pi$$
$$\phi = \tan^{-1}\left(\frac{y}{x}\right) = \tan^{-1}\frac{0}{0}$$

Spherical coordinates: $(1, \pi, \phi)$

D–3. Describe the graphs of the following equations:

a. $r = 5$, **b.** $\theta = \pi/4$, **c.** $\phi = \pi/2$

a. A sphere of radius 5 centered at the origin

b. A cone about the z-axis of internal angle $\frac{\pi}{4}$ **c.** The yz-plane

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D–4. Use Equation D.3 to determine the volume of a hemisphere.

Let the radius of the hemisphere be a. A hemisphere corresponds to $0 \le \theta \le \pi$ and $0 \le \phi \le \pi$, so

$$dV = r^2 \sin\theta dr d\theta d\phi$$
$$V = \int_0^a r^2 dr \int_0^\pi \sin\theta d\theta \int_0^\pi d\phi = \frac{2\pi a^3}{3}$$

D–5. Use Equation D.5 to determine the surface area of a hemisphere.

Let the radius of the hemisphere be a. Then the surface area of a hemisphere is

$$dA = r^2 \sin\theta d\theta d\phi$$
$$A = a^2 \int_0^\pi \sin\theta d\theta \int_0^\pi d\phi = 2\pi a^2$$

D–6. Evaluate the integral

$$I = \int_0^\pi \cos^2\theta \sin^3\theta d\theta$$

by letting $x = \cos\theta$.

If $x = \cos\theta$, then $dx = -\sin\theta d\theta$, $x = 1$ for $\theta = 0$, and $x = -1$ for $\theta = \pi$. Then

$$I = \int_0^\pi \cos^2\theta \sin^3\theta d\theta = \int_0^\pi \cos^2\theta \sin\theta(1 - \cos^2\theta) d\theta$$
$$= -\int_1^{-1} dx x^2(1 - x^2) = \int_{-1}^1 x^2 dx - \int_{-1}^1 x^4 dx$$
$$= \frac{1}{3} + \frac{1}{3} + \frac{1}{5} + \frac{1}{5} = \frac{4}{15}$$

D–7. We will learn in Chapter 6 that a $2p_y$ hydrogen atom orbital is given by

$$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}} re^{-r/2} \sin\theta \sin\phi$$

Show that ψ_{2p_y} is normalized. (Don't forget to square ψ_{2p_y} first.)

We want to show that

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{2p_y}^* \psi_{2p_y} r^2 \sin\theta dr d\theta d\phi = 1$$

First, we square ψ_{2p_y}:

$$\psi_{2p_y}^* \psi_{2p_y} = \frac{1}{32\pi} r^2 e^{-r} \sin^2\theta \sin^2\phi$$

Then

$$I = \frac{1}{32\pi} \int_0^\infty dr r^4 e^{-r} \int_0^\pi d\theta \sin^3\theta \int_0^{2\pi} \sin^2\phi d\phi$$
$$= \left(\frac{1}{32\pi}\right)(4!)\left(\frac{4}{3}\right)\left(\frac{2\pi}{2}\right) = 1$$

and we have shown that ψ_{2p_y} is normalized.

D–8. We will learn in Chapter 6 that a 2s hydrogen atomic orbital is given by

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}(2 - r)e^{-r/2}$$

Show that ψ_{2s} is normalized. (Don't forget to square ψ_{2s} first.)

We want to show that

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{2s}^* \psi_{2s} r^2 \sin\theta dr d\theta d\phi = 1$$

First, we square ψ_{2s}:

$$\psi_{2s}^*\psi_{2s} = \frac{1}{32\pi}(2-r)^2e^{-r}$$

Then

$$\begin{aligned} I &= \frac{1}{32\pi}\int_0^\infty r^2(2-r)^2e^{-r}dr\int_0^\pi d\theta\sin\theta\int_0^{2\pi}d\phi \\ &= \frac{1}{32\pi}\left(4\int_0^\infty r^2e^{-r}dr - 4\int_0^\infty r^3e^{-r}dr + \int_0^\infty r^4e^{-r}dr\right)(2)(2\pi) \\ &= \frac{1}{8}[4(2)-4(3!)+4!] = \frac{1}{8}(8) = 1 \end{aligned}$$

and ψ_{2s} is normalized.

D–9. Show that

$$Y_1^0(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$Y_1^1(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{1/2}e^{i\phi}\sin\theta$$

and

$$Y_1^{-1}(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{1/2}e^{-i\phi}\sin\theta$$

are orthonormal over the surface of a sphere.

We can show that two functions f_i and f_j are orthonormal by demonstrating that

$$\int_0^\infty\int_0^\pi\int_0^{2\pi} f_1^* f_2 r^2\sin\theta drd\theta d\phi = \delta_{ij}$$

For the functions above,

$$\begin{aligned} \int Y_1^{0*}Y_1^0 &= \frac{3}{4\pi}\int_0^\pi \sin\theta\cos^2\theta d\theta\int_0^{2\pi}d\phi \\ &= \frac{3}{4\pi}\left(\frac{-\cos^3\theta}{3}\Big|_0^\pi\right)(2\pi) = \frac{3}{2}\left(\frac{2}{3}\right) = 1 \\ \int Y_1^{1*}Y_1^1 &= \frac{3}{8\pi}\int_0^\pi d\theta\sin^3\theta\int_0^{2\pi}d\phi \\ &= \frac{3}{8\pi}\left(\frac{4}{3}\right)(2\pi) = 1 \\ \int Y_1^{-1*}Y_1^{-1} &= \frac{3}{8\pi}\int_0^\pi d\theta\sin^3\theta\int_0^{2\pi}d\phi \\ &= \frac{3}{8\pi}\left(\frac{4}{3}\right)(2\pi) = 1 \end{aligned}$$

$$\int Y_1^{0*}Y_1^1 = \int Y_1^{-1*}Y_1^0 = \frac{3}{4\sqrt{2}\pi}\int_0^\pi d\theta\cos\theta\sin^2\theta\int_0^{2\pi}e^{i\phi}d\phi = 0$$

$$\int Y_1^{0*}Y_1^{-1} = \frac{3}{4\sqrt{2}\pi}\int_0^\pi d\theta\cos\theta\sin^2\theta\int_0^{2\pi}e^{-i\phi}d\phi = 0$$

$$\int Y_1^{1*}Y_1^{-1} = \frac{3}{8\pi}\int_0^\pi d\theta\sin^3\theta\int_0^{2\pi}e^{2i\phi}d\phi = 0$$

(Recall from Problem 3–15 that $\int_0^{2\pi}e^{-i\phi}d\phi = \int_0^{2\pi}e^{i\phi}d\phi = 0$.)

D–10. Evaluate the average of $\cos\theta$ and $\cos^2\theta$ over the surface of a sphere.

To determine the average of $\cos\theta$ over the surface of a sphere, we must evaluate the integral

$$\int_0^\pi \sin\theta\cos\theta d\theta\int_0^{2\pi}d\phi = \frac{1}{2}(2\pi)\int_0^\pi \sin 2\theta d\theta = 0$$

Because this integral is equal to zero, the average of $\cos\theta$ is zero. For the average of $\cos^2\theta$ over the surface of a sphere, we must first evaluate the integral

$$\int_0^\pi \sin\theta\cos^2\theta d\theta\int_0^{2\pi}d\phi = 2\pi\int_{-1}^1 x^2dx = \frac{4\pi}{3}$$

The average of $\cos^2\theta$ over the surface of a sphere is then given by

$$\frac{\int\cos^2\theta dA}{\int dA} = \frac{4\pi}{3(4\pi)} = \frac{1}{3}$$

D–11. We shall frequently use the notation $d\mathbf{r}$ to represent the volume element in spherical coordinates. Evaluate the integral

$$I = \int d\mathbf{r}e^{-r}\cos^2\theta$$

where the integral is over all space (in other words, over all posible values of r, θ and ϕ).

$$\begin{aligned} I &= \int d\mathbf{r}e^{-r}\cos^2\theta \\ &= \int_0^\infty dr r^2e^{-r}\int_0^\pi d\theta\cos^2\theta\sin\theta\int_0^{2\pi}d\phi \\ &= (2)\left(\frac{4\pi}{3}\right) = \frac{8\pi}{3} \end{aligned}$$

D–12. Show that the two functions

$$f_1(r) = e^{-r}\cos\theta \quad \text{and} \quad f_2(r) = (2-r)e^{-r/2}\cos\theta$$

are orthogonal over all space (in other words, over all possible values of r, θ and ϕ).

If $f_1(r)$ and $f_2(r)$ are orthogonal, then

$$I = \int d\mathbf{r} f_1^*(r) f_2(r) = 0$$

We now evaluate this integral as

$$\begin{aligned} I &= \int_0^\infty dr r^2 e^{-r}(2-r)e^{-r/2} \int_0^\pi d\theta \cos^2\theta \sin\theta \int_0^{2\pi} d\phi \\ &= \int_0^\infty dr (2r^2 - r^3) e^{-3r/2} \left(\frac{4\pi}{3}\right) \\ &= \frac{8\pi}{3}\int_0^\infty dr r^2 e^{-3r/2} - \frac{4\pi}{3}\int_0^\infty dr r^3 e^{-3r/2} \\ &= \left(\frac{8\pi}{3}\right)\left(\frac{16}{27}\right) - \left(\frac{4\pi}{3}\right)\left(\frac{32}{27}\right) = 0 \end{aligned}$$

CHAPTER 5

The Harmonic Oscillator and the Rigid Rotator: Two Spectroscopic Models

PROBLEMS AND SOLUTIONS

5–1. Verify that $x(t) = A \sin\omega t + B\cos\omega t$, where $\omega = (k/m)^{1/2}$ is a solution to Newton's equation for a harmonic oscillator.

Newton's equation for a harmonic oscillator is

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0 \tag{5.3}$$

Substituting $x(t) = A\sin\omega t + B\cos\omega t$ into Newton's equation, we find

$$\begin{aligned} -A\omega^2 \sin\omega t - B\omega^2\cos\omega t + \frac{k}{m}(A\sin\omega t + B\cos\omega t) \\ = -\frac{k}{m}(A\sin\omega t + B\cos\omega t) + \frac{k}{m}(A\sin\omega t + B\cos\omega t) = 0 \end{aligned}$$

where we have used the relationship $\omega = (k/m)^{1/2}$.

5–2. Verify that $x(t) = C\sin(\omega t + \phi)$ is a solution to Newton's equation for a harmonic oscillator.

Newton's equation for a harmonic oscillator is

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0 \tag{5.3}$$

Substituting $x(t) = C\sin(\omega t + \phi)$, we find

$$-C\omega^2\sin(\omega t+\phi) + \frac{k}{m}C\sin(\omega t+\phi) = -\frac{k}{m}C\sin(\omega t+\phi) + \frac{k}{m}C\sin(\omega t+\phi) = 0$$

where we have used the relationship $\omega = (k/m)^{1/2}$.

5–3. The general solution for the classical harmonic oscillator is $x(t) = C\sin(\omega t + \phi)$. Show that the displacement oscillates between $+C$ and $-C$ with a frequency ω radian·s^{-1} or $\nu = \omega/2\pi$ cycle·s^{-1}. What is the period of the oscillations; that is, how long does it take to undergo one cycle?
