CHAPTER 5

The Harmonic Oscillator and the Rigid Rotator: Two Spectroscopic Models

The vibrational motion of a diatomic molecule can be approximated as a harmonic oscillator. In this chapter, we will first study a classical harmonic oscillator and then present and discuss the energies and the corresponding wave functions of a quantum-mechanical harmonic oscillator. We will use the quantum-mechanical energies to describe the infrared spectrum of a diatomic molecule and learn how to determine molecular force constants from vibrational spectra. Then we will model the rotational motion of a diatomic molecule by a rigid rotator. We will discuss the quantum-mechanical energies of a rigid rotator and show their relation to the rotational spectrum of a diatomic molecule. We will use the rotational spectrum of a diatomic molecule to determine the bond length of the molecule.

5–1. A Harmonic Oscillator Obeys Hooke's Law

Consider a mass m connected to a wall by a spring as shown in Figure 5.1. Suppose further that no gravitational force is acting on m so that the only force is due to

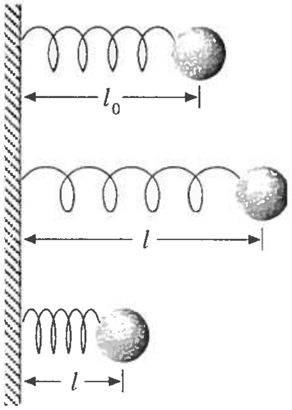

FIGURE 5.1
A mass connected to a wall by a spring. If the force acting upon the mass is directly proportional to the displacement of the spring from its undistorted length, then the force law is called Hooke's law.

the spring. If we let l_0 be the equilibrium, or undistorted, length of the spring, then the restoring force must be some function of the displacement of the spring from its equilibrium length. Let this displacement be denoted by $x = l - l_0$, where l is the length of the spring. The simplest assumption we can make about the force on m as a function of the displacement is that the force is directly proportional to the displacement and to write

$$f = -k(l - l_0) = -kx \tag{5.1}$$

The negative sign indicates that the force points to the right in Figure 5.1 if the spring is compressed ($l < l_0$) and points to the left if the spring is stretched ($l > l_0$). Equation 5.1 is called *Hooke's law* and the (positive) proportionality constant k is called the *force constant* of the spring. A small value of k implies a weak or loose spring, and a large value of k implies a stiff spring.

Newton's equation with a Hooke's law force is

$$m\frac{d^2l}{dt^2} = -k(l - l_0) \tag{5.2}$$

If we let $x = l - l_0$, then $d^2l/dt^2 = d^2x/dt^2$ (l_0 is a constant) and

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

According to Section 2–3, the general solution to this equation is (Problem 5–1)

$$x(t) = c_1 \sin \omega t + c_2 \cos \omega t \tag{5.4}$$

where

$$\omega = \left(\frac{k}{m}\right)^{1/2} \tag{5.5}$$

EXAMPLE 5–1

Show that Equation 5.4 can be written in the form

$$x(t) = A \sin(\omega t + \phi) \tag{5.6}$$

SOLUTION: The easiest way to prove this is to write

$$\sin(\omega t + \phi) = \sin \omega t \cos \phi + \cos \omega t \sin \phi$$

and substitute this into Equation 5.6 to obtain

$$\begin{aligned} x(t) &= A \cos \phi \sin \omega t + A \sin \phi \cos \omega t \\ &= c_1 \sin \omega t + c_2 \cos \omega t \end{aligned}$$

where

$$c_1 = A\cos\phi \quad \text{and} \quad c_2 = A\sin\phi$$

Equation 5.6 shows that the displacement oscillates sinusoidally, or *harmonically*, with a natural frequency $\omega = (k/m)^{1/2}$. In Equation 5.6, A is the *amplitude* of the vibration and ϕ is the *phase angle.*

Suppose we initially stretch the spring so that its initial displacement is A and then let go. The initial velocity in this case is zero and so from Equation 5.4, we have

$$x(0) = c_2 = A$$

and

$$\left(\frac{dx}{dt}\right)_{t=0} = 0 = c_1\omega$$

These two equations imply that $c_1 = 0$ and $c_2 = A$ in Equation 5.4, and so

$$x(t) = A\cos\omega t \tag{5.7}$$

The displacement versus time is plotted in Figure 5.2, which shows that the mass oscillates back and forth between A and $-A$ with a frequency of ω radians per second, or $\nu = \omega/2\pi$ cycles per second. The quantity A is called the *amplitude* of the vibration.

Let's look at the total energy of a harmonic oscillator. The force is given by Equation 5.1. Recall from physics that a force can be expressed as the negative derivative of a potential energy or that

$$f(x) = -\frac{dV}{dx} \tag{5.8}$$

so the potential energy is

$$V(x) = -\int f(x)dx + \text{constant} \tag{5.9}$$

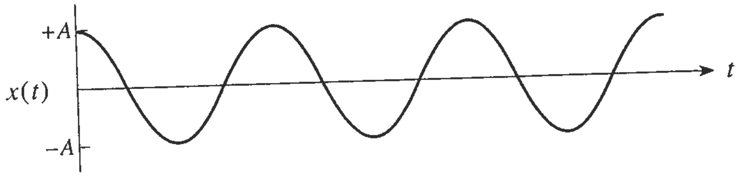

FIGURE 5.2
An illustration of the displacement of a harmonic oscillator versus time.

Using Equation 5.1 for $f(x)$, we see that

$$V(x) = \frac{k}{2}x^2 + \text{constant} \tag{5.10}$$

The constant term here is an arbitrary constant that can be used to fix the zero of energy. If we choose the potential energy of the system to be zero when the spring is undistorted ($x = 0$), then we have

$$V(x) = \frac{k}{2}x^2 \tag{5.11}$$

for the potential energy associated with a simple harmonic oscillator.

The kinetic energy is

$$K = \frac{1}{2}m\left(\frac{dl}{dt}\right)^2 = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 \tag{5.12}$$

Using Equation 5.7 for $x(t)$, we see that

$$K = \tfrac{1}{2}m\omega^2 A^2 \sin^2 \omega t \tag{5.13}$$

and

$$V = \tfrac{1}{2}kA^2 \cos^2 \omega t \tag{5.14}$$

Both K and V are plotted in Figure 5.3. The total energy is

$$E = K + V = \tfrac{1}{2}m\omega^2 A^2 \sin^2 \omega t + \tfrac{1}{2}kA^2 \cos^2 \omega t$$

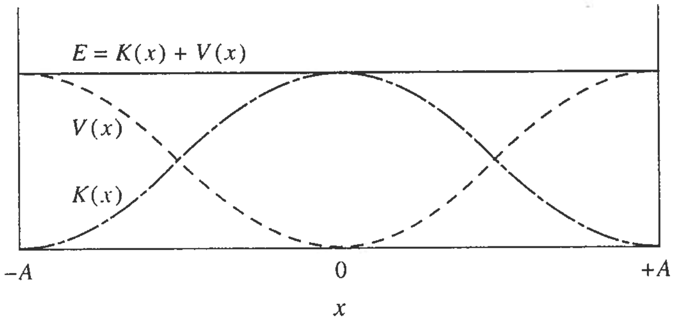

FIGURE 5.3
The kinetic energy [curve labelled $K(x)$] and the potential energy [curve labelled $V(x)$] of a harmonic oscillator during one oscillation. The spring is fully compressed at $-A$ and fully stretched at $+A$. The equilibrium length is $x = 0$. The total energy is the horizontal curve labelled E, which is the sum of $K(x)$ and $V(x)$.

If we recall that $\omega = (k/m)^{1/2}$, we see that the coefficient of the first term is $kA^2/2$, so that the total energy becomes

$$E = \frac{kA^2}{2}(\sin^2 \omega t + \cos^2 \omega t) = \frac{kA^2}{2} \tag{5.15}$$

Thus, we see that the total energy is a constant and, in particular, is equal to the potential energy at its largest displacement, where the kinetic energy is zero. Figure 5.3 shows how the total energy is distributed between the kinetic energy and the potential energy. Each oscillates in time between zero and its maximum value but in such a way that their sum is always a constant. We say that the total energy is conserved and that the system is a *conservative system.*

5–2. The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

The simple harmonic oscillator is a good model for a vibrating diatomic molecule. A diatomic molecule, however, does not look like the system pictured in Figure 5.1 but more like two masses connected by a spring as in Figure 5.4. In this case we have two equations of motion, one for each mass:

$$m_1 \frac{d^2 x_1}{dt^2} = k(x_2 - x_1 - l_0) \tag{5.16}$$

and

$$m_2 \frac{d^2 x_2}{dt^2} = -k(x_2 - x_1 - l_0) \tag{5.17}$$

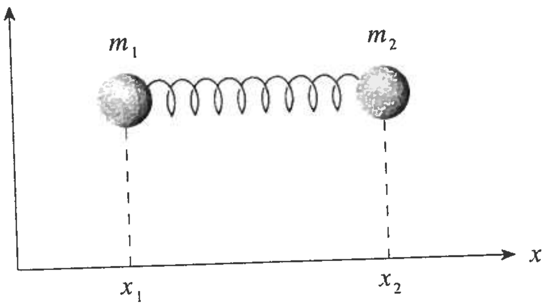

FIGURE 5.4
Two masses connected by a spring, which is a model used to describe the vibrational motion of a diatomic molecule.

where l_0 is the undistorted length of the spring. Note that if $x_2 - x_1 > l_0$, the spring is stretched and the force on mass m_1 is toward the right and that on mass m_2 is toward the left. This is why the force term in Equation 5.16 is positive and that in Equation 5.17 is negative. Note also that the force on m_1 is equal and opposite to the force on m_2, as it should be according to Newton's third law, action and reaction.

If we add Equations 5.16 and 5.17, we find that

$$\frac{d^2}{dt^2}(m_1x_1 + m_2x_2) = 0 \tag{5.18}$$

This form suggests that we introduce a *center-of-mass coordinate*

$$X = \frac{m_1x_1 + m_2x_2}{M} \tag{5.19}$$

where $M = m_1 + m_2$, so that we can write Equation 5.18 in the form

$$M\frac{d^2X}{dt^2} = 0 \tag{5.20}$$

There is no force term here, so Equation 5.20 shows that the center of mass moves uniformly in time with a constant momentum.

The motion of the two-mass or two-body system in Figure 5.4 must depend upon only the *relative* separation of the two masses, or upon the *relative coordinate*

$$x = x_2 - x_1 - l_0 \tag{5.21}$$

If we divide Equation 5.17 by m_2 and then subtract Equation 5.16 divided by m_1 we find that

$$\frac{d^2x_2}{dt^2} - \frac{d^2x_1}{dt^2} = -\frac{k}{m_2}(x_2 - x_1 - l_0) - \frac{k}{m_1}(x_2 - x_1 - l_0)$$

or

$$\frac{d^2}{dt^2}(x_2 - x_1) = -k\left(\frac{1}{m_1} + \frac{1}{m_2}\right)(x_2 - x_1 - l_0)$$

If we let

$$\frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 + m_2}{m_1m_2} = \frac{1}{\mu}$$

and introduce $x = x_2 - x_1 - l_0$ from Equation 5.21, then we have

$$\mu\frac{d^2x}{dt^2} + kx = 0 \tag{5.22}$$

The quantity μ that we have defined is called the *reduced mass*.

Equation 5.22 is an important result with a nice physical interpretation. If we compare Equation 5.22 with Equation 5.3, we see that Equation 5.22 is the same except for the substitution of the reduced mass μ. Thus, the two-body system in Figure 5.4 can be treated as easily as the one-body problem in Figure 5.1 by using the reduced mass of the two-body system. In particular, the motion of the system is governed by Equation 5.6 but with $\omega = (k/\mu)^{1/2}$. Generally, if the potential energy depends upon only the *relative* distance between two bodies, then we can introduce relative coordinates such as $x_2 - x_1$ and reduce a two-body problem to a one-body problem. This important and useful theorem of classical mechanics is discussed in Problems 5–5 and 5–6.

5–3. The Harmonic-Oscillator Approximation Results from the Expansion of an Internuclear Potential Around its Minimum

Before we discuss the quantum-mechanical treatment of a harmonic oscillator, we should discuss how good an approximation it is for a vibrating diatomic molecule. The internuclear potential for a diatomic molecule is illustrated by the solid line in Figure 5.5. Notice that the curve rises steeply to the left of the minimum, indicating the difficulty of pushing the two nuclei closer together. The curve to the right side of the equilibrium position rises intially but eventually levels off. The potential energy at large separations is essentially the bond energy. The dashed line shows the potential $\frac{1}{2}k(l - l_0)^2$ associated with Hooke's law. Although the harmonic-oscillator potential may appear to be a terrible approximation to the experimental curve, note that it is, indeed, a good approximation in the region of the minimum. This region is the

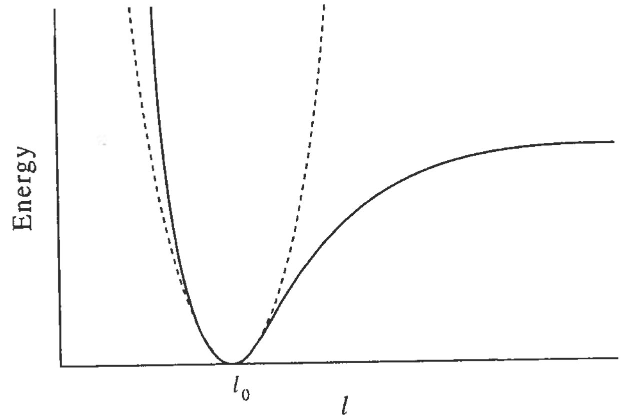

FIGURE 5.5
A comparison of the harmonic oscillator potential ($k(l - l_0)^2/2$; dashed line) with the complete internuclear potential (solid line) of a diatomic molecule. The harmonic oscillator potential is a satisfactory approximation at small displacements from the minimum.

physically important region for many molecules at room temperature. Although the harmonic oscillator unrealistically allows the displacement to vary from 0 to $+\infty$, these large displacements produce potential energies that are so large that they do not often occur in practice. The harmonic oscillator will be a good approximation for vibrations with small amplitudes.

We can put the previous discussion into mathematical terms by considering the Taylor expansion (see MathChapter I) of the potential energy $V(l)$ about the equilibrium bond length $l = l_0$. The first few terms in this expansion are

$$V(l) = V(l_0) + \left(\frac{dV}{dl}\right)_{l=l_0}(l - l_0) + \frac{1}{2!}\left(\frac{d^2V}{dl^2}\right)_{l=l_0}(l - l_0)^2 + \frac{1}{3!}\left(\frac{d^3V}{dl^3}\right)_{l=l_0}(l - l_0)^3 + \cdots \tag{5.23}$$

The first term in Equation 5.23 is a constant and depends upon where we choose the zero of energy. It is convenient to choose the zero of energy such that $V(l_0)$ equals zero and relate $V(l)$ to this convention. The second term on the right side of Equation 5.23 involves the quantity $(dV/dl)_{l=l_0}$. Because the point $l = l_0$ is the minimum of the potential energy curve, dV/dl vanishes there, so there is no linear term in the displacement in Equation 5.23. Note that dV/dl is essentially the force acting between the two nuclei, and the fact that dV/dl vanishes at $l = l_0$ means that the force acting between the nuclei is zero at this point. This is why $l = l_0$ is called the *equilibrium bond length.*

If we denote $l - l_0$ by x, $(d^2V/dl^2)_{l=l_0}$ by k, and $(d^3V/dl^3)_{l=l_0}$ by γ, Equation 5.23 becomes

$$\begin{aligned} V(x) &= \frac{1}{2}k(l - l_0)^2 + \frac{1}{6}\gamma(l - l_0)^3 + \cdots \\ &= \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \cdots \end{aligned} \tag{5.24}$$

If we restrict ourselves to small displacements, then x will be small and we can neglect the terms beyond the quadratic term in Equation 5.24, showing that the general potential energy function $V(l)$ can be approximated by a harmonic-oscillator potential. Note that the force constant is equal to the curvature of $V(l)$ at the minimum. We can consider corrections or extensions of the harmonic-oscillator model by the higher-order terms in Equation 5.24. These are called *anharmonic terms* and will be considered in Chapter 13.

EXAMPLE 5–2

An analytic expression that is a good approximation to an intermolecular potential energy curve is a *Morse potential*

$$V(l) = D(1 - e^{-\beta(l-l_0)})^2$$

First let $x = l - l_0$ so that we can write

$$V(x) = D(1 - e^{-\beta x})^2$$

where D and β are parameters that depend upon the molecule. The parameter D is the dissociation energy of the molecule measured from the minimum of $V(l)$ and β is a measure of the curvature of $V(l)$ at its minimum. Figure 5.6 shows $V(l)$ plotted against l for H_2. Derive a relation between the force constant and the parameters D and β.

SOLUTION: We now expand $V(x)$ about $x = 0$ (Equation 5.23), using

$$V(0) = 0 \qquad \left(\frac{dV}{dx}\right)_{x=0} = \{2D\beta(e^{-\beta x} - e^{-2\beta x})\}_{x=0} = 0$$

and

$$\left(\frac{d^2V}{dx^2}\right)_{x=0} = \{-2D\beta(\beta e^{-\beta x} - 2\beta e^{-2\beta x})\}_{x=0} = 2D\beta^2$$

Therefore, we can write

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

Comparing this result with Equation 5.11 gives

$$k = 2D\beta^2$$

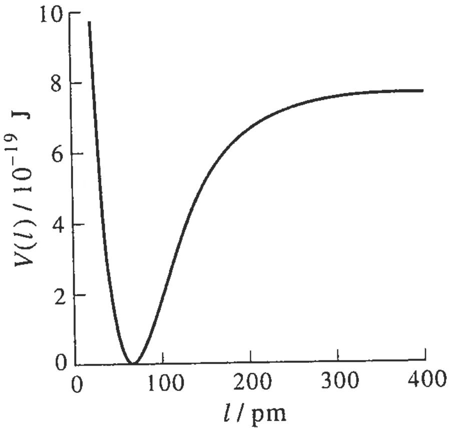

FIGURE 5.6
The Morse potential energy curve $V(l) = D(1 - e^{-\beta(l-l_0)})^2$ plotted against the internuclear displacement l for H_2. The values of the parameters for H_2 are $D = 7.61 \times 10^{-19}$ J, $\beta = 0.0193$ pm^{-1}, and $l_0 = 74.1$ pm.

5–4. The Energy Levels of a Quantum-Mechanical Harmonic Oscillator Are $E_v = \hbar\omega(v + \frac{1}{2})$ with $v = 0,\ 1,\ 2,\ \ldots$

The Schrödinger equation for a one-dimensional harmonic oscillator is

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{5.25}$$

with $V(x) = \frac{1}{2}kx^2$. Thus, we must solve the second-order differential equation

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}\left(E - \tfrac{1}{2}kx^2\right)\psi(x) = 0 \tag{5.26}$$

This differential equation, however, does not have constant coefficients, so we cannot use the method we developed in Section 2–2. In fact, when a differential equation does not have constant coefficients, there is no simple, general technique for solving it, and each case must be considered individually.

When Equation 5.26 is solved, well-behaved, finite solutions can be obtained only if the energy is restricted to the quantized values

$$\begin{aligned} E_v &= \hbar\left(\frac{k}{\mu}\right)^{1/2}\left(v + \tfrac{1}{2}\right) \\ &= \hbar\omega\left(v + \tfrac{1}{2}\right) = h\nu\left(v + \tfrac{1}{2}\right) \qquad v = 0,\ 1,\ 2,\ \ldots \end{aligned} \tag{5.27}$$

where

$$\omega = \left(\frac{k}{\mu}\right)^{1/2} \tag{5.28}$$

and

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \tag{5.29}$$

The energies are plotted in Figure 5.7. Note that the energy levels are equally spaced, with a separation $\hbar\omega$ or $h\nu$. This uniform spacing between energy levels is a property peculiar to the quadratic potential of a harmonic oscillator. Note also that the energy of the ground state, the state with $v = 0$, is $\frac{1}{2}h\nu$ and is not zero as the lowest classical energy is. This energy is called the *zero-point energy* of the harmonic oscillator and is a direct result of the Uncertainty Principle. The energy of a harmonic oscillator can be written in the form $(p^2/2\mu) + (kx^2/2)$, and so we see that a zero value for the energy would require that both p and x or, more precisely, the expectation values of $\hat{P}^2$ and $\hat{X}^2$ be simultaneously zero, in violation of the Uncertainty Principle.

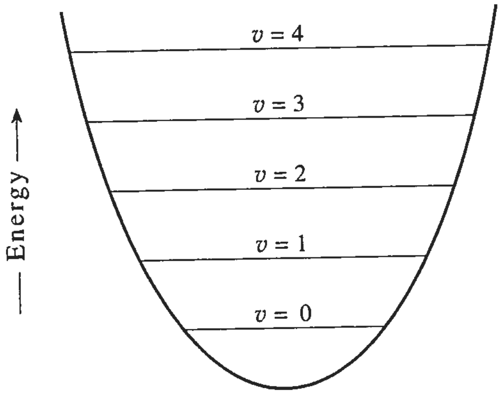

FIGURE 5.7
The energy levels of a quantum-mechanical harmonic oscillator.

5–5. The Harmonic Oscillator Accounts for the Infrared Spectrum of a Diatomic Molecule

We will discuss molecular spectroscopy in some detail in Chapter 13, but here we will discuss the spectroscopic predictions of a harmonic oscillator. If we model the potential energy function of a diatomic molecule as a harmonic oscillator, then according to Equation 5.27, the vibrational energy levels of the diatomic molecule are given by

$$E_v = \hbar \left(\frac{k}{\mu}\right)^{1/2} \left(v + \tfrac{1}{2}\right) \qquad v = 0,\ 1,\ 2,\ \ldots \tag{5.30}$$

A diatomic molecule can make a transition from one vibrational energy state to another by absorbing or emitting electromagnetic radiation whose observed frequency satisfies the Bohr frequency condition

$$\Delta E = h\nu_{\text{obs}} \tag{5.31}$$

We will prove in Chapter 13 that the harmonic-oscillator model allows transitions only between adjacent energy states, so that we have the condition that $\Delta v = \pm 1$. Such a condition is called a *selection rule*.

For absorption to occur, $\Delta v = +1$ and so

$$\Delta E = E_{v+1} - E_v = \hbar \left(\frac{k}{\mu}\right)^{1/2} \tag{5.32}$$

Thus, the observed frequency of the radiation absorbed is

$$\nu_{\text{obs}} = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \tag{5.33}$$

or

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

where the tilde indicates that the units are cm^{-1}. Furthermore, because successive energy states of a harmonic oscillator are separated by the same energy, ΔE is the same for all allowed transitions, so this model predicts that the spectrum consists of just one line whose frequency is given by Equation 5.34. This prediction is in good accord with experiment, and this line is called the *fundamental vibrational frequency*. For diatomic molecules, these lines occur at around $10^3\ \text{cm}^{-1}$, which is in the infrared region. Equation 5.34 enables us to determine force constants if the fundamental vibrational frequency is known. For example, for H^{35}Cl, $\tilde{\nu}_{\text{obs}}$ is $2.886 \times 10^3\ \text{cm}^{-1}$ and so, according to Equation 5.34, the force constant of H^{35}Cl is

$$\begin{aligned} k &= (2\pi c\tilde{\nu}_{\text{obs}})^2\mu \\ &= [2\pi(2.998 \times 10^8\ \text{m}\cdot\text{s}^{-1})(2.886 \times 10^3\ \text{cm}^{-1})(100\ \text{cm}\cdot\text{m}^{-1})]^2 \\ &\qquad \times \frac{(35.0\ \text{amu})(1.01\ \text{amu})}{(35.0 + 1.01)\ \text{amu}}(1.661 \times 10^{-27}\ \text{kg}\cdot\text{amu}^{-1}) \\ &= 4.78 \times 10^2\ \text{kg}\cdot\text{s}^{-2} = 4.78 \times 10^2\ \text{N}\cdot\text{m}^{-1} \end{aligned}$$

EXAMPLE 5–3

The infrared spectrum of $^{75}\text{Br}^{19}\text{F}$ consists of an intense line at $380\ \text{cm}^{-1}$. Calculate the force constant of $^{75}\text{Br}^{19}\text{F}$.

SOLUTION: The force constant is given by

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

The reduced mass is

$$\mu = \frac{(75.0\ \text{amu})(19.0\ \text{amu})}{(75.0 + 19.0)\ \text{amu}}(1.661 \times 10^{-27}\ \text{kg}\cdot\text{amu}^{-1}) = 2.52 \times 10^{-26}\ \text{kg}$$

and so

$$\begin{aligned} k &= [2\pi(2.998 \times 10^8\ \text{m}\cdot\text{s}^{-1})(380\ \text{cm}^{-1})(100\ \text{cm}\cdot\text{m}^{-1})]^2(2.52 \times 10^{-26}\ \text{kg}) \\ &= 129\ \text{kg}\cdot\text{s}^{-2} = 129\ \text{N}\cdot\text{m}^{-1} \end{aligned}$$

Force constants for diatomic molecules are of the order of $10^2\ \text{N}\cdot\text{m}^{-1}$. Table 5.1 lists the fundamental vibrational frequencies, force constants, and bond lengths of some diatomic molecules. We will also see in Chapter 13 that not only must $\Delta v = \pm 1$ in the harmonic-oscillator model but the dipole moment of the molecule must change as the

TABLE 5.1
The fundamental vibrational frequencies, the force constants, and bond lengths of some diatomic molecules

Molecule	$\tilde{\nu}/\text{cm}^{-1}$	$k/\text{N}\cdot\text{m}^{-1}$	Bond length/pm
H_2	4401	570	74.1
D_2	2990	527	74.1
$H^{35}Cl$	2886	478	127.5
$H^{79}Br$	2630	408	141.4
$H^{127}I$	2230	291	160.9
$^{35}Cl^{35}Cl$	554	319	198.8
$^{79}Br^{79}Br$	323	240	228.4
$^{127}I^{127}I$	213	170	266.7
$^{16}O^{16}O$	1556	1142	120.7
$^{14}N^{14}N$	2330	2243	109.4
$^{12}C^{16}O$	2143	1857	112.8
$^{14}N^{16}O$	1876	1550	115.1
$^{23}Na^{23}Na$	158	17	307.8
$^{23}Na^{35}Cl$	378	117	236.1
$^{39}K^{35}Cl$	278	84	266.7

molecule vibrates if the molecule is to absorb infrared radiation. Thus, the harmonic-oscillator model predicts that HCl absorbs in the infrared but N_2 does not. We will see that this prediction is in good agreement with experiment. There are, indeed, deviations from the harmonic-oscillator model, but we will see not only that they are fairly small but that we can systematically introduce corrections and extensions to account for them.

5–6. The Harmonic-Oscillator Wave Functions Involve Hermite Polynomials

The wave functions corresponding to the E_v for a harmonic oscillator are nondegenerate and are given by

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

where

$$\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2} \tag{5.36}$$

TABLE 5.2
The first few Hermite polynomials.

$H_0(\xi) = 1$	$H_1(\xi) = 2\xi$
$H_2(\xi) = 4\xi^2 - 2$	$H_3(\xi) = 8\xi^3 - 12\xi$
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$	$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$

The normalization constant N_v is

$$N_v = \frac{1}{(2^v v!)^{1/2}} \left(\frac{\alpha}{\pi}\right)^{1/4} \tag{5.37}$$

and the $H_v(\alpha^{1/2}x)$ are polynomials called *Hermite polynomials*. The first few Hermite polynomials are listed in Table 5.2. Note that $H_v(\xi)$ is a vth-degree polynomial in ξ. The first few harmonic oscillator wave functions are listed in Table 5.3 and plotted in Figure 5.8.

Although we have not solved the Shrödinger equation for a harmonic oscillator (Equation 5.26), we can at least show that the functions given by Equation 5.35 are solutions. For example, let's consider $\psi_0(x)$, which according to Table 5.3 is

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

Substitution of this equation into Equation 5.26 with $E_0 = \frac{1}{2}\hbar\omega$ yields

$$\frac{d^2\psi_0}{dx^2} + \frac{2\mu}{\hbar^2}\left(E_0 - \frac{1}{2}kx^2\right)\psi_0(x) = 0$$

$$\left(\frac{\alpha}{\pi}\right)^{1/4}(\alpha^2x^2e^{-\alpha x^2/2} - \alpha e^{-\alpha x^2/2}) + \frac{2\mu}{\hbar^2}\left(\frac{\hbar\omega}{2} - \frac{kx^2}{2}\right)\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \overset{?}{=} 0$$

or

$$(\alpha^2x^2 - \alpha) + \left(\frac{\mu\omega}{\hbar} - \frac{\mu k}{\hbar^2}x^2\right) \overset{?}{=} 0$$

TABLE 5.3
The first few harmonic-oscillator wave functions, Equation 5.35. The parameter $\alpha = (k\mu)^{1/2}/\hbar$.

$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$	$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$
$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}$	$\psi_3(x) = \left(\frac{\alpha^3}{9\pi}\right)^{1/4}(2\alpha x^3 - 3x)e^{-\alpha x^2/2}$

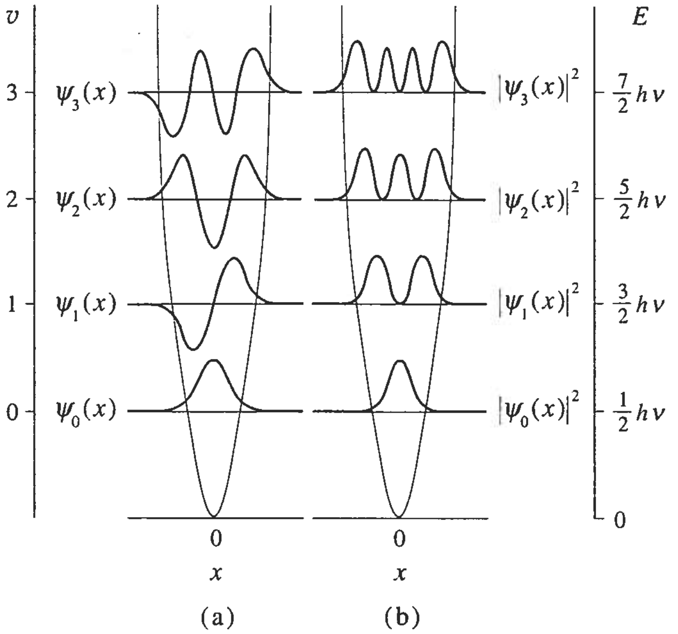

FIGURE 5.8
(a) The normalized harmonic-oscillator wave functions. (b) The probability densities for a harmonic oscillator.

Using the relations $\alpha = (k\mu/\hbar^2)^{1/2}$ and $\omega = (k/\mu)^{1/2}$, we see that everything cancels on the left side of the above expression. Thus, $\psi_0(x)$ is a solution to Equation 5.26. Problem 5–15 involves proving explicitly that $\psi_1(x)$ and $\psi_2(x)$ are solutions of Equation 5.26.

We can also show explicitly that the $\psi_v(x)$ are normalized, or that N_v given by Equation 5.37 is the normalization constant.

EXAMPLE 5–4
Show that $\psi_0(x)$ and $\psi_1(x)$ are normalized.

SOLUTION: According to Table 5.3,

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \quad \text{and} \quad \psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$$

Then

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

and

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

The integrals here are given on the inside cover of this book and are evaluated in Problem 5–17.

We can appeal to the general results of Chapter 4 to argue that the harmonic-oscillator wave functions are orthogonal. The energy eigenvalues are nondegenerate, so we have that

$$\int_{-\infty}^{\infty} \psi_v(x)\psi_{v'}(x)dx = 0 \qquad v \neq v'$$

or, more explicitly, that

$$\int_{-\infty}^{\infty} H_v(\alpha^{1/2}x)H_{v'}(\alpha^{1/2}x)e^{-\alpha x^2}dx = 0 \qquad v \neq v'$$

EXAMPLE 5–5

Show explicitly that $\psi_0(x)$ and $\psi_1(x)$ for the harmonic oscillator are orthogonal.

SOLUTION:

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \quad \text{and} \quad \psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}$$

so

$$\int_{-\infty}^{\infty} \psi_1(x)\psi_0(x)dx = \left(\frac{2\alpha^2}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} xe^{-\alpha x^2}dx = 0$$

because the integrand is an odd function of x.

Problem 5–16 has you verify that the harmonic oscillator wave functions are orthogonal for a few other cases.

5–7. Hermite Polynomials Are Either Even or Odd Functions

Recall from MathChapter B that an even function is a function that satisfies

$$f(x) = f(-x) \qquad \text{(even)} \tag{5.38}$$

and an odd function is one that satisfies

$$f(x) = -f(-x) \qquad \text{(odd)} \tag{5.39}$$

EXAMPLE 5–6

Show that the Hermite polynomials $H_v(\xi)$ are even if v is even and odd if v is odd.

SOLUTION: Using Table 5.2,

$H_0(\xi) = 1$ is even.

$H_1(\xi) = 2\xi = -2(-\xi) = -H_1(-\xi)$ and so is odd.

$H_2(\xi) = 4\xi^2 - 2 = 4(-\xi)^2 - 2 = H_2(-\xi)$ is even.

$H_3(\xi) = 8\xi^3 - 12\xi = -[8(-\xi)^3 - 12(-\xi)] = -H_3(-\xi)$ and so is odd.

Recall that if $f(x)$ is an odd function, then

$$\int_{-A}^{A} f(x)dx = 0 \qquad f(x) \text{ odd} \tag{5.40}$$

because the areas from $-A$ to 0 and 0 to A cancel. According to Equation 5.35, the harmonic-oscillator wave functions are

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

Because the $\psi_v(x)$ are even when v is an even integer and odd when v is an odd integer, $\psi_v^2(x)$ is an even function for any value of v. Therefore, $x\psi_v^2(x)$ is an odd function, and according to Equation 5.40, then,

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_v(x)x\psi_v(x)dx = 0 \tag{5.41}$$

Thus, the average displacement of a harmonic oscillator is zero for all the quantum states of a harmonic oscillator, or the average internuclear separation is the equilibrium bond length l_0.

The average momentum is given by

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_v(x)\left(-i\hbar\frac{d}{dx}\right)\psi_v(x)dx \tag{5.42}$$

The derivative of an odd (even) function is even (odd), so this integral vanishes because the integrand is the product of an odd and even function and hence is overall odd. Thus, we have that $\langle p \rangle = 0$ for a harmonic operator.

5–8. The Energy Levels of a Rigid Rotator Are $E = \hbar^2 J(J+1)/2I$

In this section we will discuss a simple model for a rotating diatomic molecule. The model consists of two point masses m_1 and m_2 at fixed distances r_1 and r_2 from their center of mass (cf. Figure 5.9). Because the distance between the two masses is fixed, this model is referred to as the *rigid-rotator model*. Even though a diatomic molecule

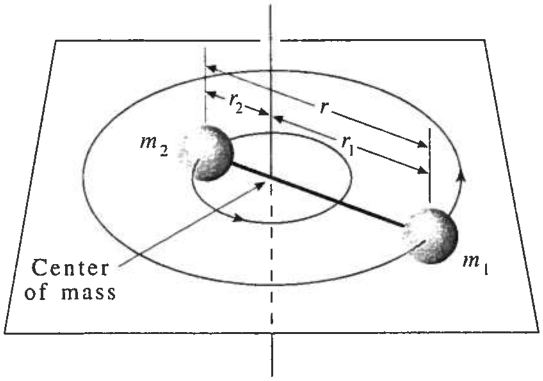

FIGURE 5.9
Two masses m_1 and m_2 shown rotating about their center of mass.

vibrates as it rotates, the vibrational amplitude is small compared with the bond length, so considering the bond length fixed is a good approximation (see Problem 5–22).

Let the molecule rotate about its center of mass at a frequency of ν_{rot} cycles per second. The velocities of the two masses are $v_1 = 2\pi r_1 \nu_{\text{rot}}$ and $v_2 = 2\pi r_2 \nu_{\text{rot}}$, which we write as $v_1 = r_1\omega$ and $v_2 = r_2\omega$, where ω (radians per second) $= 2\pi\nu_{\text{rot}}$ and is called the *angular speed* (Section 4–2). The kinetic energy of the rigid rotator is

$$\begin{aligned} K &= \tfrac{1}{2}m_1v_1^2 + \tfrac{1}{2}m_2v_2^2 = \tfrac{1}{2}(m_1r_1^2 + m_2r_2^2)\omega^2 \\ &= \tfrac{1}{2}I\omega^2 \end{aligned} \tag{5.43}$$

where I, the *moment of inertia*, is given by

$$I = m_1r_1^2 + m_2r_2^2 \tag{5.44}$$

Using the fact that the location of the center of mass is given by $m_1r_1 = m_2r_2$, the moment of inertia can be rewritten as (Problem 5–29)

$$I = \mu r^2 \tag{5.45}$$

where $r = r_1 + r_2$ (the fixed separation of the two masses) and μ is the *reduced mass* (Section 5–2). In Section 4–2, we discussed a single body of mass m rotating at a distance r from a fixed center. In that case, the moment of inertia, I, was equal to mr^2. By comparing Equation 5.45 with this result, we may consider Equation 5.45 to be an equation for the moment of inertia of a single body of mass μ rotating at a distance r from a fixed center. Thus, we have transformed a two-body problem into an equivalent one-body problem, just as we did for a harmonic oscillator in Section 5–2.

Following Equations 4.4 and 4.6, the angular momentum L is

$$L = I\omega \tag{5.46}$$

and the kinetic energy is

$$K = \frac{L^2}{2I} \tag{5.47}$$

There is no potential energy term because in the absence of any external forces (e.g., electric or magnetic), the energy of the molecule does not depend on its orientation in space. The Hamiltonian operator of a rigid rotator is therefore just the kinetic energy operator, and using the operator $\hat{K}$ given in Table 4.1 and the correspondences between linear and rotating systems given in Table 4.2, we can write the Hamiltonian operator of a rigid rotator as

$$\hat{H} = \hat{K} = -\frac{\hbar^2}{2\mu}\nabla^2 \qquad (r \text{ constant}) \tag{5.48}$$

where ∇^2 is the Laplacian operator. We encountered ∇^2 in Cartesian coordinates in Section 3–7, but if the system has a natural center of symmetry, such as one particle revolving around one fixed at the origin, then using spherical coordinates (MathChapter D) is much more convenient. Therefore, we must convert ∇^2 from Cartesian coordinates to spherical coordinates. This conversion involves a tedious exercise in the chain rule of partial differentiation, which is best left as problems (see Problems 5–30 through 5–32). The final result is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta} \tag{5.49}$$

The rigid rotator is a special case where r is a constant, so Equation 5.49 becomes

$$\nabla^2 = \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \qquad (r \text{ constant}) \tag{5.50}$$

If we use this result in Equation 5.48, we obtain

$$\hat{H} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right] \tag{5.51}$$

Because $\hat{H} = \hat{L}^2/2I$, we see we can make the correspondence

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

Note that the square of the angular momentum is a naturally occurring operator in quantum mechanics. Both θ and ϕ are unitless, so Equation 5.52 shows that the natural units of angular momentum are $\hbar$ for atomic and molecular systems. We will make use of this fact later.

The orientation of a linear rigid rotator is completely specified by the two angles θ and ϕ, so rigid-rotator wave functions depend upon only these two variables. The rigid-rotator wave functions are customarily denoted by $Y(\theta, \phi)$, so the Schrödinger equation for a rigid rotator reads

$$\hat{H} Y(\theta, \phi) = E Y(\theta, \phi)$$

or

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]Y(\theta,\phi)=EY(\theta,\phi) \tag{5.53}$$

If we multiply Equation 5.53 by $\sin^2\theta$ and let

$$\beta = \frac{2IE}{\hbar^2} \tag{5.54}$$

we find the partial differential equation

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}+(\beta\sin^2\theta)Y=0 \tag{5.55}$$

The solutions to Equation 5.55 are the rigid-rotator wave functions, which we won't need in this chapter. We will encounter Equation 5.55 when we solve the Schrödinger equation for the hydrogen atom in Chapter 6. We therefore defer discussion of the rigid-rotator wave functions until we discuss the hydrogen atom in detail. Nevertheless, you might be interested to know that the solutions to Equation 5.55 are very closely related to the s, p, d, and f orbitals of a hydrogen atom.

When we solve Equation 5.55, it turns out naturally that β, given by Equation 5.54, must obey the condition

$$\beta = J(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots \tag{5.56}$$

Using the definition of β (Equation 5.54), Equation 5.56 is equivalent to

$$E_J = \frac{\hbar^2}{2I}J(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots \tag{5.57}$$

Once again, we obtain a set of discrete energy levels. In addition to the allowed energies given by Equation 5.57, we also find that each energy level has a degeneracy g_J given by $g_J = 2J + 1$.

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5–9. The Rigid Rotator Is a Model for a Rotating Diatomic Molecule

The allowed energies of a rigid rotator are given by Equation 5.57. We will prove in Chapter 13 that electromagnetic radiation can cause a rigid rotator to undergo transitions from one state to another, and, in particular, we will prove that the selection rule for the rigid rotator says that transitions are allowed only between adjacent states or that

$$\Delta J = \pm 1 \tag{5.58}$$

In addition to the requirement that $\Delta J = \pm 1$, the molecule must also possess a permanent dipole moment to absorb electromagnetic radiation. Thus, HCl has a rotational spectrum, but N_2 does not. In the case of absorption of electromagnetic radiation, the molecule goes from a state with a quantum number J to one with $J + 1$. The energy difference, then, is

$$\begin{aligned} \Delta E = E_{J+1} - E_J &= \frac{\hbar^2}{2I}[(J+1)(J+2) - J(J+1)] \\ &= \frac{\hbar^2}{I}(J+1) = \frac{h^2}{4\pi^2 I}(J+1) \end{aligned} \tag{5.59}$$

The energy levels and the absorption transitions are shown in Figure 5.10.

Using the Bohr frequency condition $\Delta E = h\nu$, the frequencies at which the absorption transitions occur are

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

The reduced mass of a diatomic molecule is typically around 10^{-25} to 10^{-26} kg, and a typical bond distance is approximately 10^{-10} m (100 pm), so the moment of inertia of a diatomic molecule typically ranges from 10^{-45} to 10^{-46} kg·m^2. Substituting $I = 5 \times 10^{-46}$ kg·m^2 into Equation 5.60 gives that the absorption frequencies are about 2×10^{10} to 10^{11} Hz (cf. Problem 5–33). By referring to Figure 1.11 in Problem 1–1, we see that these frequencies lie in the microwave region. Consequently, rotational transitions of diatomic molecules occur in the microwave region, and the direct study of rotational transitions in molecules is called *microwave spectroscopy*.

It is common practice in microwave spectroscopy to write Equation 5.60 as

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

where

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

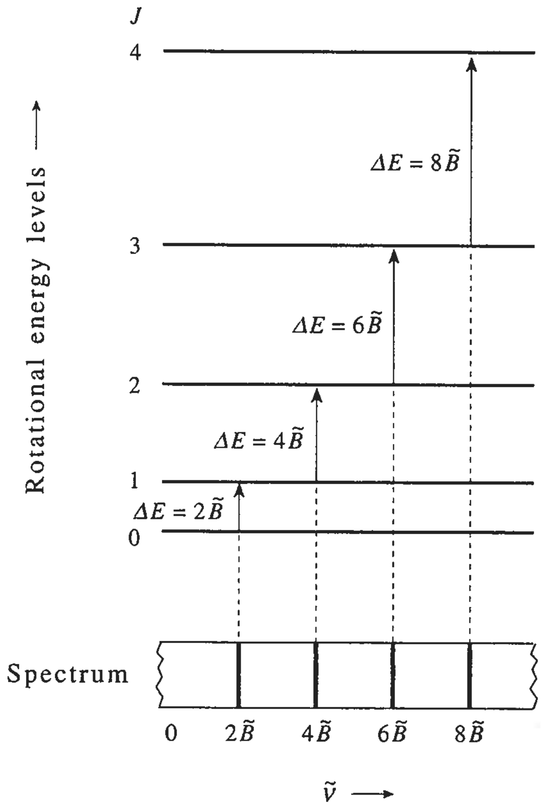


FIGURE 5.10
The energy levels and absorption transitions of a rigid rotator. The absorption transitions occur between adjacent levels, so the absorption spectrum shown below the energy levels consists of a series of equally spaced lines. The quantity $\tilde{B}$ is $h/8\pi^2cI$ (Equation 5.64).

is called the *rotational constant* of the molecule. Also, the transition frequency is commonly expressed in terms of wave numbers (cm^{-1}) rather than hertz (Hz). If we use the relation $\tilde{\nu} = \nu/c$, then Equation 5.61 becomes

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

where $\tilde{B}$ is the rotational constant expressed in units of wave numbers

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

From either Equation 5.61 or 5.63, we see that the rigid-rotator model predicts that the microwave spectrum of a diatomic molecule consists of a series of equally spaced lines with a separation of $2B$ Hz or $2\tilde{B}$ cm^{-1} as shown in Figure 5.10. From the separation between the absorption frequencies, we can determine the rotational constant and hence the moment of inertia of the molecule. Furthermore, because $I = \mu r^2$, where r

is the internuclear distance or bond length, we can determine the bond length given the transition frequencies. This procedure is illustrated in Example 5–7.

EXAMPLE 5–7

To a good approximation, the microwave spectrum of $H^{35}Cl$ consists of a series of equally spaced lines, separated by 6.26×10^{11} Hz. Calculate the bond length of $H^{35}Cl$.

SOLUTION: According to Equation 5.61, the spacing of the lines in the microwave spectrum of $H^{35}Cl$ is given by

$$2B = \frac{h}{4\pi^2 I}$$

and so

$$\frac{h}{4\pi^2 I} = 6.26 \times 10^{11}\ \text{Hz}$$

Solving this equation for I, we have

$$I = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{4\pi^2(6.26 \times 10^{11}\ \text{s}^{-1})} = 2.68 \times 10^{-47}\ \text{kg}\cdot\text{m}^2$$

The reduced mass of $H^{35}Cl$ is

$$\mu = \frac{(1.01\ \text{amu})(35.0\ \text{amu})}{36.0\ \text{amu}}(1.661 \times 10^{-27}\ \text{kg}\cdot\text{amu}^{-1}) = 1.63 \times 10^{-27}\ \text{kg}$$

Using the fact that $I = \mu r^2$, we obtain

$$r = \left(\frac{2.68 \times 10^{-47}\ \text{kg}\cdot\text{m}^2}{1.63 \times 10^{-27}\ \text{kg}}\right)^{1/2} = 1.28 \times 10^{-10}\ \text{m} = 128\ \text{pm}$$

Problems 5–34 and 5–35 give other examples of the determination of bond lengths from microwave data.

A diatomic molecule is not truly a rigid rotator, because it simultaneously vibrates, however small the amplitude. Consequently, we might expect that although the microwave spectrum of a diatomic molecule consists of a series of lines, their separation is not *exactly* constant. In Chapter 13, we will learn how to correct for the fact that the bond is not exactly rigid.

Problems

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.

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

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$\cdot$s^{-1} or $\nu = \omega/2\pi$ cycle$\cdot$s^{-1}. What is the period of the oscillations; that is, how long does it take to undergo one cycle?

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 $\langle K\rangle = \langle V\rangle$.

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

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

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

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?

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

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).

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.

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.

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

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

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 $\tilde{\nu}\tilde{x}$.

5-13. In the infrared spectrum of $H^{79}Br$, there is an intense line at 2630 cm^{-1}. Calculate the force constant of $H^{79}Br$ and the period of vibration of $H^{79}Br$.

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

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

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).

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

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

Now convert to plane polar coordinates, letting

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

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.

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.

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

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.

5-21. Show that

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

for a harmonic oscillator.

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

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 $v = 1$.

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

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

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

and

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

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

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.

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.

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

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

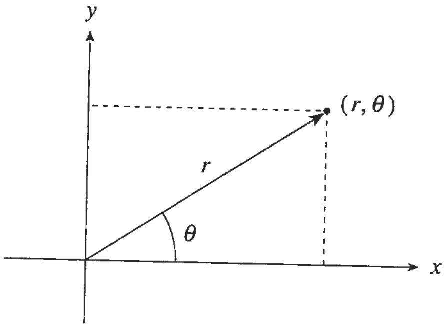
Show that $\hat{R}$ is linear and that it commutes with $\hat{H}$. Show also that the eigenvalues of $\hat{R}$ are ± 1. What are its eigenfunctions? Show that the harmonic-oscillator wave functions are eigenfunctions of $\hat{R}$. Note that they are eigenfunctions of both $\hat{H}$ and $\hat{R}$. What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

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.

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.

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

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



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.

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.

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

5-33. Show that rotational transitions of a diatomic molecule occur in the microwave region or the 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 $H^{79}Br$.

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.

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

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

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

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

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

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

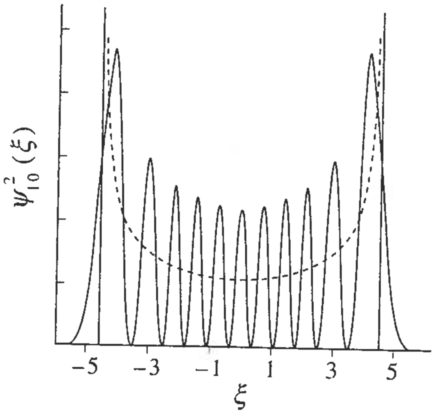


FIGURE 5.11
The probability distribution function of a harmonic oscillator in the $v = 10$ state. The dashed line is that for a classical harmonic oscillator with the same energy. The vertical lines at $\xi \approx \pm 4.6$ represents the extreme limits of the classical harmonic motion.

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.

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?

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

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

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.

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

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

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.

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

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

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 $v = 0, 1, 2, \ldots$.

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 $\hat{a}_+$.

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?

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}.

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?

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

PHYSICAL CHEMISTRY

A MOLECULAR APPROACH

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