and

$$\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2\alpha^{n+1}}$$

where $n!$ is n factorial, or $n! = n(n-1)(n-2)\cdots(1)$.

First, we demonstrate that $p(v)$ is normalized by showing that $\int_0^\infty p(v)dv = 1$:

$$\begin{aligned}\int_0^\infty p(v)dv &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^2 e^{-mv^2/2k_B T}dv \\ &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\frac{2k_B T}{4m}\left(\frac{2\pi k_B T}{m}\right)^{1/2} \\ &= \pi^{3/2}\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left(\frac{2k_B T}{m}\right)^{3/2} \\ &= 1\end{aligned}$$

Using Equation B.12, we write

$$\begin{aligned}\langle v\rangle &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2k_B T}dv \\ &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left[2\left(\frac{m}{2k_B T}\right)^2\right]^{-1} \\ &= 2\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left(\frac{2k_B T}{m}\right)^2 \\ &= \left(\frac{8k_B T}{\pi m}\right)^{1/2}\end{aligned}$$

B–7. Use the Maxwell-Boltzmann distribution in Problem B–6 to determine the average kinetic energy of a gas-phase molecule as a function of temperature. The necessary integral is given in Problem B–6.

Kinetic energy, KE, is defined as $KE = \frac{1}{2}mv^2$, so $\langle KE\rangle = \frac{1}{2}m\langle v^2\rangle$. Using Equation B.13, we write

$$\begin{aligned}\langle v^2\rangle &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^4 e^{-mv^2/2k_B T}dv \\ &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\frac{3}{8}\left(\frac{2k_B T}{m}\right)^2\left(\frac{2\pi k_B T}{m}\right)^{1/2} \\ &= \frac{3k_B T}{m}\end{aligned}$$

And so $E = \frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_B T$.

CHAPTER 3

The Schrödinger Equation and a Particle in a Box

PROBLEMS AND SOLUTIONS

3–1. Evaluate $g = \hat{A}f$, where $\hat{A}$ and f are given below:

	$\hat{A}$	f
(a)	SQRT	x^4
(b)	$\frac{d^3}{dx^3} + x^3$	e^{-ax}
(c)	$\int_0^1 dx$	$x^3 - 2x + 3$
(d)	$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$	$x^3y^2z^4$

---

a. $\text{SQRT}(x^4) = \pm x^2$

b. $\frac{d^3e^{-ax}}{dx^3} + x^3e^{-ax} = -a^3e^{-ax} + x^3e^{-ax} = e^{-ax}(x^3 - a^3)$

c. $\int_0^1 (x^3 - 2x + 3)\,dx = \left.\frac{x^4}{4} - x^2 + 3x\right|_0^1 = \frac{9}{4}$

d. $\frac{\partial^2(x^3y^2z^4)}{\partial x^2} + \frac{\partial^2(x^3y^2z^4)}{\partial y^2} + \frac{\partial^2(x^3y^2z^4)}{\partial z^2} = 6xy^2z^4 + 2x^3z^4 + 12x^3y^2z^2$

3–2. Determine whether the following operators are linear or nonlinear:

a. $\hat{A}f(x) = \text{SQR}f(x)$ [square $f(x)$]

b. $\hat{A}f(x) = f^*(x)$ [form the complex conjugate of $f(x)$]

c. $\hat{A}f(x) = 0$ [multiply $f(x)$ by zero]

d. $\hat{A}f(x) = [f(x)]^{-1}$ [take the reciprocal of $f(x)$]

e. $\hat{A}f(x) = f(0)$ [evaluate $f(x)$ at $x = 0$]

f. $\hat{A}f(x) = \ln f(x)$ [take the logarithm of $f(x)$]

An operator $\hat{A}$ is linear if $\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$ (Equation 3.9).

a.

$$\begin{aligned}\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] &= \left[c_1 f_1(x) + c_2 f_2(x)\right]^2 \\ &= c_1^2 f_1(x)^2 + 2c_1 f_1(x) c_2 f_2(x) + c_2^2 f_2(x)^2 \\ c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) &= c_1\left[f_1(x)\right]^2 + c_2\left[f_2(x)\right]^2 \\ &\neq \hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right]\end{aligned}$$

Nonlinear.

b.

$$\begin{aligned}\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] &= c_1^* f_1^*(x) + c_2^* f_2^*(x) \\ c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) &= c_1 f_1^*(x) + c_2 f_2^*(x) \\ &\neq \hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right]\end{aligned}$$

Nonlinear.

c.

$$\begin{aligned}\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] &= 0 \\ c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) &= c_1 f_1(x)0 + c_2 f_2(x) = 0 \\ &= \hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right]\end{aligned}$$

Linear.

d.

$$\begin{aligned}\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] &= \left[c_1 f_1(x) + c_2 f_2(x)\right]^{-1} \\ c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) &= \frac{c_1}{f_1(x)} + \frac{c_2}{f_2(x)} \\ &\neq \hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right]\end{aligned}$$

Nonlinear.

e.

$$\begin{aligned}\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] &= c_1 f_1(0) + c_2 f_2(0) \\ &= c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)\end{aligned}$$

Linear.

f.

$$\begin{aligned}\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] &= \ln\left[c_1 f_1(x) + c_2 f_2(x)\right] \\ c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) &= c_1 \ln f_1(x) + c_2 \ln f_2(x) \\ &\neq \hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right]\end{aligned}$$

Nonlinear.

3–3. In each case, show that $f(x)$ is an eigenfunction of the operator given. Find the eigenvalue.

	$\hat{A}$	$f(x)$
(a)	$\dfrac{d^2}{dx^2}$	$\cos \omega x$
(b)	$\dfrac{d}{dt}$	$e^{i\omega t}$
(c)	$\dfrac{d^2}{dx^2} + 2\dfrac{d}{dx} + 3$	$e^{\alpha x}$
(d)	$\dfrac{\partial}{\partial y}$	$x^2 e^{6y}$

a. $\hat{A} f(x) = \dfrac{d^2(\cos \omega x)}{dx^2} = -\omega^2 \cos \omega x$; eigenvalue $= -\omega^2$

b. $\hat{A} f(x) = \dfrac{d(e^{i\omega t})}{dt} = i\omega e^{i\omega t}$; eigenvalue $= i\omega$

c. $\hat{A} f(x) = \dfrac{d^2(e^{\alpha x})}{dx^2} + 2\dfrac{d(e^{\alpha x})}{dx} + 3e^{\alpha x} = \left(\alpha^2 + 2\alpha + 3\right) e^{\alpha x}$; eigenvalue $= \alpha^2 + 2\alpha + 3$

d. $\hat{A} f(x) = \dfrac{\partial x^2 e^{6y}}{\partial y} = 6x^2 e^{6y}$; eigenvalue $= 6$

3–4. Show that $(\cos ax)(\cos by)(\cos cz)$ is an eigenfunction of the operator,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

which is called the Lapacian operator.

$$\begin{aligned}\nabla^2(\cos ax)(\cos by)(\cos cz) &= \frac{\partial^2(\cos ax)(\cos by)(\cos cz)}{\partial x^2} + \frac{\partial^2(\cos ax)(\cos by)(\cos cz)}{\partial y^2} \\ &\quad + \frac{\partial^2(\cos ax)(\cos by)(\cos cz)}{\partial z^2} \\ &= -a^2(\cos ax)(\cos by)(\cos cz) - b^2(\cos ax)(\cos by)(\cos cz) \\ &\quad - c^2(\cos ax)(\cos by)(\cos cz) \\ &= -(a^2 + b^2 + c^2)(\cos ax)(\cos by)(\cos cz)\end{aligned}$$

The eigenvalue of the eigenfunction $(\cos ax)(\cos by)(\cos cz)$ is $-(a^2 + b^2 + c^2)$.

3–5. Write out the operator $\hat{A}^2$ for $\hat{A} =$

a. $\dfrac{d^2}{dx^2}$ b. $\dfrac{d}{dx}+x$ c. $\dfrac{d^2}{dx^2}-2x\dfrac{d}{dx}+1$

Hint: Be sure to include $f(x)$ before carrying out the operations.

For all cases, we need to determine an expression for $\hat{A}^2$ where

$$\hat{A}^2 f(x) = \hat{A}\left[\hat{A}f(x)\right]$$

a. $\hat{A}[\hat{A}f(x)] = \dfrac{d^2}{dx^2}\left[\dfrac{d^2 f(x)}{dx^2}\right] = \dfrac{d^4 f(x)}{dx^4}$

The operator $\hat{A}^2$ is then

$$\hat{A}^2 = \frac{d^4}{dx^4}$$

b.
$$\hat{A}\left[\hat{A}f(x)\right] = \left(\frac{d}{dx}+x\right)\left[\frac{df(x)}{dx}+xf(x)\right]$$
$$= \frac{d^2 f(x)}{dx^2} + x\frac{df(x)}{dx} + f(x)\frac{dx}{dx} + x\frac{df(x)}{dx} + x^2 f(x)$$
$$= \frac{d^2 f(x)}{dx^2} + 2x\frac{df(x)}{dx} + f(x) + x^2 f(x)$$

So $\hat{A}^2$ is written as

$$\hat{A}^2 = \frac{d^2}{dx^2} + 2x\frac{d}{dx} + 1 + x^2$$

c.
$$\hat{A}\left[\hat{A}f(x)\right] = \left(\frac{d^2}{dx^2} - 2x\frac{d}{dx} + 1\right)\left[\frac{d^2 f(x)}{dx^2} - 2x\frac{df(x)}{dx} + f(x)\right]$$
$$= \frac{d^4 f(x)}{dx^4} - 4x\frac{d^3 f(x)}{dx^3} + (4x^2-2)\frac{d^2 f(x)}{dx^2} + f(x)$$

So $\hat{A}^2$ is written as

$$\hat{A}^2 = \frac{d^4}{dx^4} - 4x\frac{d^3}{dx^3} + (4x^2-2)\frac{d^2}{dx^2} + 1$$

3–6. In Section 3–5, we applied the equations for a particle in a box to the π electrons in butadiene. This simple model is called the free-electron model. Using the same argument, show that the length of hexatriene can be estimated to be 867 pm. Show that the first electronic transition is predicted to occur at $2.8 \times 10^4\ \mathrm{cm}^{-1}$. (Remember that hexatriene has six π electrons.)

We assume that the π electrons move along a straight line consisting of three C=C bond lengths (3 × 135 pm), two C–C bond lengths (2 × 154 pm), and the distance of a carbon atom radius at each end (2 × 77.0 pm) or a total distance of 867 pm. Because there are six π electrons in one molecule, the first electronic transition occurs between the $n = 3$ and the $n = 4$ electronic states. Using Equation 3.21, the energy of this transition is

$$\Delta E = \frac{h^2}{8m_e a^2}(4^2 - 3^2)$$
$$= \frac{(6.626\times10^{-34}\ \mathrm{J\cdot s})^2}{8(9.11\times10^{-31}\ \mathrm{kg})(867\times10^{-12}\ \mathrm{m})^2}(16-9)$$
$$= 5.61\times10^{-19}\ \mathrm{J} = 2.82\times10^4\ \mathrm{cm}^{-1}$$

3–7. Prove that if $\psi(x)$ is a solution to the Schrödinger equation, then any constant times $\psi(x)$ is also a solution.

Because $\hat{H}$ is a linear operator,

$$\hat{H}\left[c\psi(x)\right] = c\hat{H}\psi(x) = cE\psi(x) = E\left[c\psi(x)\right]$$

and so $c\psi(x)$, where c is any constant, is a solution.

3–8. Show that the probability associated with the state ψ_n for a particle in a one-dimensional box of length a obeys the following relationships:

$$\mathrm{Prob}(0 \le x \le a/4) = \mathrm{Prob}(3a/4 \le x \le a) = \begin{cases} \dfrac{1}{4} & n \text{ even} \\[2ex] \dfrac{1}{4} - \dfrac{(-1)^{\frac{n-1}{2}}}{2\pi n} & n \text{ odd} \end{cases}$$

and

$$\mathrm{Prob}(a/4 \le x \le a/2) = \mathrm{Prob}(a/2 \le x \le 3a/4) = \begin{cases} \dfrac{1}{4} & n \text{ even} \\[2ex] \dfrac{1}{4} + \dfrac{(-1)^{\frac{n-1}{2}}}{2\pi n} & n \text{ odd} \end{cases}$$

For a particle in a one-dimensional box of length a, we know that (Equation 3.27) $\psi_n = (2/a)^{1/2}\sin(n\pi x/a)$. Now

$$\mathrm{Prob}(c \le x \le d) = \int_c^d \psi^*(x)\psi(x)dx$$
$$= \frac{2}{a}\int_c^d \sin^2\frac{n\pi x}{a}dx$$
$$= \frac{2}{a}\left[\frac{x}{2} - \frac{\sin 2n\pi x/a}{4(n\pi/a)}\right]_{x=c}^{x=d}$$
$$= \left[\frac{x}{a} - \frac{\sin 2n\pi x/a}{2n\pi}\right]_{x=c}^{x=d}$$
$$= \frac{d}{a} - \frac{\sin 2n\pi d/a}{2n\pi} - \frac{c}{a} + \frac{\sin 2n\pi c/a}{2n\pi}$$
$$= \frac{d-c}{a} - \left(\frac{1}{2n\pi}\right)\left[\sin\left(\frac{2n\pi d}{a}\right) - \sin\left(\frac{2n\pi c}{a}\right)\right]$$

For all regions under consideration, $d - c = a/4$. We can now calculate the probability associated with ψ_n for each of the four regions. (Recall that $\sin n\pi = \sin 2n\pi = 0$ for integer n.)

c	d	Prob($c \le x \le d$)
0	$\frac{a}{4}$	$\frac{1}{4} - \frac{1}{2n\pi}\sin\left(\frac{n\pi}{2}\right)$
$\frac{a}{4}$	$\frac{a}{2}$	$\frac{1}{4} - 0 + \frac{1}{2n\pi}\sin\left(\frac{n\pi}{2}\right)$
$\frac{a}{2}$	$\frac{3a}{4}$	$\frac{1}{4} - \frac{1}{2n\pi}\sin\left(\frac{3n\pi}{2}\right) + 0$
$\frac{3a}{4}$	a	$\frac{1}{4} - 0 + \frac{1}{2n\pi}\sin\left(\frac{3n\pi}{2}\right)$

For n even, $\sin\frac{n\pi}{2} = 0$; for n odd, $\sin\frac{n\pi}{2} = (-1)^{(n-1)/2}$ and $\sin\frac{3n\pi}{2} = -(-1)^{(n-1)/2}$. Therefore

$$\text{Prob}(0 \le x \le a/4) = \text{Prob}(3a/4 \le x \le a) = \begin{cases} \frac{1}{4} & n \text{ even} \\ \frac{1}{4} - \frac{(-1)^{(n-1)/2}}{2\pi n} & n \text{ odd} \end{cases}$$

and

$$\text{Prob}(a/4 \le x \le a/2) = \text{Prob}(a/2 \le x \le 3a/4) = \begin{cases} \frac{1}{4} & n \text{ even} \\ \frac{1}{4} + \frac{(-1)^{(n-1)/2}}{2\pi n} & n \text{ odd} \end{cases}$$

3–9. What are the units, if any, for the wave function of a particle in a one-dimensional box?

The normalized wavefunction $\psi(x)$ must be unitless. The normalization constant for $\psi(x)$ is $\sqrt{2/a}$ (from Equation 3.27); therefore, the wavefunction must have units of $\text{m}^{-1/2}$.

3–10. Using a table of integrals, show that

$$\int_0^a \sin^2\frac{n\pi x}{a}dx = \frac{a}{2}$$

$$\int_0^a x\sin^2\frac{n\pi x}{a}dx = \frac{a^2}{4}$$

and

$$\int_0^a x^2\sin^2\frac{n\pi x}{a}dx = \left(\frac{a}{2\pi n}\right)^3\left(\frac{4\pi^3 n^3}{3} - 2n\pi\right)$$

All these integrals can be evaluated from

$$I(\beta) = \int_0^a e^{\beta x}\sin^2\frac{n\pi x}{a}dx$$

Show that the above integrals are given by $I(0)$, $I'(0)$, and $I''(0)$, respectively, where the primes denote differentiation with respect to β. Using a table of integrals, evaluate $I(\beta)$ and then the above three integrals by differentiation.

In MathChapter B, Problems B–1 and B–2, we evaluated the integrals $\int_0^a p(x)dx$ and $\int_0^a xp(x)dx$ where $p(x)$ was given by

$$p(x)dx = \frac{2}{a}\sin^2\frac{n\pi x}{a}dx$$

Using the results from Problems B–1 and B–2 gives the numerical results for the integrals considered in the first part of the problem. Now consider

$$I(\beta) = \int_0^a e^{\beta x}\sin^2\frac{n\pi x}{a}dx$$

Taking the first and second derivatives of $I(\beta)$ with respect to β gives

$$I'(\beta) = \int_0^a xe^{\beta x}\sin^2\frac{n\pi x}{a}dx$$
$$I''(\beta) = \int_0^a x^2e^{\beta x}\sin^2\frac{n\pi x}{a}dx$$

The corresponding expressions for $I(0)$, $I'(0)$, and $I''(0)$ are

$$I(0) = \int_0^a \sin^2\frac{n\pi x}{a}dx$$
$$I'(0) = \int_0^a x\sin^2\frac{n\pi x}{a}dx$$
$$I''(0) = \int_0^a x^2\sin^2\frac{n\pi x}{a}dx$$

Generally, from a table of integrals, we can write

$$\int e^{\beta x}\sin^2 bx dx = \frac{e^{\beta x}}{2\beta} - \frac{e^{\beta x}}{\beta^2 + 4b^2}\left(\frac{\beta\cos 2bx}{2} + b\sin 2bx\right)$$

and so

$$I(\beta) = \frac{e^{\beta a} - 1}{2\beta} - \frac{\beta}{2}\left(\frac{e^{\beta a} - 1}{\beta^2 + 4n^2\pi^2a^{-2}}\right)$$

Now we use the Maclaurin series and the series expansion of $e^{\beta a}$ (MathChapter J):

$$I(\beta) = I(0) + \beta I'(0) + \frac{\beta^2}{2}I''(0) + O(\beta^3)$$
$$I(\beta) = \frac{a}{2} + \frac{a^2}{4}\beta + \frac{a^3}{12}\beta^2 - \frac{1}{4n^2\pi^2a^{-2}}\left(\frac{\beta^2 a}{2} + \frac{\beta^3 a^2}{4}\right) + O(\beta^3)$$
$$= \frac{a}{2} + \frac{a^2}{4}\beta + \left(\frac{a^3}{6} - \frac{a^3}{4\pi^2n^2}\right)\frac{\beta^2}{2} + O(\beta^3)$$

Therefore,

$$I(0) = \frac{a}{2} \qquad I'(0) = \frac{a^2}{4} \qquad I''(0) = \frac{a^3}{6} - \frac{a^3}{4\pi^2n^2}$$

3–11. Show that

$$\langle x\rangle = \frac{a}{2}$$

for all the states of a particle in a box. Is this result physically reasonable?

$$\langle x\rangle = \int_0^a x\psi^*(x)\psi(x)dx$$
$$= \frac{2}{a}\int_0^a x\sin^2\frac{n\pi x}{a}dx$$
$$= \frac{2}{a}\cdot\frac{a^2}{4} = \frac{a}{2}$$

For any n, $\langle x\rangle = a/2$. This result is physically reasonable and is discussed in detail in the text.

3–12. Show that $\langle p\rangle = 0$ for all states of a one-dimensional box of length a.

From Equation 3.37,

$$\langle p\rangle = \frac{2}{a}\int_0^a \sin\frac{n\pi x}{a}\left(-i\hbar\frac{d}{dx}\right)\sin\frac{n\pi x}{a}dx$$
$$= -\frac{2i\hbar n\pi}{a^2}\int_0^a \sin\frac{n\pi x}{a}\cos\frac{n\pi x}{a}dx$$
$$= 0$$

This result holds for any integer value of n.

3–13. Show that

$$\sigma_x = (\langle x^2\rangle - \langle x\rangle^2)^{1/2}$$

for a particle in a box is less than a, the width of the box, for any value of n. If σ_x is the uncertainty in the position of the particle, could σ_x ever be larger than a?

Use Equations 3.31 and 3.32 for $\langle x\rangle$ and $\langle x^2\rangle$:

$$\langle x\rangle = \frac{a}{2} \qquad \langle x^2\rangle = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}$$

$$\sigma_x = (\langle x^2\rangle - \langle x\rangle^2)^{1/2} = \left(\frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} - \frac{a^2}{4}\right)^{1/2}$$
$$= a\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)^{1/2}$$

For $\sigma_x \geq a$,

$$\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)^{1/2} \geq 1$$
$$\frac{\pi^2 n^2 - 6}{12\pi^2 n^2} \geq 1$$

$$\pi^2 n^2 - 6 \geq 12\pi^2 n^2$$
$$\pi^2 n^2 \geq 12\pi^2 n^2 + 6$$

This inequality cannot be satisfied for any value of n, so $\sigma_x < a$ for all n.

3–14. Using the trigonometric identity

$$\sin 2\theta = 2\sin\theta\cos\theta$$

show that

$$\int_0^a \sin\frac{n\pi x}{a}\cos\frac{n\pi x}{a}dx = 0$$

$$\int_0^a \sin\frac{n\pi x}{a}\cos\frac{n\pi x}{a}dx = \frac{1}{2}\int_0^a \sin\frac{2\pi n x}{a}dx$$
$$= \frac{1}{2}\left(\frac{-a}{2\pi n}\cos\frac{2\pi n x}{a}\right)\Big|_0^a = 0$$

3–15. Prove that

$$\int_0^a e^{\pm i2\pi n x/a}dx = 0 \qquad n \neq 0$$

$$\int_0^a e^{\pm i2\pi n x/a}dx = \int_0^a \cos\frac{2\pi n x}{a}dx \pm i\int_0^a \sin\frac{2\pi n x}{a}dx$$

The integrals on the right side of this equation go over complete cycles of the cosine and sine functions, and so both are equal to zero if $n \neq 0$. If $n = 0$, the integral on the left side of this equation is a and the first integral on the right side of this equation is also a.

3–16. Using the trigonometric identity

$$\sin\alpha\sin\beta = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta)$$

show that the particle-in-a-box wave functions (Equations 3.27) satisfy the relation

$$\int_0^a \psi_n^*(x)\psi_m dx = 0 \qquad m \neq n$$

(The asterisk in this case is superfluous because the functions are real.) If a set of functions satisfies the above integral condition, we say that the set is *orthogonal* and, in particular, that $\psi_m(x)$ is orthogonal to $\psi_n(x)$. If, in addition, the functions are normalized, then we say that the set is *orthonormal*.

If $n \neq m$,

$$\int_0^a \psi_n^*(x)\psi_m dx = \frac{2}{a}\int_0^a \sin\frac{n\pi x}{a}\sin\frac{m\pi x}{a}dx$$
$$= \frac{1}{a}\int_0^a \cos\frac{(n-m)\pi x}{a}dx - \frac{1}{a}\int_0^a \cos\frac{(n+m)\pi x}{a}dx$$

$$= \frac{1}{(n-m)\pi} \sin \frac{(n-m)\pi x}{a}\Big|_0^a - \frac{1}{(n+m)\pi} \sin \frac{(n+m)\pi x}{a}\Big|_0^a$$
$$= \frac{1}{(n-m)\pi} \sin(n-m)\pi - \frac{1}{(n+m)\pi} \sin(n+m)\pi$$
$$= 0$$

because $\sin N\pi = 0$ for integer values of N. Note that if $n = m$,

$$\int_0^a \psi_n^*(x)\psi_n dx = \frac{1}{a}\int_0^a dx - \frac{1}{a}\int_0^a \cos \frac{2n\pi x}{a} dx$$
$$= 1$$

and so the particle-in-a-box wave functions are orthonormal.

3–17. Prove that the set of functions

$$\psi_n(x) = (2a)^{-1/2} e^{i\pi n x/a} \qquad n = 0, \pm 1, \pm 2, \ldots$$

is orthonormal (cf. Problem 3–16) over the interval $-a \leq x \leq a$. A compact way to express orthonormality in the ψ_n is to write

$$\int_{-a}^{a} \psi_m^*(x)\psi_n dx = \delta_{mn}$$

The symbol δ_{mn} is called a Kroenecker delta and is defined by

$$\delta_{mn} = 1 \qquad \text{if } m = n$$
$$= 0 \qquad \text{if } m \neq n$$

For $n = m$, we have

$$\int_{-a}^{a} \psi_m^*(x)\psi_n dx = \frac{1}{2a}\int_{-a}^{a} e^{-in\pi x/a} e^{in\pi x/a} = \frac{1}{2a}\int_{-a}^{a} dx = 1$$

For $n \neq m$,

$$\int_{-a}^{a} \psi_m^*(x)\psi_n dx = \frac{1}{2a}\int_{-a}^{a} e^{i\pi(n-m)x/a} dx$$
$$= \frac{1}{2a}\int_{-a}^{a}\left[\cos\frac{\pi(n-m)x}{a} + i\sin\frac{\pi(n-m)x}{a}\right] dx$$

Both integrals here are taken over complete cycles of sine and cosine, and so vanish. This set of functions is therefore orthonormal over the stated interval.

3–18. Show that the set of functions

$$\phi_n(\theta) = (2\pi)^{-1/2} e^{in\theta} \qquad 0 \leq \theta \leq 2\pi$$

is orthonormal (Problem 3–16).

When $n = m$, we have

$$\int_0^{2\pi} \phi_n^*(\theta)\phi_n(\theta) d\theta = \frac{1}{2\pi}\int_0^{2\pi} e^{i(n-n)\theta} d\theta = \frac{1}{2\pi}\int_0^{2\pi} d\theta = 1$$

When $n \neq m$, we have

$$\int_0^{2\pi} \phi_m^*(\theta)\phi_n(\theta) d\theta = \frac{1}{2\pi}\int_0^{2\pi} e^{i(n-m)\theta} d\theta$$

We encountered the above integral in Problem 3–17 and showed that it is equal to zero, so the set of functions ϕ_n is orthonormal.

3–19. In going from Equation 3.34 to 3.35, we multiplied Equation 3.34 from the left by $\psi^*(x)$ and then integrated over all values of x to obtain Equation 3.35. Does it make any difference whether we multiplied from the left or the right?

It does not make a difference whether we multiply from the left or the right. Realize that $\hat{H}\psi_n(x)$ is just a function; $\hat{H}$ has already operated on $\psi_n(x)$.

3–20. Calculate $\langle x \rangle$ and $\langle x^2 \rangle$ for the $n = 2$ state of a particle in a one-dimensional box of length a. Show that

$$\sigma_x = \frac{a}{4\pi}\left(\frac{4\pi^2}{3} - 2\right)^{1/2}$$

We will use the equations for a particle in a one-dimensional box

$$\langle x \rangle = \frac{a}{2} \tag{3.31}$$

$$\langle x^2 \rangle = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} \tag{3.32}$$

$$\sigma_x = \frac{a}{2\pi n}\left(\frac{\pi^2 n^2}{3} - 2\right)^{1/2} \tag{3.33}$$

For $n = 2$,

$$\langle x \rangle = \frac{a}{2}$$

$$\langle x^2 \rangle = \frac{a^2}{3} - \frac{a^2}{8\pi^2}$$

$$\sigma_x = \frac{a}{4\pi}\left(\frac{4\pi^2}{3} - 2\right)^{1/2}$$

3–21. Calculate $\langle p \rangle$ and $\langle p^2 \rangle$ for the $n = 2$ state of a particle in a one-dimensional box of length a. Show that

$$\sigma_p = \frac{h}{a}$$

We will use the equations from the chapter

$$\langle p \rangle = 0 \tag{3.38}$$

$$\langle p^2 \rangle = \frac{n^2\pi^2\hbar^2}{a^2} = \sigma_p^2 \tag{3.40}$$

$$\sigma_p = \frac{n\pi\hbar}{a} = \frac{nh}{2a}$$

For $n = 2$, $\sigma_p = \dfrac{h}{a}$ and $\langle p^2 \rangle = \dfrac{h^2}{a^2}$.

3–22. Consider a particle of mass m in a one-dimensional box of length a. Its average energy is given by

$$\langle E \rangle = \frac{1}{2m}\langle p^2 \rangle$$

Because $\langle p \rangle = 0$, $\langle p^2 \rangle = \sigma_p^2$, where σ_p can be called the uncertainty in p. Using the Uncertainty Principle, show that the energy must be at least as large as $\hbar^2/8ma^2$ because σ_x, the uncertainty in x, cannot be larger than a.

From Equation 3.43 and the condition $\sigma_x \le a$,

$$\frac{\hbar}{2\sigma_p} < \sigma_x \le a$$

Then

$$\frac{\hbar}{2a} \le \sigma_p$$

and so

$$\frac{\hbar^2}{4a^2} \le \sigma_p^2 \tag{1}$$

We are given that $\langle p^2 \rangle = \sigma_p^2$, so we write

$$\frac{\sigma_p^2}{2m} = \frac{\langle p^2 \rangle}{2m} = \langle E \rangle \tag{2}$$

Substituting Equation 2 into Equation 1 gives

$$\frac{\hbar^2}{8ma^2} \le \langle E \rangle$$

3–23. Discuss the degeneracies of the first few energy levels of a particle in a three-dimensional box when all three sides have a different length.

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{3.57}$$

Even if $a \ne b \ne c$, the energy levels will not necessarily be degenerate.

3–24. Show that the normalized wave function for a particle in a three-dimensional box with sides of length a, b, and c is

$$\psi(x, y, z) = \left(\frac{8}{abc}\right)^{1/2} \sin\frac{n_x\pi x}{a} \sin\frac{n_y\pi y}{b} \sin\frac{n_z\pi z}{c}$$

We can separate $\psi(x, y, z)$ into three one-dimensional wavefunctions $X(x)$, $Y(y)$, and $Z(z)$ such that $\psi(x, y, z) = X(x)Y(y)Z(z)$. These three one-dimensional wavefunctions have the same form and boundary conditions as the one we treated in Section 3–5, and so (as in Section 3–9)

$$X(x) = A_x \sin\frac{n_x\pi x}{a} \qquad n_x = 1, 2, 3, \ldots$$

$$Y(y) = A_y \sin\frac{n_y\pi y}{b} \qquad n_y = 1, 2, 3, \ldots$$

$$Z(z) = A_z \sin\frac{n_z\pi z}{c} \qquad n_z = 1, 2, 3, \ldots$$

To normalize ψ, we require that

$$\psi(x, y, z)\psi^*(x, y, z) = 1 = (A_xA_yA_z)^2 \int_0^a \sin^2\frac{n_x\pi x}{a}dx \int_0^b \sin^2\frac{n_y\pi y}{b}dy \int_0^c \sin^2\frac{n_z\pi z}{c}dz$$

In Problem 3–10, we learned that $\displaystyle\int_0^a \sin^2\frac{n\pi x}{a}dx = \frac{a}{2}$. Thus

$$\psi(x, y, z)\psi^*(x, y, z) = 1 = (A_xA_yA_z)^2 \left(\frac{a}{2}\right)\left(\frac{b}{2}\right)\left(\frac{c}{2}\right)$$

or

$$A_xA_yA_z = \left(\frac{8}{abc}\right)^{1/2}$$

3–25. Show that $\langle \mathbf{p} \rangle = 0$ for the ground state of a particle in a three-dimensional box with sides of length a, b, and c.

$$\hat{\mathbf{P}} = -i\hbar\left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}\right) \tag{3.58}$$

$$\begin{aligned}
\langle \mathbf{p} \rangle &= \int_0^a dx \int_0^b dy \int_0^c dz\, \psi^*(x, y, z)\hat{\mathbf{P}}\psi(x, y, z) \\
&= -i\hbar\mathbf{i} \int_0^a \sin\frac{n_x\pi x}{a}\frac{\partial}{\partial x}\left(\sin\frac{n_x\pi x}{a}\right)dx \int_0^b \sin^2\frac{n_y\pi y}{b}dy \int_0^c \sin^2\frac{n_z\pi z}{c}dz \\
&\quad -i\hbar\mathbf{j} \int_0^a \sin^2\frac{n_x\pi x}{a}dx \int_0^b \sin\frac{n_y\pi y}{b}\frac{\partial}{\partial y}\left(\sin\frac{n_y\pi y}{b}\right)dy \int_0^c \sin^2\frac{n_z\pi z}{c}dz \\
&\quad -i\hbar\mathbf{k} \int_0^a \sin^2\frac{n_x\pi x}{a}dx \int_0^b \sin^2\frac{n_y\pi y}{b}dy \int_0^c \sin\frac{n_z\pi z}{c}\frac{\partial}{\partial z}\left(\sin\frac{n_z\pi z}{a}\right)dz
\end{aligned}$$

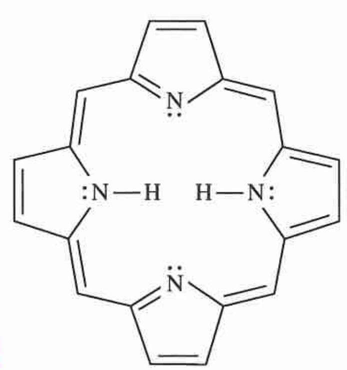
Each of these three sets of integrals has a multiplicative factor like $\int_0^a \sin\frac{n_x \pi x}{a} \cos\frac{n_x \pi x}{a} dx$ that results from taking a derivative. We have previously shown (Problem 3–14) that such an integral is equal to zero, and so we have $\langle \mathbf{p} \rangle = 0$ for a particle in a three-dimensional box.

3–26. What are the degeneracies of the first four energy levels for a particle in a three-dimensional box with $a = b = 1.5c$?

$$E = \frac{h^2}{8m}\left(\frac{n_x^2 + n_y^2 + 2.25n_z^2}{a^2}\right) \tag{3.57}$$

Energy level	(n_x, n_y, n_z)	Degeneracy	$E/(h^2/8ma^2)$
E_{111}	(1, 1, 1)	1	4.25
E_{211}	(2, 1, 1)(1, 2, 1)	2	7.25
E_{221}	(2, 2, 1)	1	10.25
E_{112}	(1, 1, 2)	1	11
E_{311}	(3, 1, 1)(1, 3, 1)	2	12.25
E_{212}	(2, 1, 2)(1, 2, 2)	2	14
E_{133}	(1, 3, 3)	1	30.25

3–27. Many proteins contain metal porphyrin molecules. The general structure of the porphyrin molecule is



This molecule is planar and so we can approximate the π electrons as being confined inside a square. What are the energy levels and degeneracies of a particle in a square of side a? The porphyrin molecule has 18 π electrons. If we approximate the length of the molecule by 1000 pm, then what is the predicted lowest energy absorption of the porphyrin molecule? (The experimental value is $\approx$ 17 000 cm^{-1}.)

$$E_{n_x n_y} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2) \tag{3.57}$$

$E_{n_x n_y}$ is singly degenerate for $n_x = n_y$ and doubly degenerate for $n_x \neq n_y$.

Energy level	(n_x, n_y)	Degeneracy
E_{11}	(1, 1)	1
E_{12}	(1, 2) (2, 1)	2
E_{22}	(2, 2)	1
E_{31}	(3, 1) (1, 3)	2
E_{23}	(3, 2) (2, 3)	2
E_{41}	(4, 1) (1, 4)	2
E_{33}	(3, 3)	1
E_{42}	(4, 2) (2, 4)	2
E_{43}	(4, 3) (3, 4)	2

Because each energy level can hold 2 π-electrons, the lowest energy absorption of the porphyrin molecule will be that which excites an electron from the E_{42} state to the E_{43} state. Then

$$\begin{aligned}\Delta E &= \frac{h^2}{8m_e a^2}(n_{x,2}^2 + n_{y,2}^2 - n_{x,1}^2 - n_{y,1}^2)\\ &= \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{8(9.11 \times 10^{-31}\ \text{kg})(1000 \times 10^{-12}\ \text{m})^2}(4^2 + 3^2 - 4^2 - 2^2)\\ &= 3.012 \times 10^{-19}\ \text{J}\end{aligned}$$

Because $E = hc\tilde{\nu}$, $\tilde{\nu} = 1.52 \times 10^4$ cm^{-1}.

3–28. The Schrödinger equation for a particle of mass m constrained to move on a circle of radius a is

$$-\frac{\hbar^2}{2I}\frac{d^2\psi}{d\theta^2} = E\psi(\theta) \qquad 0 \le \theta \le 2\pi$$

where $I = ma^2$ is the moment of inertia and θ is the angle that describes the position of the particle around the ring. Show by direct substitution that the solutions to this equation are

$$\psi(\theta) = Ae^{in\theta}$$

where $n = \pm(2IE)^{1/2}/\hbar$. Argue that the appropriate boundary condition is $\psi(\theta) = \psi(\theta + 2\pi)$ and use this condition to show that

$$E = \frac{n^2\hbar^2}{2I} \qquad n = 0, \pm1, \pm2, \ldots$$

Show that the normalization constant A is $(2\pi)^{-1/2}$. Discuss how you might use these results for a free-electron model of benzene.

We can write the differential equation as

$$\frac{d^2\psi}{d\theta^2} + \frac{2EI}{\hbar^2}\psi(\theta) = 0$$

Substituting $\psi(\theta) = Ae^{in\theta}$ gives

$$-n^2Ae^{in\theta} + \frac{2EI}{\hbar^2}Ae^{in\theta} = 0$$

or $n = \pm(2IE)^{1/2}/\hbar$. Because the particle is moving in a circle, it must return to any designated point after traveling 2π radians: $\psi(\theta) = \psi(\theta + 2\pi)$. Then

$$e^{in\theta} = e^{in(\theta+2\pi)}$$
$$1 = e^{i2\pi n}$$
$$1 = \cos 2\pi n + i \sin 2\pi n$$

This is true only if n is an integer. In that case,

$$E = \frac{n^2\hbar^2}{2I} \qquad n = 0, \pm 1, \pm 2, \ldots$$

To normalize $\psi(x)$, we require that

$$A^2 \int_0^{2\pi} e^{in\theta}e^{-in\theta} d\theta = 1$$

$$A^2 \int_0^{2\pi} d\theta = 1$$

so

$$A = \frac{1}{\sqrt{2\pi}}$$

There are six π electrons in benzene. If we model the electrons of a benzene molecule as described above, there will be two electrons in each of the three energy levels $n = 0$ and ± 1. The first electronic transition would be a $n = 1 \rightarrow n = 2$ transition, and the frequency associated with this transition would be given by the expression

$$\tilde{\nu} = \frac{\hbar}{4\pi c I}(2^2 - 1^2)$$

3–29. Set up the problem of a particle in a box with its walls located at $-a$ and $+a$. Show that the energies are equal to those of a box with walls located at 0 and $2a$. (These energies may be obtained from the results that we derived in the chapter simply by replacing a by $2a$.) Show, however, that the wave functions are not the same and in this case are given by

$$\psi_n(x) = \frac{1}{a^{1/2}} \sin \frac{n\pi x}{2a} \qquad n \text{ even}$$
$$= \frac{1}{a^{1/2}} \cos \frac{n\pi x}{2a} \qquad n \text{ odd}$$

Does it bother you that the wave functions seem to depend upon whether the walls are located at $\pm a$ or 0 and $2a$? Surely the particle "knows" only that it has a region of length $2a$ in which to move and cannot be affected by where you place the origin for the two sets of wave functions. What does this tell you? Do you think that any experimentally observable properties depend upon where you choose to place the origin of the x-axis? Show that $\sigma_x\sigma_p > \hbar/2$, exactly as we obtained in Section 3–8.

The general solution of the Schrödinger equation for a particle in a one-dimensional box is (Section 3–5)

$$\psi(x) = A \cos kx + B \sin kx \qquad k = \frac{(2mE)^{1/2}}{\hbar}$$

We have the boundary conditions $\psi(-a) = \psi(a) = 0$, so

$$\psi(-a) = A\cos(-ka) + B\sin(-ka) = A\cos ka - B\sin ka = 0$$

and

$$\psi(a) = A\cos(ka) + B\sin(ka) = A\cos ka + B\sin ka = 0$$

Adding and subtracting these two equations gives

$$A\cos ka = 0 \quad \text{and} \quad B\sin ka = 0$$

The general solution to these equations is to set

$$k = \frac{n\pi}{2a}$$

where $n = 1, 2, \ldots$ and to satisfy the boundary conditions by setting $B = 0$ when n is odd and $A = 0$ when n is even. Thus

$$\psi_n(x) = B \sin \frac{n\pi x}{2a} \qquad n \text{ even}$$
$$= A \cos \frac{n\pi x}{2a} \qquad n \text{ odd}$$

The normalization constants A and B are both equal to $a^{-1/2}$. We find E through the defined variable k:

$$\frac{(2mE)^{1/2}}{\hbar} = \frac{n\pi}{2a}$$
$$E = \frac{h^2n^2}{32ma^2}$$

When we solved the Schrödinger equation for the boundary conditions $\psi(0) = \psi(2a) = 0$ (Section 3–5), we found

$$E_n = \frac{h^2n^2}{8m(2a)^2} \qquad n = 1, 2, \cdots$$

which is the same result as that for a box with walls located at $\pm a$. Realize that the wave functions are independent of where the walls are located; however, how we define our coordinate system will change the way we express the wave function mathematically. No experimentally observable properties depend upon how we define our coordinate system - the coordinate system is a purely hypothetical construct which does not impact any observable system. Since σ_x and σ_p are observable properties, $\sigma_x\sigma_p \geq \hbar/2$ as in Section 3.8.

3–30. For a particle moving in a one-dimensional box, the mean value of x is $a/2$, and the mean square deviation is $\sigma_x^2 = (a^2/12)[1 - (6/\pi^2n^2)]$. Show that as n becomes very large, this value agrees with the classical value. The classical probability distribution is uniform,

$$p(x)dx = \frac{1}{a}dx \qquad 0 \leq x \leq a$$
$$= 0 \qquad \text{otherwise}$$

Classically,

$$\langle x \rangle = \frac{1}{a}\int_0^a x dx = \frac{a}{2} \quad \text{and} \quad \langle x^2 \rangle = \frac{1}{a}\int_0^a x^2 dx = \frac{a^2}{3}$$

so

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle = \frac{a^2}{12}$$

For the particle in a box,

$$\lim_{n\to\infty} \sigma^2 = \lim_{n\to\infty} \frac{a^2}{12}\left[1 - \frac{6}{\pi^2 n^2}\right] = \frac{a^2}{12}$$

3–31. This problem shows that the intensity of a wave is proportional to the square of its amplitude. Figure 3.7 illustrates the geometry of a vibrating string. Because the velocity at any point of the string is $\partial u/\partial t$, the kinetic energy of the entire string is

$$K = \int_0^l \frac{1}{2}\rho \left(\frac{\partial u}{\partial t}\right)^2 dx$$

where ρ is the linear mass density of the string. The potential energy is found by considering the increase of length of the small arc PQ of length ds in Figure 3.7. The segment of the string along that arc has increased its length from dx to ds. Therefore, the potential energy associated with this increase is

$$V = \int_0^l T(ds - dx)$$

where T is the tension in the string. Using the fact that $(ds)^2 = (dx)^2 + (du)^2$, show that

$$V = \int_0^l T\left\{\left[1 + \left(\frac{\partial u}{\partial x}\right)^2\right]^{1/2} - 1\right\} dx$$

Using the fact that $(1 + x)^{1/2} \approx 1 + (x/2)$ for small x, show that

$$V = \frac{1}{2}T \int_0^l \left(\frac{\partial u}{\partial x}\right)^2 dx$$

for small displacements. The total energy of the vibrating string is the sum of K and V and so

$$E = \frac{\rho}{2}\int_0^l \left(\frac{\partial u}{\partial t}\right)^2 dx + \frac{T}{2}\int_0^l \left(\frac{\partial u}{\partial x}\right)^2 dx$$

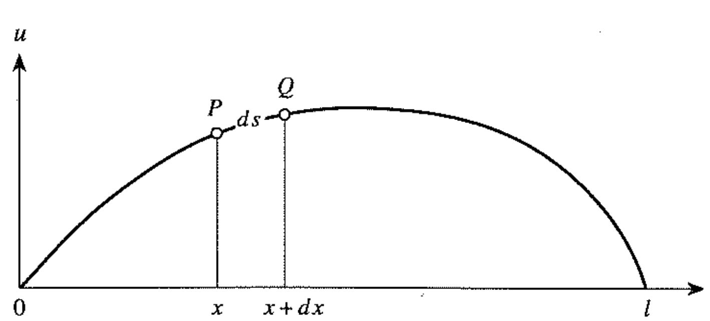


FIGURE 3.7
The geometry of a vibrating string.

We showed in Chapter 2 (Equations 2.23 through 2.25) that the nth normal mode can be written in the form

$$u_n(x, l) = D_n \cos(\omega_n t + \phi_n) \sin\frac{n\pi x}{l}$$

where $\omega_n = v n\pi/l$. Using this equation, show that

$$K_n = \frac{\pi^2 v^2 n^2 \rho}{4l} D_n^2 \sin^2(\omega_n t + \phi_n)$$

and

$$V_n = \frac{\pi^2 n^2 T}{4l} D_n^2 \cos^2(\omega_n t + \phi_n)$$

Using the fact that $v = (T/\rho)^{1/2}$, show that

$$E_n = \frac{\pi^2 v^2 n^2 \rho}{4l} D_n^2$$

Note that the total energy, or intensity, is proportional to the square of the amplitude. Although we have shown this proportionality only for the case of a vibrating string, it is a general result and shows that the intensity of a wave is proportional to the square of the amplitude. If we had carried everything through in complex notation instead of sines and cosines, then we would have found that E_n is proportional to $|D_n|^2$ instead of just D_n^2. Generally, there are many normal modes present at the same time, and the complete solution is (Equation 2.25)

$$u(x, t) = \sum_{n=1}^{\infty} D_n \cos(\omega_n t + \phi_n) \sin\frac{n\pi x}{l}$$

Using the fact that (see Problem 3–16)

$$\int_0^l \sin\frac{n\pi x}{l} \sin\frac{m\pi x}{l} dx = 0 \qquad \text{if } m \neq n$$

show that

$$E_n = \frac{\pi^2 v^2 \rho}{4l} \sum_{n=1}^{\infty} n^2 D_n^2$$

We begin with the potential energy associated with the vibrating string,

$$\begin{aligned} V &= \int_0^l T(ds - dx) \\ &= \int_0^l T\left[\left(dx^2 + du^2\right)^{1/2} - dx\right] \\ &= \int_0^l T\left\{\left[1 + \left(\frac{\partial u}{\partial x}\right)^2\right]^{1/2} - 1\right\} dx \end{aligned}$$

Using the fact that $(1 + x)^{1/2} \approx 1 + x/2$ for small x, we obtain

$$V \approx \int_0^l T\left[1 + \frac{1}{2}\left(\frac{\partial u}{\partial x}\right)^2 - 1\right] dx \approx \frac{T}{2}\int_0^l \left(\frac{\partial u}{\partial x}\right)^2 dx$$

Starting with the equation for the nth normal mode

$$u_n(x, l) = D_n \cos(\omega_n t + \phi_n) \sin\frac{n\pi x}{l}$$

we obtain the partial derivatives

$$\frac{\partial u_n}{\partial t} = -\omega_n D_n \sin(\omega_n t + \phi_n) \sin\frac{n\pi x}{l}$$

and

$$\frac{\partial u_n}{\partial x} = \frac{n\pi}{l} D_n \cos(\omega_n t + \phi_n) \cos\frac{n\pi x}{l}$$

where $\omega_n = vn\pi/l$. Thus,

$$\begin{aligned} K_n &= \frac{\rho}{2}\int_0^l \left(\frac{\partial u_n}{\partial t}\right)^2 dx \\ &= \frac{\rho}{2}\int_0^l \omega_n^2 D_n^2 \sin^2(\omega_n t + \phi_n)\sin^2\frac{n\pi x}{l}dx \\ &= \frac{\omega_n^2 D_n^2 \rho}{2}\int_0^l \sin^2(\omega_n t + \phi_n)\sin^2\frac{n\pi x}{l}dx \\ &= \frac{n^2\pi^2 v^2 \rho}{2l^2} D_n^2 \sin^2(\omega_n t + \phi_n)\int_0^l \sin^2\frac{n\pi x}{l}dx \\ &= \frac{n^2\pi^2 v^2 \rho}{4l} D_n^2 \sin^2(\omega_n t + \phi_n) \end{aligned}$$

and

$$\begin{aligned} V_n &= \frac{T}{2}\int_0^l \left(\frac{\partial u_n}{\partial x}\right)^2 dx \\ &= \frac{T}{2}\int_0^l \frac{n^2\pi^2}{l^2} D_n^2 \cos^2(\omega_n t + \phi_n)\cos^2\frac{n\pi x}{l}dx \\ &= \frac{Tn^2\pi^2}{2l^2} D_n^2 \cos^2(\omega_n t + \phi_n)\int_0^l \cos^2\frac{n\pi x}{l}dx \\ &= \frac{Tn^2\pi^2}{4l} D_n^2 \cos^2(\omega_n t + \phi_n) \end{aligned}$$

where $T = \rho v^2$. The total energy is given by

$$\begin{aligned} E_n &= V_n + K_n \\ &= \frac{n^2\pi^2 v^2\rho}{4l} D_n^2 \sin^2(\omega_n t + \phi_n) + \frac{Tn^2\pi^2}{4l} D_n^2 \cos^2(\omega_n t + \phi_n) \\ &= \frac{n^2\pi^2 v^2\rho}{4l} D_n^2 \sin^2(\omega_n t + \phi_n) + \frac{v^2\rho n^2\pi^2}{4l} D_n^2 \cos^2(\omega_n t + \phi_n) \\ &= \frac{n^2\pi^2 v^2\rho}{4l} D_n^2 \left[\sin^2(\omega_n t + \phi_n) + \cos^2(\omega_n t + \phi_n)\right] \\ &= \frac{n^2\pi^2 v^2\rho}{4l} D_n^2 \end{aligned}$$

Now, using the complete solution, we find

$$\begin{aligned} \sum_{n=1}^{\infty} u_n(x,t) &= \sum_{n=1}^{\infty} D_n \cos(\omega_n t + \phi_n)\sin\frac{n\pi x}{l} \\ \frac{\partial u_n}{\partial t} &= -\sum_{n=1}^{\infty} \omega_n D_n \sin(\omega_n t + \phi_n)\sin\frac{n\pi x}{l} \\ \frac{\partial u_n}{\partial x} &= \sum_{n=1}^{\infty} \frac{n\pi}{l} D_n \cos(\omega_n t + \phi_n)\cos\frac{n\pi x}{l} \end{aligned}$$

To find V and K, use the identity from Problem 3–16

$$\int_0^l \sin\frac{n\pi x}{l}\sin\frac{m\pi x}{l}dx = \int_0^l \cos\frac{n\pi x}{l}\cos\frac{m\pi x}{l}dx = \frac{l}{2}\delta_{nm}$$

We then have

$$\begin{aligned} \sum_{n=1}^{\infty} K_n &= \frac{\rho}{2}\int_0^l \left(\frac{\partial u_n}{\partial t}\right)^2 dx \\ &= \frac{\rho}{2}\int_0^l \left(\sum_{n=1}^{\infty} -\omega_n D_n \sin(\omega_n t + \phi_n)\sin\frac{n\pi x}{l}\right)\left(\sum_{m=1}^{\infty} -\omega_m D_m \sin(\omega_m t + \phi_m)\sin\frac{m\pi x}{l}\right)dx \\ &= \frac{\rho}{2}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \omega_n\omega_m D_n D_m \sin(\omega_n t + \phi_n)\sin(\omega_m t + \phi_m)\int_0^l \sin\frac{n\pi x}{l}\sin\frac{m\pi x}{l}dx \\ &= \frac{\rho}{2}\sum_{n=1}^{\infty} \omega_n^2 D_n^2 \sin^2(\omega_n t + \phi_n)\left(\frac{l}{2}\right) \\ &= \frac{\rho\pi^2 v^2}{4l}\sum_{n=1}^{\infty} n^2 D_n^2 \sin^2(\omega_n t + \phi_n) \end{aligned}$$

and

$$\begin{aligned} \sum_{n=1}^{\infty} V_n &= \frac{T}{2}\int_0^l \left(\frac{\partial u_n}{\partial x}\right)^2 dx \\ &= \frac{T}{2}\int_0^l \left(\sum_{n=1}^{\infty} \frac{n\pi}{l} D_n \cos(\omega_n t + \phi_n)\cos\frac{n\pi x}{l}\right)\left(\sum_{m=1}^{\infty} \frac{m\pi}{l} D_m \cos(\omega_m t + \phi_m)\cos\frac{m\pi x}{l}\right)dx \\ &= \frac{T\pi^2}{2l^2}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} nm D_n D_m \cos(\omega_n t + \phi_n)\cos(\omega_m t + \phi_m)\int_0^l \cos\frac{n\pi x}{l}\cos\frac{m\pi x}{l}dx \\ &= \frac{T\pi^2}{2l^2}\sum_{n=1}^{\infty} n^2 D_n^2 \cos^2(\omega_n t + \phi_n)\left(\frac{l}{2}\right) \\ &= \frac{\pi^2 v^2 \rho}{4l}\sum_{n=1}^{\infty} n^2 D_n^2 \cos^2(\omega_n t + \phi_n) \end{aligned}$$

Finally,

$$\begin{aligned} \sum_{n=1}^{\infty} E_n &= \sum_{n=1}^{\infty} V_n + \sum_{n=1}^{\infty} K_n \\ &= \frac{\pi^2 v^2\rho}{4l}\sum_{n=1}^{\infty} n^2 D_n^2 \cos^2(\omega_n t + \phi_n) + \frac{\rho\pi^2 v^2}{4l}\sum_{n=1}^{\infty} n^2 D_n^2 \sin^2(\omega_n t + \phi_n) \\ &= \frac{\pi^2 v^2\rho}{4l}\sum_{n=1}^{\infty} n^2 D_n^2 \left[\cos^2(\omega_n t + \phi_n) + \sin^2(\omega_n t + \phi_n)\right] \\ &= \frac{\pi^2 v^2\rho}{4l}\sum_{n=1}^{\infty} n^2 D_n^2 \end{aligned}$$

3–32. The quantized energies of a particle in a box result from the boundary conditions, or from the fact that the particle is restricted to a finite region. In this problem, we investigate the quantum-mechanical problem of a free particle, one that is not restricted to a finite region. The potential energy $V(x)$ is equal to zero and the Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0 \qquad -\infty < x < \infty$$

Note that the particle can lie anywhere along the x-axis in this problem. Show that the two solutions of this Schrödinger equation are

$$\psi_1(x) = A_1 e^{i(2mE)^{1/2}x/\hbar} = A_1 e^{ikx}$$

and

$$\psi_2(x) = A_2 e^{-i(2mE)^{1/2}x/\hbar} = A_2 e^{-ikx}$$

where

$$k = \frac{(2mE)^{1/2}}{\hbar}$$

Show that if E is allowed to take on negative values, then the wave functions become unbounded for large x. Therefore, we will require that the energy, E, be a positive quantity. We saw in our discussion of the Bohr atom that negative energies correspond to bound states and positive energies correspond to unbound states, and so our requirement that E be positive is consistent with the picture of a free particle. To get a physical interpretation of the states that $\psi_1(x)$ and $\psi_2(x)$ describe, operate on $\psi_1(x)$ and $\psi_2(x)$ with the momentum operator $\hat{P}$ (Equation 3.11), and show that

$$\hat{P}\psi_1 = -i\hbar\frac{d\psi_1}{dx} = \hbar k\psi_1$$

and

$$\hat{P}\psi_2 = -i\hbar\frac{d\psi_2}{dx} = -\hbar k\psi_2$$

Notice that these are eigenvalue equations. Our interpretation of these two equations is that ψ_1 describes a free particle with fixed momentum $\hbar k$ and that ψ_2 describes a particle with fixed momentum $-\hbar k$. Thus, ψ_1 describes a particle moving to the right and ψ_2 describes a particle moving to the left, both with a fixed momentum. Notice also that there are no restrictions on k, and so the particle can have any value of momentum. Now show that

$$E = \frac{\hbar^2 k^2}{2m}$$

Notice that the energy is not quantized; the energy of the particle can have any positive value in this case because no boundaries are associated with this problem. Last, show that $\psi_1^*(x)\psi_1(x) = A_1^*A_1 = |A_1|^2 =$ constant and that $\psi_2^*(x)\psi_2(x) = A_2^*A_2 = |A_2|^2 =$ constant. Discuss this result in terms of the probabilistic interpretation of $\psi^*\psi$. Also discuss the application of the Uncertainty Principle to this problem. What are σ_p and σ_x?

From Example 2–4, we know that the solutions to this Schrödinger equation are

$$\psi_1(x) = A_1 e^{ikx} \qquad \psi_2(x) = A_2 e^{-ikx}$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}$$

Suppose E can be less than zero. Then $k \to i(-2mE)^{1/2}/\hbar$ and

$$\lim_{x\to\infty}\psi_2(x) = \lim_{x\to\infty} A_2 e^{x\sqrt{-2mE}/\hbar}$$

diverges. Therefore, E must be positive. Using Equation 3.11 for the momentum operator, we find

$$\begin{aligned}
\hat{P}\psi_1 &= -i\hbar\frac{d\psi_1}{dx} = -i\hbar\frac{d}{dx}\left(A_1 e^{ikx}\right)\\
&= -i^2\hbar k A_1 e^{ikx} = \hbar k A_1 e^{ikx} = \hbar k\psi_1(x)\\
\hat{P}\psi_2 &= -i\hbar\frac{d\psi_2}{dx} = -i\hbar\frac{d}{dx}\left(A_2 e^{-ikx}\right)\\
&= i^2\hbar k A_2 e^{-ikx} = -\hbar k A_2 e^{-ikx} = -\hbar k\psi_1(x)
\end{aligned}$$

For a free particle, all energy is kinetic energy. The possible values of the momentum of a free particle are $\hbar k$ and $-\hbar k$. Using $E = p^2/2m$, we find that

$$E = \frac{p^2}{2m} = \frac{(\pm\hbar k)^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

Finally,

$$\begin{aligned}
\psi_1^*(x)\psi_1(x) &= \left(A_1^* e^{-ikx}\right)\left(A_1 e^{ikx}\right)\\
&= A_1^*A_1 = \left|A_1\right|^2 = \text{constant}\\
\psi_2^*(x)\psi_2(x) &= \left(A_2^* e^{ikx}\right)\left(A_2 e^{-ikx}\right)\\
&= A_2^*A_2 = \left|A_2\right|^2 = \text{constant}
\end{aligned}$$

Since $\psi^*(x)\psi(x)$ is a constant, the particle is equally likely to be found anywhere along the x axis. Thus, there is an infinite uncertainty in the location of the particle. This is consistent with the Uncertainty Principle because the momentum of the particle is known exactly ($\sigma_p = 0$).

3–33. Derive the equation for the allowed energies of a particle in a one-dimensional box by assuming that the particle is described by standing de Broglie waves within the box.

The de Broglie relationship is

$$\lambda = \frac{h}{p} \tag{1.12}$$

Because the waves are standing waves, an integral number of half-wavelengths will fit into the box, or

$$\frac{n\lambda}{2} = a \qquad \text{and} \qquad \frac{nh}{2p} = a$$

Solving for p gives

$$p = \frac{nh}{2a}$$

and the corresponding energy is

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{1}{2m}\frac{n^2h^2}{4a^2} = \frac{n^2h^2}{8ma^2}$$

3–34. We can use the Uncertainty Principle for a particle in a box to argue that free electrons cannot exist in a nucleus. Before the discovery of the neutron, one might have thought that a nucleus of atomic number Z and mass number A is made up of A protons and $A - Z$ electrons, that is, just enough electrons such that the net nuclear charge is $+Z$. Such a nucleus would have an atomic number Z and mass number A. In this problem, we will use Equation 3.41 to *estimate* the energy of an electron confined to a region of nuclear size. The diameter of a typical nucleus is approximately 10^{-14} m. Substitute $a = 10^{-14}$ m into Equation 3.41 and show that σ_p is

$$\sigma_p \gtrsim 3 \times 10^{-20}\ \text{kg}\cdot\text{m}\cdot\text{s}^{-1}$$

Show that

$$E = \frac{\sigma_p^2}{2m} = 5 \times 10^{-10}\ \text{J}$$
$$\approx 3000\ \text{MeV}$$

where millions of electron volts (MeV) is the common nuclear physics unit of energy. It is observed experimentally that electrons emitted from nuclei as β radiation have energies of only a few MeV, which is far less than the energy we have calculated above. Argue, then, that there can be no free electrons in nuclei because they should be ejected with much higher energies than are found experimentally.

$$\sigma_p = \frac{n\pi\hbar}{a} = \frac{nh}{2a} \tag{3.41}$$

For $n = 1$ and $a = 10^{-14}$ m,

$$\sigma_p = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{2(1 \times 10^{-14}\ \text{m})} \approx 3 \times 10^{-20}\ \text{kg}\cdot\text{m}\cdot\text{s}^{-1}$$

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{\sigma_p^2}{2m} \qquad \text{(Problem 3–23)}$$

and in this case

$$E \approx \frac{(3 \times 10^{-20}\ \text{kg}\cdot\text{m}\cdot\text{s}^{-1})^2}{2(9.11 \times 10^{-31}\ \text{kg})} \approx 5 \times 10^{-10}\ \text{J} \approx 3000\ \text{MeV}$$

Because no nuclei emit electrons with energies on the order of 1000 MeV, we assume such electrons do not exist in nuclei; therefore, there can be no free electrons in nuclei. (Electrons with energies of only a few MeV are the result of a neutron decaying into a proton and an electron in the nucleus.)

3–35. We can use the wave functions of Problem 3–29 to illustrate some fundamental symmetry properties of wave functions. Show that the wave functions are alternately symmetric and antisymmetric or even and odd with respect to the operation $x \to -x$, which is a reflection through the $x = 0$ line. This symmetry property of the wave function is a consequence of the symmetry of the Hamiltonian operator, as we now show. The Schrödinger equation may be written as

$$\hat{H}(x)\psi_n(x) = E_n\psi_n(x)$$

Reflection through the $x = 0$ line gives $x \to -x$ and so

$$\hat{H}(-x)\psi_n(-x) = E_n\psi_n(-x)$$

Now show that $\hat{H}(x) = \hat{H}(-x)$ (i.e., that $\hat{H}$ is symmetric) for a particle in a box, and so show that

$$\hat{H}(x)\psi_n(-x) = E_n\psi_n(-x)$$

Thus, we see that $\psi_n(-x)$ is also an eigenfunction of $\hat{H}$ belonging to the same eigenvalue E_n. Now, if only one eigenfunction is associated with each eigenvalue (the state is nondegenerate), then argue that $\psi_n(x)$ and $\psi_n(-x)$ must differ only by a multiplicative constant [i.e., that $\psi_n(x) = c\psi_n(-x)$]. By applying the inversion operation again to this equation, show that $c = \pm 1$ and that all the wave functions must be either even or odd with respect to reflection through the $x = 0$ line because the Hamiltonian operator is symmetric. Thus, we see that the symmetry of the Hamiltonian operator influences the symmetry of the wave functions. A general study of symmetry uses group theory, and this example is actually an elementary application of group theory to quantum-mechanical problems. We will study group theory in Chapter 12.

Consider the wavefunctions found in Problem 3–29. For odd n

$$\psi_n(-x) = \frac{1}{a^{1/2}}\cos\left(-\frac{n\pi x}{2a}\right) = \frac{1}{a^{1/2}}\cos\left(\frac{n\pi x}{2a}\right) = \psi_n(x)$$

and the wavefunctions for odd n are symmetric. For even n

$$\psi_n(-x) = \frac{1}{a^{1/2}}\sin\left(-\frac{n\pi x}{2a}\right) = -\frac{1}{a^{1/2}}\sin\left(\frac{n\pi x}{2a}\right) = -\psi_n(x)$$

and the wavefunctions for even n are antisymmetric. We will now show that $\hat{H}(x)$ is an even function of x:

$$\hat{H}(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$
$$\hat{H}(-x) = -\frac{\hbar^2}{2m}\frac{d^2}{d(-x)^2} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} = \hat{H}(x)$$

Now we have shown that $E_n\psi_n(-x) = \hat{H}(x)\psi_n(-x) = \hat{H}(x)\psi_n(x)$. If the state is nondegenerate, $\psi_n(-x) = c\psi_n(x)$. Repeating the operation, we find

$$\psi_n(-x) = c\psi_n(x) = c^2\psi_n(-x)$$

which leads to the conclusion that $c = \pm 1$ and consequently to the conclusion that all $\psi_n(x)$ are either even or odd with respect to reflection through the $x = 0$ line. Thus the symmetry of the Hamiltonian influences the symmetry of its eigenfunctions (assuming a nondegenerate system).
