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

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

We now evaluate this integral as

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

CHAPTER 5

The Harmonic Oscillator and the Rigid Rotator: Two Spectroscopic Models

PROBLEMS AND SOLUTIONS

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

Newton's equation for a harmonic oscillator is

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

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

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

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

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

Newton's equation for a harmonic oscillator is

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

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

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

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

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

Consider the general solution $x(t) = C\sin(\omega t + \phi)$. Because the sine function varies from +1 to -1, the value of x varies from $+C$ to $-C$. To find the period of oscillation, we determine the smallest nonzero value of τ that satisfies the condition

$$\begin{aligned}\sin(\omega t + \phi) &= \sin[\omega(t+\tau)+\phi]\\ &= \sin(\omega t + \phi + \omega\tau)\\ &= \sin(\omega t+\phi)\cos\omega\tau + \cos(\omega t+\phi)\sin\omega\tau\end{aligned}$$

This condition is met when τ satisfies the two conditions

$$\cos\omega\tau = 1 \qquad \sin\omega\tau = 0$$

or, equivalently,

$$\omega\tau = 2\pi n \qquad n = 1, 2, \ldots$$

The smallest value of τ is then $2\pi/\omega$, which is the time it takes for the oscillator to undergo one cycle. The frequency of oscillation is

$$\nu = \frac{1}{\tau} = \frac{\omega}{2\pi}$$

5–4. From Problem 5–3, we see that the period of a harmonic vibration is $\tau = 1/\nu$. The average of the kinetic energy over one cycle is given by

$$\langle K\rangle = \frac{1}{\tau}\int_0^\tau \frac{m\omega^2C^2}{2}\cos^2(\omega t+\phi)dt$$

Show that $\langle K\rangle = E/2$ where E is the total energy. Show also that $\langle V\rangle = E/2$, where the instantaneous potential energy is given by

$$V = \frac{kC^2}{2}\sin^2(\omega t+\phi)$$

Interpret the result $\langle K\rangle = \langle V\rangle$.

We start with the general equation for a harmonic oscillator $x = C\sin(\omega t+\phi)$ (Problem 5–2). The total energy of this oscillator is

$$E = K + U = \frac{m}{2}\left(\frac{dx}{dt}\right)^2 + \frac{kx^2}{2}$$

where we have used Equations 5.11 and 5.12 for K and U. Substituting $x(t)$ into this expression gives

$$\begin{aligned}E &= \frac{m}{2}\omega^2C^2\cos^2(\omega t+\phi) + \frac{k}{2}C^2\sin^2(\omega t+\phi)\\ &= \frac{k}{2}C^2\left[\cos^2(\omega t+\phi)+\sin^2(\omega t+\phi)\right] = \frac{k}{2}C^2\end{aligned}$$

Now

$$\begin{aligned}\langle K\rangle &= \frac{1}{\tau}\int_0^\tau \frac{m\omega^2C^2}{2}\cos^2(\omega t+\phi)dt\\ &= \frac{m\omega C^2}{2\tau}\int_\phi^{\omega\tau+\phi}\cos^2 x\,dx\end{aligned}$$

$$\begin{aligned}&= \frac{m\omega C^2}{2\tau}\left[\frac{x}{2}+\sin 2x\right]_\phi^{\omega\tau+\phi}\\ &= \frac{m\omega C^2}{2\tau}\left[\frac{\omega\tau}{2}+\frac{\sin 2(\omega\tau+\phi)-\sin 2\phi}{4}\right]\\ &= \frac{m\omega C^2}{2\tau}\left[\frac{\omega\tau}{2}+\frac{\sin 2\omega\tau\cos 2\phi+\cos 2\omega\tau\sin 2\phi-\sin 2\phi}{4}\right]\\ &= \frac{m\omega C^2}{2\tau}\left[\frac{\omega\tau}{2}+\frac{\sin 4\pi\cos 2\phi+\cos 4\pi\sin 2\phi-\sin 2\phi}{4}\right]\\ &= \frac{m\omega^2C^2}{4} = \frac{kC^2}{4} = \frac{E}{2}\end{aligned}$$

where we have used the fact that $\tau = 2\pi/\omega$ (Problem 5–3). Likewise,

$$\begin{aligned}\langle V\rangle &= \frac{kC^2}{2\tau}\int_0^\tau \sin^2(\omega t+\phi)dt\\ &= \frac{kC^2}{2\tau}\int_0^\tau [1-\cos^2(\omega t+\phi)]dt\\ &= \frac{kC^2}{2} - \frac{kC^2}{2\tau\omega}\left(\frac{\omega\tau}{2}\right) = \frac{kC^2}{4} = \frac{E}{2}\end{aligned}$$

The motion of a harmonic oscillator is such that $\langle K\rangle = \langle V\rangle$ over a cycle of motion.

5–5. Consider two masses m_1 and m_2 in one dimension, interacting through a potential that depends only upon their relative separation $(x_1 - x_2)$, so that $V(x_1, x_2) = V(x_1 - x_2)$. Given that the force acting upon the jth particle is $f_j = -(\partial V/\partial x_j)$, show that $f_1 = -f_2$. What law is this? Newton's equations for m_1 and m_2 are

$$m_1\frac{d^2x_1}{dt^2} = -\frac{\partial V}{\partial x_1} \quad\text{and}\quad m_2\frac{d^2x_2}{dt^2} = -\frac{\partial V}{\partial x_2}$$

Now introduce center-of-mass and relative coordinates by

$$X = \frac{m_1x_1+m_2x_2}{M} \qquad x = x_1 - x_2$$

where $M = m_1 + m_2$, and solve for x_1 and x_2 to obtain

$$x_1 = X + \frac{m_2}{M}x \quad\text{and}\quad x_2 = X - \frac{m_1}{M}x$$

Show that Newton's equations in these coordinates are

$$m_1\frac{d^2X}{dt^2} + \frac{m_1m_2}{M}\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x}$$

and

$$m_2\frac{d^2X}{dt^2} - \frac{m_1m_2}{M}\frac{d^2x}{dt^2} = +\frac{\partial V}{\partial x}$$

Now add these two equations to find

$$M\frac{d^2X}{dt^2} = 0$$

Interpret this result. Now divide the first equation by m_1 and the second by m_2 and subtract to obtain

$$\frac{d^2x}{dt^2} = -\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial V}{\partial x}$$

or

$$\mu\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x}$$

where $\mu = m_1m_2/(m_1 + m_2)$ is the reduced mass. Interpret this result, and discuss how the original two-body problem has been reduced to two one-body problems.

The forces acting on masses 1 and 2 are

$$f_1 = -\frac{\partial V}{\partial x_1} \qquad f_2 = -\frac{\partial V}{\partial x_2} = \frac{\partial V}{\partial x_1} = -f_1$$

where we obtain the second equality from the fact that $V(x_1, x_2) = V(x_1 - x_2)$. This is Newton's second law: for every action there is an equal and opposite reaction. Now use the definitions of center-of-mass, X, and relative coordinates, x,

$$X = \frac{m_1x_1 + m_2x_2}{M} \quad (1) \qquad x = x_1 - x_2 \quad (2)$$

Multiply Equation 1 by M and Equation 2 by m_2 and add to find

$$x_1 = X + \frac{m_2}{M}x \qquad (3)$$

Now multiply Equation 1 by M and Equation 2 by m_1 and subtract to find

$$x_2 = X - \frac{m_1}{M}x \qquad (4)$$

Substitute Equations 3 and 4 into Newton's equations to obtain

$$m_1\frac{d^2x_1}{dt^2} = m_1\frac{d^2\left(X + \frac{m_2}{M}x\right)}{dt^2} = m_1\frac{d^2X}{dt^2} + \frac{m_1m_2}{M}\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x} \qquad (5)$$

and

$$m_2\frac{d^2x_2}{dt^2} = m_1\frac{d^2\left(X - \frac{m_1}{M}x\right)}{dt^2} = m_2\frac{d^2X}{dt^2} - \frac{m_2m_1}{M}\frac{d^2x}{dt^2} = \frac{\partial V}{\partial x} \qquad (6)$$

where we have set $\partial V/\partial x_1 = \partial V/\partial x$. Add Equations 5 and 6 to find

$$M\frac{d^2X}{dt^2} = 0$$

The physical interpretation of this equation is that the center of mass moves at a constant velocity. Now divide Equation 5 by m_1 and Equation 6 by m_2 and subtract the results to obtain

$$\frac{d^2x}{dt^2} = -\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial V}{\partial x} \qquad (7)$$

If we define $\mu = m_1m_2/(m_1 + m_2)$, then we can write Equation 7 as

$$\mu\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x}$$

This is the equation of mass for a body of mass μ moving under a force $-\partial V/\partial x$. We were able to reduce the two-body problem because we could express the forces acting on body 1 in terms of the forces acting on body 2.

5–6. Extend the results of Problem 5–5 to three dimensions. Realize that in three dimensions the relative separation is given by

$$r_{12} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}$$

We can treat the x-, y-, and z-dimensions individually because these directions are orthogonal. The equations in the x-direction are the same as in Problem 5–5. To find the equations in the y and z-directions, we can substitute y or z in place of x (and Y or Z in place of X) in the equations of Problem 5–5. We then find that

$$\mu\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x} \qquad \mu\frac{d^2y}{dt^2} = -\frac{\partial V}{\partial y} \qquad \mu\frac{d^2z}{dt^2} = -\frac{\partial V}{\partial z}$$

or

$$\mu\frac{d^2\mathbf{r}}{dt^2} = -\nabla V$$

which is the three-dimensional extension of Problem 5–5.

5–7. Calculate the value of the reduced mass of a hydrogen atom. Take the masses of the electron and proton to be $9.109\,390 \times 10^{-31}$ kg and $1.672\,623 \times 10^{-27}$ kg, respectively. What is the percent difference between this result and the rest mass of an electron?

$$\mu = \frac{m_1m_2}{m_1 + m_2} = \frac{(9.109\,390 \times 10^{-31}\text{ kg})(1.672\,623 \times 10^{-27}\text{ kg})}{1.673\,534 \times 10^{-27}\text{ kg}}$$
$$= 9.104\,432 \times 10^{-31}\text{ kg}$$

The percent difference between this result and the rest mass of an electron is

$$\frac{9.109\,390 \times 10^{-31}\text{ kg} - 9.104\,432 \times 10^{-31}\text{ kg}}{9.109\,390 \times 10^{-31}\text{ kg}} = 0.05\%$$

5–8. Show that the reduced mass of two equal masses, m, is $m/2$.

Setting $m_1 = m_2 = m$, we find that

$$\mu = \frac{m_1m_2}{m_1 + m_2} = \frac{m^2}{2m} = \frac{m}{2}$$

5–9. Example 5–2 shows that a Maclaurin expansion of a Morse potential leads to

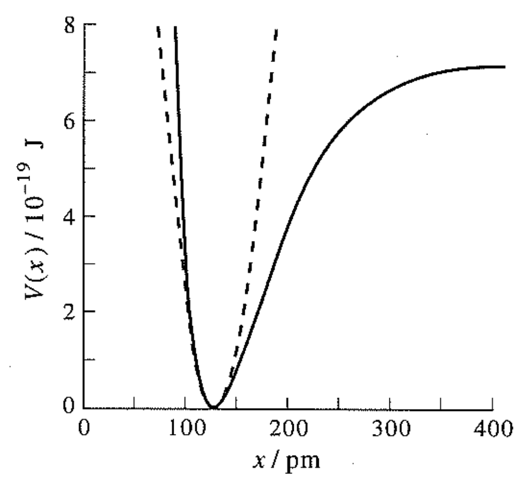
$$V(x) = D\beta^2x^2 + \cdots$$

Given that $D = 7.31 \times 10^{-19}$ J·molecule^{-1} and $\beta = 1.81 \times 10^{10}$ m^{-1} for HCl, calculate the force constant of HCl. Plot the Morse potential for HCl, and plot the corresponding harmonic oscillator potential on the same graph (cf. Figure 5.5).

Because $V(x) = kx^2/2$ for a harmonic oscillator,

$$k = 2D\beta^2 = 2(7.31 \times 10^{-19} \text{ J·molecule}^{-1})(1.81 \times 10^{10} \text{ m}^{-1})^2 = 479 \text{ N·m}^{-1}$$

The bond length of HCl (l_0) is 127.5 pm (Table 5.1). The graph below shows the Morse potential $V(x) = D[1 - e^{-\beta(l-l_0)}]^2$ (solid line) and the harmonic oscillator potential $V(x) = \frac{1}{2}k(l - l_0)^2$ (dashed line) for HCl.



5–10. Use the result of Example 5–2 and Equation 5.34 to show that

$$\beta = 2\pi c\tilde{\nu}\left(\frac{\mu}{2D}\right)^{1/2}$$

Given that $\tilde{\nu} = 2886$ cm^{-1} and $D = 440.2$ kJ·mol^{-1} for $H^{35}Cl$, calculate β. Compare your result with that in Problem 5–9.

$$\tilde{\nu}_{\text{obs}} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \qquad (5.34)$$

Example 5–2 shows that $k = 2D\beta^2$, which upon substituting into Equation 5.34 gives

$$\tilde{\nu}_{\text{obs}} = \frac{1}{2\pi c}\left(\frac{2D\beta^2}{\mu}\right)^{1/2}$$

Solving for β,

$$\beta = 2\pi c\tilde{\nu}_{\text{obs}}\left(\frac{\mu}{2D}\right)^{1/2}$$

For $H^{35}Cl$,

$$\begin{aligned}\beta &= 2\pi c\tilde{\nu}_{\text{obs}}\left(\frac{\mu}{2D}\right)^{1/2} \\ &= 2\pi(2.998 \times 10^8 \text{ m·s}^{-1})\left(2886 \text{ cm}^{-1} \times \frac{100 \text{ cm}}{1 \text{ m}}\right) \\ &\quad \left[\frac{\left(\frac{1.008 \times 34.97}{1.008 + 34.97}\right)(1.661 \times 10^{-27} \text{ kg})}{2\left(\frac{440.2 \times 10^3 \text{ J·mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}\right)}\right]^{1/2} \\ &= 1.81 \times 10^{10} \text{ m}^{-1}\end{aligned}$$

which is the same as the value for β given in the previous problem.

5–11. Carry out the Maclaurin expansion of the Morse potential in Example 5–2 through terms in x^4. Express γ in Equation 5.24 in terms of D and β.

$$\begin{aligned}V(x) &= D\left(1 - e^{-\beta x}\right)^2 \\ &= D\left\{1 - \left[1 - \beta x + \frac{1}{2}\beta^2x^2 - \frac{1}{6}\beta^3x^3 + O(x^4)\right]\right\}^2 \\ &= D\left[\beta x - \frac{1}{2}\beta^2x^2 + \frac{1}{6}\beta^3x^3 - O(x^4)\right]^2 \\ &= D\beta^2x^2\left[1 - \frac{1}{2}\beta x + \frac{1}{6}\beta^2x^2 - O(x^3)\right]^2 \\ &= D\beta^2x^2\left[1 - \beta x + \frac{1}{3}\beta^2x^2 + \frac{1}{4}\beta^2x^2 + O(x^3)\right] \\ &= D\left[\beta^2x^2 - \beta^3x^3 + \frac{7}{12}\beta^4x^4 + O(x^5)\right]\end{aligned}$$

By comparing this result to Equation 5.24, we see that

$$\gamma = -6D\beta^3$$

5–12. It turns out that the solution of the Schrödinger equation for the Morse potential can be expressed as

$$\tilde{E}_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\nu}\tilde{x}\left(v + \frac{1}{2}\right)^2$$

where

$$\tilde{x} = \frac{hc\tilde{\nu}}{4D}$$

Given that $\tilde{\nu} = 2886$ cm^{-1} and $D = 440.2$ kJ·mol^{-1} for $H^{35}Cl$, calculate $\tilde{x}$ and $\tilde{\nu}\tilde{x}$.

$$\tilde{x} = \frac{(6.626\times10^{-34}\ \text{J·s})(2.998\times10^{8}\ \text{m·s}^{-1})(2886\ \text{cm}^{-1})(100\ \text{cm·m}^{-1})}{4\left(\dfrac{440.2\times10^{3}\ \text{J·mol}^{-1}}{6.022\times10^{23}\ \text{mol}^{-1}}\right)}$$

$$= 0.01961$$

$$\tilde{\nu}\tilde{x} = (2886\ \text{cm}^{-1})(0.01961) = 56.59\ \text{cm}^{-1}$$

5–13. In the infrared spectrum of $H^{79}Br$, there is an intense line at 2559 cm^{-1}. Calculate the force constant of $H^{79}Br$ and the period of vibration of $H^{79}Br$.

$$\tilde{\nu}_{\text{obs}} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \qquad (5.34)$$

$$\begin{aligned} k &= (2\pi c\tilde{\nu}_{\text{obs}})^2\mu \\ &= \left[2\pi(2.998\times10^{10}\ \text{cm·s}^{-1})(2559\ \text{cm}^{-1})\right]^2 \\ &\quad\times\left[\frac{(1.008\ \text{amu})(78.92\ \text{amu})}{79.93\ \text{amu}}\right](1.661\times10^{-27}\ \text{kg·amu}^{-1}) \\ &= 384\ \text{N·m}^{-1} \end{aligned}$$

The period of vibration is

$$T = \frac{1}{\nu} = \frac{1}{c\tilde{\nu}} = 1.30\times10^{-14}\ \text{s}$$

5–14. The force constant of $^{79}Br^{79}Br$ is 240 N·m^{-1}. Calculate the fundamental vibrational frequency and the zero-point energy of $^{79}Br^{79}Br$.

$$\tilde{\nu}_{\text{obs}} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \qquad (5.34)$$

$$\tilde{\nu}_{\text{obs}} = \frac{1}{2\pi(2.998\times10^{10}\ \text{cm·s}^{-1})}\left\{\frac{240\ \text{N·m}^{-1}}{\left[\dfrac{(78.92\ \text{amu})^2}{78.92\ \text{amu}+78.92\ \text{amu}}\right](1.66\times10^{-27}\ \text{kg·amu}^{-1})}\right\}^{1/2}$$

$$= 321\ \text{cm}^{-1}$$

We use Equation 5.27 to find the zero point energy:

$$E_0 = \tfrac{1}{2}h\nu = \tfrac{1}{2}hc\tilde{\nu} = 3.19\times10^{-21}\ \text{J}$$

5–15. Verify that $\psi_1(x)$ and $\psi_2(x)$ given in Table 5.3 satisfy the Schrödinger equation for a harmonic oscillator.

The Schrödinger equation for a harmonic oscillator is

$$\frac{d^2\psi_v}{dx^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{1}{2}kx^2\right)\psi_v = 0 \qquad (5.26)$$

where $E_v = h\nu(v+\frac{1}{2})$. From Table 5.3,

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$$

where $\alpha = (k\mu)^{1/2}/\hbar$. Substituting ψ_1 into the Schrödinger equation with $v = 1$ gives

$$\begin{aligned} \frac{d^2\psi_1}{dx^2} + \frac{2\mu}{\hbar^2}\left(E_1 - \frac{1}{2}kx^2\right)\psi_1 &= 0 \\ \frac{d}{dx}\left[\left(\frac{4\alpha^3}{\pi}\right)^{1/4}\left(e^{-\alpha x^2/2} - \alpha x^2 e^{-\alpha x^2/2}\right)\right] + \frac{2\mu}{\hbar^2}\left(\frac{3h\nu}{2} - \frac{1}{2}kx^2\right)\left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2} &= 0 \\ -3\alpha x e^{-\alpha x^2/2} + \alpha^2 x^3 e^{-\alpha x^2/2} + \left(\frac{3h\mu\nu}{\hbar^2} - \frac{k\mu x^2}{\hbar^2}\right) x e^{-\alpha x^2/2} &= 0 \\ -3\alpha x + \alpha^2 x^3 + \frac{3}{\hbar}(2\pi\nu)\mu x - \alpha^2 x^3 &= 0 \\ -3\alpha x + 3\alpha x &= 0 \end{aligned}$$

where $k = (2\pi\nu)^2\mu$. Substituting ψ_2 into the Schrödinger equation with $v = 2$ gives

$$\begin{aligned} \frac{d^2\psi_2}{dx^2} + \frac{2\mu}{\hbar^2}\left(E_2 - \frac{1}{2}kx^2\right)\psi_2 &= 0 \\ \left(\frac{\alpha}{4\pi}\right)^{1/4}\frac{d}{dx}\left[4\alpha x e^{-\alpha x^2/2} - \alpha x(2\alpha x^2 - 1)e^{-\alpha x^2/2}\right] & \\ + \frac{2\mu}{\hbar^2}\left(\frac{5h\nu}{2} - \frac{1}{2}kx^2\right)\left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2} &= 0 \\ (5\alpha - 11\alpha^2x^2 + 2\alpha^3x^4)e^{-\alpha x^2/2} + \left(\frac{5h\mu\nu}{\hbar^2} - \frac{k\mu}{\hbar^2}x^2\right)(2\alpha x^2 - 1)e^{-\alpha x^2/2} &= 0 \\ 5\alpha - 11\alpha^2x^2 + 2\alpha^3x^4 - \frac{5}{\hbar}(2\pi\nu)\mu + \alpha^2x^2 + \frac{10}{\hbar}(2\pi\nu)\mu\alpha x^2 - 2\alpha^3x^4 &= 0 \\ 5\alpha - 11\alpha^2x^2 - 5\alpha + 11\alpha^2x^2 &= 0 \end{aligned}$$

Both ψ_1 and ψ_2 are solutions to the Schrödinger equation.

5–16. Show explicitly for a harmonic oscillator that $\psi_0(x)$ is orthogonal to $\psi_1(x)$, $\psi_2(x)$, and $\psi_3(x)$ and that $\psi_1(x)$ is orthogonal to $\psi_2(x)$ and $\psi_3(x)$ (see Table 5.3).

From Table 5.3, we have

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$$

$$\psi_3(x) = \left(\frac{\alpha^3}{9\pi}\right)^{1/4}(2\alpha x^3 - 3x)e^{-\alpha x^2/2}$$

There are five integrals we must evaluate to show orthogonality. Three have integrands that are odd functions of x, and so are zero.

$$\int_{-\infty}^{\infty} dx\psi_0(x)\psi_1(x) = \int_{-\infty}^{\infty} dx\psi_0(x)\psi_3(x) = \int_{-\infty}^{\infty} dx\psi_1(x)\psi_2(x) = 0$$

This leaves the integrals with even integrands to be evaluated explicitly.

$$\begin{aligned}\int_{-\infty}^{\infty} dx\psi_0(x)\psi_2(x) &= 2\left(\frac{\alpha}{\pi}\right)^{1/4}\left(\frac{\alpha}{4\pi}\right)^{1/4}\int_0^{\infty} dx(2\alpha x^2-1)e^{-\alpha x^2}\\ &= 2\left(\frac{\alpha}{\pi}\right)^{1/4}\left(\frac{\alpha}{4\pi}\right)^{1/4}\left[2\alpha\left(\frac{1}{4\alpha}\right)\left(\frac{\pi}{\alpha}\right)^{1/2}-\left(\frac{\pi}{4\alpha}\right)^{1/2}\right]\\ &= 0\end{aligned}$$

and

$$\begin{aligned}\int_{-\infty}^{\infty} dx\psi_1(x)\psi_3(x) &= 2\left(\frac{4\alpha^3}{\pi}\right)^{1/4}\left(\frac{\alpha^3}{9\pi}\right)^{1/4}\int_0^{\infty} dx(2\alpha x^4-3x^2)e^{-\alpha x^2}\\ &= 2\left(\frac{4\alpha^3}{\pi}\right)^{1/4}\left(\frac{\alpha^3}{9\pi}\right)^{1/4}\left[2\alpha\left(\frac{3}{8\alpha^2}\right)\left(\frac{\pi}{\alpha}\right)^{1/2}-3\alpha^{1/2}\left(\frac{1}{4\alpha}\right)\left(\frac{\pi}{\alpha}\right)^{1/2}\right]\\ &= 0\end{aligned}$$

5–17. To normalize the harmonic-oscillator wave functions and calculate various expectation values, we must be able to evaluate integrals of the form

$$I_v(a) = \int_{-\infty}^{\infty} x^{2v}e^{-ax^2}dx \qquad v = 0,\ 1,\ 2,\ \ldots$$

We can simply either look them up in a table of integrals or continue this problem. First, show that

$$I_v(a) = 2\int_0^{\infty} x^{2v}e^{-ax^2}dx$$

The case $v = 0$ can be handled by the following trick. Show that the square of $I_0(a)$ can be written in the form

$$I_0^2(a) = 4\int_0^{\infty}\int_0^{\infty} dxdye^{-a(x^2+y^2)}$$

Now convert to plane polar coordinates, letting

$$r^2 = x^2 + y^2 \quad \text{and} \quad dxdy = rdrd\theta$$

Show that the appropriate limits of integration are $0 \le r < \infty$ and $0 \le \theta \le \pi/2$ and that

$$I_0^2(a) = 4\int_0^{\pi/2} d\theta \int_0^{\infty} drre^{-ar^2}$$

which is elementary and gives

$$I_0^2(a) = 4\cdot\frac{\pi}{2}\cdot\frac{1}{2a} = \frac{\pi}{a}$$

or that

$$I_0(a) = \left(\frac{\pi}{a}\right)^{1/2}$$

Now prove that the $I_v(a)$ may be obtained by repeated differentiation of $I_0(a)$ with respect to a and, in particular, that

$$\frac{d^v I_0(a)}{da^v} = (-1)^v I_v(a)$$

Use this result and the fact that $I_0(a) = (\pi/a)^{1/2}$ to generate $I_1(a)$, $I_2(a)$, and so forth.

The function $I_v(a)$ is an even function, and so

$$I_v(a) = 2\int_0^{\infty} x^{2v}e^{-ax^2}dx$$

Because the function $I(a)$ depends only on a, we can write

$$I_0^2(a) = 4\int_0^{\infty} dxe^{-ax^2}\int_0^{\infty} dye^{-ay^2} = 4\int_0^{\infty}\int_0^{\infty} dxdye^{-a(x^2+y^2)}$$

We realize that we are integrating over the entire first quadrant, so our limits of integration in polar coordinates are $0 \le r < \infty, 0 \le \theta \le \pi/2$. In polar coordinates, $dx\,dy = r\,dr\,d\theta$ and $x^2 + y^2 = r^2$, and so we can write

$$\begin{aligned}I_0^2(a) &= 4\int_0^{\pi/2} d\theta\int_0^{\infty} drre^{-ar^2}\\ &= 2\pi\left(\frac{1}{2a}\right) = \frac{\pi}{a}\end{aligned}$$

Now differentiate $I_0(a)$ with respect to a:

$$\begin{aligned}\frac{dI_0}{da} &= -\int_{-\infty}^{\infty} dxx^2e^{-ax^2} = -I_1(a)\\ \frac{d^2I_0}{da} &= \int_{-\infty}^{\infty} dxx^4e^{-ax^2} = I_2(a)\end{aligned}$$

Extrapolating to the nth derivative gives the general solution

$$\frac{d^v I_0(a)}{da^v} = (-1)^v I_v(a)$$

Because $I_0(a) = (\pi/a)^{1/2}$, $I_1 = (\pi/a)^{1/2}/2a$, $I_2 = 3(\pi/a)^{1/2}/4a^2$, and so forth.

5–18. Prove that the product of two even functions is even, that the product of two odd functions is even, and that the product of an even and an odd function is odd.

Recall that an even function is one for which $f(x) = f(-x)$ and an odd function is one for which $f(x) = -f(-x)$. Let $P(x)$ be the product of two functions $f(x)$ and $q(x)$. For two even functions,

$$P(x) = f(x)g(x) = f(-x)g(-x) = P(-x)$$

so the product of two even functions is even. For two odd functions,

$$P(x) = f(x)g(x) = -f(-x)[-g(-x)] = f(-x)g(-x) = P(-x)$$

so the product of two odd functions is also even. For one odd and one even function,

$$P(x) = f(x)g(x) = [-f(-x)]g(-x) = -f(-x)g(-x) = -P(-x)$$

so the product of one odd and one even function is odd.

5–19. Prove that the derivative of an even (odd) function is odd (even).

If $f(x)$ is even, it can be represented by a power series of the form

$$f(x) = f_0 + f_2x^2 + f_4x^4 + O(x^6)$$

where the only allowed values of n in x^n are even. The derivative of this function is

$$f'(x) = 2f_2x + 4f_4x^3 + O(x^5)$$

which is an odd function expressed in a power series. Similarly, if $g(x)$ is odd, it can be represented by

$$g(x) = f_1x + f_3x^3 + f_5x^5 + O(x^7)$$

where the only allowed values of n in x^n are odd, and its derivative is

$$g'(x) = f_1 + 3f_3x^2 + 5f_5x^4 + O(x^6)$$

which is an even function.

5–20. Show that

$$\langle x^2\rangle = \int_{-\infty}^{\infty} \psi_2(x)x^2\psi_2(x)dx = \frac{5}{2}\frac{\hbar}{(\mu k)^{1/2}}$$

for a harmonic oscillator. Note that $\langle x^2\rangle^{1/2}$ is the square root of the mean of the square of the displacement (the *root-mean-square displacement*) of the oscillator.

From Table 5.3, $\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$. So

$$\begin{aligned}
\langle x^2\rangle &= \int_{-\infty}^{\infty} \psi_2(x)x^2\psi_2(x)dx \\
&= 2\left(\frac{\alpha}{4\pi}\right)^{1/2}\int_0^{\infty} dx(2\alpha x^2 - 1)^2x^2e^{-\alpha x^2} \\
&= \left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^{\infty} dx(4\alpha^2x^6 - 4\alpha x^4 + x^2)e^{-\alpha x^2} \\
&= \left(\frac{\alpha}{\pi}\right)^{1/2}\left[4\alpha^2\left(\frac{15}{16\alpha^3}\right) - 4\alpha\left(\frac{3}{8\alpha^2}\right) + \left(\frac{1}{4\alpha}\right)\right]\left(\frac{\pi}{\alpha}\right)^{1/2} \\
&= \frac{5}{2\alpha} = \frac{5}{2}\frac{\hbar}{(\mu k)^{1/2}}
\end{aligned}$$

5–21. Show that

$$\langle p^2\rangle = \int_{-\infty}^{\infty} \psi_2(x)\hat{P}^2\psi_2(x)dx = \frac{5}{2}\hbar(\mu k)^{1/2}$$

for a harmonic oscillator.

From Table 5.3 and Table 4.1, $\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$ and $\hat{P} = -i\hbar d/dx$. So

$$\begin{aligned}
\langle p^2\rangle &= \int_{-\infty}^{\infty} \psi_2(x)\hat{P}^2\psi_2(x)dx \\
&= 2\left(\frac{\alpha}{4\pi}\right)^{1/2}\int_0^{\infty} dx(2\alpha x^2 - 1)e^{-\alpha x^2/2}\left\{-\hbar^2\frac{d^2}{dx^2}\left[(2\alpha x^2 - 1)e^{-\alpha x^2/2}\right]\right\} \\
&= -\hbar^2\left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^{\infty} dx(2\alpha x^2 - 1)e^{-\alpha x^2}\left(5\alpha - 11\alpha^2x^2 + 2\alpha^3x^4\right) \\
&= -\hbar^2\left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^{\infty} dx\left(4\alpha^4x^6 - 24\alpha^3x^4 + 21\alpha^2x^2 - 5\alpha\right)e^{-\alpha x^2} \\
&= -\hbar^2\left(\frac{\alpha}{\pi}\right)^{1/2}\left[4\alpha^4\left(\frac{15}{16\alpha^3}\right) - 24\alpha^3\left(\frac{3}{8\alpha^2}\right) + 21\alpha^2\left(\frac{1}{4\alpha}\right) - 5\alpha\left(\frac{1}{4}\right)\right]\left(\frac{\pi}{\alpha}\right)^{1/2} \\
&= \hbar^2\frac{5}{2}\alpha = \frac{5}{2}\hbar(\mu k)^{1/2}
\end{aligned}$$

5–22. Using the fundamental vibrational frequencies of some diatomic molecules given below, calculate the root-mean-square displacement (see Problem 5–20) in the $v = 0$ state and compare it with the equilibrium bond length (also given below).

Molecule	$\tilde{\nu}/\text{cm}^{-1}$	l_0/pm
H_2	4401	74.1
$^{35}Cl^{35}Cl$	554	198.8
$^{14}N^{14}N$	2330	109.4

We will use Equation 5.34 to find k. Solving for k gives

$$k = (2\pi c\tilde{\nu})^2\mu$$

The root-mean-square displacement is given by $\langle x^2\rangle^{1/2}$. For the ground state,

$$\begin{aligned}
\langle x^2\rangle &= \int_{-\infty}^{\infty} \psi_0(x)x^2\psi_0(x)dx \\
&= 2\left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^{\infty} x^2e^{-\alpha x^2}dx \\
&= 2\left(\frac{\alpha}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left(\frac{1}{4\alpha}\right) = \frac{1}{2\alpha} = \frac{\hbar}{2(\mu k)^{1/2}} \\
&= \frac{\hbar}{4\pi c\tilde{\nu}\mu}
\end{aligned}$$

and so the root-mean-square displacement of the molecule is

$$\langle x^2\rangle^{1/2} = \left(\frac{\hbar}{4\pi c\tilde{\nu}\mu}\right)^{1/2}$$

For H_2,

$$\begin{aligned}
\langle x^2\rangle^{1/2} &= \left\{\frac{1.055\times 10^{-34}\ \text{J}\cdot\text{s}}{4\pi(2.998\times 10^{10}\ \text{cm}\cdot\text{s}^{-1})(4401\ \text{cm}^{-1})\left[\left(\frac{1.008}{2}\right)(1.661\times 10^{-27}\ \text{kg})\right]}\right\}^{1/2} \\
&= 8.718\times 10^{-12}\ \text{m} = 8.718\ \text{pm}
\end{aligned}$$

For $^{35}Cl^{35}Cl$,

$$\langle x^2\rangle^{1/2} = \left\{\frac{1.055\times10^{-34}\ \text{J}\cdot\text{s}}{4\pi(2.998\times10^{10}\ \text{cm}\cdot\text{s}^{-1})(554\ \text{cm}^{-1})\left[\left(\frac{34.97}{2}\right)(1.661\times10^{-27}\ \text{kg})\right]}\right\}^{1/2}$$
$$= 4.172\times10^{-12}\ \text{m} = 4.172\ \text{pm}$$

and finally, for $^{14}N^{14}N$,

$$\langle x^2\rangle^{1/2} = \left\{\frac{1.055\times10^{-34}\ \text{J}\cdot\text{s}}{4\pi(2.998\times10^{10}\ \text{cm}\cdot\text{s}^{-1})(2330\ \text{cm}^{-1})\left[\frac{14.003}{2}(1.661\times10^{-27}\ \text{kg})\right]}\right\}^{1/2}$$
$$= 3.215\times10^{-12}\ \text{m} = 3.215\ \text{pm}$$

These values are all much smaller than the equilibrium bond lengths.

5–23. Prove that

$$\langle K\rangle = \langle V(x)\rangle = \frac{E_v}{2}$$

for a one-dimensional harmonic oscillator for $v = 0$ and $v = 1$.

The operators for $V(x)$ and $K(x)$ given in Table 4.1, the expressions for $\psi_v(x)$ given in Table 5.3, and Equation 5.30 for the vibrational energy levels are

$$\hat{V}(x) = \frac{kx^2}{2}$$
$$\hat{K}(x) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}$$
$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$
$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$$
$$E_v = \hbar\left(\frac{k}{\mu}\right)^{1/2}\left(v+\frac{1}{2}\right)$$

For $v = 0$,

$$\langle K\rangle = \int_{-\infty}^{\infty} dx\,\psi_0(x)\left(\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2}\right)\psi_0(x)$$
$$= -\frac{\hbar^2}{\mu}\left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^{\infty} dx\,e^{-\alpha x^2}\left[\alpha^2x^2-\alpha\right]$$
$$= -\frac{\hbar^2}{\mu}\left(\frac{\alpha}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left[\alpha^2\left(\frac{1}{4\alpha}\right)-\alpha\left(\frac{1}{2}\right)\right] = \frac{\hbar^2\alpha}{4\mu}$$
$$= \frac{\hbar}{4}\left(\frac{k}{\mu}\right)^{1/2} = \frac{E_0}{2}$$

and

$$\langle V\rangle = \int_{-\infty}^{\infty} dx\,\psi_0(x)\left(\frac{kx^2}{2}\right)\psi_0(x)$$
$$= k\left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^{\infty} dx\,x^2e^{-\alpha x^2}$$
$$= k\left(\frac{\alpha}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\frac{1}{4\alpha} = \frac{k}{4\alpha} = \frac{\hbar}{4}\left(\frac{k}{\mu}\right)^{1/2} = \frac{E_0}{2}$$

For $v = 1$,

$$\langle K\rangle = \int_{-\infty}^{\infty} dx\,\psi_1(x)\left(\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2}\right)\psi_1(x)$$
$$= -\frac{\hbar^2}{\mu}\left(\frac{4\alpha^3}{\pi}\right)^{1/2}\int_0^{\infty} dx\,e^{-\alpha x^2}\left(\alpha^2x^4-3\alpha x^2\right)$$
$$= -\frac{\hbar^2}{\mu}\left(\frac{4\alpha^3}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left[\alpha^2\left(\frac{3}{8\alpha^2}\right)-3\alpha\left(\frac{1}{4\alpha}\right)\right]$$
$$= \frac{3\hbar^2\alpha}{4\mu} = \frac{3\hbar}{4}\left(\frac{k}{\mu}\right)^{1/2} = \frac{E_1}{2}$$

and

$$\langle V\rangle = \int_{-\infty}^{\infty} dx\,\psi_1(x)\left(\frac{kx^2}{2}\right)\psi_1(x)$$
$$= k\left(\frac{4\alpha^3}{\pi}\right)^{1/2}\int_0^{\infty} dx\,x^4e^{-\alpha x^2}$$
$$= k\left(\frac{4\alpha^3}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left(\frac{3}{8\alpha^2}\right) = \frac{3k}{4\alpha}$$
$$= \frac{3\hbar}{4}\left(\frac{k}{\mu}\right)^{1/2} = \frac{E_1}{2}$$

5–24. There are a number of general relations between the Hermite polynomials and their derivatives (which we will not derive). Some of these are

$$\frac{dH_v(\xi)}{d\xi} = 2\xi H_v(\xi) - H_{v+1}(\xi)$$

$$H_{v+1}(\xi) - 2\xi H_v(\xi) + 2vH_{v-1}(\xi) = 0$$

and

$$\frac{dH_v(\xi)}{d\xi} = 2vH_{v-1}(\xi)$$

Such connecting relations are called *recursion formulas*. Verify these formulas explicitly using the first few Hermite polynomials given in Table 5.2.

We will verify these formulas for $v = 0$, 1, and 2. The Hermite polynomials for these values of v are

$$H_0(\xi) = 1 \qquad H_1(\xi) = 2\xi \qquad H_2(\xi) = 4\xi^2 - 2$$

Using the first recursion formula, we have

$$\frac{dH_0(\xi)}{d\xi} = 2\xi H_0(\xi) - H_1(\xi)$$

or

$$0 = 2\xi(1) - 2\xi = 0$$

For $v = 1$,

$$\frac{dH_1(\xi)}{d\xi} = 2\xi H_1(\xi) - H_2(\xi)$$
$$2 = 2\xi(2\xi) - (4\xi^2 - 2) = 2$$

Using the second recursion fromula for $v = 1$, we have

$$H_2(\xi) - 2\xi H_1(\xi) + 2vH_0(\xi) = 0$$
$$4\xi^2 - 2 - 2\xi(2\xi) + 2 = 0$$

The third recursion formula is

$$\frac{dH_v(\xi)}{d\xi} = 2vH_{v-1}(\xi)$$

For $v = 1$, we have

$$2 = (2)(1)(1) = 2$$

and for $v = 2$, we have

$$8\xi = (2)(2)(2\xi) = 8\xi$$

5–25. Use the recursion formulas for the Hermite polynomials given in Problem 5–24 to show that $\langle p\rangle = 0$ and $\langle p^2\rangle = \hbar(\mu k)^{1/2}(v + \frac{1}{2})$. Remember that the momentum operator involves a differentiation with respect to x, not ξ.

$$\langle p\rangle = \int_{-\infty}^{\infty} dx\psi_v(x)\hat{P}_x\psi_v(x)$$
$$= -i\hbar\int_{-\infty}^{\infty} dx\psi_v(x)\frac{d\psi_v(x)}{dx}$$

In Example 5–6 we learned that $H_v(x)$ is an even function of x if v is even and is an odd function of x if v is odd. Because $e^{-\alpha x^2/2}$ is an even function of x, ψ_v is an even function of x if v is even and an odd function of x if v is odd (Problem 5–18). Also, the quantity $d\psi_v/dx$ is an even function if v is odd and is an odd function if v is even (Problem 5–19). Therefore, the integrand of $\langle p\rangle$ will always be the product of one odd and one even function, and is therefore an odd function (Problem 5–18). Because the integrand is integrated over all space, $\langle p\rangle = 0$. Now consider

$$\langle p^2\rangle = \int_{-\infty}^{\infty} dx\psi_v(x)\hat{P}^2\psi_v(x)$$
$$= -\hbar^2\int_{-\infty}^{\infty} dx\psi_v(x)\frac{d^2\psi_v(x)}{dx^2}$$

We use the Schrödinger equation for a harmonic oscillator

$$\frac{d^2\psi_v}{dx^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{1}{2}kx^2\right)\psi_v(x) = 0$$

to write

$$\begin{aligned}\langle p^2\rangle &= 2\mu\int_{-\infty}^{\infty} dx\psi_v(x)\left(E_v - \frac{1}{2}kx^2\right)\psi_v(x)\\ &= 2\mu E_v - k\mu\int_{-\infty}^{\infty} dx\psi_v(x)x^2\psi_v(x)\\ &= 2\mu\hbar\omega\left(v + \frac{1}{2}\right)\frac{-k\mu}{\alpha^{3/2}}\int_{-\infty}^{\infty} d\xi N_vH_v(\xi)\xi^2N_vH_v(\xi)e^{-\xi^2} \qquad (1)\end{aligned}$$

Using the second recursion relation in Problem 5–24, we have

$$\begin{aligned}\xi^2H_v(\xi) &= \xi\left[vH_{v-1}(\xi) + \frac{1}{2}H_{v+1}(\xi)\right]\\ &= v\left[(v-1)H_{v-2}(\xi) + \frac{1}{2}H_v(\xi)\right] + \frac{1}{2}\left[(v+1)H_v(\xi) + \frac{1}{2}H_{v+2}(\xi)\right]\\ &= v(v-1)H_{v-2}(\xi) + \left(v + \frac{1}{2}\right)H_v(\xi) + \frac{1}{4}H_{v+2}(\xi)\end{aligned}$$

Substituting this result into the integral of Equation 1 above gives three integrals, only one of which is nonzero (Section 5–6), so

$$\begin{aligned}\langle p^2\rangle &= 2\mu\hbar\omega\left(v + \frac{1}{2}\right) - \frac{k\mu}{\alpha^{3/2}}\int_{-\infty}^{\infty} d\xi N_vH_v\xi N_v\left(v + \frac{1}{2}\right)H_v(\xi)e^{-\xi^2}\\ &= 2\mu\hbar\omega\left(v + \frac{1}{2}\right) - \frac{k\mu}{\alpha}\left(v + \frac{1}{2}\right)\int_{-\infty}^{\infty}\psi_v(x)\psi_v(x)dx\\ &= 2\hbar(\mu k)^{1/2}\left(v + \frac{1}{2}\right) - \hbar(\mu k)^{1/2}\left(v + \frac{1}{2}\right)\\ &= \hbar(\mu k)^{1/2}\left(v + \frac{1}{2}\right)\end{aligned}$$

5–26. It can be proved generally that

$$\langle x^2\rangle = \frac{1}{\alpha}\left(v + \tfrac{1}{2}\right) = \frac{\hbar}{(\mu k)^{1/2}}\left(v + \tfrac{1}{2}\right)$$

and that

$$\langle x^4\rangle = \frac{3}{4\alpha^2}(2v^2 + 2v + 1) = \frac{3\hbar^2}{4\mu k}(2v^2 + 2v + 1)$$

for a harmonic oscillator. Verify these formulas explicitly for the first two states of a harmonic oscillator.

$$\begin{aligned}\langle x^2\rangle_{v=0} &= \left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^2e^{-\alpha x^2}dx\\ &= 2\left(\frac{\alpha}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left(\frac{1}{4\alpha}\right)\\ &= \frac{1}{2\alpha} = \frac{\hbar}{2(\mu k)^{1/2}}\end{aligned}$$

$$\langle x^4\rangle_{v=0} = \left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^4 e^{-\alpha x^2}dx$$
$$= 2\left(\frac{\alpha}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left(\frac{3}{8\alpha^2}\right)$$
$$= \frac{3}{4\alpha^2} = \frac{3\hbar^2}{4\mu k}$$
$$\langle x^2\rangle_{v=1} = \left(\frac{4\alpha^3}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^4 e^{-\alpha x^2}dx$$
$$= 2\left(\frac{4\alpha^3}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left(\frac{3}{8\alpha^2}\right)$$
$$= \frac{3}{2\alpha} = \frac{3\hbar}{2(\mu k)^{1/2}}$$
$$\langle x^4\rangle_{v=1} = \left(\frac{4\alpha^3}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^6 e^{-\alpha x^2}dx$$
$$= 2\left(\frac{4\alpha^3}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left(\frac{15}{16\alpha^3}\right)$$
$$= \frac{15}{4\alpha^2} = \frac{15\hbar^2}{4\mu k}$$

5–27. This problem is similar to Problem 3–35. Show that the harmonic-oscillator wave functions are alternately even and odd functions of x because the Hamiltonian operator obeys the relation $\hat{H}(x) = \hat{H}(-x)$. Define a reflection operator $\hat{R}$ by

$$\hat{R}u(x) = u(-x)$$

Show that $\hat{R}$ is linear and that it commutes with $\hat{H}$. Show also that the eigenvalues of $\hat{R}$ are ± 1. What are its eigenfunctions? Show that the harmonic-oscillator wave functions are eigenfunctions of $\hat{R}$. Note that they are eigenfunctions of both $\hat{H}$ and $\hat{R}$. What does this observation say about $\hat{H}$ and $\hat{R}$?

Consider the Schrödinger equation of a harmonic oscillator

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

Replace x by $-x$ and use the fact that $\hat{H}(x) = \hat{H}(-x)$ to obtain

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

Both $\psi_n(-x)$ and $\psi_n(x)$ are eigenfunctions of $\hat{H}(x)$ corresponding to the eigenvalue E_n. Because the system is nondegenerate, these eigenfunctions can differ by only a multiplicative constant c. We can write this as $\psi_n(x) = c\psi_n(-x)$. But $\psi_n(-x) = c\psi_n(x)$, and so $c = \pm 1$ (as in Problem 3–35). Thus ψ_n is always either even or odd. Moreover, because $H_v(x)$ is even when v is even and odd when v is odd, and because

$$\psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2} \tag{5.35}$$

$\psi_v(x)$ is even when v is even and odd when v is odd. Now define $\hat{R}$ as $\hat{R}u(x) = u(-x)$. $\hat{R}$ is linear because

$$\hat{R}\left[c_1u_1(x) + c_2u_2(x)\right] = c_1u_1(-x) + c_2u_2(-x)$$
$$= c_1\hat{R}u_1(x) + c_2\hat{R}u_2(x)$$

Because $\hat{R}\psi_n(x) = \psi_n(-x) = \pm\psi_n(x)$, we see that the eigenvalues of $\hat{R}$ are ± 1 and the eigenfunctions are $\psi_n(x)$. Because $\hat{H}$ and $\hat{R}$ have mutual eigenfunctions, they commute.

5–28. Use Ehrenfest's theorem (Problem 4–27) to show that $\langle p_x\rangle$ does not depend upon time for a one-dimensional harmonic oscillator.

$$\frac{d\langle p_x\rangle}{dt} = \left\langle -\frac{dV}{dx}\right\rangle = \langle -kx\rangle = 0$$

because $\langle x\rangle$ is the integral of an odd function. The fact that $d\langle p_x\rangle/dt = 0$ means that $\langle p_x\rangle$ does not depend upon time.

5–29. Show that the moment of inertia for a rigid rotator can be written as $I = \mu r^2$, where $r = r_1 + r_2$ (the fixed separation of the two masses) and μ is the reduced mass.

By definition, at the center of mass

$$m_1r_1 = m_2r_2 \qquad I = m_1r_1^2 + m_2r_2^2 \qquad \mu = \frac{m_1m_2}{m_1+m_2}$$

Now $r_1 = r - r_2$ and $r_2 = r - r_1$, so we can write the first equaiton as either $m_1(r - r_2) = m_2r_2$ or $m_2(r - r_1) = m_1r_1$. Solving these expressions for r_1 and r_2 gives

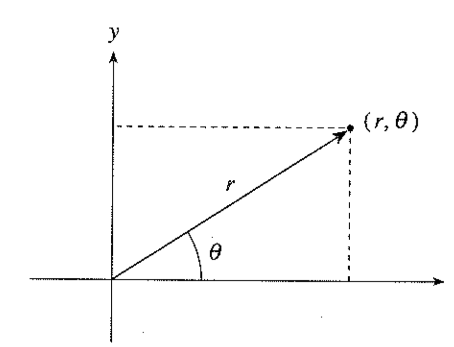
$$r_2 = \frac{m_1r}{m_1+m_2} \qquad r_1 = \frac{m_2r}{m_1+m_2}$$

Substituting these results into the expression of I gives

$$I = m_1r_1^2 + m_2r_2^2$$
$$= \frac{m_1m_2}{m_1+m_2}\left[\frac{m_1+m_2}{m_2}\left(\frac{m_2r}{m_1+m_2}\right)^2 + \frac{m_1+m_2}{m_1}\left(\frac{m_1r}{m_1+m_2}\right)^2\right]$$
$$= \mu\left[\left(\frac{m_2}{m_1+m_2} + \frac{m_1}{m_1+m_2}\right)r^2\right]$$
$$= \mu r^2$$

5–30. Consider the transformation from Cartesian coordinates to plane polar coordinates where

$$x = r\cos\theta \qquad r = (x^2+y^2)^{1/2}$$
$$y = r\sin\theta \qquad \theta = \tan^{-1}\left(\frac{y}{x}\right) \tag{1}$$



If a function $f(r,\theta)$ depends upon the polar coordinates r and θ, then the chain rule of partial differentiation says that

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial x}\right)_y + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial x}\right)_y \tag{2}$$

and that

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial y}\right)_x + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial y}\right)_x \tag{3}$$

For simplicity, we will assume r is constant so that we can ignore terms involving derivatives with respect to r. In other words, we will consider a particle that is constrained to move on the circumference of a circle. This system is sometimes called a *particle on a ring*. Using Equations 1 and 2, show that

$$\left(\frac{\partial f}{\partial x}\right)_y = -\frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r \quad \text{and} \quad \left(\frac{\partial f}{\partial y}\right)_x = \frac{\cos\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r \qquad (r \text{ fixed}) \tag{4}$$

Now apply Equation 2 again to show that

$$\begin{aligned}\left(\frac{\partial^2 f}{\partial x^2}\right)_y &= \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)_y\right] = \left[\frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial x}\right)_y\right]_r \left(\frac{\partial \theta}{\partial x}\right)_y \\ &= \left\{\frac{\partial}{\partial \theta}\left[-\frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r\right]\right\}_r \left(-\frac{\sin\theta}{r}\right) \\ &= \frac{\sin\theta\cos\theta}{r^2}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\sin^2\theta}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r \qquad (r \text{ fixed})\end{aligned}$$

Similarly, show that

$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = -\frac{\sin\theta\cos\theta}{r^2}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\cos^2\theta}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r \qquad (r \text{ fixed})$$

and that

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} \longrightarrow \frac{1}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r \qquad (r \text{ fixed})$$

Now show that the Schrödinger equation for a particle of mass m constrained to move on a circle of radius r is (see Problem 3–28)

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

where $I = mr^2$ is the moment of inertia.

First use Equations 1 to find the partial derivatives of r and θ with respect to x and y:

$$\left(\frac{\partial r}{\partial x}\right)_y = \left(\frac{\partial (x^2+y^2)^{1/2}}{\partial x}\right)_y = \frac{x}{(x^2+y^2)^{1/2}} = \cos\theta$$

$$\left(\frac{\partial r}{\partial y}\right)_x = \left(\frac{\partial (x^2+y^2)^{1/2}}{\partial y}\right)_x = \frac{y}{(x^2+y^2)^{1/2}} = \sin\theta$$

$$\begin{aligned}\left(\frac{\partial \theta}{\partial x}\right)_y &= \left(\frac{\partial \tan^{-1}\left(\frac{y}{x}\right)}{\partial x}\right)_y = \frac{1}{1+\left(\frac{y}{x}\right)^2}\left(-\frac{y}{x^2}\right) \\ &= -\frac{y}{x^2+y^2} = -\frac{r\sin\theta}{r^2} = -\frac{\sin\theta}{r}\end{aligned}$$

$$\begin{aligned}\left(\frac{\partial \theta}{\partial y}\right)_x &= \left(\frac{\partial \tan^{-1}\left(\frac{y}{x}\right)}{\partial y}\right)_x = \frac{1}{1+\left(\frac{y}{x}\right)^2}\left(\frac{1}{x}\right) \\ &= \frac{x}{x^2+y^2} = \frac{\cos\theta}{r}\end{aligned}$$

Now substitute into Equations 2 and 3 to find Equations 4:

$$\left(\frac{\partial f}{\partial x}\right)_y = 0 + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial x}\right)_y = -\frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r$$

$$\left(\frac{\partial f}{\partial y}\right)_x = 0 + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial y}\right)_x = \frac{\cos\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r$$

where r is fixed. Now (keeping r fixed)

$$\begin{aligned}\left(\frac{\partial^2 f}{\partial x^2}\right)_y &= \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)_y\right] = \left[\frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial x}\right)_y\right]_r \left(\frac{\partial \theta}{\partial x}\right)_y \\ &= \left\{\frac{\partial}{\partial \theta}\left[-\frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r\right]\right\}_r \left(-\frac{\sin\theta}{r}\right) \\ &= \frac{\sin\theta\cos\theta}{r^2}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\sin^2\theta}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r\end{aligned}$$

and

$$\begin{aligned}\left(\frac{\partial^2 f}{\partial y^2}\right)_x &= \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial y}\right)_x\right] = \left[\frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial y}\right)_x\right]_r \left(\frac{\partial \theta}{\partial y}\right)_x \\ &= \left\{\frac{\partial}{\partial \theta}\left[\frac{\cos\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r\right]\right\}_r \left(\frac{\cos\theta}{r}\right) \\ &= -\frac{\sin\theta\cos\theta}{r^2}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\cos^2\theta}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r\end{aligned}$$

giving

$$\begin{aligned}\nabla^2 f &= \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} \\ &= \frac{\sin^2\theta + \cos^2\theta}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r \\ &= \frac{1}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r\end{aligned}$$

The Schrödinger equation for the particle is

$$\begin{aligned}-\frac{\hbar^2}{2m}\nabla^2\psi_n(\theta) &= E\psi_n(\theta) \\ -\frac{\hbar^2}{2mr^2}\frac{\partial^2\psi_n(\theta)}{\partial\theta^2} &= E\psi_n(\theta) \\ -\frac{\hbar^2}{2I}\frac{\partial^2\psi_n(\theta)}{\partial\theta^2} &= E\psi_n(\theta)\end{aligned}$$

5–31. Generalize Problem 5–30 to the case of a particle moving in a plane under the influence of a central force; in other words, convert

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

to plane polar coordinates, this time without assuming that r is a constant. Use the method of separation of variables to separate the equation for this problem. Solve the angular equation.

We can use the partial derivatives we found in the previous problem and Equations 2 and 3 to write

$$\left(\frac{\partial f}{\partial x}\right)_y = \cos\theta\left(\frac{\partial f}{\partial r}\right)_\theta - \frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r$$
$$\left(\frac{\partial f}{\partial y}\right)_x = \sin\theta\left(\frac{\partial f}{\partial r}\right)_\theta + \frac{\cos\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r$$

Now (as before)

$$\begin{aligned}
\left(\frac{\partial^2 f}{\partial x^2}\right)_y &= \left(\frac{\partial r}{\partial x}\right)_y\left[\frac{\partial}{\partial r}\left(\frac{\partial f}{\partial x}\right)_y\right] + \left(\frac{\partial \theta}{\partial x}\right)_y\left[\frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial x}\right)_y\right]\\
&= \cos\theta\left[\cos\theta\left(\frac{\partial^2 f}{\partial r^2}\right)_\theta + \frac{\sin^2\theta}{r^2}\left(\frac{\partial f}{\partial \theta}\right)_r - \frac{\sin\theta}{r}\left(\frac{\partial^2 f}{\partial r\partial\theta}\right)\right]\\
&\quad - \frac{\sin\theta}{r}\left[-\sin\theta\left(\frac{\partial f}{\partial r}\right)_\theta + \cos\theta\left(\frac{\partial^2 f}{\partial\theta\partial r}\right) - \frac{\cos\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r - \frac{\sin\theta}{r}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r\right]\\
&= \cos^2\theta\left(\frac{\partial^2 f}{\partial r^2}\right)_\theta - \frac{2\cos\theta\sin\theta}{r}\left(\frac{\partial^2 f}{\partial r\partial\theta}\right)\\
&\quad + \frac{2\cos\theta\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\sin^2\theta}{r}\left(\frac{\partial f}{\partial r}\right)_\theta + \frac{\sin^2\theta}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r
\end{aligned}$$

and

$$\begin{aligned}
\left(\frac{\partial^2 f}{\partial y^2}\right)_x &= \left(\frac{\partial r}{\partial y}\right)_x\left[\frac{\partial}{\partial r}\left(\frac{\partial f}{\partial y}\right)_x\right] + \left(\frac{\partial \theta}{\partial y}\right)_x\left[\frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial y}\right)_x\right]\\
&= \sin\theta\left[\sin\theta\left(\frac{\partial^2 f}{\partial r^2}\right)_\theta - \frac{\cos\theta}{r^2}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\cos\theta}{r}\left(\frac{\partial^2 f}{\partial r\partial\theta}\right)\right]\\
&\quad + \frac{\cos\theta}{r}\left[\cos\theta\left(\frac{\partial f}{\partial r}\right)_\theta + \sin\theta\left(\frac{\partial^2 f}{\partial\theta\partial r}\right) - \frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\cos\theta}{r}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r\right]\\
&= \sin^2\theta\left(\frac{\partial^2 f}{\partial r^2}\right)_\theta + \frac{2\cos\theta\sin\theta}{r}\left(\frac{\partial^2 f}{\partial r\partial\theta}\right)\\
&\quad - \frac{2\cos\theta\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\cos^2\theta}{r}\left(\frac{\partial f}{\partial r}\right)_\theta + \frac{\cos^2\theta}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r
\end{aligned}$$

giving

$$\nabla^2 f = \left(\frac{\partial^2 f}{\partial x^2}\right)_y + \left(\frac{\partial^2 f}{\partial y^2}\right)_x = \left(\frac{\partial^2 f}{\partial r^2}\right)_\theta + \frac{1}{r}\left(\frac{\partial f}{\partial r}\right)_\theta + \frac{1}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r$$

Now consider the Schrödinger equation of a particle moving in a plane under the influence of a central force:

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2}\right] + V(r)\psi(r,\theta) = E\psi(r,\theta)$$
$$-\hbar^2\left[r^2\frac{\partial^2\psi}{\partial r^2} + r\frac{\partial\psi}{\partial r}\right] - \hbar^2\frac{\partial^2\psi}{\partial\theta^2} + 2\mu r^2\left[V(r) - E\right]\psi = 0$$

Let $\psi(r,\theta) = R(r)\Theta(\theta)$ to get

$$-\frac{\hbar^2}{R}\left[r^2\frac{d^2R}{dr^2} + r\frac{dR}{dr}\right] + 2\mu r^2[V - E] - \frac{\hbar^2}{\Theta}\frac{d^2\Theta}{d\theta^2} = 0$$

Separating the equation, we get the two equations

$$p^2 = -\frac{\hbar^2}{R}\left[r^2\frac{d^2R}{dr^2} + r\frac{dR}{dr}\right] + 2\mu r^2[V - E]$$
$$q^2 = -\frac{\hbar^2}{\Theta}\frac{d^2\Theta}{d\theta^2}$$

where $p^2 + q^2 = 0$. Using the second of these equations, we find

$$\frac{d^2\Theta}{d\theta^2} + \frac{q^2}{\hbar^2}\Theta = 0$$

The general solution to this equation (Example 2–4) is

$$\Theta(\theta) = c_1 e^{\pm ni\theta} = E\cos(n\theta + \phi)$$

where $n = q/\hbar$.

5–32. Using Problems 5–30 and 5–31 as a guide, convert ∇^2 from three-dimensional Cartesian coordinates to spherical coordinates.

This is an extremely long and tedious exercise in partial differentiation. We can avoid this tedium by approaching the problem another way. Let q_1, q_2, and q_3 be any suitable set of coordinates and let x, y, and z be given by

$$x = x(q_1, q_2, q_3) \qquad y = y(q_1, q_2, q_3) \qquad z = z(q_1, q_2, q_3)$$

For example, for spherical coordinates $q_1 = r$, $q_2 = \theta$ and $q_3 = \phi$. We give here without proof (the proof is actually straightforward, although lengthy) a general formula for ∇^2 in terms of q_1, q_2, and q_3:

$$\nabla^2 f = \frac{1}{h_1h_2h_3}\left[\frac{\partial}{\partial q_1}\left(\frac{h_2h_3}{h_1}\frac{\partial f}{\partial q_1}\right) + \frac{\partial}{\partial q_2}\left(\frac{h_3h_1}{h_2}\frac{\partial f}{\partial q_2}\right) + \frac{\partial}{\partial q_3}\left(\frac{h_1h_2}{h_3}\frac{\partial f}{\partial q_3}\right)\right]$$

where

$$h_j^2 = \left(\frac{\partial x}{\partial q_j}\right)^2 + \left(\frac{\partial y}{\partial q_j}\right)^2 + \left(\frac{\partial z}{\partial q_j}\right)^2$$

We can now apply this formula to spherical coordinates, where $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, and $z = r\cos\theta$. Using the above formula, we find

$$h_1^2 = \left(\frac{\partial x}{\partial r}\right)^2 + \left(\frac{\partial y}{\partial r}\right)^2 + \left(\frac{\partial z}{\partial r}\right)^2 = \sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi + \cos^2\theta$$
$$h_1 = \left[\sin^2\theta(\cos^2\phi + \sin^2\phi) + \cos^2\theta\right]^{1/2} = 1$$

Likewise,

$$h_2^2 = \left(\frac{\partial x}{\partial \theta}\right)^2 + \left(\frac{\partial y}{\partial \theta}\right)^2 + \left(\frac{\partial z}{\partial \theta}\right)^2 = r^2\cos^2\theta\cos^2\phi + r^2\cos^2\theta\sin^2\phi + r^2\sin^2\theta$$

$$h_2 = r\left[\cos^2\theta(\cos^2\phi + \sin^2\phi) + \sin^2\theta\right]^{1/2} = r$$

and

$$h_3^2 = \left(\frac{\partial x}{\partial \phi}\right)^2 + \left(\frac{\partial y}{\partial \phi}\right)^2 + \left(\frac{\partial z}{\partial \phi}\right)^2 = r^2\sin^2\theta\sin^2\phi + r^2\sin^2\theta\cos^2\phi$$

$$h_3 = r\left[\sin^2\theta(\sin^2\phi + \cos^2\phi)\right]^{1/2} = r\sin\theta$$

Then

$$\nabla^2 f = \frac{1}{r^2\sin\theta}\left[\frac{\partial}{\partial r}\left(r^2\sin\theta\frac{\partial f}{\partial r}\right) + \frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) + \frac{\partial}{\partial \phi}\left(\frac{1}{\sin\theta}\frac{\partial f}{\partial \phi}\right)\right]$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial \phi^2}$$

5–33. Show that rotational transitions of a diatomic molecule occur in the microwave region or the far infrared region of the spectrum.

Assuming that the diatomic molecule can be treated as a rigid rotator, the frequency of a rotational transition is

$$\nu = \frac{h}{4\pi^2 I}(J+1) \qquad J = 0, 1, 2, \ldots \tag{5.60}$$

From Section 5–9, a typical moment of inertia for a diatomic molecule is 5×10^{-46} kg·m^2. The observed frequency is therefore an integral multiple of

$$\nu = \frac{6.626 \times 10^{-34}\text{ J·s}}{4\pi^2(5 \times 10^{-46}\text{ kg·m}^2)} = 3.4 \times 10^{10}\text{ s}^{-1}$$

Frequencies in the vicinity of this value occur in the microwave or far infrared region of the spectrum.

5–34. In the far infrared spectrum of $H^{79}Br$, there is a series of lines separated by 16.72 cm^{-1}. Calculate the values of the moment of inertia and the internuclear separation in $H^{79}Br$.

Assuming that $H^{79}Br$ can be treated as a rigid rotator,

$$\tilde{\nu} = 2\tilde{B}(J+1) \qquad J = 0, 1, 2, \ldots \tag{5.63}$$

$$\tilde{B} = \frac{h}{8\pi^2 cI} \tag{5.64}$$

The lines in the spectrum are separated by 16.72 cm^{-1}, so

$$\Delta\tilde{\nu} = 2\tilde{B} = \frac{2h}{8\pi^2 cI}$$

$$16.72\text{ cm}^{-1} = \frac{2(6.626 \times 10^{-34}\text{ J·s})}{8\pi^2(2.998 \times 10^{10}\text{ cm·s}^{-1})I}$$

$$I = 3.35 \times 10^{-47}\text{ kg·m}^2$$

We can find μ for $H^{79}Br$:

$$\mu = \frac{(78.9)(1.01)}{79.91}(1.661 \times 10^{-27}\text{ kg}) = 1.653 \times 10^{-27}\text{ kg}$$

Now we can use the relationship $r = (I/\mu)^{1/2}$ to find r.

$$r = \left(\frac{3.35 \times 10^{-47}\text{ kg·m}^2}{1.653 \times 10^{-27}\text{ kg}}\right)^{1/2} = 1.42 \times 10^{-10}\text{ m} = 142\text{ pm}$$

5–35. The $J = 0$ to $J = 1$ transition for carbon monoxide ($^{12}C^{16}O$) occurs at 1.153×10^5 MHz. Calculate the value of the bond length in carbon monoxide.

Assuming that $^{12}C^{16}O$ can be treated as a rigid rotator,

$$\nu = 2B(J+1) \qquad J = 0, 1, 2, \ldots \tag{5.61}$$

$$B = \frac{h}{8\pi^2 I} \tag{5.62}$$

For the $J = 0$ to $J = 1$ transition,

$$\frac{1}{2}\nu = B = \frac{h}{8\pi^2 I}$$

$$\frac{1}{2}(1.153 \times 10^{11}\text{ s}^{-1}) = \frac{6.626 \times 10^{-34}\text{ J·s}}{8\pi^2\mu r^2}$$

We can find μ and use the relationship $r = (I/\mu)^{1/2}$ to find r.

$$\mu = \frac{(12.00)(15.99)}{27.99}(1.661 \times 10^{-27}\text{ kg}) = 1.139 \times 10^{-26}\text{ kg}$$

$$r = \left[\frac{6.626 \times 10^{-34}\text{ J·s}}{4\pi^2(1.139 \times 10^{-26}\text{ kg})(1.153 \times 10^{11}\text{ s}^{-1})}\right]^{1/2}$$

$$= 1.13 \times 10^{-10}\text{ m} = 113\text{ pm}$$

5–36. Figure 5.11 compares the probability distribution associated with the harmonic oscillator wave function $\psi_{10}(\xi)$ to the classical distribution. This problem illustrates what is meant by the classical distribution. Consider

$$x(t) = A\sin(\omega t + \phi)$$

which can be written as

$$\omega t = \sin^{-1}\left(\frac{x}{A}\right) - \phi$$

Now

$$dt = \frac{\omega^{-1}dx}{\sqrt{A^2 - x^2}} \qquad (1)$$

This equation gives the time that the oscillator spends between x and $x + dx$. We can convert Equation 1 to a probability distribution in x by dividing by the time that it takes for the oscillator to go from $-A$ to A. Show that this time is π/ω and that the probability distribution in x is

$$p(x)dx = \frac{dx}{\pi\sqrt{A^2 - x^2}} \qquad (2)$$

Show that $p(x)$ is normalized. Why does $p(x)$ achieve its maximum value at $x = \pm A$? Now use the fact that $\xi = \alpha^{1/2}x$, where $\alpha = (k\mu/\hbar^2)^{1/2}$, to show that

$$p(\xi)d\xi = \frac{d\xi}{\pi\sqrt{\alpha A^2 - \xi^2}} \qquad (3)$$

Show that the limits of ξ are $\pm(\alpha A^2)^{1/2} = \pm(21)^{1/2}$, and compare this result to the vertical lines shown in Figure 5.11. [*Hint*: You need to use the fact that $kA^2/2 = E_{10}$ ($v = 10$).] Finally, plot Equation 3 and compare your result with the curve in Figure 5.11.

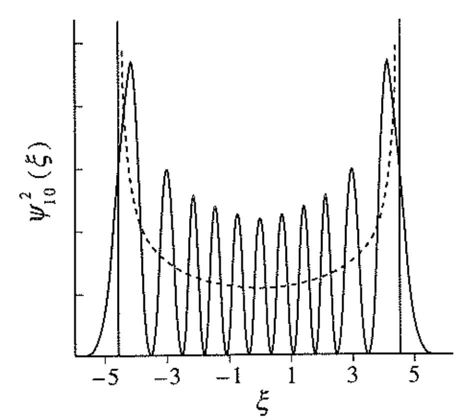


FIGURE 5.11
The probability distribution function of a harmonic oscillator in the $v = 10$ state. The dashed line is that for a classical harmonic oscillator with the same energy. The vertical lines at $\xi \approx \pm 4.6$ represents the extreme limits of the classical harmonic motion.

The variable ω is the angular velocity of the oscillator, defined as $\omega = 2\pi\nu$ where ν is in cycles per second. In going from $-A$ to A the function $x(t)$ goes through $\frac{1}{2}$ cycle, so

$$\omega = \frac{2\pi\left(\frac{1}{2}\text{ cycle}\right)}{t} \qquad t = \frac{\pi}{\omega}$$

Substitute $\omega^{-1} = t\pi^{-1}$ into Equation 1 and divide by t:

$$\frac{dt}{t} = \frac{dx}{\pi\sqrt{A^2 - x^2}}$$

Interpreting dt/t as a probability distribution in x, we find

$$p(x)dx = \frac{dx}{\pi\sqrt{A^2 - x^2}} \qquad (2)$$

To show that this expression is normalized, we integrate over the time period we are observing:

$$\int_{-A}^{A}\frac{dx}{\pi\sqrt{A^2 - x^2}} = \frac{1}{\pi}\sin^{-1}\frac{x}{A}\Big|_{-A}^{A} = 1$$

The maximum values of $p(x)$ are at $x = \pm A$ because these are the points at which the classical harmonic oscillator has zero velocity. Substituting $\xi = \alpha^{1/2}x$ and $d\xi = \alpha^{1/2}dx$,

$$p(\xi)d\xi = \frac{d\xi}{\pi\sqrt{\alpha A^2 - \xi^2}}$$

Since the limits of x are $\pm A$, the limits of ξ are $\pm\alpha^{1/2}A = \pm\sqrt{\alpha A^2}$. But $kA^2/2 = E_{10} = \frac{21}{2}\hbar\omega$, so $A^2 = 21\hbar/(\mu k)^{1/2}$. Also, $\alpha = (\mu k)^{1/2}/\hbar$, so $(\alpha A^2)^{1/2} = (21)^{1/2} = 4.58$. The plot of Equation 3 is given by the dashed curve in Figure 5.11.

5–37. Compute the value of $\hat{L}^2 Y(\theta, \phi)$ for the following functions:

a. $1/(4\pi)^{1/2}$ **b.** $(3/4\pi)^{1/2}\cos\theta$

c. $(3/8\pi)^{1/2}\sin\theta e^{i\phi}$ **d.** $(3/8\pi)^{1/2}\sin\theta e^{-i\phi}$

Do you find anything interesting about the results?

Equation 5.52 is

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \qquad (5.52)$$

a. $\hat{L}^2\left[\frac{1}{(4\pi)^{1/2}}\right] = 0$ because $1/(4\pi)^{1/2}$ is independent of θ and ϕ.

b. $$\hat{L}^2\left(\sqrt{\frac{3}{4\pi}}\cos\theta\right) = -\hbar^2\left(\frac{3}{4\pi}\right)^{1/2}[-2\cos\theta] = 2\hbar^2\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

c. $$\hat{L}^2\left(\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}\right) = -\hbar^2\left(\frac{3}{8\pi}\right)^{1/2}\left[\frac{\cos^2\theta - \sin^2\theta}{\sin\theta} - \frac{1}{\sin\theta}\right]e^{i\phi}$$
$$= -\hbar^2\left(\frac{3}{8\pi}\right)^{1/2}[-2\sin\theta]e^{i\phi} = 2\hbar^2\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{i\phi}$$

d. $\hat{L}^2\left(\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}\right) = \hat{L}^2\left(\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}\right)$, which we evaluated in c.

All of the spherical harmonics examined are eigenfunctions of $\hat{L}^2$ and the eigenvalues are multiples of $\hbar^2$. This is a general result.

Problems 5–38 through 5–43 develop an alternative method for determining the eigenvalues and eigenfunctions of a one-dimensional harmonic oscillator.

5–38. The Schrödinger equation for a one-dimensional harmonic oscillator is

$$\hat{H}\psi(x) = E\psi(x)$$

where the Hamiltonian operator is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

where $k = \mu\omega^2$ is the force constant. Let $\hat{P}$ and $\hat{X}$ be the operators for momentum and position, respectively. If we define $\hat{p} = (\mu\hbar\omega)^{-1/2}\hat{P}$ and $\hat{x} = (\mu\omega/\hbar)^{1/2}\hat{X}$, show that

$$\hat{H} = \frac{\hat{P}^2}{2\mu} + \frac{k}{2}\hat{X}^2 = \frac{\hbar\omega}{2}(\hat{p}^2 + \hat{x}^2)$$

Use the definitions of $\hat{p}$ and $\hat{x}$ to show that

$$\hat{p} = -i\frac{d}{dx}$$

and

$$\hat{p}\hat{x} - \hat{x}\hat{p} = [\hat{p}, \hat{x}] = -i$$

Recall that $\hat{P} = -i\hbar(d/d\hat{X})$ and $\hat{X} = x$, so

$$\begin{aligned}\hat{H} &= \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{kx^2}{2} = \frac{1}{2\mu}(-\hbar^2)\frac{d^2}{dx^2} + \frac{\mu\omega^2x^2}{2}\\ &= \frac{1}{2\mu}\hat{P}^2 + \frac{\mu\omega^2}{2}\hat{X}^2\\ &= \frac{\mu\hbar\omega}{2\mu}\hat{p}^2 + \frac{\mu\omega^2\hbar}{2\mu\omega}\hat{x}^2\\ &= \frac{\hbar\omega}{2}(\hat{p}^2 + \hat{x}^2)\end{aligned}$$

Now

$$\hat{p} = (\mu\hbar\omega)^{-1/2}\hat{P} = \frac{1}{(\mu\omega\hbar)^{1/2}}\left(-i\hbar\frac{\partial}{\partial X}\right) = -i\frac{d}{d\hat{x}}$$

and

$$\begin{aligned}\hat{p}\hat{x}f - \hat{x}\hat{p}f &= -i\left(f + x\frac{df}{dx}\right) + ix\frac{df}{dx} = -if\\ \hat{p}\hat{x} - \hat{x}\hat{p} &= -i\end{aligned}$$

5–39. We will define the operators $\hat{a}_-$ and $\hat{a}_+$ to be

$$\hat{a}_- = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{p}) \quad \text{and} \quad \hat{a}_+ = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{p}) \tag{1}$$

where $\hat{x}$ and $\hat{p}$ are given in Problem 5–38. Show that

$$\hat{a}_-\hat{a}_+ = \tfrac{1}{2}(\hat{x}^2 + i[\hat{p}, \hat{x}] + \hat{p}^2) = \tfrac{1}{2}(\hat{p}^2 + \hat{x}^2 + 1) \tag{2}$$

and that

$$\hat{a}_+\hat{a}_- = \tfrac{1}{2}(\hat{p}^2 + \hat{x}^2 - 1) \tag{3}$$

Now show that the Hamiltonian operator for the one-dimensional harmonic oscillator can be written as

$$\hat{H} = \frac{\hbar\omega}{2}(\hat{a}_-\hat{a}_+ + \hat{a}_+\hat{a}_-)$$

Now show that $\hat{a}_-\hat{a}_+ + \hat{a}_+\hat{a}_-$ is equal to $2\hat{a}_+\hat{a}_- + 1$ so that the Hamiltonian operator can be written as

$$\hat{H} = \hbar\omega\left(\hat{a}_+\hat{a}_- + \tfrac{1}{2}\right)$$

The operator $\hat{a}_+\hat{a}_-$ is called the number operator, which we will denote by $\hat{v}$, and using this definition we obtain

$$\hat{H} = \hbar\omega\left(\hat{v} + \tfrac{1}{2}\right) \tag{4}$$

Comment on the functional form of this result. What do you expect are the eigenvalues of the number operator? Without doing any calculus, explain why $\hat{v}$ must be a Hermitian operator.

$$\begin{aligned}\hat{a}_-\hat{a}_+ &= \tfrac{1}{2}(\hat{x} + i\hat{p})(\hat{x} - i\hat{p})\\ &= \tfrac{1}{2}\left[\hat{x}^2 + i(\hat{p}\hat{x} - \hat{x}\hat{p}) + \hat{p}^2\right]\\ &= \tfrac{1}{2}(\hat{p}^2 + \hat{x}^2 + 1) \qquad (1)\\ \hat{a}_+\hat{a}_- &= \tfrac{1}{2}(\hat{x} - i\hat{p})(\hat{x} + i\hat{p})\\ &= \tfrac{1}{2}\left[\hat{x}^2 + i(\hat{x}\hat{p} - \hat{p}\hat{x}) + \hat{p}^2\right]\\ &= \tfrac{1}{2}(\hat{p}^2 + \hat{x}^2 - 1) \qquad (2)\end{aligned}$$

Adding Equations 1 and 2 gives

$$\hat{p}^2 + \hat{x}^2 = \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+$$

and using this result and the result of Problem 5–38 gives

$$\hat{H} = \frac{\hbar\omega}{2}(\hat{p}^2 + \hat{x}^2) = \frac{\hbar\omega}{2}(\hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+)$$

Now

$$2\hat{a}_+\hat{a}_- = \hat{p}^2 + \hat{x}^2 - 1$$

so

$$2\hat{a}_+\hat{a}_- + 1 = \hat{p}^2 + \hat{x}^2 = \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+$$

and we can write

$$\hat{H} = \frac{\hbar\omega}{2}(2\hat{a}_+\hat{a}_- + 1) = \hbar\omega\left(\hat{a}_+\hat{a}_- + \tfrac{1}{2}\right)$$

Letting $\hat{v} = \hat{a}_+\hat{a}_-$, we find $\hat{H} = \hbar\omega(\hat{v} + \frac{1}{2})$. The eigenvalues of $\hat{v}$ must correspond to the v of Section 5–9. The operator $\hat{v}$ must be Hermitian because $\hat{H}$ is Hermitian.

5–40. In this problem, we will explore some of the properties of the operators introduced in Problem 5–39. Let ψ_v and E_v be the wave functions and energies of the one-dimensional harmonic oscillator. Start with

$$\hat{H}\psi_v = \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\psi_v = E_v\psi_v$$

Multiply from the left by $\hat{a}_-$ and use Equation 2 of Problem 5–39 to show that

$$\hat{H}(\hat{a}_-\psi_v) = (E_v - \hbar\omega)(\hat{a}_-\psi_v)$$

or that

$$\hat{a}_-\psi_v \propto \psi_{v-1}$$

Also show that

$$\hat{H}(\hat{a}_+\psi_v) = (E_v + \hbar\omega)(\hat{a}_+\psi_v)$$

or that

$$\hat{a}_+\psi_v \propto \psi_{v+1}$$

Thus, we see that $\hat{a}_+$ operating on ψ_v gives ψ_{v+1} (to within a constant) and that $\hat{a}_-\psi_v$ gives ψ_{v-1} to within a constant. The operators $\hat{a}_+$ and $\hat{a}_-$ are called *raising* or *lowering operators*, or simply *ladder operators*. If we think of each rung of a ladder as a quantum state, then the operators $\hat{a}_+$ and $\hat{a}_-$ enable us to move up and down the ladder once we know the wave function of a single rung.

From the previous problem,

$$\hat{H}\psi_v = \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\psi_v = E_v\psi_v$$

Multiplying from the left by a_- gives

$$\hbar\omega\left(\hat{a}_-\hat{a}_+\hat{a}_- + \frac{1}{2}\hat{a}_-\right)\psi_v = E_v\hat{a}_-\psi_v$$

Now use the relation $\hat{a}_-\hat{a}_+ = \hat{a}_+\hat{a}_- + 1$ from Problem 5–39 to obtain

$$\hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{3}{2}\right)\hat{a}_-\psi_v = E_v\hat{a}_-\psi_v$$

$$\hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\hat{a}_-\psi_v = (E_v - \hbar\omega)\hat{a}_-\psi_v$$

Because $\hat{H} = \hat{a}_+\hat{a}_- + \frac{1}{2}$, we have

$$\hat{H}(\hat{a}_-\psi_v) = (E_v - \hbar\omega)(\hat{a}_-\psi_v)$$

$$\hat{a}_-\psi_v \propto \psi_{v-1}$$

Likewise, starting with

$$\hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\psi_v = E_v\psi_v$$

Multiplying from the left by a_+ gives

$$\hbar\omega\left(\hat{a}_+\hat{a}_+\hat{a}_- + \frac{1}{2}\hat{a}_+\right)\psi_v = E_v\hat{a}_+\psi_v$$

Now use the relation $\hat{a}_+\hat{a}_- = \hat{a}_-\hat{a}_+ - 1$ from Problem 5–39 to obtain

$$\hbar\omega\left(\hat{a}_+\hat{a}_- - \frac{1}{2}\right)\hat{a}_+\psi_v = E_v\hat{a}_+\psi_v$$

$$\hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2} - 1\right)\hat{a}_+\psi_v = E_v\hat{a}_+\psi_v$$

$$\hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\hat{a}_+\psi_v = (E_v + \hbar\omega)\hat{a}_+\psi_v$$

Because $\hat{H} = \hat{a}_+\hat{a}_- + \frac{1}{2}$, we have

$$\hat{H}(\hat{a}_+\psi_v) = (E_v + \hbar\omega)(\hat{a}_+\psi_v)$$

$$\hat{a}_+\psi_v \propto \psi_{v+1}$$

5–41. Use the fact that $\hat{x}$ and $\hat{p}$ are Hermitian in the number operator defined in Problem 5–39 to show that

$$\int \psi_v^*\hat{v}\psi_v dx \geq 0$$

$$\begin{aligned}\int \psi_v^*\hat{v}\psi_v dx &= \int \psi_v^*\hat{a}_+\hat{a}_-\psi_v dx \\ &= \frac{1}{\sqrt{2}}\int \psi_v^*\hat{x}\hat{a}_-\psi_v dx - \frac{i}{\sqrt{2}}\int \psi_v^*\hat{p}\hat{a}_-\psi_v dx \\ &= \frac{1}{\sqrt{2}}\int (\hat{x}\psi_v)^*\hat{a}_-\psi_v dx - \frac{i}{\sqrt{2}}\int (\hat{p}\psi_v)^*\hat{a}_-\psi_v dx \\ &= \frac{1}{\sqrt{2}}\int (\hat{x}\psi_v)^*\hat{a}_-\psi_v dx + \frac{1}{\sqrt{2}}\int (i\hat{p}\psi_v)^*\hat{a}_-\psi_v dx \\ &= \int (\hat{a}_-\psi_v)^*(\hat{a}_-\psi_v)dx \\ &= \int |\hat{a}_-\psi_v|^2 dx \geq 0\end{aligned}$$

5–42. In Problem 5–41, we proved that $v \geq 0$. Because $\hat{a}_-\psi_v \propto \psi_{v-1}$ and $v \geq 0$, there must be some minimal value of v, v_{min}. Argue that $\hat{a}_-\psi_{v_{\text{min}}} = 0$. Now multiply $\hat{a}_-\psi_{v_{\text{min}}} = 0$ by $\hat{a}_+$ and use Equation 3 of Problem 5–39 to prove that $v_{\text{min}} = 0$, and that $v = 0, 1, 2, \ldots$.

The natural zero-point for $\hat{a}_-$ is when it acts on $\psi_{v_{min}}$, since the lowest quantum state has already been reached and ψ cannot be lowered any further. Therefore we define $\hat{a}_-\psi_{v_{min}} = 0$.

$$\begin{aligned}
\hat{a}_-\psi_{v_{min}} &= 0\\
\hat{a}_+\hat{a}_-\psi_{v_{min}} &= 0\\
\hbar\omega\hat{a}_+\hat{a}_-\psi_{v_{min}} &= 0\\
\frac{\hbar\omega}{2}(\hat{p}^2 + \hat{x}^2 - 1)\psi_{v_{min}} &= 0\\
(\hat{H} - \frac{\hbar\omega}{2})\psi_{v_{min}} &= 0\\
\hat{H}\psi_{v_{min}} &= \frac{\hbar\omega}{2}\psi_{v_{min}}
\end{aligned}$$

Because Equation 4 of Problem 5–38 states that $\hat{H} = \hbar\omega(\hat{v} + \frac{1}{2})$, $\psi_{v_{min}}$ treated in this problem must be the eigenfunction of $\hat{v} = 0$. Therefore, $v_{min} = 0$.

5–43. Using the definition of $\hat{a}_-$ given in Problem 5–39 and the fact that $\hat{a}_-\psi_0 = 0$, determine the unnormalized wave function $\psi_0(x)$. Now determine the unnormalized wave function $\psi_1(x)$ using the operator $\hat{a}_+$.

$$\begin{aligned}
\hat{a}_-\psi_0 &= 0\\
\frac{1}{\sqrt{2}}(\hat{x} + i\hat{p})\psi_0 &= 0\\
x\psi_0 + \frac{d\psi_0}{dx} &= 0\\
\frac{d\psi_0}{\psi_0} &= -x dx\\
\psi_0 &= e^{-x^2/2}
\end{aligned}$$

Since $\psi_1 \sim \hat{a}_+\psi_0 \sim \hat{x}\psi_0 - i\hat{p}\psi_0$, and

$$\hat{x}\psi_0 - i\hat{p}\psi_0 = x\psi_0 - \frac{d\psi_0}{dx} = 2xe^{-x^2/2} = 2x\psi_0$$

we can write

$$\psi_1 \sim xe^{-x^2/2}$$

Problems 5–44 through 5–47 apply the idea of reduced mass to the hydrogen atom.

5–44. Given the development of the concept of reduced mass in Section 5–2, how do you think the energy of a hydrogen atom (Equation 1.22) will change if we do not assume that the proton is fixed at the origin?

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} \qquad (1.22)$$

Instead of using m_e, we will need to use μ, since the distance from the center of mass to the proton will not be zero.

5–45. In Example 1–8, we calculated the value of the Rydberg constant to be 109 737 cm^{-1}. What is the calculated value if we replace m_e in Equation 1.25 by the reduced mass? Compare your answer with the experimental result, 109 677.6 cm^{-1}.

From Problem 5–7, the reduced mass of hydrogen is $\mu = 9.104\,431 \times 10^{-31}$ kg $= 0.999\,455\,6 m_e$.

$$R_H = \frac{m_e e^4}{8\varepsilon_0^2 ch^3} \qquad (1.25)$$

Replacing m_e with μ gives a new R_H value of

$$(109\,737.2 \text{ cm}^{-1})(0.999\,455\,6) = 109\,677.5 \text{ cm}^{-1}$$

which differs from the experimental result by about 1×10^{-4}%.

5–46. Calculate the reduced mass of a deuterium atom. Take the mass of a deuteron to be $3.343\,586 \times 10^{-27}$ kg. What is the value of the Rydberg constant for a deuterium atom?

$$\begin{aligned}
\mu &= \frac{(9.109\,390 \times 10^{-31} \text{ kg})(3.343\,586 \times 10^{-27} \text{ kg})}{9.109\,390 \times 10^{-31} \text{ kg} + 3.343\,586 \times 10^{-27} \text{ kg}}\\
&= 9.106\,909 \times 10^{-31} \text{ kg} = 0.999\,727\,7 m_e
\end{aligned}$$

$$R_H = (109\,737.2 \text{ cm}^{-1})(0.999\,727\,7) = 109\,707.3 \text{ cm}^{-1}$$

5–47. Calculate the ratio of the frequencies of the lines in the spectra of atomic deuterium and atomic hydrogen.

The ratio of the frequencies of the lines in these spectra is the same as the ratios of the Rydberg constants found in Problems 5–45 and 5–46:

$$\frac{109\,707.3 \text{ cm}^{-1}}{109\,677.5 \text{ cm}^{-1}} = 1.000\,272$$
