CHAPTER 4

Some Postulates and General Principles of Quantum Mechanics

PROBLEMS AND SOLUTIONS

4–1. Which of the following candidates for wave functions are normalizable over the indicated intervals?

a. $e^{-x^2/2}$ $(-\infty, \infty)$ **b.** e^{x} $(0, \infty)$ **c.** $e^{i\theta}$ $(0, 2\pi)$

d. $\sinh x$ $(0, \infty)$ **e.** xe^{-x} $(0, \infty)$

Normalize those that can be normalized. Are the others suitable wave functions?

Only the functions given by (a), (c), and (e) can be normalized. The functions given by (b) and (d) diverge as $x \to \infty$. If a function cannot be normalized, it is not a suitable wave function. Therefore (b) and (d) are not suitable wave functions. We now normalize the functions given by (a), (c), and (e).

a.

$$A^2 \int_{-\infty}^{\infty} e^{-x^2} dx = 1$$

$$2A^2 \int_{0}^{\infty} e^{-x^2} dx = 2A^2 \left(\frac{\pi}{4}\right)^{1/2} = 1$$

$$A = \left(\frac{1}{\pi}\right)^{1/4}$$

recalling that e^{-x^2} is an even function.

c.

$$A^2 \int_{0}^{2\pi} e^{-i\theta} e^{i\theta} d\theta = 1$$

$$A^2 \int_{0}^{2\pi} d\theta = A^2(2\pi) = 1$$

$$A = \left(\frac{1}{2\pi}\right)^{1/2}$$

e.

$$A^2 \int_{0}^{\infty} x^2 e^{-2x} dx = 1$$

$$\frac{A^2}{4} = 1$$

$$A = 2$$

4–2. Which of the following wave functions are normalized over the indicated two-dimensional intervals?

a. $e^{-(x^2+y^2)/2}$ $\quad 0 \le x < \infty$, $0 \le y < \infty$

b. $e^{-(x+y)/2}$ $\quad 0 \le x < \infty$, $0 \le y < \infty$

c. $\left(\dfrac{4}{ab}\right)^{1/2} \sin\dfrac{\pi x}{a} \sin\dfrac{\pi y}{b}$ $\quad 0 \le x \le a$, $0 \le y \le b$

Normalize those that aren't.

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a.

$$\int_0^\infty dx \int_0^\infty dy e^{-(x^2+y^2)} = \int_0^\infty dx e^{-x^2} \int_0^\infty dy e^{-y^2}$$
$$= \left(\frac{\pi}{4}\right)^{1/2}\left(\frac{\pi}{4}\right)^{1/2}$$
$$= \frac{\pi}{4}$$

Therefore, to normalize the function, it must be multiplied by $\dfrac{2}{\sqrt{\pi}}$.

b.

$$\int_0^\infty dx \int_0^\infty dy e^{-(x+y)} = \int_0^\infty dx e^{-x} \int_0^\infty dy e^{-y} = 1$$

This function is normalized.

c.

$$\left(\frac{4}{ab}\right)\int_0^a dx \sin^2\frac{\pi x}{a}\int_0^b dy \sin^2\frac{\pi y}{b} = \left(\frac{4}{ab}\right)\left(\frac{a}{2}\right)\left(\frac{b}{2}\right) = 1$$

This function is normalized.

4–3. Why does $\psi^*\psi$ have to be everywhere real, nonnegative, finite, and of definite value?

This is required if $\psi^*\psi$ is to be a measure of probability.

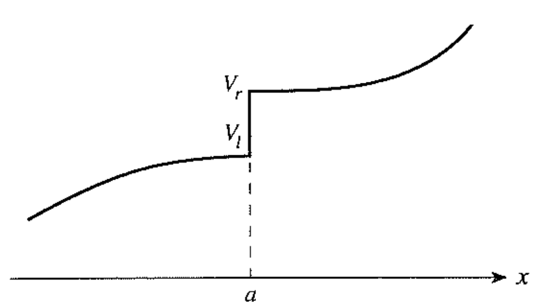
4–4. In this problem, we will prove that the form of the Schrödinger equation imposes the condition that the first derivative of a wave function be continuous. The Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0$$

If we integrate both sides from $a - \epsilon$ to $a + \epsilon$, where a is an arbitrary value of x and ϵ is infinitesimally small, then we have

$$\left.\frac{d\psi}{dx}\right|_{x=a+\epsilon} - \left.\frac{d\psi}{dx}\right|_{x=a-\epsilon} = \frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon}[V(x) - E]\psi(x)dx$$

Now show that $d\psi/dx$ is continuous if $V(x)$ is continuous.
Suppose now that $V(x)$ is *not* continuous at $x = a$, as in



Show that

$$\left.\frac{d\psi}{dx}\right|_{x=a+\epsilon} - \left.\frac{d\psi}{dx}\right|_{x=a-\epsilon} = \frac{2m}{\hbar^2}[V_l + V_r - 2E]\psi(a)\epsilon$$

so that $d\psi/dx$ is continuous even if $V(x)$ has a *finite* discontinuity. What if $V(x)$ has an infinite discontinuity, as in the problem of a particle in a box? Are the first derivatives of the wave functions continuous at the boundaries of the box?

We start with

$$\left.\frac{d\psi}{dx}\right|_{x=a+\epsilon} - \left.\frac{d\psi}{dx}\right|_{x=a-\epsilon} = \frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon}[V(x) - E]\psi(x)dx \tag{1}$$

Because $V(x)$ is continuous, $\lim_{\epsilon\to 0} V(a \pm \epsilon) = V(a)$. We already know that $\psi(x)$ is continuous, so

$$\lim_{\epsilon\to 0}\frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon}[V(x) - E]\psi(x)dx = \frac{2m}{\hbar^2}[V(a) - E]\,\psi(a)\lim_{\epsilon\to 0}\int_{a-\epsilon}^{a+\epsilon}dx = 0 \tag{2}$$

Combining Equations 1 and 2 shows that

$$\lim_{\epsilon\to 0}\left(\left.\frac{d\psi}{dx}\right|_{x=a+\epsilon} - \left.\frac{d\psi}{dx}\right|_{x=a-\epsilon}\right) = 0$$

and therefore, $d\psi/dx$ is continuous. Now suppose that $V(x)$ has a finite discontinuity at $x = a$. We divide the integral into two parts, $a - \epsilon$ to a and a to $a + \epsilon$:

$$\frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon}[V(x) - E]\psi(x)dx = \frac{2m}{\hbar^2}\left[\int_{a-\epsilon}^{a}[V_l(x) - E]\psi(x)dx + \int_a^{a+\epsilon}[V_r(x) - E]\psi(x)dx\right]$$
$$= \frac{2m}{\hbar^2}\left\{\left[V_l(a) - E\right]\psi(a)\int_{a-\epsilon}^{a}dx + \left[V_r(a) - E\right]\psi(a)\int_a^{a+\epsilon}dx\right\}$$
$$= \frac{2m}{\hbar^2}\left[V_l(a) + V_r(a) - 2E\right]\psi(a)\epsilon$$

Because $\lim_{\epsilon\to 0}\left[V_l(a) + V_r(a) - 2E\right]\psi(a)\epsilon = 0$, $d\psi/dx$ remains continuous even though $V(x)$ has a finite discontinuity. If $V(x)$ has an infinite discontinuity at an arbitrary point a, however, we cannot approach a from one side and therefore cannot integrate the expression $\frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon}[V(x) - E]\psi(x)dx$. This implies that $d\psi/dx$ is no longer a continuous function at a. For this reason, the first derivatives of the wave functions of a particle in a box are not continuous at (and only at) the boundaries of the box.

4–5. Determine whether the following functions are acceptable or not as state functions over the indicated intervals.

a. $\dfrac{1}{x}$ $\quad (0, \infty)$

b. $e^{-2x}\sinh x$ $\quad (0, \infty)$

c. $e^{-x}\cos x$ $\quad (0, \infty)$

d. e^{x} $\quad (-\infty, \infty)$

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a. Unacceptable because it cannot be normalized.

b. Acceptable.

c. Acceptable.

d. Unacceptable because it cannot be normalized.

4–6. Calculate the values of $\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2$ for a particle in a box in the state described by

$$\psi(x) = \left(\frac{630}{a^9}\right)^{1/2} x^2(a-x)^2 \qquad 0 \le x \le a$$

Using Postulate 4, $\langle E \rangle$ is given by

$$\langle E \rangle = \int_0^a \psi^*(x)\hat{H}\psi(x)dx \tag{4.11}$$

and $\langle E^2 \rangle$ is given by

$$\langle E^2 \rangle = \int_0^a \psi^*(x)\hat{H}^2\psi(x)dx$$

We are interested in σ_E^2 for the state described by

$$\psi^*(x) = \psi(x) = \left(\frac{630}{a^9}\right)^{1/2} x^2(a-x)^2$$

To evaluate $\langle E \rangle$ and $\langle E^2 \rangle$, we will need to know the first four derivatives of ψ. These are given by

$$\begin{aligned}
\frac{d\psi(x)}{dx} &= \left(\frac{630}{a^9}\right)^{1/2}\left[2x(a-x)^2 - 2x^2(a-x)\right]\\
\frac{d^2\psi(x)}{dx^2} &= \left(\frac{630}{a^9}\right)^{1/2}\left[2(a-x)^2 - 4x(a-x) - 4x(a-x) + 2x^2\right]\\
&= \left(\frac{630}{a^9}\right)^{1/2}(2a^2 - 12ax + 12x^2)\\
\frac{d^3\psi(x)}{dx^3} &= \left(\frac{630}{a^9}\right)^{1/2}(-12a + 24x)\\
\frac{d^4\psi(x)}{dx^4} &= \left(\frac{630}{a^9}\right)^{1/2}(24)
\end{aligned}$$

Using these results,

$$\begin{aligned}
\langle E \rangle &= \int_0^a \psi^*(x)\left(-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}\right)dx\\
&= -\frac{\hbar^2}{2m}\int_0^a \left(\frac{630}{a^9}\right)x^2(a-x)^2\left(2a^2 - 12ax + 12x^2\right)dx\\
&= -\frac{630\hbar^2}{2ma^9}\int_0^a x^2(a-x)^2\left(2a^2 - 12ax + 12x^2\right)dx\\
&= -\frac{630\hbar^2}{2ma^9}\left[\int_0^a 2a^2x^2(a-x)^2dx + \int_0^a -12ax^3(a-x)^2dx + \int_0^a 12x^4(a-x)^2dx\right]
\end{aligned}$$

or

$$\langle E \rangle = \frac{6\hbar^2}{ma^2} \tag{1}$$

We used the general integral

$$\int_0^1 x^m(1-x)^n dx = \frac{m!n!}{(m+n+1)!} \tag{2}$$

to evaluate the integrals in the last step to obtain Equation 1. We now evaluate $\langle E^2 \rangle$, which is given by

$$\langle E^2 \rangle = \int_0^a \psi^*(x)\hat{H}^2\psi(x)dx$$

Substituting in the appropriate quantities gives

$$\begin{aligned}
\langle E^2 \rangle &= \int_0^a \psi^*(x)\left(\frac{\hbar^4}{4m^2}\frac{d^4\psi(x)}{dx^4}\right)dx\\
&= \frac{630\hbar^4}{4m^2a^9}\int_0^a x^2(a-x)^2(24)dx
\end{aligned}$$

or

$$\langle E^2 \rangle = \frac{126\hbar^4}{m^2a^4} \tag{3}$$

Using Equations 1 and 3 gives

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{126\hbar^4}{m^2a^4} - \frac{36\hbar^4}{m^2a^4} = \frac{90\hbar^4}{m^2a^4}$$

4–7. Consider a free particle constrained to move over the rectangular region $0 \le x \le a$, $0 \le y \le b$. The energy eigenfunctions of this system are

$$\psi_{n_x,n_y}(x,y) = \left(\frac{4}{ab}\right)^{1/2}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b} \qquad \begin{array}{l} n_x = 1, 2, 3, \ldots \\ n_y = 1, 2, 3, \ldots \end{array}$$

The Hamiltonian operator for this system is

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

Show that if the system is in one of its eigenstates, then

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = 0$$

If the system is in one of its eigenstates, then

$$\begin{aligned}
\hat{H}\psi_{n_xn_y} &= E_{n_xn_y}\psi_{n_xn_y}\\
\hat{H}^2\psi_{n_xn_y} &= E_{n_xn_y}^2\psi_{n_xn_y}
\end{aligned}$$

Therefore,

$$\begin{aligned}
\langle E \rangle &= \int\int \psi_{n_xn_y}^*\hat{H}\psi_{n_xn_y} = \int\int \psi_{n_xn_y}^*E_{n_xn_y}\psi_{n_xn_y}\\
&= E_{n_xn_y}\int\int \psi_{n_xn_y}^*\psi_{n_xn_y} = E_{n_xn_y}\\
\langle E^2 \rangle &= \int\int \psi_{n_xn_y}^*\hat{H}^2\psi_{n_xn_y} = \int\int \psi_{n_xn_y}^*E_{n_xn_y}^2\psi_{n_xn_y}\\
&= E_{n_xn_y}^2\int\int \psi_{n_xn_y}^*\psi_{n_xn_y} = E_{n_xn_y}^2
\end{aligned}$$

and $\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = 0$.

4–8. The momentum operator in two dimensions is

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

Using the wave function given in Problem 4–7, calculate the value of $\langle p\rangle$ and then

$$\sigma_p^2 = \langle p^2\rangle - \langle p\rangle^2$$

Compare your result with σ_p^2 in the one-dimensional case.

We find

$$\langle p\rangle = \int_0^a dx\int_0^b dy\psi^*_{n_x n_y}(x,y)\left[-i\hbar\left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y}\right)\right]\psi_{n_x n_y}(x,y)$$
$$= -\frac{4i\hbar}{ab}\int_0^a dx\int_0^b dy\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\left(\mathbf{i}\frac{n_x\pi}{a}\cos\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b} + \mathbf{j}\frac{n_y\pi}{b}\sin\frac{n_x\pi x}{a}\cos\frac{n_y\pi y}{b}\right)$$
$$= 0$$

and

$$\langle p^2\rangle = \int_0^a dx\int_0^b dy\psi^*_{n_x n_y}(x,y)\left[-\hbar^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\right]\psi_{n_x n_y}(x,y)$$
$$= \frac{4\hbar^2}{ab}\int_0^a dx\int_0^b dy\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\left(\frac{n_x^2\pi^2}{a^2} + \frac{n_y^2\pi^2}{b^2}\right)\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}$$
$$= \pi^2\hbar^2\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right) = \frac{h^2}{4}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

$$\sigma_p^2 = \langle p^2\rangle - \langle p\rangle^2 = \langle p^2\rangle = \frac{h^2}{4}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

This is an extension of the result in the one-dimensional case (Problem 3–25).

4–9. Suppose that a particle in a two-dimensional box (cf. Problem 4–7) is in the state

$$\psi(x,y) = \frac{30}{(a^5b^5)^{1/2}}x(a-x)y(b-y)$$

Show that $\psi(x,y)$ is normalized, and then calculate the value of $\langle E\rangle$ associated with the state described by $\psi(x,y)$.

First, we show that $\psi(x,y)$ is normalized.

$$\int_0^a dx\int_0^b dy\psi^*\psi = \frac{900}{a^5b^5}\int_0^a dx\, x^2(a-x)^2\int_0^b dy\, y^2(b-y)^2$$
$$= \frac{900}{a^5b^5}\left[\frac{(2)(2a^5)}{5!}\right]\left[\frac{(2)(2b^5)}{5!}\right]$$
$$= 1$$

We used Equation 2 of Problem 4–6 to evaluate the integrals over dx and dy. To find $\langle E\rangle$, we evaluate

$$\langle E\rangle = \frac{900}{a^5b^5}\int_0^a dx\int_0^b dy\, x(a-x)y(b-y)\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right)(ax-x^2)(by-y^2)\right]$$
$$= \frac{900\hbar^2}{ma^5b^5}\int_0^a dx\int_0^b dy\, x(a-x)y(b-y)\,[y(b-y) + x(a-x)]$$
$$= \frac{900\hbar^2}{ma^5b^5}\left[\int_0^a dx\int_0^b dy\, x(a-x)y^2(b-y)^2 + \int_0^a dx\int_0^b dy\, x^2(a-x)^2y(b-y)\right]$$
$$= \frac{900\hbar^2}{ma^5b^5}\left[\left(\frac{a^3}{3!}\right)\left(\frac{4b^5}{5!}\right) + \left(\frac{4a^5}{5!}\right)\left(\frac{b^3}{3!}\right)\right]$$
$$= \frac{5\hbar^2}{m}\left(\frac{1}{a^2} + \frac{1}{b^2}\right)$$

4–10. Show that

$$\psi_0(x) = \pi^{-1/4}e^{-x^2/2}$$
$$\psi_1(x) = (4/\pi)^{1/4}xe^{-x^2/2}$$
$$\psi_2(x) = (4\pi)^{-1/4}(2x^2-1)e^{-x^2/2}$$

are orthonormal over the interval $-\infty < x < \infty$.

All of the functions are real, so $\psi^*(x) = \psi(x)$. We want to show that

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

$$\int_{-\infty}^{\infty}\psi_0^2(x)dx = \frac{2}{\pi^{1/2}}\int_0^{\infty}e^{-x^2}dx = 1$$
$$\int_{-\infty}^{\infty}\psi_1^2(x)dx = \frac{4}{\pi^{1/2}}\int_0^{\infty}x^2e^{-x^2}dx = 1$$
$$\int_{-\infty}^{\infty}\psi_2^2(x)dx = \frac{1}{2\pi^{1/2}}\int_0^{\infty}(2x^2-1)^2e^{-x^2}dx$$
$$= \frac{1}{\pi^{1/2}}\left[4\left(\frac{3\pi^{1/2}}{8}\right) - 4\left(\frac{\pi^{1/2}}{4}\right) + \frac{\pi^{1/2}}{2}\right] = 1$$
$$\int_{-\infty}^{\infty}\psi_0(x)\psi_1(x) = \left(\frac{2}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}xe^{-x^2}dx = 0$$
$$\int_{-\infty}^{\infty}\psi_0(x)\psi_2(x) = \frac{1}{(2\pi)^{1/2}}\left[\int_{-\infty}^{\infty}2x^2e^{-x^2}dx - \int_{-\infty}^{\infty}e^{-x^2}dx\right]$$
$$= \frac{1}{(2\pi)^{1/2}}(\pi^{1/2} - \pi^{1/2}) = 0$$
$$\int_{-\infty}^{\infty}\psi_1(x)\psi_2 = \frac{1}{\pi^{1/2}}\int_{-\infty}^{\infty}x(2x^2-1)e^{-x^2} = 0$$

The last integral is easy to evaluate because the integrand is an odd function and the integral is over a symmetric interval.

4–11. Show that the polynomials

$$P_0(x) = 1, \qquad P_1(x) = x, \qquad \text{and} \qquad P_2(x) = \tfrac{1}{2}(3x^2 - 1)$$

satisfy the orthogonality relation

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

where δ_{ln} is the Kroenecker delta (Equation 4.30).

Again, all the functions are real, so $P_n^*(x) = P_n(x)$.

$$\int_{-1}^{1} P_0^2(x)dx = \int_{-1}^{1} dx = 2$$
$$\int_{-1}^{1} P_1^2(x)dx = \int_{-1}^{1} x^2 dx = \frac{2}{3}$$
$$\int_{-1}^{1} P_0^2(x)dx = \frac{1}{2}\int_{0}^{1} (9x^4 - 6x^2 + 1)dx = \frac{2}{5}$$
$$\int_{-1}^{1} P_0(x)P_1(x)dx = \int_{-1}^{1} xdx = 0$$
$$\int_{-1}^{1} P_0(x)P_2(x)dx = \int_{0}^{1} (3x^2 - 1)dx = 0$$
$$\int_{-1}^{1} P_1(x)P_2(x)dx = \frac{1}{2}\int_{-1}^{1} (3x^3 - x)dx = 0$$

4–12. Show that the set of functions $(2/a)^{1/2}\cos(n\pi x/a)$, $n = 0, 1, 2, \ldots$ is orthonormal over the interval $0 \le x \le a$.

Because the functions are real, $\psi_n^*(x) = \psi_n(x)$.

$$\int_0^a \psi_n(x)\psi_m(x)dx = \frac{2}{a}\int_0^a \cos\frac{n\pi x}{a}\cos\frac{m\pi x}{a}dx$$
$$= \delta_{nm}$$

This integral was solved explicitly in Problem 3–18.

4–13. Prove that if δ_{nm} is the Kroenecker delta

$$\delta_{nm} = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases}$$

then

$$\sum_{n=1}^{\infty} c_n\delta_{nm} = c_m$$

and

$$\sum_n\sum_m a_n b_m \delta_{nm} = \sum_n a_n b_n$$

These results will be used later.

The sum $\sum_{n=1}^{\infty} c_n\delta_{nm} = c_m$ because every term is equal to zero except for those where $n = m$. Now

$$\sum_n\sum_m a_n b_m \delta_{nm} = \sum_n a_n\left(\sum_m b_m\delta_{nm}\right) = \sum_n a_n b_n$$

where we used the first result to evaluate $\sum_m b_m\delta_{nm}$.

4–14. Determine whether or not the following pairs of operators commute.

	$\hat{A}$	$\hat{B}$
(a)	$\frac{d}{dx}$	$\frac{d^2}{dx^2} + 2\frac{d}{dx}$
(b)	x	$\frac{d}{dx}$
(c)	SQR	SQRT
(d)	$x^2\frac{d}{dx}$	$\frac{d^2}{dx^2}$

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a.

$$\hat{A}\hat{B}f = \frac{d}{dx}\left(\frac{d^2f}{dx^2} + 2\frac{df}{dx}\right) = \frac{d^3f}{dx^3} + 2\frac{d^2f}{dx^2}$$
$$\hat{B}\hat{A}f = \left(\frac{d^2}{dx^2} + 2\frac{d}{dx}\right)\frac{df}{dx} = \frac{d^3f}{dx^3} + 2\frac{d^2f}{dx^2}$$
$$\hat{A}\hat{B}f = \hat{B}\hat{A}f$$

This pair of operators commutes.

b.

$$\hat{A}\hat{B}f = x\frac{df}{dx}$$
$$\hat{B}\hat{A}f = \frac{d}{dx}(xf) = f + x\frac{df}{dx}$$
$$\hat{A}\hat{B}f \neq \hat{B}\hat{A}f$$

This pair of operators does not commute.

c.

$$\hat{A}\hat{B}f = [\text{SQRT}(f)]^2 = (\pm f^{1/2})^2 = f$$
$$\hat{B}\hat{A}f = \text{SQRT}(f^2) = \pm f$$
$$\hat{A}\hat{B}f \neq \hat{B}\hat{A}f$$

This pair of operators does not commute.

d.

$$\hat{A}\hat{B}f = x^2\frac{d}{dx}\left(\frac{d^2f}{dx^2}\right) = x^2\frac{d^3f}{dx^3}$$
$$\hat{B}\hat{A}f = \frac{d^2}{dx^2}\left(x^2\frac{df}{dx}\right) = x^2\frac{d^3f}{dx^3} + 4x\frac{d^2f}{dx^2} + 2\frac{df}{dx}$$
$$\hat{A}\hat{B}f \neq \hat{B}\hat{A}f$$

This pair of operators does not commute.

4–15. In ordinary algebra, $(P+Q)(P-Q)=P^2-Q^2$. Expand $(\hat{P}+\hat{Q})(\hat{P}-\hat{Q})$. Under what conditions do we find the same result as in the case of ordinary algebra?

$$(\hat{P}+\hat{Q})(\hat{P}-\hat{Q})=\hat{P}^2-\hat{Q}^2+\hat{Q}\hat{P}-\hat{P}\hat{Q}=\hat{P}^2-\hat{Q}^2+\left[\hat{Q},\hat{P}\right]$$

In order for this result to equal the result found in ordinary algebra, $\hat{P}$ and $\hat{Q}$ must commute.

4–16. Evaluate the commutator $[\hat{A},\hat{B}]$, where $\hat{A}$ and $\hat{B}$ are given below.

	$\hat{A}$	$\hat{B}$
(a)	$\dfrac{d^2}{dx^2}$	x
(b)	$\dfrac{d}{dx}-x$	$\dfrac{d}{dx}+x$
(c)	$\displaystyle\int_0^x dx$	$\dfrac{d}{dx}$
(d)	$\dfrac{d^2}{dx^2}-x$	$\dfrac{d}{dx}+x^2$

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a.

$$\hat{A}\hat{B}f=\frac{d^2}{dx^2}(xf)=2\frac{df}{dx}+x\frac{d^2f}{dx^2}$$

$$\hat{B}\hat{A}f=x\frac{d^2f}{dx^2}$$

$$[\hat{A},\hat{B}]=\hat{A}\hat{B}f-\hat{B}\hat{A}f=2\frac{d}{dx}$$

b.

$$\hat{A}\hat{B}f=\left(\frac{d}{dx}-x\right)\left(\frac{df}{dx}+xf\right)=\frac{d^2f}{dx^2}+f-x^2f$$

$$\hat{B}\hat{A}f=\left(\frac{d}{dx}+x\right)\left(\frac{df}{dx}-xf\right)=\frac{d^2f}{dx^2}-f-x^2f$$

$$[\hat{A},\hat{B}]=2$$

c.

$$\hat{A}\hat{B}f=\int_0^x dx'\frac{df}{dx'}=f(x)-f(0)$$

$$\hat{B}\hat{A}f=\frac{d}{dx}\int_0^x dx'f(x')=f(x)$$

$$[\hat{A},\hat{B}]f=-f(0)$$

d.

$$\hat{A}\hat{B}f=\left(\frac{d^2}{dx^2}-x\right)\left(\frac{df}{dx}+x^2f\right)=\frac{d^3f}{dx^3}+x^2\frac{d^2f}{dx^2}+3x\frac{df}{dx}+(2-x^3)f$$

$$\hat{B}\hat{A}f=\left(\frac{d}{dx}+x^2\right)\left(\frac{d^2f}{dx^2}-xf\right)=\frac{d^3f}{dx^3}+x^2\frac{d^2f}{dx^2}-x\frac{df}{dx}-(1+x^3)f$$

$$[\hat{A},\hat{B}]=4x\frac{d}{dx}+3$$

4–17. Referring to Table 4.1 for the operator expressions for angular momentum, show that

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

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

and

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

(Do you see a pattern here to help remember these commutation relations?) What do these expressions say about the ability to measure the components of angular momentum simultaneously?

$$\hat{L}_x\hat{L}_yf=\left[-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\right]\left[-i\hbar\left(z\frac{\partial f}{\partial x}-x\frac{\partial f}{\partial z}\right)\right]$$

$$=-\hbar^2\left(y\frac{\partial f}{\partial x}+yz\frac{\partial^2f}{\partial z\partial x}-xy\frac{\partial^2f}{\partial z^2}-z^2\frac{\partial^2f}{\partial x\partial y}+xz\frac{\partial^2f}{\partial y\partial z}\right)$$

$$\hat{L}_y\hat{L}_xf=\left[-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\right]\left[-i\hbar\left(y\frac{\partial f}{\partial z}-z\frac{\partial f}{\partial y}\right)\right]$$

$$=-\hbar^2\left(yz\frac{\partial^2f}{\partial x\partial z}-z^2\frac{\partial^2f}{\partial x\partial y}-xy\frac{\partial^2f}{\partial z^2}+x\frac{\partial f}{\partial y}+xz\frac{\partial^2f}{\partial z\partial y}\right)$$

$$\left[\hat{L}_x,\hat{L}_y\right]=-\hbar^2\left(y\frac{\partial}{\partial x}-x\frac{\partial}{\partial y}\right)=i\hbar\left[-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\right]$$

$$=i\hbar\hat{L}_z$$

In the same way, we can show $[\hat{L}_y,\hat{L}_z]=i\hbar\hat{L}_x$ and $[\hat{L}_z,\hat{L}_x]=i\hbar\hat{L}_y$. The pattern involves the cyclic permutation of x, y, and z. Since no combination of the operators $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ commutes, it is not possible to simultaneously measure any two of the three components of angular momentum to arbitrary precision (as discussed in Section 4–6).

4–18. Defining

$$\hat{L}^2=\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2$$

show that $\hat{L}^2$ commutes with each component separately. What does this result tell you about the ability to measure the square of the total angular momentum and its components simultaneously?

$$\hat{L}_x^2\hat{L}_x-\hat{L}_x\hat{L}_x^2=0$$

$$\hat{L}_y^2\hat{L}_x-\hat{L}_x\hat{L}_y^2=\hat{L}_y^2\hat{L}_x-\left(\hat{L}_y\hat{L}_x+i\hbar\hat{L}_z\right)\hat{L}_y$$

$$\hat{L}_z^2\hat{L}_x-\hat{L}_x\hat{L}_z^2=\hat{L}_z^2\hat{L}_x-\left(\hat{L}_z\hat{L}_x-i\hbar\hat{L}_y\right)\hat{L}_z$$

$$\left[\hat{L}^2,\hat{L}_x\right]=0+\hat{L}_y^2\hat{L}_x-\hat{L}_y\hat{L}_x\hat{L}_y-i\hbar\hat{L}_z\hat{L}_y+\hat{L}_z^2\hat{L}_x-\hat{L}_z\hat{L}_x\hat{L}_z+i\hbar\hat{L}_y\hat{L}_z$$

$$=\hat{L}_y\left(\hat{L}_y\hat{L}_x-\hat{L}_x\hat{L}_y\right)+\hat{L}_z\left(\hat{L}_z\hat{L}_x-\hat{L}_x\hat{L}_z\right)-i\hbar\left(\hat{L}_z\hat{L}_y-\hat{L}_y\hat{L}_z\right)$$

$$=\hat{L}_y\left(-i\hbar\hat{L}_z\right)+\hat{L}_z\left(i\hbar\hat{L}_y\right)-i\hbar\left(-i\hbar\hat{L}_x\right)$$

$$=i\hbar\left(\hat{L}_z\hat{L}_y-\hat{L}_y\hat{L}_z\right)-\hbar^2\hat{L}_x$$

$$=i\hbar\left(-i\hbar\hat{L}_x\right)-\hbar^2\hat{L}_x=0$$

In a similar way, we can show that $\hat{L}^2$ commutes with $\hat{L}_y$ and $\hat{L}_z$. This result tells us that we can simultaneously measure the square of the total angular momentum and any of its components to arbitrary precision (as discussed in Section 4–6).

4–19. In Chapter 6 we will use the operators

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y$$

and

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y$$

Show that

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

$$[\hat{L}_z, \hat{L}_+] = \hbar\hat{L}_+$$

and that

$$[\hat{L}_z, \hat{L}_-] = -\hbar\hat{L}_-$$

$$\hat{L}_+\hat{L}_- = \left(\hat{L}_x + i\hat{L}_y\right)\left(\hat{L}_x - i\hat{L}_y\right) = \hat{L}_x^2 + i\hat{L}_y\hat{L}_x - i\hat{L}_x\hat{L}_y + \hat{L}_y^2$$
$$= \hat{L}_x^2 + \hat{L}_y^2 + i[\hat{L}_y, \hat{L}_x] = \hat{L}_x^2 + \hat{L}_y^2 + \hbar\hat{L}_z = \hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z$$

where we used the fact that $\hat{L}_x^2 + \hat{L}_y^2 = \hat{L}^2 - \hat{L}_z^2$.

$$\left[\hat{L}_z, \hat{L}_+\right] = \hat{L}_z\hat{L}_x + i\hat{L}_z\hat{L}_y - \hat{L}_x\hat{L}_z - i\hat{L}_y\hat{L}_z$$
$$= [\hat{L}_z, \hat{L}_x] + i[\hat{L}_z, \hat{L}_y] = i\hbar\hat{L}_y + \hbar\hat{L}_x$$
$$= \hbar\hat{L}_+$$
$$\left[\hat{L}_z, \hat{L}_-\right] = [\hat{L}_z, \hat{L}_x] - i[\hat{L}_z, \hat{L}_y] = i\hbar\hat{L}_y - \hbar\hat{L}_x$$
$$= -\hbar\hat{L}_-$$

4–20. Consider a particle in a two-dimensional box. Determine $[\hat{X}, \hat{P}_y]$, $[\hat{X}, \hat{P}_x]$, $[\hat{Y}, \hat{P}_y]$, and $[\hat{Y}, \hat{P}_x]$.

From Equation 3.56, we have

$$\psi(x, y) = \left(\frac{4}{ab}\right)^{1/2} \sin\frac{n_x\pi x}{a} \sin\frac{n_y\pi y}{b}$$

a.

$$\hat{X}\hat{P}_y\psi = x\left(-i\hbar\frac{\partial\psi}{\partial y}\right)$$
$$= -i\hbar\left(\frac{4}{ab}\right)^{1/2}\frac{n_y\pi x}{b}\sin\frac{n_x\pi x}{a}\cos\frac{n_y\pi y}{b}$$
$$\hat{P}_y\hat{X}\psi = -i\hbar\frac{\partial}{\partial y}\left(x\left(\frac{4}{ab}\right)^{1/2}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\right)$$
$$= -i\hbar\left(\frac{4}{ab}\right)^{1/2}\frac{n_y\pi x}{b}\sin\frac{n_x\pi x}{a}\cos\frac{n_y\pi y}{b}$$
$$\left[\hat{X}, \hat{P}_y\right] = \hat{X}\hat{P}_y - \hat{P}_y\hat{X} = 0$$

b.

$$\hat{X}\hat{P}_x\psi = x\left(-i\hbar\frac{\partial\psi}{\partial x}\right)$$
$$= -i\hbar\left(\frac{4}{ab}\right)^{1/2}\frac{n_x\pi x}{a}\cos\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}$$
$$\hat{P}_x\hat{X}\psi = -i\hbar\frac{\partial}{\partial x}\left(x\left(\frac{4}{ab}\right)^{1/2}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\right)$$
$$= -i\hbar\left(\frac{4}{ab}\right)^{1/2}\left(\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b} + \frac{n_x\pi x}{a}\cos\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\right)$$
$$= -i\hbar\psi - i\hbar\left(\frac{4}{ab}\right)^{1/2}\frac{n_x\pi x}{a}\cos\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}$$
$$\left[\hat{X}, \hat{P}_x\right] = \hat{X}\hat{P}_x - \hat{P}_x\hat{X} = i\hbar$$

c.

$$\hat{Y}\hat{P}_y\psi = y\left(-i\hbar\frac{\partial\psi}{\partial y}\right)$$
$$= -i\hbar\left(\frac{4}{ab}\right)^{1/2}\frac{n_y\pi y}{b}\sin\frac{n_x\pi x}{a}\cos\frac{n_y\pi y}{b}$$
$$\hat{P}_y\hat{Y}\psi = -i\hbar\frac{\partial}{\partial y}\left(y\left(\frac{4}{ab}\right)^{1/2}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\right)$$
$$= -i\hbar\left(\frac{4}{ab}\right)^{1/2}\left(\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b} + \frac{n_y\pi y}{b}\sin\frac{n_x\pi x}{a}\cos\frac{n_y\pi y}{b}\right)$$
$$= -i\hbar\psi - i\hbar\left(\frac{4}{ab}\right)^{1/2}\frac{n_y\pi y}{b}\sin\frac{n_x\pi x}{a}\cos\frac{n_y\pi y}{b}$$
$$\left[\hat{Y}, \hat{P}_y\right] = \hat{Y}\hat{P}_y - \hat{P}_y\hat{Y} = i\hbar$$

d.

$$\hat{Y}\hat{P}_x\psi = y\left(-i\hbar\frac{\partial\psi}{\partial x}\right)$$
$$= -i\hbar\left(\frac{4}{ab}\right)^{1/2}\frac{n_x\pi y}{a}\cos\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}$$
$$\hat{P}_x\hat{Y}\psi = -i\hbar\frac{\partial}{\partial x}\left(y\left(\frac{4}{ab}\right)^{1/2}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\right)$$
$$= -i\hbar\left(\frac{4}{ab}\right)^{1/2}\frac{n_x\pi y}{a}\cos\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}$$
$$\left[\hat{Y}, \hat{P}_x\right] = \hat{Y}\hat{P}_x - \hat{P}_x\hat{Y} = 0$$

4–21. Can the position and total angular momentum of any electron be measured simultaneously to arbitrary precision?

Yes. The position and total angular momentum operators are vector operators given by $\hat{\mathbf{R}} = \mathbf{i}\hat{x} + \mathbf{j}\hat{y} + \mathbf{k}\hat{z}$ and $\hat{\mathbf{L}} = \mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z$. We are interested in whether $\hat{\mathbf{R}}$ and $\hat{\mathbf{L}}$ commute.

$$\begin{aligned}[\hat{\mathbf{R}}, \hat{\mathbf{L}}] &= [\mathbf{i}\hat{x} + \mathbf{j}\hat{y} + \mathbf{k}\hat{z}, \mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z] \\ &= [\hat{x}, \hat{L}_x] + [\hat{y}, \hat{L}_y] + [\hat{z}, \hat{L}_z] \\ &= 0\end{aligned}$$

where we have used the fact that $\mathbf{i}\cdot\mathbf{i} = \mathbf{j}\cdot\mathbf{j} = \mathbf{k}\cdot\mathbf{k} = 1$ and $\mathbf{i}\cdot\mathbf{j} = \mathbf{j}\cdot\mathbf{k} = \mathbf{k}\cdot\mathbf{i} = 0$ (MathChapter C). Therefore, the position and total angular momentum of any electron can be measured simultaneously to arbitrary precision.

4–22. Can the angular momentum and kinetic energy of a particle be measured simultaneously to arbitrary precision?

Yes. The proof is similar to that in Problem 4–21.

$$\begin{aligned}[\hat{\mathbf{K}}, \hat{\mathbf{L}}] &= [\hat{K}_x, \hat{L}_x] + [\hat{K}_y, \hat{L}_y] + [\hat{K}_z, \hat{L}_z] \\ &= 0\end{aligned}$$

We see from this that the kinetic energy and angular momentum of the electron can be simultaneously measured to arbitrary precision.

4–23. Using the result of Problem 4–20, what are the "uncertainty relationships" $\Delta x \Delta p_y$ and $\Delta y \Delta p_x$ equal to?

Because $[\hat{X}, \hat{P}_y]$ and $[\hat{Y}, \hat{P}_x]$ are both equal to zero (Problem 4–20), the "uncertainty relationships" are $\Delta x \Delta p_y = \Delta y \Delta p_x = 0$. This means that the quantities x, p_y and y, p_x can be measured simultaneously to arbitrary precision.

4–24. We can define functions of operators through their Taylor series (MathChapter I). For example, we define the operator exp $(\hat{S})$ by

$$e^{\hat{S}} = \sum_{n=0}^{\infty} \frac{(\hat{S})^n}{n!}$$

Under what conditions does the equality

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}}$$

hold?

Let $\hat{I}$ be the identity operator. Then

$$\begin{aligned}e^{\hat{A}+\hat{B}} &= \hat{I} + \hat{A} + \hat{B} + \frac{(\hat{A}+\hat{B})^2}{2!} + O[(\hat{A}+\hat{B})^3] \\ &= \hat{I} + \hat{A} + \hat{B} + \frac{\hat{A}^2}{2} + \frac{\hat{B}^2}{2} + \frac{\hat{A}\hat{B}}{2} + \frac{\hat{B}\hat{A}}{2} + O[(\hat{A}+\hat{B})^3]\end{aligned}$$

and

$$\begin{aligned}e^{\hat{A}} e^{\hat{B}} &= \left[\hat{I} + \hat{A} + \frac{\hat{A}^2}{2} + O(\hat{A}^3)\right]\left[\hat{I} + \hat{B} + \frac{\hat{B}^2}{2} + O(\hat{B}^3)\right] \\ &= \hat{I} + \hat{A} + \hat{B} + \frac{\hat{A}^2}{2} + \frac{\hat{B}^2}{2} + \hat{A}\hat{B} + O[(\hat{A}+\hat{B})^3]\end{aligned}$$

These two expressions are equivalent only if $[\hat{A}, \hat{B}] = 0$; in other words, only if $\hat{A}$ and $\hat{B}$ commute.

4–25. In this chapter, we learned that if ψ_n is an eigenfunction of the time-independent Schrödinger equation, then

$$\Psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar}$$

Show that if ψ_m and ψ_n are both stationary states of $\hat{H}$, then the state

$$\Psi(x,t) = c_m \psi_m(x) e^{-iE_m t/\hbar} + c_n \psi_n(x) e^{-iE_n t/\hbar}$$

satisfies the time-dependent Schrödinger equation.

Postulate 5 gives the time-dependent Schrödinger equation as

$$\hat{H}\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

We will substitute Ψ into each side of this equation separately to show that the equivalence holds. The left side becomes

$$\begin{aligned}\hat{H}\Psi &= \hat{H}\left[c_m \psi_m e^{-iE_m t/\hbar} + c_n \psi_n e^{-iE_n t/\hbar}\right] \\ &= E_m c_m \psi_m e^{-iE_m t/\hbar} + E_n c_n \psi_n e^{-iE_n t/\hbar}\end{aligned}$$

and the right side is

$$\begin{aligned}i\hbar \frac{\partial \Psi}{\partial t} &= i\hbar \left(\frac{-iE_m}{\hbar} c_m \psi_m e^{-iE_m t\hbar} - \frac{iE_n}{\hbar} c_n \psi_n e^{-iE_n t\hbar}\right) \\ &= c_m E_m \psi_m e^{-iE_m t/\hbar} + c_n E_n \psi_n e^{-iE_n t/\hbar}\end{aligned}$$

4–26. Starting with

$$\langle x \rangle = \int \Psi^*(x,t) x \Psi(x,t) dx$$

and the time-dependent Schrödinger equation, show that

$$\frac{d\langle x \rangle}{dt} = \int \Psi^* \frac{i}{\hbar}(\hat{H}x - x\hat{H})\Psi dx$$

Given that

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

show that

$$\hat{H}x - x\hat{H} = -2\frac{\hbar^2}{2m}\frac{d}{dx} = -\frac{\hbar^2}{m}\frac{i}{\hbar}\hat{P}_x = -\frac{i\hbar}{m}\hat{P}_x$$

Finally, substitute this result into the equation for $d\langle x\rangle/dt$ to show that

$$m\frac{d\langle x\rangle}{dt} = \langle \hat{P}_x\rangle$$

Interpret this result.

$$\langle x\rangle = \int \Psi^* x \Psi dx$$

$$\frac{d\langle x\rangle}{dt} = \int \frac{\partial \Psi^*}{\partial t} x\Psi dx + \int \Psi^* x \frac{\partial \Psi}{\partial t} dx$$

Using Postulate 5 to express $\partial\Psi/\partial t$, we can write

$$\frac{d\langle x\rangle}{dt} = -\frac{1}{i\hbar}\int (\hat{H}\Psi)^* x\Psi dx + \frac{1}{i\hbar}\int \Psi^* x(\hat{H}\Psi) dx$$

Because $\hat{H}$ is Hermitian, this is equivalent to

$$\begin{aligned}\frac{d\langle x\rangle}{dt} &= -\frac{1}{i\hbar}\int \Psi^* \hat{H} x\Psi dx + \frac{1}{i\hbar}\int \Psi^* x(\hat{H}\Psi) dx \\ &= \frac{i}{\hbar}\int \Psi^*(\hat{H}x - x\hat{H})\Psi dx \qquad (1)\end{aligned}$$

Now, using the given expression for $\hat{H}$, we find that

$$\begin{aligned}(\hat{H}x - x\hat{H})f &= \left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]xf - x\left[\frac{-\hbar^2}{2m}\frac{d^2 f}{dx^2} + V(x)f\right] \\ &= \frac{-\hbar^2 x}{2m}\frac{d^2 f}{dx^2} = \frac{-2\hbar^2}{2m}\frac{df}{dx} + V(x)xf + \frac{+\hbar^2 x}{2m}\frac{d^2 f}{dx^2} - xV(x)f \\ (\hat{H}x - x\hat{H}) &= \frac{-\hbar^2}{m}\frac{d}{dx} = \frac{-\hbar^2}{m}\frac{i}{\hbar}\hat{P}_x \\ &= \frac{-i\hbar}{m}\hat{P}_x \qquad (2)\end{aligned}$$

Substituting Equation 2 into Equation 1 gives

$$m\frac{d\langle x\rangle}{dt} = \langle \hat{P}_x\rangle$$

which is the quantum mechanical equivalent of the classical definition of linear momentum, $p = mv$.

4–27. Generalize the result of Problem 4–26 and show that if F is any dynamical quantity, then

$$\frac{d\langle F\rangle}{dt} = \int \Psi^* \frac{i}{\hbar}(\hat{H}\hat{F} - \hat{F}\hat{H})\Psi dx$$

Use this equation to show that

$$\frac{d\langle \hat{P}_x\rangle}{dt} = \left\langle -\frac{dV}{dx}\right\rangle$$

Interpret this result. This last equation is known as *Ehrenfest's theorem*.

Replace x by $\hat{F}$ in the first part of the previous problem to show that

$$\frac{d\langle F\rangle}{dt} = \int \Psi^* \frac{i}{\hbar}(\hat{H}\hat{F} - \hat{F}\hat{H})\Psi dx \qquad (1)$$

Now consider the case where $\hat{F} = \hat{P}_x$:

$$\begin{aligned}\hat{H}\hat{P}_x &= -i\hbar \hat{H}\frac{d}{dx} \\ &= -\frac{\hbar^2}{2m}(-i\hbar)\frac{d^3}{dx^3} - i\hbar V(x)\frac{d}{dx} \\ \hat{P}_x\hat{H} &= -i\hbar\left(-\frac{\hbar^2}{2m}\right)\frac{d^3}{dx^3} - i\hbar V(x)\frac{d}{dx} - i\hbar\frac{dV}{dx} \\ \left[\hat{H}, \hat{P}_x\right] &= \hat{H}\hat{P}_x - \hat{P}_x\hat{H} = i\hbar\frac{dV}{dx}\end{aligned}$$

Substituting this result into Equation 1 gives

$$\frac{d\langle \hat{P}_x\rangle}{dt} = -\int \Psi^* \frac{dV}{dx}\Psi dx = \left\langle -\frac{dV}{dx}\right\rangle$$

Ehrenfest's theorem is the quantum mechanical equivalent of Newton's law, $F = ma$.

4–28. The fact that eigenvalues, which correspond to physically observable quantities, must be real imposes a certain condition on quantum-mechanical operators. To see what this condition is, start with

$$\hat{A}\psi = a\psi \qquad (1)$$

where $\hat{A}$ and ψ may be complex, but a must be real. Multiply Equation 1 from the left by ψ^* and then integrate to obtain

$$\int \psi^* \hat{A}\psi d\tau = a\int \psi^*\psi d\tau = a \qquad (2)$$

Now take the complex conjugate of Equation 1, multiply from the left by ψ, and then integrate to obtain

$$\int \psi \hat{A}^*\psi^* d\tau = a^* = a \qquad (3)$$

Equate the left sides of Equations 2 and 3 to give

$$\int \psi^* \hat{A}\psi d\tau = \int \psi \hat{A}^*\psi^* d\tau \qquad (4)$$

This is the condition that an operator must satisfy if its eigenvalues are to be real. Such operators are called Hermitian operators.

We start with

$$\hat{A}\psi = a\psi \qquad (1)$$

Multiplying Equation 1 from the left by ψ^* and then integrating gives

$$\int \psi^* \hat{A}\psi d\tau = \int \psi^* a\psi d\tau = a\int \psi^*\psi d\tau = a \qquad (2)$$

The complex conjugate of Equation 1 is

$$\hat{A}^*\psi^* = a^*\psi^*$$

Multiplying this expression from the left by ψ and then integrating gives

$$\int \psi\hat{A}^*\psi^* d\tau = \int \psi a^*\psi^* d\tau = a^* \int \psi\psi^* d\tau = a \qquad (2)$$

because we have imposed the restriction that a is real. Equating Equations 2 and 3 shows that if a is real, then

$$\int \psi^*\hat{A}\psi d\tau = \int \psi\hat{A}^*\psi^* d\tau$$

4–29. In this problem, we will prove that not only are the eigenvalues of Hermitian operators real but that their eigenfunctions are orthogonal. Consider the two eigenvalue equations

$$\hat{A}\psi_n = a_n\psi_n \quad \text{and} \quad \hat{A}\psi_m = a_m\psi_m$$

Multiply the first equation by ψ_m^* and integrate; then take the complex conjugate of the second, multiply by ψ_n, and integrate. Subtract the two resulting equations from each other to get

$$\int_{-\infty}^{\infty} \psi_m^*\hat{A}\psi_n dx - \int_{-\infty}^{\infty} \psi_n\hat{A}^*\psi_m^* dx = (a_n - a_m^*)\int_{-\infty}^{\infty} \psi_m^*\psi_n dx$$

Because $\hat{A}$ is Hermitian, the left side is zero, and so

$$(a_n - a_m^*)\int_{-\infty}^{\infty} \psi_m^*\psi_n dx = 0$$

Discuss the two possibilities $n = m$ and $n \neq m$. Show that $a_n = a_n^*$, which is just another proof that the eigenvalues are real. When $n \neq m$, show that

$$\int_{-\infty}^{\infty} \psi_m^*\psi_n dx = 0 \qquad m \neq n$$

if the system is nondegenerate. Are ψ_m and ψ_n necessarily orthogonal if they are degenerate?

Carrying out the stated steps gives

$$\int \psi_m^*\hat{A}\psi_n d\tau = a_n \int \psi_m^*\psi_n d\tau$$

$$\int \psi_n\hat{A}^*\psi_m^* d\tau = a_m^* \int \psi_n\psi_m^* d\tau = a_m^* \int \psi_m^*\psi_n d\tau$$

Subtracting these two expressions gives

$$\int \psi_m^*\hat{A}\psi_n d\tau - \int \psi_n\hat{A}^*\psi_m^* d\tau = (a_n - a_m^*)\int \psi_m^*\psi_n d\tau = 0$$

We set this last equation equal to zero because (as stated in the question) $\hat{A}$ is Hermitian. If $n = m$, then the integral $\int \psi_m^*\psi_n d\tau$ is equal to one and so the above equation tells us that $a_n = a_m^*$ $(= a_n^*)$. In other words, a must be real. If $n \neq m$, for a non-degenerate system $(a_n - a_m^*)$ will be nonzero and so

$$\int \psi_m^*\psi_n d\tau = 0 \qquad n \neq m$$

Note that ψ_m and ψ_n are not necessarily orthogonal if they are degenerate, because a_n can equal a_m^*.

4–30. All the operators in Table 4.1 are Hermitian. In this problem, we show how to determine if an operator is Hermitian. Consider the operator $\hat{A} = d/dx$. If $\hat{A}$ is Hermitian, it will satisfy Equation 4 of Problem 4–28. Substitute $\hat{A} = d/dx$ into Equation 4 and integrate by parts to obtain

$$\int_{-\infty}^{\infty} \psi^*\frac{d\psi}{dx}dx = \Big|_{-\infty}^{\infty} \psi^*\psi\Big| - \int_{-\infty}^{\infty} \psi\frac{d\psi^*}{dx}dx$$

For a wave function to be normalizable, it must vanish at infinity, so the first term on the right side is zero. Therefore, we have

$$\int_{-\infty}^{\infty} \psi^*\frac{d}{dx}\psi dx = -\int_{-\infty}^{\infty} \psi\frac{d}{dx}\psi^* dx$$

For an arbitrary function $\psi(x)$, d/dx does *not* satisfy Equation 4 of Problem 4–28, so it is *not* Hermitian.

We will use the fact that $\int v\, du = uv - \int u\, dv$. Let ψ^* be v and $\frac{d\psi}{dx}dx$ be du. Then

$$\int_{-\infty}^{\infty} \psi^*\frac{d\psi}{dx}dx = \Big|\psi^*\psi\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi\frac{d\psi^*}{dx}dx$$
$$= -\int_{-\infty}^{\infty} \psi\frac{d}{dx}\psi^* dx$$

4–31. Following the procedure in Problem 4–30, show that the momentum operator is Hermitian.

$$\int_{-\infty}^{\infty} \psi^*\hat{P}_x\psi dx = \int_{-\infty}^{\infty} \psi^*\left(-i\hbar\frac{d\psi}{dx}\right)dx$$
$$= -i\hbar\Big|_{-\infty}^{\infty} \psi^*\psi\Big| + \int_{-\infty}^{\infty} i\hbar\psi\frac{d\psi^*}{dx}dx$$
$$= \int_{-\infty}^{\infty}\left[-i\hbar\frac{d}{dx}\psi(x)\right]^*\psi dx$$
$$= \int_{-\infty}^{\infty}\left(\hat{P}_x^*\psi^*\right)\psi dx$$

The momentum operator is Hermitian.

4–32. Specify which of the following operators are Hermitian: id/dx, d^2/dx^2, and id^2/dx^2. Assume that $-\infty < x < \infty$ and that the functions on which these operators operate are appropriately well behaved at infinity.

We must determine whether the operator satisfies the condition

$$\int_{-\infty}^{\infty} f^*(x)\hat{A}f(x)dx = \int_{-\infty}^{\infty} f(x)\hat{A}^*f^*(x)dx$$

If the operator satisfies this equation, then it is Hermitian (Section 4–5).

a.

$$\int_{-\infty}^{\infty} f^*\left(i\frac{df}{dx}\right)dx = i\int_{-\infty}^{\infty} f^*\frac{df}{dx}dx = i\left[\left|_{-\infty}^{\infty} f^*f\right| - \int_{-\infty}^{\infty} f\frac{df^*}{dx}dx\right]$$

$$= -i\int_{-\infty}^{\infty} f\frac{df^*}{dx}dx = \int_{-\infty}^{\infty} f\left(-i\frac{d}{dx}\right)f^*dx$$

$$= \int_{-\infty}^{\infty} f\left(i\frac{d}{dx}\right)^* f^*dx$$

This operator is Hermitian.

b.

$$\int_{-\infty}^{\infty} f^*\left(\frac{d^2f}{dx^2}\right)dx = \left|_{-\infty}^{\infty} f^*\frac{df}{dx}\right| - \int_{-\infty}^{\infty}\frac{df^*}{dx}\frac{df}{dx}dx$$

$$= -\left|_{-\infty}^{\infty}\frac{df^*}{dx}f\right| + \int_{-\infty}^{\infty}\frac{d^2f^*}{dx^2}f\,dx$$

$$= \int_{-\infty}^{\infty} f\left(\frac{d^2}{dx^2}\right)f^*dx = \int_{-\infty}^{\infty} f\left(\frac{d^2}{dx^2}\right)^* f^*dx$$

This operator is Hermitian.

c.

$$\int_{-\infty}^{\infty} f^*\left(i\frac{d^2f}{dx^2}\right)dx = \left|_{-\infty}^{\infty} f^*i\frac{df}{dx}\right| - i\int_{-\infty}^{\infty}\frac{df^*}{dx}\frac{df}{dx}dx$$

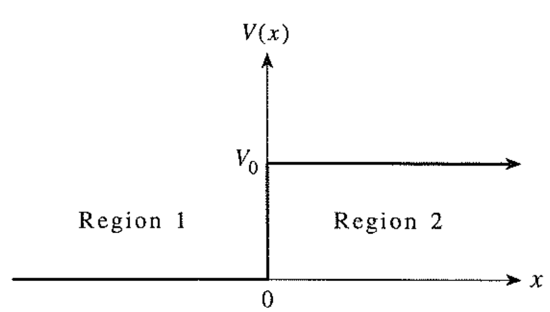
$$= -i\left|_{-\infty}^{\infty} f\frac{df^*}{dx}\right| + i\int_{-\infty}^{\infty} f\frac{d^2f^*}{dx^2}dx$$

$$= -\int_{-\infty}^{\infty} f\left(i\frac{d^2}{dx^2}\right)^* f^*dx$$

This operator is not Hermitian.

Problems 4–33 through 4–38 deal with systems with piece-wise constant potentials.

4–33. Consider a particle moving in the potential energy



whose mathematical form is

$$V(x) = \begin{matrix} 0 & x < 0 \\ V_0 & x > 0 \end{matrix}$$

where V_0 is a constant. Show that if $E > V_0$, then the solutions to the Schrödinger equation in the two regions (1 and 2) are (see Problem 3–32)

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \qquad x < 0 \tag{1}$$

and

$$\psi_2(x) = Ce^{ik_2x} + De^{-ik_2x} \qquad x > 0 \tag{2}$$

where

$$k_1 = \left(\frac{2mE}{\hbar^2}\right)^{1/2} \quad\text{and}\quad k_2 = \left(\frac{2m(E-V_0)}{\hbar^2}\right)^{1/2} \tag{3}$$

As we learned in Problem 3–32, e^{ikx} represents a particle traveling to the right and e^{-ikx} represents a particle traveling to the left. Let's consider a particle traveling to the right in region 1. If we wish to exclude the case of a particle traveling to the left in region 2, we set $D = 0$ in Equation 2. The physical problem we have set up is a particle of energy E incident on a potential barrier of height V_0. The squares of the coefficients in Equation 1 and 2 represent the probability that the particle is traveling in a certain direction in a given region. For example, $|A|^2$ is the probabillity that the particle is traveling with momentum $+\hbar k_1$ (Problem 3–32) in the region $x < 0$. If we consider many particles, N_0, instead of just one, then we can interpret $|A|^2N_0$ to be the number of particles with momentum $\hbar k_1$ in the region $x < 0$. The number of these particles that pass a given point per unit time is given by $v|A|^2N_0$, where the velocity v is given by $\hbar k_1/m$. Now apply the conditions that $\psi(x)$ and $d\psi/dx$ must be continuous at $x = 0$ (see Problem 4–4) to obtain

$$A + B = C$$

and

$$k_1(A - B) = k_2C$$

Now define a quantity

$$R = \frac{v_1|B|^2N_0}{v_1|A|^2N_0} = \frac{\hbar k_1|B|^2N_0/m}{\hbar k_1|A|^2N_0/m} = \frac{|B|^2}{|A|^2}$$

and show that

$$R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2$$

Similarly, define

$$T = \frac{v_2|C|^2N_0}{v_1|A|^2N_0} = \frac{\hbar k_2|C|^2N_0/m}{\hbar k_1|A|^2N_0/m} = \frac{k_2|C|^2}{k_1|A|^2}$$

and show that

$$T = \frac{4k_1k_2}{(k_1 + k_2)^2}$$

The symbols R and T stand for reflection coefficient and transmission coefficient, respectively. Give a physical interpretation of these designations. Show that $R + T = 1$. Would you have expected the particle to have been reflected even though its energy, E, is greater than the barrier height, V_0? Show that $R \to 0$ and $T \to 1$ as $V_0 \to 0$.

Region 1 ($x < 0$):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} = E\psi_1$$

The solution to this differential equation is

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \qquad k_1 = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

Region 2 ($x > 0$):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V_0\psi_2 = E\psi_2$$

giving

$$\psi_2(x) = Ce^{ik_2x} + De^{-ik_2x} \qquad k_2 = \left[\frac{2m(E-V_0)}{\hbar^2}\right]^{1/2}$$

Let $D = 0$ as stated in the problem. Now we impose the boundary conditions $\psi(0) = 0$ and $d\psi/dx = 0$ at $x = 0$, so

$$\psi_1(0) = \psi_2(0) \qquad \left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_2}{dx}\right|_{x=0}$$

This gives

$$A + B = C \quad (1) \qquad k_1A - k_1B = k_2C \quad (2)$$

If we multiply Equation 1 by k_2 and subtract the result from Equation 2, we can obtain

$$\frac{B}{A} = \frac{k_1 - k_2}{k_2 + k_1}$$

$$R = \frac{|B|^2}{|A|^2} = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 \qquad (3)$$

If we multiply Equation 1 by k_1 and add the result to Equation 2, we can obtain

$$\frac{C}{A} = \frac{2k_1}{k_1 + k_2}$$

$$T = \frac{k_2|C|^2}{k_1|A|^2} = \frac{4k_1k_2}{(k_1 + k_2)^2} \qquad (4)$$

The quantity R is the proportion of the wavefunction that is reflected back into region 1 and T is the proportion of the wavefunction that is transmitted into region 2. Therefore, $R + T = 1$, which is in agreement with the sum of Equations 3 and 4.

$$R + T = \frac{4k_1k_2 + k_1^2 - 2k_1k_2 + k_2^2}{(k_1 + k_2)^2} = \frac{(k_1 + k_2)^2}{(k_1 + k_2)^2} = 1$$

In a classical treatment of the problem, the particle would not be reflected when its energy was greater than the barrier height. This is a quantum mechanical effect. As $V_0 \to 0$, $k_1 \to k_2$, and so $R \to 0$ and $T \to 1$.

4–34. Show that $R = 1$ for the system described in Problem 4–33 but with $E < V_0$. Discuss the physical interpretation of this result.

Region 1 ($x < 0$):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} = E\psi_1$$

giving

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \qquad k_1 = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

Region 2 ($x > 0$):

$$\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + (E - V_0)\psi_2 = 0$$

giving

$$\psi_2(x) = Ce^{\beta x} + De^{-\beta x} \qquad \beta = \left[\frac{2m(V_0 - E)}{\hbar^2}\right]^{1/2}$$

Now, β must be real because $E < V_0$. This means that for ψ to remain finite as $x \to \infty$, C must equal zero. The boundary conditions give

$$\psi_1(0) = \psi_2(0) \qquad \left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_2}{dx}\right|_{x=0}$$

$$A + B = D \qquad ik_1A - ik_1B = -\beta D$$

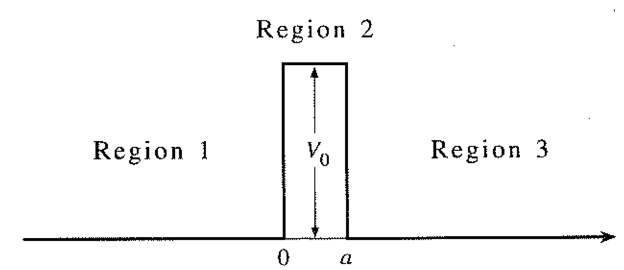
We can now use these relationships between the coefficients to solve for R as in Problem 4–33.

$$\frac{B}{A} = \frac{\beta + ik_1}{-\beta + ik_1}$$

$$R = \left|\frac{B}{A}\right|^2 = \frac{(\beta + ik_1)(\beta - ik_1)}{(-\beta + ik_1)(-\beta - ik_1)} = 1$$

This result tells us that all the particles will be reflected by the barrier.

4–35. In this problem, we introduce the idea of *quantum-mechanical tunneling*, which plays a central role in such diverse processes as the α-decay of nuclei, electron-transfer reactions, and hydrogen bonding. Consider a particle in the potential energy regions as shown below.



Mathematically, we have

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & 0 < x < a \\ 0 & x > a \end{cases}$$

Show that if $E < V_0$, the solution to the Schrödinger equation in each region is given by

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \qquad x < 0 \qquad (1)$$

$$\psi_2(x) = Ce^{k_2x} + De^{-k_2x} \qquad 0 < x < a \qquad (2)$$

and

$$\psi_3(x) = Ee^{ik_1x} + Fe^{-ik_1x} \qquad x > a \tag{3}$$

where

$$k_1 = \left(\frac{2mE}{\hbar^2}\right)^{1/2} \quad \text{and} \quad k_2 = \left(\frac{2m(V_0 - E)}{\hbar^2}\right)^{1/2} \tag{4}$$

If we exclude the situation of the particle coming from large positive values of x, then $F = 0$ in Equation 3. Following Problem 4–33, argue that the transmission coefficient, the probability the particle will get past the barrier, is given by

$$T = \frac{|E|^2}{|A|^2} \tag{5}$$

Now use the fact that $\psi(x)$ and $d\psi/dx$ must be continuous at $x = 0$ and $x = a$ to obtain

$$A + B = C + D \qquad ik_1(A - B) = k_2(C - D) \tag{6}$$

and

$$Ce^{k_2a} + De^{-k_2a} = Ee^{ik_1a} \qquad k_2Ce^{k_2a} - k_2De^{-k_2a} = ik_1Ee^{ik_1a} \tag{7}$$

Eliminate B from Equations 6 to get A in terms of C and D. Then solve Equations 7 for C and D in terms of E. Substitute these results into the equation for A in terms of C and D to get the intermediate result

$$2ik_1A = [(k_2^2 - k_1^2 + 2ik_1k_2)e^{k_2a} + (k_1^2 - k_2^2 + 2ik_1k_2)e^{-k_2a}]\frac{Ee^{ik_1a}}{2k_2}$$

Now use the relations $\sinh x = (e^x - e^{-x})/2$ and $\cosh x = (e^x + e^{-x})/2$ (Problem A–11) to get

$$\frac{E}{A} = \frac{4ik_1k_2e^{-ik_1a}}{2(k_2^2 - k_1^2)\sinh k_2a + 4ik_1k_2\cosh k_2a}$$

Now multiply the right side by its complex conjugate and use the relation $\cosh^2 x = 1 + \sinh^2 x$ to get

$$T = \left|\frac{E}{A}\right|^2 = \frac{4}{4 + \dfrac{(k_1^2 + k_2^2)^2}{k_1^2k_2^2}\sinh^2 k_2a}$$

Finally, use the definition of k_1 and k_2 to show that the probability the particle gets through the barrier (even though it does not have enough energy!) is

$$T = \frac{1}{1 + \dfrac{v_0^2}{4\varepsilon(v_0 - \varepsilon)}\sinh^2(v_0 - \varepsilon)^{1/2}} \tag{8}$$

or

$$T = \frac{1}{1 + \dfrac{\sinh^2[v_0^{1/2}(1 - r)^{1/2}]}{4r(1 - r)}} \tag{9}$$

where $v_0 = 2ma^2V_0/\hbar^2$, $\varepsilon = 2ma^2E/\hbar$, and $r = E/V_0 = \varepsilon/v_0$. Figure 4.3 shows a plot of T versus r. To plot T versus r for values of $r > 1$, you need to use the relation $\sinh ix = i\sin x$ (Problem A–11). What would the classical result look like?

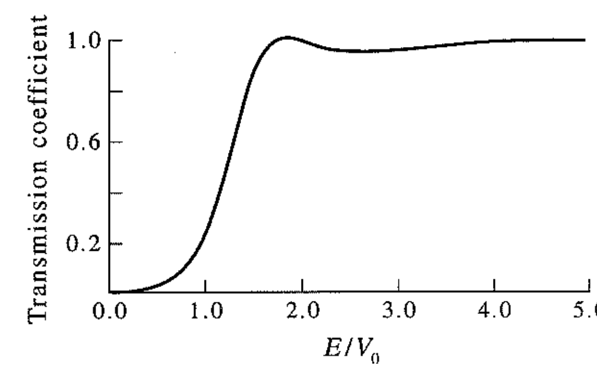


FIGURE 4.3
A plot of the probability that a particle of energy E will penetrate a barrier of height V_0 plotted against the ratio E/V_0 (Equation 9 of Problem 4–35).

Region 1: $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2} = E\psi_1$, giving

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \qquad x < 0 \tag{1}$$

Region 2: $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2} + V_0\psi_2 = E\psi_2$, giving

$$\psi_2(x) = Ce^{k_2x} + De^{-k_2x} \qquad 0 < x < a \tag{2}$$

Region 3: $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2} = E\psi_3$, giving

$$\psi_3(x) = Ee^{ik_1x} + Fe^{-ik_1x} \qquad x > a \tag{3}$$

where

$$k_1 = \left(\frac{2mE}{\hbar^2}\right)^{1/2} \quad \text{and} \quad k_2 = \left(\frac{2m(V_0 - E)}{\hbar^2}\right)^{1/2} \tag{4}$$

Let $F = 0$ (given in the problem). Now we will use the boundary conditions

$$\psi_1(0) = \psi_2(0) \qquad \left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_2}{dx}\right|_{x=0}$$

to find

$$A + B = C + D \qquad ik_1(A - B) = k_2(C - D) \tag{6}$$

and the boundary conditions

$$\psi_2(a) = \psi_3(a) \qquad \left.\frac{d\psi_2}{dx}\right|_{x=a} = \left.\frac{d\psi_3}{dx}\right|_{x=a}$$

to find

$$Ce^{k_2a} + De^{-k_2a} = Ee^{ik_1a} \qquad k_2Ce^{k_2a} - k_2De^{-k_2a} = ik_1Ee^{ik_1a} \tag{7}$$

Following the steps suggested in the problem,

$$ik_1[A - (C + D - A)] = k_2(C - D)$$

$$2ik_1A = (ik_1 + k_2)C + (ik_1 - k_2)D \tag{8}$$

and

$$2k_2 C e^{k_2 a} = (k_2 + ik_1) E e^{ik_1 a}$$

$$C = \frac{(k_2 + ik_1) E e^{ik_1 a}}{2k_2 e^{k_2 a}} \tag{9}$$

$$2k_2 D e^{-k_2 a} = (k_2 - ik_1) E e^{ik_1 a}$$

$$D = \frac{(k_2 - ik_1) E e^{ik_1 a}}{2k_2 e^{-k_2 a}} \tag{10}$$

Substituting Equations 9 and 10 into Equation 8 gives

$$\begin{aligned} 2ik_1 A &= (ik_1 + k_2)\frac{(k_2 + ik_1) E e^{ik_1 a}}{2k_2 e^{k_2 a}} + (ik_1 - k_2)\frac{(k_2 - ik_1) E e^{ik_1 a}}{2k_2 e^{-k_2 a}} \\ &= \frac{E e^{ik_1 a}}{2k_2}\left[\frac{(k_2 + ik_1)^2}{e^{k_2 a}} + \frac{-(ik_1 - k_2)^2}{e^{-k_2 a}}\right] \\ &= \frac{E e^{ik_1 a}}{2k_2}\left[(k_2^2 - k_1^2 + 2ik_1k_2)e^{-k_2 a} + (k_1^2 - k_2^2 + 2ik_1k_2)e^{k_2 a}\right] \end{aligned}$$

which can be written as

$$\begin{aligned} \frac{E}{A} &= \frac{4ik_1k_2 e^{-ik_1 a}}{k_1^2(e^{k_2 a} - e^{-k_2 a}) - k_2^2(e^{k_2 a} - e^{-k_2 a}) + 2ik_1k_2(e^{k_2 a} + e^{-k_2 a})} \\ &= \frac{4ik_1k_2 e^{-ik_1 a}}{2(k_2^2 - k_1^2)\sinh k_2 a + 4ik_1k_2 \cosh k_2 a} \end{aligned} \tag{11}$$

To find T, we need to evaluate

$$T = \left|\frac{E}{A}\right|^2$$

Using Equation 11, we obtain

$$\begin{aligned} T &= \frac{(4ik_1k_2 e^{-ik_1 a})(-4ik_1k_2 e^{-ik_1 a})}{(2(k_2^2 - k_1^2)\sinh k_2 a + 4ik_1k_2\cosh k_2 a)(2(k_2^2 - k_1^2)\sinh k_2 a - 4ik_1k_2\cosh k_2 a)} \\ &= \frac{16k_1^2k_2^2}{4(k_2^2 - k_1^2)^2 \sinh^2 k_2 a + 16k_1^2k_2^2\cosh^2 k_2 a} \end{aligned}$$

Using the identity $\cosh^2 x = 1 + \sinh^2 x$, we have

$$\begin{aligned} T &= \frac{16k_1^2k_2^2}{(4k_2^4 - 8k_1^2k_2^2 + 4k_1^4)\sinh^2 k_2 a + 16k_1^2k_2^2\sinh^2 k_2 a + 16k_1^2k_2^2} \\ &= \frac{16k_1^2k_2^2}{4(k_2^2 + k_1^2)^2\sinh^2 k_2 a + 16k_1^2k_2^2} = \frac{4}{4 + \dfrac{(k_1^2 + k_2^2)^2}{k_1^2k_2^2}\sinh^2 k_2 a} \end{aligned}$$

Using the definitions of k_1 and k_2 in Equation 4 gives

$$T = \frac{4}{4 + \dfrac{\left[\frac{2mE}{\hbar^2} + \frac{2m(V_0 - E)}{\hbar^2}\right]^2}{\left(\frac{2mE}{\hbar^2}\right)\left[\frac{2m(V_0 - E)}{\hbar^2}\right]}\sinh^2\left[\left(\dfrac{2ma^2}{\hbar^2}\right)^{1/2}(V_0 - E)^{1/2}\right]}$$

Now let $v_0 = 2ma^2 V_0/\hbar^2$, $\varepsilon = 2ma^2 E/\hbar$, and $r = E/V_0 = \varepsilon/v_0$ to find

$$\begin{aligned} T &= \frac{4}{4 + \dfrac{v_0^2}{\varepsilon(v_0 - \varepsilon)}\sinh^2(v_0 - \varepsilon)^{1/2}} \\ &= \frac{1}{1 + \dfrac{v_0^2}{4\varepsilon(v_0 - \varepsilon)}\sinh^2(v_0 - \varepsilon)^{1/2}} \\ &= \frac{1}{1 + \dfrac{\sinh^2[v_0^{1/2}(1 - r)^{1/2}]}{4r(1 - r)}} \end{aligned}$$

The classical result would have a discontinuity at $E = V_0$; if $E < V_0$ the probability that the particle would penetrate the barrier would be zero, and if $E > V_0$ the probability that the particle would penetrate the barrier would be one.

4–36. Use the result of Problem 4–35 to determine the probability that an electron with a kinetic energy 8.0×10^{-21} J will tunnel through a 1.0 nm thick potential barrier with $V_0 = 12.0 \times 10^{-21}$ J.

The probability of the electron tunneling through the barrier is given by the expression for T in Problem 4–35,

$$T = \frac{1}{1 + \dfrac{\sinh^2[v_0^{1/2}(1 - r)^{1/2}]}{4r(1 - r)}}$$

First we calculate the values of the variables in this expression.

$$\begin{aligned} r &= \frac{E}{V_0} = \frac{8}{12} = \frac{2}{3} \\ v_0 &= \frac{2ma^2 V_0}{\hbar^2} \\ &= \frac{2(9.1094 \times 10^{-31}\text{ kg})(1.0 \times 10^{-9}\text{ m})^2(12.0 \times 10^{-21}\text{ J})}{(1.0546 \times 10^{-34}\text{ J·s})^2} \\ &= 2.0 \end{aligned}$$

Now substitute into Equation 7 from Problem 4–35:

$$\begin{aligned} T &= \frac{1}{1 + \dfrac{\sinh^2[v_0^{1/2}(1 - r)^{1/2}]}{4r(1 - r)}} \\ &= \frac{1}{1 + \dfrac{\sinh^2[(2.0)^{1/2}(\frac{1}{3})^{1/2}]}{4(\frac{2}{3})(\frac{1}{3})}} \\ &= 0.52 \end{aligned}$$

4–37. Problem 4–35 gives that the probability of a particle of relative energy E/V_0 will penetrate a rectangular potential barrier of height V_0 and thickness a is

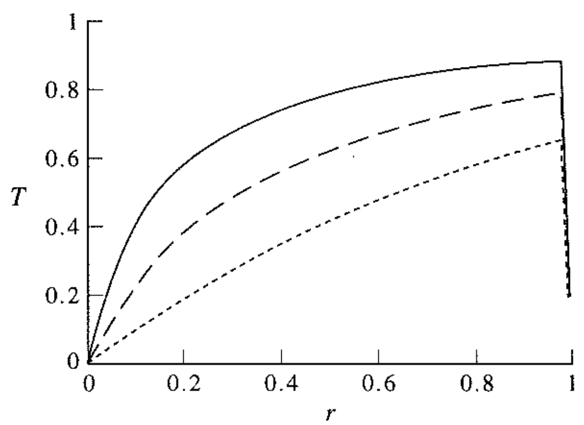
$$T = \frac{1}{1 + \dfrac{\sinh^2[v_0^{1/2}(1-r)^{1/2}]}{4r(1-r)}}$$

where $v_0 = 2mV_0a^2/\hbar^2$ and $r = E/V_0$. What is the limit of T as $r \to 1$? Plot T against r for $v_0 = 1/2$, 1, and 2. Interpret your results.

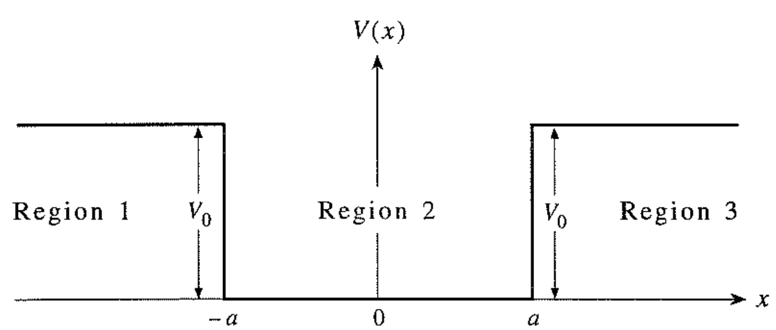
Use the fact that $\sinh x = x + x^3/6 + \cdots$ to write

$$T = \frac{1}{1 + \dfrac{v_0(1-r)}{4r(1-r)} + \cdots} = \frac{1}{1 + v_0/4} \qquad \text{as} \qquad r \to 1$$

In the graph below, the solid line is the graph of T versus r for $v_0 = 1/2$, the dashed line is the graph of T versus r for $v_0 = 1$, and the dotted line is the graph of T versus r for $v_0 = 2$.



4–38. In this problem, we will consider a particle in a *finite* potential well



whose mathematical form is

$$V(x) = \begin{cases} V_0 & x < -a \\ 0 & -a < x < a \\ V_0 & x > a \end{cases} \tag{1}$$

Note that this potential describes what we have called a "particle in a box" if $V_0 \to \infty$. Show that if $0 < E < V_0$, the solution to the Schrödinger equation in each region is

$$\begin{aligned} \psi_1(x) &= Ae^{k_1x} & x &< -a \\ \psi_2(x) &= B\sin\alpha x + C\cos\alpha x & -a &< x < a \\ \psi_3(x) &= De^{-k_1x} & x &> a \end{aligned} \tag{2}$$

where

$$k_1 = \left(\frac{2m(V_0 - E)}{\hbar^2}\right)^{1/2} \quad \text{and} \quad \alpha = \left(\frac{2mE}{\hbar^2}\right)^{1/2} \tag{3}$$

Now apply the conditions that $\psi(x)$ and $d\psi/dx$ must be continuous at $x = -a$ and $x = a$ to obtain

$$Ae^{-k_1a} = -B\sin\alpha a + C\cos\alpha a \tag{4}$$

$$De^{-k_1a} = B\sin\alpha a + C\cos\alpha a \tag{5}$$

$$k_1Ae^{-k_1a} = \alpha B\cos\alpha a + \alpha C\sin\alpha a \tag{6}$$

and

$$-k_1De^{-k_1a} = \alpha B\cos\alpha a - \alpha C\sin\alpha a \tag{7}$$

Add and subtract Equations 4 and 5 and add and subtract Equations 6 and 7 to obtain

$$2C\cos\alpha a = (A + D)e^{-k_1a} \tag{8}$$

$$2B\sin\alpha a = (D - A)e^{-k_1a} \tag{9}$$

$$2\alpha C\sin\alpha a = k_1(A + D)e^{-k_1a} \tag{10}$$

and

$$2\alpha B\cos\alpha a = -k_1(D - A)e^{-k_1a} \tag{11}$$

Now divide Equation 10 by Equation 8 to get

$$\frac{\alpha\sin\alpha a}{\cos\alpha a} = \alpha\tan\alpha a = k_1 \qquad (D \neq -A \text{ and } C \neq 0) \tag{12}$$

and then divide Equation 11 by Equation 9 to get

$$\frac{\alpha\cos\alpha a}{\sin\alpha a} = \alpha\cot\alpha a = -k_1 \quad \text{and} \quad (D \neq A \text{ and } B \neq 0) \tag{13}$$

Referring back to Equation 3, note that Equations 12 and 13 give the allowed values of E in terms of V_0. It turns out that these two equations cannot be solved simultaneously, so we have two sets of equations

$$\alpha\tan\alpha a = k_1 \tag{14}$$

and

$$\alpha\cot\alpha a = -k_1 \tag{15}$$

Let's consider Equation 14 first. Multiply both sides by a and use the definitions of α and k_1 to get

$$\left(\frac{2ma^2E}{\hbar^2}\right)^{1/2}\tan\left(\frac{2ma^2E}{\hbar^2}\right)^{1/2}=\left[\frac{2ma^2}{\hbar^2}(V_0-E)\right]^{1/2} \tag{16}$$

Show that this equation simplifies to

$$\varepsilon^{1/2}\tan\varepsilon^{1/2}=(v_0-\varepsilon)^{1/2} \tag{17}$$

where $\varepsilon = 2ma^2E/\hbar^2$ and $v_0 = 2ma^2V_0/\hbar^2$. Thus, if we fix v_0 (actually $2ma^2V_0/\hbar^2$), then we can use Equation 17 to solve for the allowed values of ε (actually $2ma^2E/\hbar^2$). Equation 17 cannot be solved analytically, but if we plot both $\varepsilon^{1/2}\tan\varepsilon^{1/2}$ and $(v_0-\varepsilon)^{1/2}$ versus ε on the same graph, then the solutions are given by the intersections of the two curves. Show that the intersections occur at $\varepsilon = 2ma^2E/\hbar^2 = 1.47$ and 11.37 for $v_0 = 12$. The other value(s) of ε are given by the solutions to Equation 15, which are obtained by finding the intersection of $-\varepsilon^{1/2}\cot\varepsilon^{1/2}$ and $(v_0-\varepsilon)^{1/2}$ plotted against ε. Show that $\varepsilon = 2ma^2E/\hbar^2 = 5.68$ for $v_0 = 12$. Thus, we see there are only three bound states for a well of depth $V_0 = 12\hbar^2/2ma^2$. The important point here is not the numerical values of E, but the fact that there is only a finite number of bound states. Show that there are only two bound states for $v_0 = 2ma^2V_0/\hbar^2 = 4$.

Region 1: $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2}+V_0\psi_1=E\psi_1$, giving

$$\psi_1(x)=Ae^{k_1x}$$

(We ignore the solution $c_2e^{-k_1x}$ because if the particle goes from region 2 into region 1, it must be traveling to the left.)

Region 2: $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2}=E\psi_2$, giving

$$\psi_2(x)=B\sin\alpha x+C\cos\alpha x$$

as in Example 2–4.

Region 3: $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2}+V_0\psi_3=E\psi_3$, giving

$$\psi_3(x)=De^{-k_1x} \qquad x>a$$

(We ignore the solution $c_1e^{k_1x}$ because if the particle goes from region 2 into region 3, it must be traveling to the right.) In the above expressions

$$k_1=\left(\frac{2m(V_0-E)}{\hbar^2}\right)^{1/2} \quad \text{and} \quad \alpha=\left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

Now use the boundary condition equations $\psi_1(-a)=\psi_2(-a)$, $\psi_2(a)=\psi_3(a)$, $d\psi_1/dx=d\psi_2/dx$ at $x=-a$, and $d\psi_2/dx=d\psi_3/dx$ at $x=a$ to find

$$Ae^{-k_1a}=-B\sin\alpha a+C\cos\alpha a \tag{4}$$

$$B\sin\alpha a+C\cos\alpha a=De^{-k_1a} \tag{5}$$

$$k_1Ae^{-k_1a}=\alpha B\cos\alpha a+\alpha C\sin\alpha a \tag{6}$$

$$-k_1De^{-k_1a}=\alpha B\cos\alpha a-\alpha C\sin\alpha a \tag{7}$$

Adding and subtracting Equations 4 and 5 gives

$$2C\cos\alpha a=(A+D)e^{-k_1a} \tag{8}$$

$$2B\sin\alpha a=(D-A)e^{-k_1a} \tag{9}$$

Adding and subtracting Equations 6 and 7 gives

$$2\alpha C\sin\alpha a=k_1(A+D)e^{-k_1a} \tag{10}$$

$$2\alpha B\cos\alpha a=-k_1(D-A)e^{-k_1a} \tag{11}$$

Now divide Equation 10 by Equation 8 and Equation 11 by Equation 9 to obtain

$$\frac{\alpha\sin\alpha a}{\cos\alpha a}=\alpha\tan\alpha a=k_1 \qquad (D\neq -A \text{ and } C\neq 0) \tag{12}$$

$$\frac{\alpha\cos\alpha a}{\sin\alpha a}=\alpha\cot\alpha a=-k_1 \qquad (D\neq A \text{ and } B\neq 0) \tag{13}$$

We now have two sets of equations:

$$\alpha\tan\alpha a=k_1 \tag{14}$$

$$\alpha\cot\alpha a=-k_1 \tag{15}$$

The result that $A=\pm D$ implies that the chance of the particle leaving the finite well through one side of the well is equal to the chance that it will leave the finite well through its other side. Using the definitions of α and k_1 (Equation 3) and multiplying Equation 14 by a, we find

$$\left(\frac{2ma^2E}{\hbar^2}\right)^{1/2}\tan\left(\frac{2ma^2E}{\hbar^2}\right)^{1/2}=\left[\frac{2ma^2}{\hbar^2}(V_0-E)\right]^{1/2} \tag{16}$$

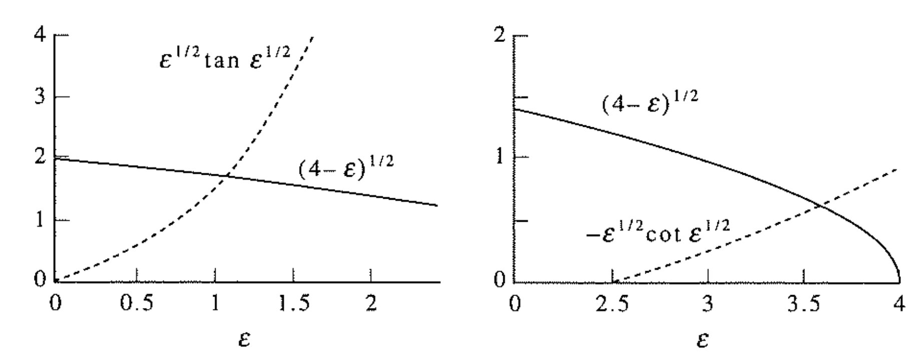
If we let $\varepsilon = 2ma^2E/\hbar^2$ and $v_0 = 2ma^2V_0/\hbar^2$, we obtain

$$\varepsilon^{1/2}\tan\varepsilon^{1/2}=(v_0-\varepsilon)^{1/2} \tag{17}$$

Likewise, we can obtain the expression

$$-\varepsilon^{1/2}\cot\varepsilon^{1/2}=(v_0-\varepsilon)^{1/2} \tag{18}$$

by going through the same procedure with Equation 15. The solutions to Equations 17 and 18 are shown graphically for $v_0 = 12$ in the captioned figure. The solutions for $v_0 = 4$ are shown in the figure below. Because these graphs show two intersections, there are two bound states for $v_0 = 4$.



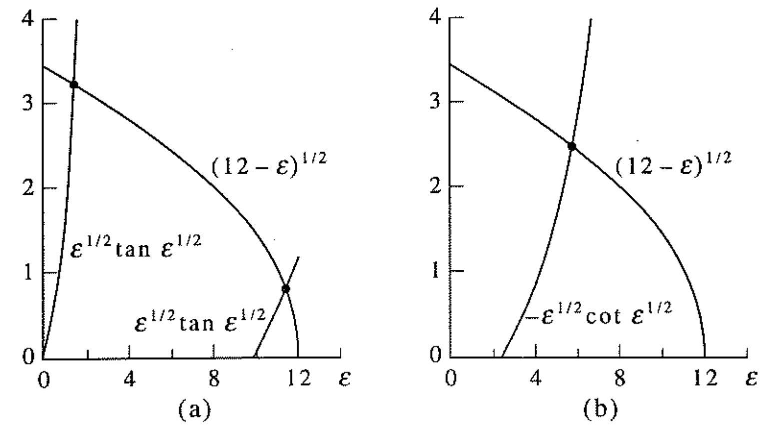


FIGURE 4.4
(a) Plots of both $\varepsilon^{1/2}\tan\varepsilon^{1/2}$ and $(12-\varepsilon)^{1/2}$ versus ε. The intersections of the curves give the allowed values of ε for a one-dimensional potential well of depth $V_0 = 12\hbar^2/2ma^2$. (b) Plots of both $-\varepsilon^{1/2}\cot\varepsilon^{1/2}$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

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

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. $(1, 0, 0)$

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

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