Chapter 24: The Quantum Mechanics of Rotation and Vibration

Do molecular rotation and vibration have zero point energies? What happens to rotational and vibrational motions at absolute zero?

The molecular degrees of freedom include translation, rotation, vibration, and electronic energies. The particle in a box is a model for the translational degree of freedom. We now consider rotation and vibration. The rotational and vibrational energies of molecules are quantized. The energies of the quantum levels are determined by molecular structure, through the bond lengths, angles, and bond strengths. The energy level spacings are a sensitive measure of molecular structure and are experimentally determined using spectroscopy. In this way, light absorption and emission are primary tools for experimental determination of molecular structure. The harmonic oscillator is a useful model for molecular vibration. The rigid rotor is a useful model for molecular rotation. The rigid rotor is a good introduction to the theory of angular momentum. The theory of angular momentum is integral to atomic and molecular structure theory. The harmonic oscillator and rigid rotor are good examples of the applications of the postulates of quantum mechanics. Understanding the quantization of vibration and rotation help us learn how to think quantum mechanically.

   The rotation and low frequency vibrations of molecules contribute to the heat capacity, internal energy, enthalpy, Helmholtz energy, and Gibbs energy. The Gibbs energy determines the thermodynamic force for chemical change at constant temperature and pressure, $\Delta_r G° = –RT \ln K_p$. The conclusion is that rotation and vibration play a role in determining the extent of chemical reactions. Therefore, molecular vibration and rotation have an effect on structure-function relationships.

   The harmonic oscillator follows directly from our treatment of the particle in a box, so we begin with the harmonic oscillator, after a brief review of the classical treatment of vibration.

24.1 A Brief Review of Classical Mechanics: Vibration

The fundamental vibration frequency of a single mass m suspended by a spring with force constant k is $v_o = 1/2\pi \sqrt{k/m}$, Eq. 8.13.11. The fundamental vibration frequency of a diatomic molecule is expressible in the same functional form. Consider a diatomic molecule with bond length r and atomic masses m_1 and m_2. The center of mass of a diatomic molecule is the "balance point," Figure 24.1.1, where r_1 is the distance from mass m_1 to the center of mass and r_2 is the distance from mass m_2 to the center of mass:

$$m_1 r_1 = m_2 r_2 \qquad\qquad 24.1.1$$

(a). vibration   (b). rotation

Figure 24.1.1: The center of mass of a molecule defines the origin for vibration and rotation. The center of mass, cm, is closer to the heavier atom than the lighter atom.

Translation describes the motion of the center of mass. The bond length is given by the sum, $r = r_1 + r_2$. The distances to the center of mass can be related to the bond length. Adding $m_2 r_1$ to both sides of Eq. 24.1.1 gives:

$$m_1 r_1 + m_2 r_1 = m_2 r_2 + m_2 r_1 \qquad\qquad 24.1.2$$

Gathering common factors gives $(m_1 + m_2)r_1 = m_2(r_1 + r_2) = m_2 r$ and then solving for r_1 gives:

$$r_1 = \frac{m_2}{m_1 + m_2} r \qquad\qquad 24.1.3$$

Using parallel steps, adding $m_1 r_2$ to both sides of Eq. 24.1.1 gives for r_2:

$$r_2 = \frac{m_1}{m_1 + m_2} r \qquad\qquad 24.1.4$$

The last two equations show that r_1 and r_2 are mass weighted fractions of the full bond length. If m_2 is larger, then r_1 is longer to achieve equal leverage.

The kinetic energy of a diatomic molecule is given by the sum of the kinetic energies of the two atoms, with reference to the center of mass:

$$E_k = \tfrac{1}{2}\, m_1 \left(\frac{dr_1}{dt}\right)^2 + \tfrac{1}{2}\, m_2 \left(\frac{dr_2}{dt}\right)^2 \qquad\qquad \text{(diatomic)} \qquad 24.1.5$$

However, r_1 and r_2 are related to the bond length by Eqs. 24.1.3 and 24.1.4:

$$E_k = \tfrac{1}{2}\, \frac{m_1 m_2^2}{(m_1 + m_2)^2}\left(\frac{dr}{dt}\right)^2 + \tfrac{1}{2}\, \frac{m_1^2 m_2}{(m_1 + m_2)^2}\left(\frac{dr}{dt}\right)^2 \qquad\qquad \text{(diatomic)} \qquad 24.1.6$$

Collecting terms gives:

$$E_k = \tfrac{1}{2}\, \frac{m_1 m_2^2 + m_1^2 m_2}{(m_1 + m_2)^2}\left(\frac{dr}{dt}\right)^2 = \tfrac{1}{2}\, \frac{m_1 m_2 (m_2 + m_1)}{(m_1 + m_2)^2}\left(\frac{dr}{dt}\right)^2 \qquad\qquad \text{(diatomic)} \qquad 24.1.7$$

Canceling the common factor in the numerator and denominator gives the kinetic energy for the diatomic oscillator as:

$$E_k = \tfrac{1}{2}\, \frac{m_1 m_2}{m_1 + m_2}\left(\frac{dr}{dt}\right)^2 = \tfrac{1}{2}\, \mu \left(\frac{dr}{dt}\right)^2 \qquad\qquad \text{(diatomic)} \qquad 24.1.8$$

where μ is the **reduced mass** of the diatomic molecule:

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \qquad\qquad \text{(diatomic)} \qquad 24.1.9$$

The reduced mass is the effective vibrational mass of the diatomic molecule. The extension is defined as the deviation of the bond length from the equilibrium value: $x \equiv r - r_o$. The velocity is related to the extension through:

$$\frac{dx}{dt} = \frac{d(r - r_o)}{dt} = \frac{dr}{dt} \qquad\qquad 24.1.10$$

since the equilibrium bond length is a constant. The kinetic energy of vibration of a diatomic molecule then reduces to the same form as for a single mass, with m replaced by μ:

$$E_k = \frac{1}{2}\,\mu\left(\frac{dx}{dt}\right)^2 \qquad\qquad\qquad\qquad\qquad \text{(diatomic)} \qquad 24.1.11$$

The Vibrational Restoring Force is Proportional to the Extension: The force for a harmonic oscillator is given by Hooke's Law, $F(x) = -kx$. The corresponding potential energy is $V(x) = \frac{1}{2}\,kx^2$. The solutions to the classical harmonic oscillator are sinusoidal with frequency ν_o; please review Addendum 8.13. The fundamental vibration frequency for a diatomic harmonic oscillator is given by Eq. 8.13.11:

$$\nu_o = \frac{1}{2\pi}\sqrt{k/\mu} \qquad\qquad \omega_o = 2\pi\nu_o \qquad \omega_o = \sqrt{k/\mu} \qquad\qquad \text{(harmonic)} \qquad 24.1.12$$

For larger molecules, normal mode analysis provides the reduced mass and fundamental vibration frequency for each normal mode (Section 8.11).

24.2 Vibration

The Harmonic Oscillator is a Model for Molecular Vibrations: We begin by considering the ground state of the harmonic oscillator. Subsequently, we will build the excited states, based on the ground state.
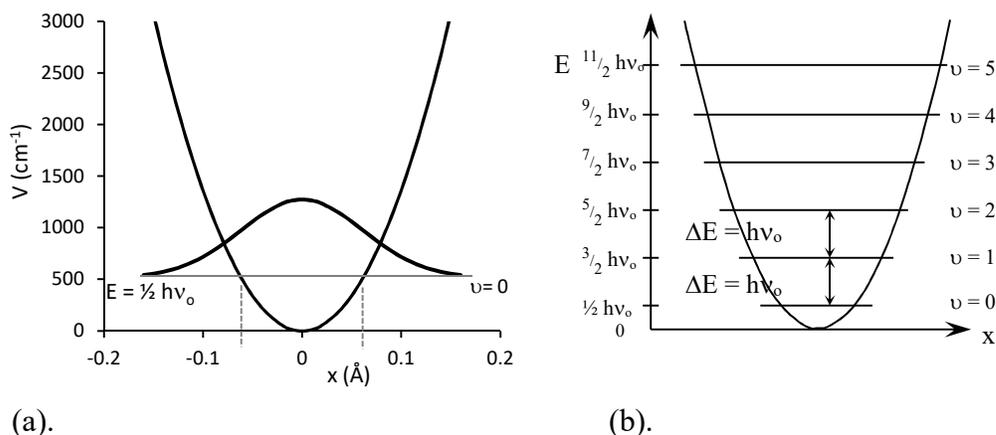
Figure 24.2.1: (a). A Gaussian wave function has high curvature in the middle of the energy well, were the potential energy is at minimum. The wave function asymptotically approaches zero more gradually than the particle in a box wave function, tunneling past the classical turning points (dotted lines). (b). The energy states for the harmonic oscillator are equally spaced with $\Delta E = h\nu_o$.

The Schrödinger equation for one-dimensional problems always takes the same general form, Eq. 23.3.1. The potential energy function for the harmonic oscillator is purely multiplicative, so the quantum operator is equivalent to the classical potential, Exercise 23.7.3:

$$\hat{V}(x) = \frac{1}{2}\,kx^2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 24.2.1$$

The Schrödinger equation for the one-dimensional harmonic oscillator is then:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi + \tfrac{1}{2}\,k x^2\,\Psi = E\Psi \qquad\qquad 24.2.2$$

The parabolic potential is similar to the particle in a box, but the potential energy increases gradually at the extremes, Figure 24.2.1. A good guess for a wave function is a form with large curvature in the middle of the potential energy well and a gradual approach to zero at the extremes. A Gaussian wave function is an appropriate trial wave function for the ground state:

$$\Psi_o(x) = N_o\, e^{-\frac{1}{2}\alpha^2 x^2} \qquad\qquad 24.2.3$$

with α as a constant and N_o the normalization. The first derivative is given by:

$$\frac{d\Psi_o}{dx} = N_o(-\tfrac{1}{2}\,\alpha^2)(2x)\,e^{-\frac{1}{2}\alpha^2 x^2} = -\,N_o\,\alpha^2 x\,e^{-\frac{1}{2}\alpha^2 x^2} = -\,\alpha^2 x\Psi_o \qquad\qquad 24.2.5$$

(see *General Pattern* ℘5 for an introduction to the Gaussian distribution and its derivatives). The second derivative is obtained using the product rule for $x\Psi_o$ and Eq. 24.2.5:

$$\begin{aligned}\frac{d^2\Psi_o}{dx^2} &= -\,\alpha^2\left[x\,\frac{d\Psi_o}{dx} + \Psi_o\,\frac{dx}{dx}\right]\\ &= -\,\alpha^2\,[x(-\,\alpha^2 x\,)\Psi_o + \Psi_o]\\ &= \alpha^4 x^2\,\Psi_o - \alpha^2\,\Psi_o\end{aligned} \qquad\qquad 24.2.6$$

Substituting the second derivative into Eq. 24.2.2 gives:

$$-\frac{\hbar^2}{2m}(\alpha^4 x^2\,\Psi_o - \alpha^2\,\Psi_o) + \tfrac{1}{2}\,k x^2\Psi_o = E\Psi_o \qquad\qquad 24.2.7$$

All the operators have been applied and only functions remain, so we no longer need to worry about the order of operations. Dividing both sides of the equation by the wave function gives:

$$-\frac{\hbar^2}{2m}\,\alpha^4 x^2 + \frac{\hbar^2}{2m}\,\alpha^2 + \tfrac{1}{2}k x^2 = E \qquad\qquad 24.2.8$$

The range for the displacement is $-\infty \le x \le \infty$. The only way for the left-side of the last equation to always equal a constant is for the terms in x to cancel, giving:

$$E = \frac{\hbar^2\alpha^2}{2m} \qquad\text{or}\qquad \alpha = \frac{\sqrt{2mE}}{\hbar} \qquad\qquad 24.2.9$$

(Notice that we used similar reasoning for the 3D-particle in a box, Eq. 23.6.9). The energy is in a familiar form; for a free particle and for a particle in a box the energy is $E = \hbar^2 k^2/2m$, Eq. 23.4.4. This similarity suggests that the Gaussian form is appropriate for the harmonic oscillator. However, the terms in x must cancel:

$$-\frac{\hbar^2}{2m}\,\alpha^4 x^2 + \tfrac{1}{2}\,k x^2 = 0 \qquad\text{or}\qquad -\frac{\hbar^2}{m}\,\alpha^4 + k = 0 \qquad\qquad 24.2.10$$

This last equation determines the value of α:

$$\alpha^4 = \frac{mk}{\hbar^2} \qquad\text{or}\qquad \alpha^2 = \frac{\sqrt{mk}}{\hbar} = \frac{m}{\hbar}\sqrt{k/m} = \frac{m\omega_o}{\hbar} \qquad\qquad 24.2.11$$

In this last equation, we have rearranged to show the relationship of α to the fundamental vibration frequency, Eq. 24.1.12. Substituting α back into the energy, Eq. 24.2.9 gives:

$$E_o = \frac{\hbar^2\alpha^2}{2m} = \frac{1}{2}\,\hbar\omega_o = \frac{1}{2}\,\frac{h}{2\pi}\,2\pi\nu_o = \frac{1}{2}\,h\nu_o \qquad\qquad 24.2.12$$

The energy is quantized; the energy of the ground state is a fixed value, which is determined by the force constant and mass of the oscillator. The harmonic oscillator has a zero-point energy; the ground state energy is non-zero. At absolute zero Kelvin, the molecule still vibrates. The classical turning points occur when the total energy is equal to the potential energy, $E = V(x)$. However, the quantum mechanical wave function has significant intensity beyond the classical turning points, Figure 24.2.1. The wave function tunnels into the barrier at each extreme, beyond the classical turning points. The quantum mechanical harmonic oscillator has strikingly different behavior than the classical oscillator. However, the fundamental vibration frequency is the same for quantum and classical problems.

The final wave function must be normalized, $\int_{-\infty}^{\infty} \Psi^2(x)\,dx = 1$. We will leave the normalization integral as a homework problem. The normalization constant is:

$$N_o = \left(\frac{\alpha^2}{\pi}\right)^{1/4} \qquad\qquad 24.2.13$$

Using Eq. 24.2.11 for α^2 gives the final wave function as:

$$\Psi(x) = \left(\frac{m\omega_o}{\hbar\pi}\right)^{1/4} e^{-\frac{m\omega_o}{2\hbar}x^2} \qquad\qquad 24.2.14$$

We now need to consider excited states of the oscillator.

The Harmonic Oscillator is Quantized: The energy levels for the harmonic oscillator are quantized with quantum number υ, which ranges from $\upsilon = 0, 1, 2, \ldots, \infty$:

$$E_\upsilon = h\nu_o(\upsilon + \tfrac{1}{2}) \qquad\qquad 24.2.15$$

This result will be proved in Sec. 24.7. The energy states are equally spaced, which we can determine by considering any two adjacent energy levels, υ and $\upsilon+1$:

$$\Delta E = E_{\upsilon+1} - E_\upsilon = h\nu_o(\upsilon + 1 + \tfrac{1}{2}) - h\nu_o(\upsilon + \tfrac{1}{2}) = h\nu_o \qquad\qquad 24.2.16$$

The absorption of light results in transitions between adjacent vibrational energy levels, Figure 24.2.1b.

Example 24.2.1: *Bond Force Constants*
The fundamental vibrational transition in the infrared spectrum of the diatomic molecule $^{16}O^{19}F$ is 1029. cm^{-1} (Figure 24.2.1a). Calculate the bond force constant.

Answer: Given $\tilde{\nu}_o = 1029.$ cm^{-1} with $\nu_o = c\tilde{\nu}_o$, the reduced mass using mono-isotopic masses is:

$$\mu = \frac{(15.9949 \text{ g mol}^{-1})(18.9984 \text{ g mol}^{-1})}{(15.9949 \text{ g mol}^{-1} + 18.9984 \text{ g mol}^{-1})} \, (1 \text{ mol}/6.02214 \times 10^{23})(1 \text{ kg}/1000 \text{ g})$$

$$= 1.44199 \times 10^{-26} \text{ kg}$$

Solving Eq. 24.1.12 for the force constant gives: $k = 4\pi^2 \tilde{v}_o^2 c^2 \mu = 541.8 \text{ N m}^{-1}$

This result is typical for a single covalent bond (draw the Lewis dot structure for OF).

Excited State Wave Functions are Built from the Ground State Wave Function: The ground state, Eq. 24.2.3, has no nodes. Higher energy states have larger curvature, requiring nodes. The quantum number υ gives the number of nodes, Figure 24.2.2. The nodal properties can be introduced into excited state wave functions by multiplying the ground state wave function by a polynomial, $\Psi_\upsilon(x) = $ (polynomial) $\Psi_o(x)$. The polynomial is chosen to have the number of zeros equal to the number of nodes. For the first excited state, $\upsilon = 1$:

$$\Psi_1(x) = \text{(polynomial)} \, \Psi_o(x) = (ax + b) \, \Psi_o(x) \qquad\qquad (\upsilon = 1) \qquad 24.2.17$$

where the polynomial, $ax + b$, has one zero and a and b are constants. A plot of $ax + b$ is a straight line, Figure 24.2.2a. The product of the straight line and the ground state is shown in Figure 24.2.2b for $\upsilon = 1$. The ground state is said to give the asymptotic form of the wave function. The asymptotic form describes the approach of the wave function to zero for large magnitude displacements, $x \rightarrow \pm\infty$. An excited state wave function is given as the appropriate polynomial multiplied by the asymptotic form, which guarantees the proper approach to zero.

(a).   (b).
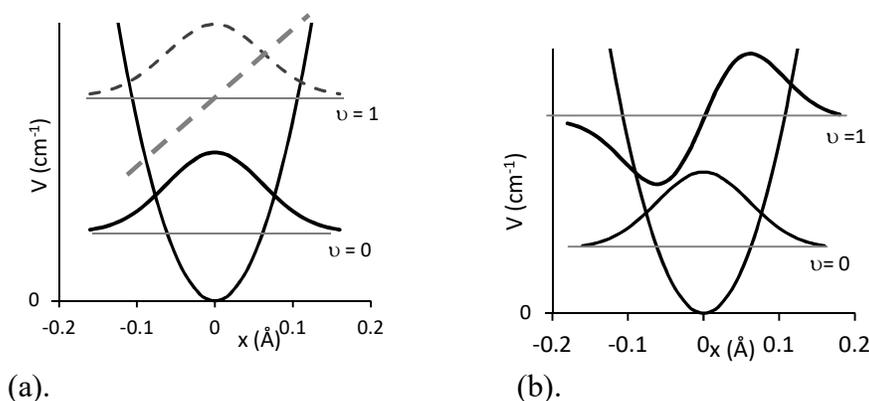
Figure 24.2.2: (a). Harmonic oscillator excited states are a product of the ground state wave function and a polynomial that has the number of zeros = number of nodes = υ. A linear polynomial is required for one node, $ax + b$. (b). The ground and first excited state.

The polynomials are well known and are called the **Hermite polynomials**. The **order** of the Hermite polynomial corresponds to the vibrational quantum number, H_υ. The Hermite polynomials arise in many different circumstances and are tabulated in reference sources and Table 24.1.1. The polynomials are often listed as a function of the dimensionless quantity, $y = \alpha x$. The harmonic oscillator wave functions are given as:

$$\Psi_\upsilon(y) = N_\upsilon H_\upsilon(y)\, e^{-\frac{1}{2} y^2} \qquad\qquad 24.2.18$$

where N_υ is the normalization constant. The Hermite polynomials are the solutions of the **Hermite equation**:

$$\frac{d^2 H_\upsilon}{dy^2} - 2y\, \frac{dH_\upsilon}{dy} + 2\upsilon\, H_\upsilon = 0 \qquad\qquad 24.2.19$$

In the next section we will show that the Schrödinger equation for the harmonic oscillator reduces to the Hermite equation. For now, we will simply use the results.

Table 24.1.1: Hermite Polynomials and Harmonic Oscillator Wave functions, $y = \alpha x$.

υ	$H_\upsilon(y)$	$H_\upsilon(\alpha x)$	$\Psi_\upsilon(\alpha x)$
0	1	1	$(\alpha/\pi^{\frac{1}{2}})^{\frac{1}{2}}\, e^{-\frac{1}{2}\, \alpha^2 x^2}$
1	$2y$	$2\alpha x$	$(\alpha/2\pi^{\frac{1}{2}})^{\frac{1}{2}}\, (2\alpha x)\, e^{-\frac{1}{2}\, \alpha^2 x^2}$
2	$4y^2 - 2$	$4\alpha^2 x^2 - 2$	$(\alpha/8\pi^{\frac{1}{2}})^{\frac{1}{2}}\, (4\alpha^2 x^2 - 2) e^{-\frac{1}{2}\, \alpha^2 x^2}$
3	$8y^3 - 12y$	$8\alpha^3 x^3 - 12\alpha x$	$(\alpha/48\pi^{\frac{1}{2}})^{\frac{1}{2}}\, (8\alpha^3 x^3 - 12\alpha x)\, e^{-\frac{1}{2}\, \alpha^2 x^2}$

The solutions to the Hermite equation are generated using a **recursion relationship**:

$$H_{\upsilon+1} = 2y\, H_\upsilon - 2\upsilon\, H_{\upsilon-1} \qquad\qquad 24.2.20$$

The recursion relationship acts as a generator for all the excited states of the harmonic oscillator. The expression is called a recursion relationship because each successive polynomial is generated recursively from the polynomials of lower order. For example, the Hermite polynomial for $\upsilon = 2$ is a function of H_1 and H_o as:

$$H_2 = 2y\, H_1 - 2\, H_o \qquad \text{or} \qquad H_2 = 2y(2y) - 2(1) = 4y^2 - 2 \qquad\qquad 24.2.21$$

The second order Hermite polynomial is a quadratic polynomial, which has two nodes, Figure 24.2.3a. The product of H_2 with the ground state gives an excited state wave function with $\upsilon = 2$ and two nodes, Figure 24.2.3b for $\upsilon = 2$.

Another handy result is that the integrals of products involving two Hermite polynomials, with quantum numbers υ' and υ, are known:

$$\int_{-\infty}^{\infty} H_{\upsilon'}\, e^{-\frac{1}{2} y^2}\, H_\upsilon\, e^{-\frac{1}{2} y^2}\, dy \quad = 0 \qquad\qquad \text{if } \upsilon' \neq \upsilon$$

$$= \pi^{\frac{1}{2}}\, 2^\upsilon\, \upsilon! \qquad \text{if } \upsilon' = \upsilon \qquad\qquad 24.2.22$$

If $\upsilon' \neq \upsilon$, the integral corresponds to the orthogonality integral. The integral then guarantees orthogonality of the final harmonic oscillator wave functions. If $\upsilon' = \upsilon$, the integral corresponds to the normalization integral. Using the change of variables $dy = \alpha\, dx$ with $\int_{-\infty}^{\infty} \Psi^2(x)\, dx = N_\upsilon^2\, \alpha \int_{-\infty}^{\infty} H_\upsilon^2\, e^{-y^2}\, dy = 1$ and Eq. 24.2.22 gives the normalization constant as:

$$N_\upsilon = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^\upsilon\, \upsilon!} \right)^{\frac{1}{2}} \qquad\qquad 24.2.23$$

The result is a complete set of orthonormal solutions to the quantum harmonic oscillator.
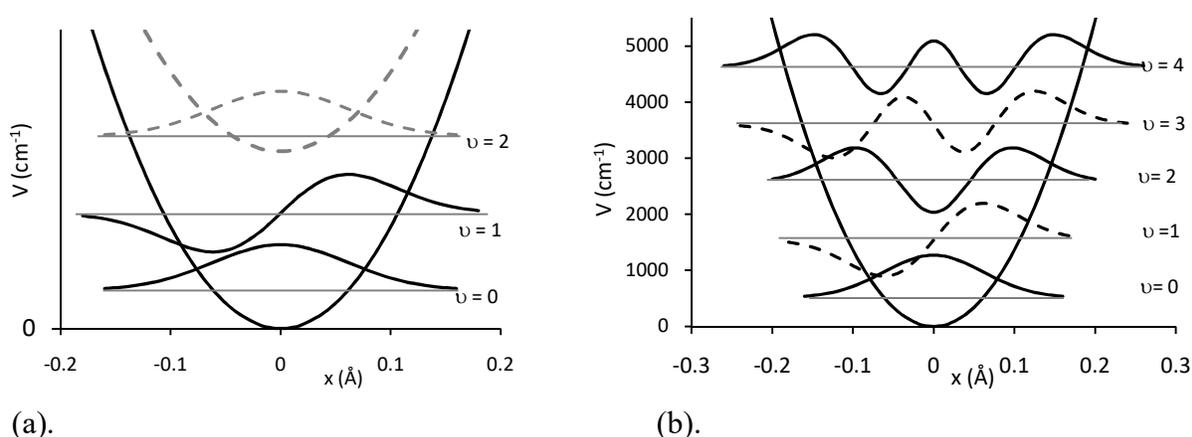
Figure 24.2.3: Excited state wave functions are the product of a normalization constant, the Hermite polynomial of order υ, and the ground state asymptotic form. (a). For $\upsilon = 2$, the polynomial is quadratic, which has two zeros. (b). The harmonic oscillator wave functions.

24.3 The Hermite Equation

The Harmonic Oscillator Schrödinger Equation Reduces to the Hermite Equation: To show that the Schrödinger equation for the harmonic oscillator reduces to the Hermite equation, we first multiply the harmonic oscillator Schrödinger equation, Eq. 24.2. 2, by $2m/\hbar^2$:

$$-\frac{d^2}{dx^2}\Psi_\upsilon + \frac{2mk}{2\hbar^2}x^2\Psi_\upsilon = \frac{2mE_\upsilon}{\hbar^2}\Psi_\upsilon \qquad\qquad 24.3.1$$

The coefficient of second term is α^4, Eq. 24.2.11. The energy of the ground state is given by Eq. 24.2.12, which rearranges to give:

$$E_o = \frac{\hbar^2\alpha^2}{2m} \qquad\qquad giving \qquad\qquad \frac{2m}{\hbar^2} = \frac{\alpha^2}{E_o} \qquad\qquad 24.3.2$$

Substituting this last expression into the right-side of Eq. 24.3.1 and also substituting in α^4 from Eq. 24.2.11 gives the simplified form:

$$-\frac{d^2}{dx^2}\Psi_\upsilon + \alpha^4 x^2 = \alpha^2\varepsilon_\upsilon \Psi_\upsilon \qquad\qquad with \qquad \varepsilon_\upsilon = \frac{E_\upsilon}{E_o} \qquad\qquad 24.3.3$$

The last expression can be put into more general form using the change of variables: $y = \alpha x$. The derivatives for the change in variables are determined using the chain rule:

$$\frac{d}{dx} = \frac{d}{dy}\frac{dy}{dx} = \alpha\frac{d}{dy} \qquad\qquad\qquad \frac{d^2}{dx^2} = \alpha^2\frac{d^2}{dy^2} \qquad\qquad 24.3.4$$

Substituting Eq. 24.3.4 for d^2/dx^2 and $x^2 = y^2/\alpha^2$ into Eq. 24.3.3 gives:

$$-\alpha^2\frac{d^2}{dy^2}\Psi_\upsilon + \alpha^2 y^2 \Psi_\upsilon = \alpha^2 \varepsilon_\upsilon \Psi_\upsilon \qquad\qquad 24.3.5$$

Dividing by α^2 gives the general, dimensionless form:

$$-\frac{d^2}{dy^2}\,\Psi_\upsilon + y^2\,\Psi_\upsilon = \varepsilon_\upsilon\,\Psi_\upsilon \qquad\qquad\text{(dimensionless)} \qquad 24.3.6$$

where the energy is given in multiples of the ground state energy:

$$\varepsilon_\upsilon = \frac{E_\upsilon}{E_o} = \frac{h\nu_o(\upsilon + \tfrac{1}{2})}{\tfrac{1}{2}\,h\nu_o} = 2\upsilon + 1 \qquad\qquad 24.3.7$$

Substituting in this last equation, substituting in the wave function from Eq. 24.2.18, and dividing both sides of Eq. 24.3.6 by the normalization constant, N_υ, gives:

$$\frac{d^2}{dy^2}\,H_\upsilon\,e^{-y^2/2} - y^2\,H_\upsilon\,e^{-y^2/2} + (2\upsilon + 1)\,H_\upsilon\,e^{-y^2/2} = 0 \qquad\qquad 24.3.8$$

Taking the derivative of the unnormalized wave function, $H_\upsilon\,e^{-y^2/2}$, using the product rule gives:

$$\frac{d}{dy}\,H_\upsilon\,e^{-y^2/2} = H_\upsilon\,(-y)\,e^{-y^2/2} + e^{-y^2/2}\,\frac{dH_\upsilon}{dy} \qquad\qquad 24.3.9$$

The second derivative is:

$$\frac{d^2}{dy^2}\,H_\upsilon\,e^{-y^2/2} = H_\upsilon\,[y^2\,e^{-y^2/2} - e^{-y^2/2}] + (-y)\,e^{-y^2/2}\,\frac{dH_\upsilon}{dy} + e^{-y^2/2}\,\frac{d^2H_\upsilon}{dy^2} + \frac{dH_\upsilon}{dy}\,(-y)\,e^{-y^2/2}$$

$$24.3.10$$

and collecting terms gives:

$$\frac{d^2}{dy^2}\,H_\upsilon\,e^{-y^2/2} = e^{-y^2/2}\,\frac{d^2H_\upsilon}{dy^2} - 2y\,e^{-y^2/2}\,\frac{dH_\upsilon}{dy} + H_\upsilon\,(y^2 - 1)\,e^{-y^2/2} \qquad\qquad 24.3.11$$

Substituting the second derivative into Eq. 24.3.8 and dividing both sides of the equation by $e^{-y^2/2}$ gives:

$$\frac{d^2H_\upsilon}{dy^2} - 2y\,\frac{dH_\upsilon}{dy} + H_\upsilon\,(y^2 - 1) - y^2\,H_\upsilon + (2\upsilon + 1)\,H_\upsilon = 0 \qquad\qquad 24.3.12$$

Several terms cancel in the last equation to give the Hermite equation:

$$\frac{d^2H_\upsilon}{dy^2} - 2y\,\frac{dH_\upsilon}{dy} + 2\upsilon\,H_\upsilon = 0 \qquad\qquad 24.3.13$$

To solve this equation, H_υ is assumed to be a polynomial, which upon substitution into the Hermite equation results in the recursion relationship, Eq. 24.2.20. The Hermite equation also plays an important role in probability, statistics, and combinatorics. We next consider rotation.

24.4 A Brief Review of Classical Mechanics: Rotation and Angular Momentum

Angular Momentum: A correspondence can be described between linear and angular momentum. The linear momentum is $p = mv$. The angular momentum is often denoted L. Consider a mass m rotating around the origin at radius r with tangential velocity v, Figure 24.4.1a. A quick experiment can determine whether the angular momentum is given by $L \overset{?}{=} mvr$ or $L \overset{?}{=} mv/r$. A small object is set spinning on a string. Without any other change, pulling in some

string decreases r. The object spins faster, increasing the tangential velocity. As the radius decreases, the tangential velocity increases for a constant angular momentum, giving $L = mvr$ as the proper relationship.

The tangential velocity, dx/dt, is related to the angular velocity, $d\phi/dt$, Figure 24.4.1b. Consider the mass rotating by an infinitesimal angle $d\phi$. For an infinitesimal angle, the linear distance traveled is equal to the arc length subtended by the angle, $dx = r\, d\phi$. Taking the derivative with respect to time gives the linear velocity as:

$$v = \frac{dx}{dt} = r\frac{d\phi}{dt} \qquad \text{or} \quad v = r\omega \qquad\qquad 24.4.1$$

where the angular velocity is denoted as $\omega = d\phi/dt$.

(a). $L = mvr$ 　　　　　　　　　　(b). $L = mr^2\omega$
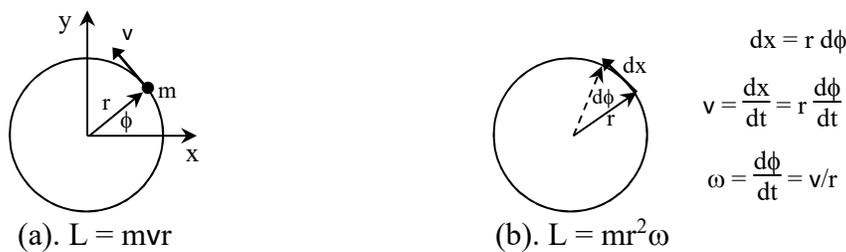
Figure 24.4.1: (a). Angular momentum is determined by the mass, tangential velocity, and distance from the origin, r. (b). The angular velocity is $\omega = d\phi/dt = v/r$ and then $L = mr^2\omega$.

Substituting the last expression into $L = mvr$ gives the angular momentum as $L = mr^2\omega$. Defining the moment of inertia as $I = mr^2$ gives the angular momentum as:

$$L = I\omega \qquad\qquad 24.4.2$$

which shows a useful correspondence with the linear momentum, $p = mv$. The moment of inertia acts as the effective rotational mass. The time derivative of the linear momentum is the force, and the time derivative of the angular momentum is the torque. The kinetic energy of a rotating mass also corresponds to the linear case and is given by $E_k = L^2/2I$, Table 24.4.1.

Table 24.4.1: Linear and Angular Momentum have a Direct Correspondence.

Linear momentum		Angular Momentum	
momentum:	$p = mv$	$L = I\omega$	
effective mass:	m	$I = \Sigma\, m_i\, r_i^2$	
acceleration:	$\dfrac{dp}{dt} = F$　force	$\dfrac{dL}{dt} = T$	torque: twisting force
kinetic energy:	$E_k = \dfrac{p^2}{2m}$	$E_k = \dfrac{L^2}{2I}$	
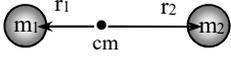
For a molecule, the mass of every atom contributes to the moment of inertia. For a linear molecule with n atoms:

$$I = \sum_{i=1}^{n} m_i r_i^2 \qquad \text{(linear)} \qquad 24.4.3$$

where the distances are measured to the center of mass of the molecule. The molecule rotates about the center of mass, Figure 24.1.1. Consider again a diatomic molecule with bond length r and atomic masses m_1 and m_2. Eqs. 24.1.3 and 24.1.4 give the distances from the masses to the center of mass. Useful relationships are obtained by multiplying Eq. 24.1.1 by r_1 or r_2, respectively:

$$m_1 r_1^2 = m_2 r_1 r_2 \qquad\qquad 24.4.4$$
$$m_1 r_1 r_2 = m_2 r_2^2 \qquad\qquad 24.4.5$$

Reversing Eq. 24.4.4 and adding Eq.24.4.5 gives:

$$(m_1 + m_2) r_1 r_2 = m_1 r_1^2 + m_2 r_2^2 \qquad\qquad 24.4.6$$

Using Eq. 24.4.3, the moment of inertia of the diatomic molecule is:

$$I = \sum_{i=1}^{n} m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2 \qquad \text{(diatomic)} \qquad 24.4.7$$

Substituting Eq. 24.4.6 into the last equation gives:

$$I = (m_1 + m_2) r_1 r_2 \qquad \text{(diatomic)} \qquad 24.4.8$$

Substituting Eqs. 24.1.3 and 24.1.4 for r_1 and r_2 into Eq. 24.4.8 gives:

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 \qquad \text{(diatomic)} \qquad 24.4.9$$

Substituting the definition of the reduced mass, Eq. 24.1.9, into Eq. 24.4.9 results in:

$$I = \mu r^2 \qquad \text{(diatomic)} \qquad 24.4.10$$

The reduced mass is the effective rotational mass of the diatomic molecule. The moment of inertia for a diatomic molecule reduces to the same form as a single rotating mass, so solutions to the equation of motion for a single mass apply equally to diatomic molecules.

The theory of angular momentum is the same, regardless of the degree of freedom under study. As a consequence, once the wave functions and energy levels for different angular momentum states have been determined for one system, the results apply to all angular momentum problems. Different symbols are used for different examples of angular momentum: J for rotating molecules, L for electronic angular momentum in atoms and molecules, S for angular momentum of electrons, and I for angular momentum of nuclei. We will use L for the general case, and then specialize according to the particular problem, where all the symbols are interchangeable, Table 24.4.2.

Table 24.4.2: The Symbols for Angular Momentum are Interchangeable.

Degree of Freedom	Conventional Symbol
Molecular rotation	J
Electronic angular momentum	L
Intrinsic angular momentum of electrons	S
Intrinsic angular momentum of nuclei (NMR)	I
Intrinsic angular momentum of light	S

24.5 Angular Momentum and Molecular Rotation

The Rigid Rotor is a Model for Molecular Rotation: A good model for molecular rotation is to assume that the bond lengths and angles in the molecule are fixed and independent of the rotational state of the molecule. This model is called the **rigid rotor** approximation. In this section we focus on the general case, which is a single mass with fixed distance to the origin, and then apply the results to diatomic molecules. We start with rotation in a plane for simplicity, and then use the results from rotation in a plane to build the wave functions for rotation on the surface of a sphere.

Rotation in a Plane is Quantized: A mass m rotating about the origin at fixed distance r has classical angular momentum $L = mr^2\omega = mr^2(d\phi/dt)$ and kinetic energy $E_k = L^2/2I$. Rotation in a plane involves one angular dimension, Figure 24.5.1a. The angle between the vector pointing to the mass and the x-axis is called the azimuthal angle, ϕ, with $0 \le \phi \le 2\pi$. No potential energy acts on the particle, $V(\phi) = 0$. The total energy is given by the kinetic energy.

(a).   (b). stationary-state   (c). non-stationary
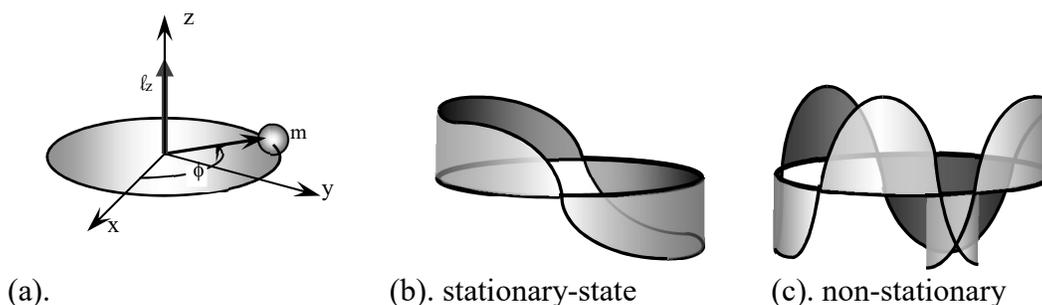
Figure 24.5.1: (a). Rotation in the x-y plane is a function of the azimuthal angle, ϕ. (b). The wave function must constructively interfere with itself at $\phi + 2\pi$: allowed orbitals give $m_\ell = 0, \pm1, \pm2,\ldots$ (c). Orbitals that don't constructively interfere do not give stationary states.

The Schrödinger equation for rotation in a plane is:

$$-\frac{\hbar^2}{2I}\left(\frac{\partial^2 \Psi}{\partial \phi^2}\right) = E\Psi \qquad\qquad (0 \le \phi \le 2\pi) \qquad\qquad 24.5.1$$

This equation is in the same form as a free particle, except that the distance x has been replaced by the angle ϕ. The wave function is also in the same form:

$$\Psi_{m_\ell} = a\, e^{im_\ell\phi} \qquad\qquad 24.5.2$$

where m_ℓ is a constant and a is the normalization constant. To find the energy for rotation, the derivatives are given by:

$$\left(\frac{\partial\Psi_{m_\ell}}{\partial\phi}\right) = a\, im_\ell\, e^{im_\ell\phi} = im_\ell\Psi_{m_\ell} \qquad \left(\frac{\partial^2\Psi_{m_\ell}}{\partial\phi^2}\right) = -\,a\, m_\ell^2\, e^{im_\ell\phi} = -\, m_\ell^2\, \Psi_{m_\ell} \qquad 24.5.3$$

Substituting the second derivative into the Schrödinger equation, Eq. 24.5.1, gives:

$$-\frac{\hbar^2}{2I}\left(-\, m_\ell^2\, \Psi_{m_\ell}\right) = E\, \Psi_{m_\ell} \qquad\qquad 24.5.4$$

Only functions remain, so that dividing both sides of the last equation by Ψ_{m_ℓ} determines the energy as:

$$E_{m_\ell} = \frac{\hbar^2 m_\ell^2}{2I} \qquad\qquad 24.5.5$$

This last equation is in the same general form as for a free particle, the particle in a box, and the harmonic oscillator, 24.2.12, with m_ℓ the constant. Are there any restrictions on the allowable values for m_ℓ? The boundary condition for the wave function is that the amplitude of the wave function must be the same at a given angle ϕ and $\phi+2\pi$ to allow for constructive interference on subsequent transits around the plane of rotation, Figure 24.5.1b:

$$a\, e^{im_\ell\phi} = a\, e^{im_\ell(\phi+2\pi)} \qquad\qquad 24.5.6$$

Factoring the exponential on the right into two terms gives:

$$e^{im_\ell\phi} = e^{im_\ell\phi}\, e^{im_\ell\, 2\pi} \quad\text{or}\quad 1 = e^{im_\ell\, 2\pi} \qquad\qquad 24.5.7$$

The Euler identity gives the boundary condition as:

$$e^{im_\ell\, 2\pi} = \cos 2\pi m_\ell + i \sin 2\pi m_\ell = 1 \qquad\qquad 24.5.8$$

which shows that m_ℓ must be an integer:

$$m_\ell = 0, \pm1, \pm2, \pm3, \ldots \qquad\qquad 24.5.9$$

The requirement of constructive overlap gives quantized stationary-states, as we also showed for the Bohr atom. The lowest energy state with $m_\ell = 0$ gives zero energy, Eq. 24.5.5. Rotation does not have a zero-point energy. Molecules cease rotation at absolute zero Kelvin. The spacing between successive energy states diverges as m_ℓ^2. Positive values for m_ℓ correspond to counter-clockwise rotation and negative values clockwise rotation, using the "right-hand rule." The direction of the angular momentum vector is along the z-axis. In direct analogy with linear momentum, Eq. 23.4.21, the angular momentum around the z-axis is given by the quantum operator:

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \qquad\qquad 24.5.10$$

The rigid rotor wave function is an eigenfunction of the z-component of the angular momentum:

$$\hat{L}_z \, \Psi_{m\ell} = \frac{\hbar}{i} \frac{\partial \Psi_{m\ell}}{\partial \phi} = \hbar m_\ell \Psi_{m\ell} \qquad\qquad 24.5.11$$

where the eigenvalue is:

$$L_z = \hbar m_\ell \qquad\qquad 24.5.12$$

Repeated observations of the total energy and the angular momentum around the z-axis always give the same results, because the 2D-rigid rotor wave function is an eigenfunction of both $\hat{\mathcal{H}}$ and $\hat{L}_z$ (Postulate III, Sec. 23.7). The quantum number m_ℓ gives the number of planar nodes that include the z-axis, Figure 24.5.2. For the $m_\ell = 0$ wave function, the particle has no angular momentum and can then be found with equal probability anywhere around the circumference. Increasing number of nodes gives increasing angular curvature, energy, and angular momentum.

$$m_\ell = 0 \qquad\qquad m_\ell = \pm 1 \qquad\qquad m_\ell = \pm 2$$
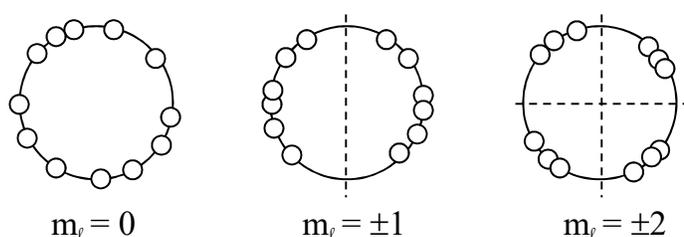
Figure 24.5.2: The azimuthal quantum number m_ℓ gives the number of planar nodes that include the z-axis. Greater curvature gives greater kinetic energy. The real part of the wave function is depicted. The z-axis extends out of the plane of the page.

Building upon our understanding of rotation in a plane we now consider rotation in three dimensions. However, first we need to consider the use of spherical polar coordinates to specify the position of the particle.

Spherical Polar Coordinates are Used for Spherically Symmetric Systems: For a spherically symmetric system, the spherical polar coordinate system is useful for determining the position of a particle as it moves around the origin. The distance of the particle from the origin is r, Figure 24.5.3a. The polar angle, θ, is the angle between the z-axis and the vector that points to the particle. The azimuthal angle, ϕ, is the angle between the x-axis and the projection of the vector onto the xy-plane. We considered motion in the xy-plane as a function of ϕ in the last section.
   To completely cover all space, the ranges for the coordinates are:

$$0 \le r \le \infty \qquad 0 \le \theta \le \pi \qquad 0 \le \phi \le 2\pi \qquad\qquad 24.5.13$$

The projection of the position vector onto the z-axis is $r \cos \theta$. The projection of the position vector onto the xy-plane has length $r \sin \theta$, Figure 24.5.3b. The transformation between spherical polar coordinates and Cartesian coordinates is then given by:

$$r = \sqrt{x^2 + y^2 + z^2}$$
$$x = r \sin \theta \cos \phi$$
$$y = r \sin \theta \sin \phi$$
$$z = r \cos \theta \qquad\qquad 24.5.14$$

(a).   (b).   (c).
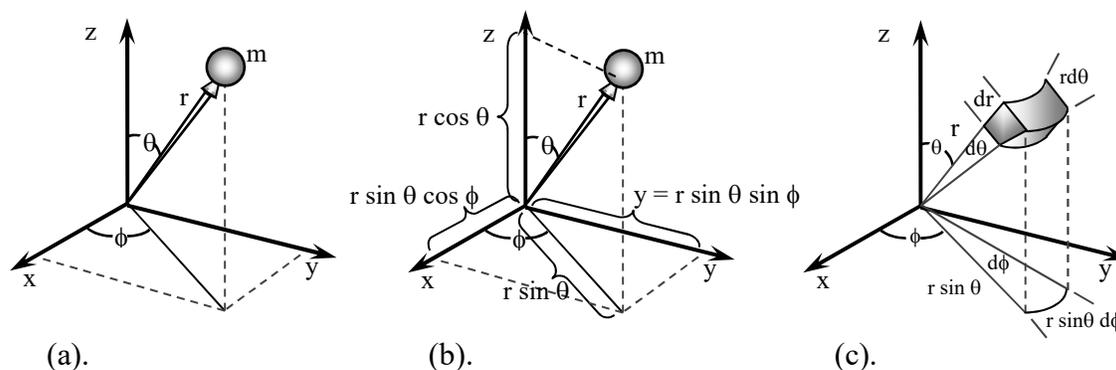
Figure 24.5.3: (a). Spherical polar coordinates, r, θ, and φ completely specify the position of the particle. (b). The transformation from r, θ, φ to x, y, z. (c). The volume element in three-space.

Consider a change in r, θ, and φ from r to r + dr, θ to θ + dθ, and φ to φ + dφ. The corresponding sides of the small volume element that are swept out by these differential changes are dr, r dθ, and r sin θ dφ, Figure 24.5.3c. The volume element in three-space is the product of these sides:

$$d\tau = dx\ dy\ dz = dr\ (r\ d\theta)(r\ \sin\theta\ d\phi) = r^2\sin\theta\ dr\ d\theta\ d\phi \qquad 24.5.15$$

Please see Addendum 24.8.1 for additional information on integration in multiple dimensions. The integrals over all possible θ values and over all possible φ values are:

$$\int_0^\pi \sin\theta\ d\theta = [-\cos\theta\ |_0^\pi = 1 + 1 = 2 \qquad \text{and} \qquad \int_0^{2\pi} d\phi = [\ \phi\ |_0^{2\pi} = 2\pi \qquad 24.5.16$$

The angular portion of the integral over all space is then just 4π:

$$\int_0^\pi \int_0^{2\pi} \sin\theta\ d\theta\ d\phi = 4\pi \qquad 24.5.17$$

Angular Momentum in 3-Dimensions: Rotation of a mass in a plane has one component of angular momentum, perpendicular to the plane, $L = mr^2\omega$. Rotation in three-dimensions gives angular momentum components about three orthogonal axes. The definition of the angular momentum vector is given by the cross product relationship, $\vec{L} = \vec{r} \times \vec{p}$, where $\vec{r}$ is the position vector, which extends from the origin to the particle with components (x, y, z), and $\vec{p}$ is the linear momentum of the particle. The cross product can be resolved into the components along the $\vec{i}, \vec{j}$, and $\vec{k}$ directions by finding the determinant:

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (y\ p_z - z\ p_y)\ \vec{i} - (x\ p_z - z\ p_x)\ \vec{j} + (x\ p_y - y\ p_x)\ \vec{k} \qquad 24.5.18$$

For rotation in the xy-plane the angular momentum vector is in the "z-direction," that is along the unit vector $\vec{k}$, Figure 24.5.1. The quantum mechanical operators corresponding to the components of the angular momentum are:

$$\hat{L}_x = (\hat{y}\,\hat{p}_z - \hat{z}\,\hat{p}_y) = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = (\hat{z}\,\hat{p}_x - \hat{x}\,\hat{p}_z) = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = (\hat{x}\,\hat{p}_y - \hat{x}\,\hat{p}_x) = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \qquad 24.5.19$$

Using the coordinate transformations in Eqs. 24.5.14, the angular momentum components in spherical polar coordinates are:

$$\hat{L}_x = \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = \frac{\hbar}{i}\left(\frac{\partial}{\partial\phi}\right) \qquad 24.5.20$$

The result for the $\hat{L}_z$ operator verifies Eq. 24.5.10, which we obtained by analogy with linear momentum. The square of the total angular momentum is given by the Pythagorean theorem and Eqs. 24.5.20 as:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] \qquad 24.5.21$$

The 3-dimensional Schrödinger equation, Eq. 23.6.3, is:

$$-\frac{\hbar^2}{2m}\nabla^2\,\Psi + \hat{V}(x,y,z) = E\,\Psi \quad \text{with } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad (23.6.3)\ 24.5.22$$

The curvature can be recast into spherical polar coordinates to give:

$$\nabla^2 = \frac{1}{r}\left(\frac{\partial^2}{\partial r^2}\right)r + \left(\frac{1}{r^2}\right)\Lambda^2 \qquad 24.5.23$$

where Λ^2 is related to the square of the total angular momentum operator by:

$$\hat{L}^2 = (\text{angular momentum operator})^2 = -\hbar^2\Lambda^2 \qquad 24.5.24$$

The first term of Eq. 24.5.23 determines the "wiggliness" of the wave function for motion toward or away from the origin, which is called the radial direction. The term in Λ^2 determines the "wiggliness" of the wave function as it wraps around the origin:

$$\Lambda^2 = \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) + \left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) \qquad 24.5.25$$

The Schrödinger equation for the 3D-rigid rotor is most conveniently cast in spherical polar coordinates.

Example 24.5.1: *Angular Momentum Coordinate Conversion*

Show that $\hat{L}_z = \hbar/i \, (\partial/\partial\phi)$.

Answer: The chain rule gives: $\left(\dfrac{\partial}{\partial\phi}\right) = \left(\dfrac{\partial x}{\partial\phi}\right)\left(\dfrac{\partial}{\partial x}\right) + \left(\dfrac{\partial y}{\partial\phi}\right)\left(\dfrac{\partial}{\partial y}\right) + \left(\dfrac{\partial z}{\partial\phi}\right)\left(\dfrac{\partial}{\partial z}\right)$

The derivatives are evaluated using the coordinate transformations given in Eqs. 24.5.14:

$$\left(\frac{\partial x}{\partial\phi}\right) = -\,r \sin\theta \sin\phi = -\,y \qquad \left(\frac{\partial y}{\partial\phi}\right) = r \sin\theta \cos\phi = x \qquad \left(\frac{\partial z}{\partial\phi}\right) = 0$$

Substitution of the derivatives into $(\partial/\partial\phi)$ gives:

$$\left(\frac{\partial}{\partial\phi}\right) = -\,y\left(\frac{\partial}{\partial x}\right) + x\left(\frac{\partial}{\partial y}\right) \qquad \text{and} \qquad \hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \frac{\hbar}{i}\left(\frac{\partial}{\partial\phi}\right)$$

as given in Eqs. 24.5.19 and 24.5.20. The derivations of the remaining Eqs. 24.5.20 are algebraically more intricate, but this example gives the general idea of the procedure.

Rotation in 3D Involves Two Angular Dimensions: The 3-dimensional rigid rotor corresponds to the motion of a particle of mass m on the surface of a sphere with fixed radius r. The potential energy is zero, $V = 0$. The Schrödinger equation, Eq. 24.5.17, reduces to:

$$-\frac{\hbar^2}{2m}\nabla^2\,\Psi = E\,\Psi \tag{24.5.26}$$

For the rigid rotor, r is constant so the derivative with respect to r in the curvature, Eq. 25.5.23, is zero giving:

$$-\frac{\hbar^2}{2mr^2}\Lambda^2\Psi = E\,\Psi \tag{24.5.27}$$

The moment of inertia is defined as mr^2 for a single mass rotating about the origin:

$$-\frac{\hbar^2}{2I}\Lambda^2\Psi = E\,\Psi \tag{24.5.28}$$

Since there is no potential energy for rotation, the total energy is entirely kinetic energy. Using Eqs. 24.5.24 and 24.5.28, the kinetic energy operator is $\hat{E}_k = \hat{L}^2/2I$, which flows quite naturally from the curvature, as anticipated from Table 24.4.1. The curvature involves angles θ and ϕ. The corresponding motions are separable so that the overall wave function is expressed as the product of one-dimensional wave functions (see Sec. 23.6 for the equivalent process for the 3D-particle in a box):

$$\Psi = \Theta(\theta)\Phi(\phi) \tag{24.5.29}$$

The ϕ dependent portion is already familiar to us and is given by the wave function for motion in the xy-plane, Eq. 24.5.2:

$$\Phi(\phi) = \left(\frac{1}{2\pi}\right)^{\!\!1/2} e^{im_\ell\phi} \qquad\qquad m_\ell = 0, \pm1, \pm2, \pm3, \dots. \tag{24.5.30}$$

The complete wave function is well known; the solutions are called spherical harmonics, Y_{ℓ,m_ℓ}:

$$\Psi = Y_{\ell,m_\ell} = \Theta(\theta)\Phi(\phi) \tag{24.5.31}$$

The spherical harmonics are the eigenfunctions of the square of the total angular momentum:

$$-\hbar^2\,\Lambda^2 Y_{\ell,m_\ell} = \hbar^2\,\ell\,(\ell+1)\,Y_{\ell,m_\ell} \tag{24.5.32}$$

where ℓ is the **angular momentum quantum number** and m_ℓ is the **magnetic quantum number**. The angular momentum quantum number is restricted to positive integers, $\ell = 0, 1, 2, \dots$. The eigenvalue is the square of the total angular momentum:

$$L^2 = \hbar^2\,\ell\,(\ell+1) \tag{24.5.33}$$

and the magnitude of the total angular momentum is then the square root of the last expression:

$$|L| = \hbar\,\sqrt{\ell\,(\ell+1)} \tag{24.5.34}$$

The spherical harmonics for $\ell = 0, 1, 2$ are listed in Table 24.5.1. You are already familiar with these functions because they are identical to the angular portions of atomic orbitals, where $\ell = 0$ are "s"-type, $\ell = 1$ are "p"-type, and $\ell = 2$ are "d"-type orbitals, Figure 24.5.4. The real parts of the ϕ dependent portions are depicted in Figure 24.5.2.

Dividing Eq. 24.5.32 by 2I gives the rigid rotor Schrödinger equation:

$$-\frac{\hbar^2}{2I}\Lambda^2 Y_{\ell,m_\ell} = E_\ell\,Y_{\ell,m_\ell} \tag{24.5.35}$$

Dividing Eq. 24.5.32 by 2I gives the total rotational energy eigenvalue as:

$$E_\ell = \frac{\hbar^2}{2I}\ell\,(\ell+1) \tag{24.5.36}$$

The z-axis projection of the angular momentum is given using Eqs. 24.5.11 and 24.5.12 as:

$$\hat{L}_z\,Y_{\ell,m_\ell} = \frac{\hbar}{i}\frac{\partial Y_{\ell,m_\ell}}{\partial\phi} = \hbar m_\ell\,Y_{\ell,m_\ell} \qquad\qquad L_z = \hbar m_\ell \tag{24.5.37}$$

Table 24.5.1: Spherical Harmonics

ℓ	m_ℓ	Y_{ℓ,m_ℓ}
0	0	$(1/4\pi)^{1/2}$
1	0	$(3/4\pi)^{1/2}\cos\theta$
	±1	$\pm(3/8\pi)^{1/2}\sin\theta\,e^{\pm i\phi}$
2	0	$(5/16\pi)^{1/2}\,(3\cos^2\theta - 1)$
	±1	$\pm(15/8\pi)^{1/2}\cos\theta\sin\theta\,e^{\pm i\phi}$
	±2	$\pm(15/32\pi)^{1/2}\sin^2\theta\,e^{\pm i2\phi}$

A useful way to visualize the spherical harmonics is to use node counting. The nodes for rotational motion are planes of zero wave function amplitude that pass through the origin. The planar nodes are called **angular nodes**. The total number of angular nodes is equal to the angular momentum quantum number, ℓ. The number of angular nodes that include the z-axis is equal to m_ℓ, Figure 24.5.4. The total energy, Eq. 24.5.36, is dependent only on ℓ. The energy is proportional to the curvature. The number of nodes increases as the curvature increases, so the total number of angular nodes indicates the total angular momentum and the rotational energy. The number of angular nodes that include the z-axis cannot exceed the total number of nodes, so the restrictions on the quantum numbers are then:

$$\ell = 0, 1, 2, \ldots \quad \text{and} \quad m_\ell = 0, \pm 1, \ldots, \pm\ell \qquad\qquad 24.5.38$$

This result for m_ℓ will be proved in Sec. 24.7. If $\ell = 0$, then m_ℓ can only be 0, and the lowest energy state is non-degenerate. If $\ell = 1$, then $m_\ell = 0, \pm 1$, where positive m_ℓ values are for counter-clockwise rotation and the negative are for clockwise. The $\ell = 1$ level is triply degenerate, $g_\ell = 3$. In general, the degeneracy is:

$$g_\ell = 2\,\ell + 1 \qquad\qquad 24.5.39$$

$$\ell = 1, m_\ell = 0 \qquad\qquad \ell = 2, m_\ell = 0 \qquad\qquad \ell = 2, m_\ell = \pm 1$$
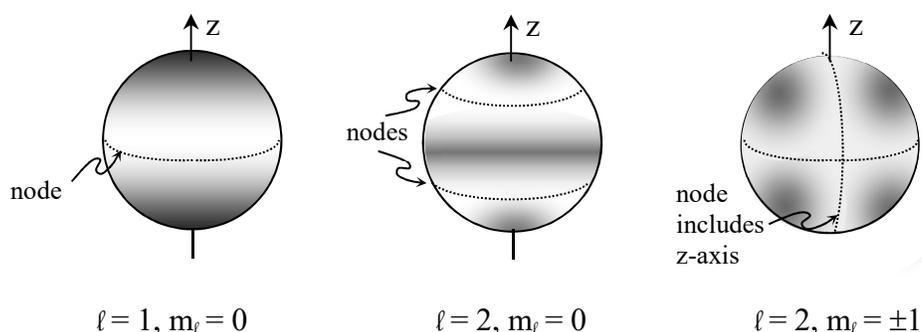
Figure 24.5.4: The rigid rotor wave functions are the spherical harmonics Y_{ℓ,m_ℓ}. The real parts of the spherical harmonic wave functions are shown.

The energy levels diverge for increasing ℓ, Figure 24.5.5. Transitions between adjacent energy levels are excited by light absorption in the microwave region of the spectrum or by light scattering. For example, microwave ovens operate by exciting rotational transitions in the water molecules in your food.

For the specific case of a rotating linear molecule, the angular momentum quantum number is denoted J and the projection on the z-axis is m_J. For molecular rotation, Eq. 24.5.36 becomes:

$$E_J = \frac{\hbar^2}{2I} J(J + 1) \qquad J = 0, 1, 2, \ldots \quad \text{and} \quad m_J = 0, \pm 1, \ldots, \pm J \qquad g_J = 2J + 1 \qquad 24.5.40$$

In wave numbers, the energy levels are called the **rotational term values**, $\tilde{F}_J$:

$$\tilde{F}_J = \frac{E_J}{hc} = \tilde{B}\, J(J + 1) \qquad\qquad \text{with} \quad \tilde{B} = \frac{\hbar}{4\pi Ic} \qquad\qquad 24.5.41$$

where $\tilde{B}$ is the **rotational constant**, which is dependent on the molecular geometry.
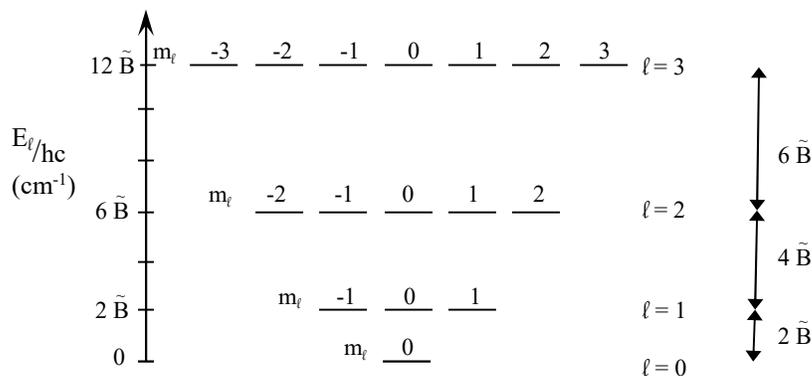
Figure 24.5.5: Energy levels for the rigid rotor diverge with increasing ℓ. The degeneracy is $g_\ell = 2\ell + 1$. For the specific case of a rotating molecule, $\ell = J$ and $m_\ell = m_J$.

For a diatomic molecule $I = \mu r^2$, so the value of $\tilde{B}$ determines the bond length. In joules:

$$E_J = \tilde{B}hc\, J\,(J + 1) \qquad\qquad 24.5.42$$

The energy difference between adjacent energy levels is:

$$\Delta E = E_{J+1} - E_J = \tilde{B}hc[(J+1)(J+1+1) - J(J+1)] = 2\tilde{B}hc(J+1) \qquad 24.5.43$$

where J is the quantum number for the lower level, Figure 24.5.5.

The Spin States of Electrons and Nuclei Correspond to Different Angular Momentum States: Electrons, protons, neutrons, and photons also carry angular momentum. The angular momentum of elementary particles is often called **intrinsic angular momentum**, since the effect is evident in a non-interacting, isolated particle. The intrinsic angular momentum of a particle is also called its **spin**.[1] The quantized angular momentum states for the electron were observed in 1922 by Stern and Gerlach using silver and alkali atoms and in 1927 by Phipps and Taylor using hydrogen atoms.[2] A stream of hydrogen atoms is deflected into two discrete beams by an inhomogeneous magnetic field, Figure 24.5 6.
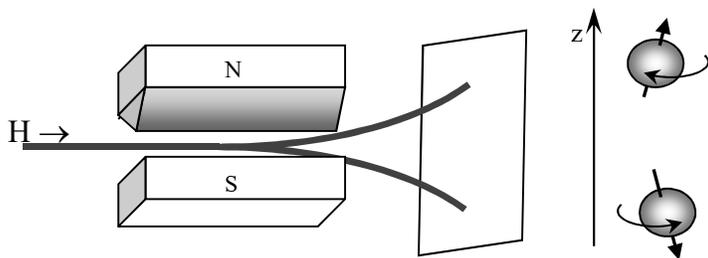
Figure 24.5.6: (a). The Stern-Gerlach experiment with hydrogen atoms. The projection of the electron angular momentum on the external magnetic field axis is restricted to two discrete values, $m_s = \pm\frac{1}{2}\,\hbar$, giving two spatially separated beams of atoms. The two spin states can be modeled as spin up with counter-clockwise rotation and spin down with clockwise rotation.

The hydrogen atom has one electron that can have two projections of its angular momentum vector on the external field direction. The external field determines the unique axis, which is arbitrarily chosen as the z-axis by convention. The presence of only two spin states suggests that the intrinsic angular momentum quantum number of the electron is $s = \frac{1}{2}$ and the corresponding projection of the angular momentum on the z-axis can be only $m_s = \pm\frac{1}{2}$. The observation is called **space quantization**, since the orientation of the spin angular momentum is an angular, spatial dimension. The full relativistic quantum mechanical theory by P. A. M. Dirac in 1928 provides a rigorous theoretical foundation for the intrinsic angular momentum of the electron. The spin quantum numbers of the proton and neutron are also $\frac{1}{2}$. We will provide experimental evidence that the spin quantum number of the photon is $s = 1$.

Based on the universal nature of angular momentum, we can represent the allowed spin states of the electron by wave functions α for $m_s = +\frac{1}{2}$ and β for $m_s = -\frac{1}{2}$. The α state is called "spin up" and the β state "spin down." Following Eqs. 24.5.32 and 24.5.37, the spin wave functions, α and β, are eigenfunctions of both the square of the total angular momentum and the z-axis projection of the angular momentum:

$$\hat{S}^2\,\alpha = \hbar^2\,s(s+1)\,\alpha \qquad\qquad S_z\,\alpha = +\tfrac{1}{2}\,\hbar\,\alpha$$
$$\hat{S}^2\,\beta = \hbar^2\,s(s+1)\,\beta \qquad\qquad S_z\,\beta = -\tfrac{1}{2}\,\hbar\,\beta \qquad\qquad 24.5.44$$

The magnitude of the angular momentum of the electron is then:

$$|S| = \hbar\,\sqrt{s(s+1)} = \hbar\,\sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1)} = \sqrt{\tfrac{3}{4}}\,\hbar \qquad\qquad 24.5.45$$

A common analogy is to picture the electron as a sphere spinning counter-clockwise for $m_s = \frac{1}{2}$ and clockwise for $m_s = -\frac{1}{2}$. In effect, the elementary particle acts like a subatomic gyroscope. However, this analogy is not supported by theory, since the existence of any internal structure for the electron is currently unknown. The spinning sphere analogy should not be taken literally; the effect is purely quantum mechanical. The spin states for the proton and neutron are also governed by Eqs. 24.5.44 and 24.5.45. Photons are a special case, however.

The intrinsic angular momentum quantum number for a photon is $s = 1$. Based on our work so far, the projection of the angular momentum on the z-axis is expected to be $m_s \overset{?}{=} -1, 0, +1$. However, because a photon is travelling at the speed of light, the relativistic theory gives only two projections, $m_s = -1$ and $+1$. The two m_s values correspond to left- and right-circularly polarized light. The two allowed m_s values for the photon have an important effect on the conservation of angular momentum in spectroscopic transitions.

24.6 Angular Momentum Vector Diagrams

The allowed angular momentum m_ℓ states and the effect of the commutation relations for the projections of the angular momentum are conveniently illustrated using angular momentum vector diagrams. The commutation relationships among the components of the angular momentum determine the ability of experiments to determine precise values for the projections of the angular momentum. Using Eqs. 24.5.19, the x and y components of the angular momentum do not commute and cannot be determined simultaneously to arbitrary precision:

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

The full set of commutation relationships is:

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \qquad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \qquad 24.6.1$$
$$[\hat{L}^2, \hat{L}_x] = 0 \qquad [\hat{L}^2, \hat{L}_y] = 0 \qquad [\hat{L}^2, \hat{L}_z] = 0 \qquad 24.6.2$$

The result is that only one component of the angular momentum can be determined simultaneously with arbitrary precision along with $\hat{L}^2$.

   The angular momentum vector can be drawn as a vector diagram. Consider first $\ell = 1$ and $m_\ell = +1$. The length of the vector is given by the magnitude of the total angular momentum, Eq. 24.5.34, and the projection on the z-axis is given by 24.5.37:

$$|L| = \hbar\sqrt{\ell(\ell+1)} = |L| = \hbar\sqrt{1(1+1)} = \sqrt{2}\,\hbar = 1.414\,\hbar$$
$$L_z = \hbar m_\ell = +1\,\hbar \qquad\qquad 24.6.3$$

The projection on the z-axis is less than the length of the vector, so the angular momentum vector must be tilted with respect to the z-axis. The angle is given by $\cos^{-1}(1/\sqrt{2}) = 45°$. A single observation for each of $m_\ell = -1, 0, +1$ is shown in Figure 24.6.1a. The angular momentum is quantized in space, by a fixed orientation with respect to the z-axis. However, the commutation relationships show that two projections of the angular momentum cannot be determined simultaneously with arbitrary precision, Eq. 24.6.1. Only $\hat{L}^2$ and one of the projections can be determined precisely simultaneously, Eq. 24.6.2. If L^2 and L_z are known precisely from the quantum numbers ℓ and m_ℓ, then the projections on the x- and y-axes must be uncertain. As a consequence repeated observations have different projections on the x- and y-axes and $\langle\hat{L}_x\rangle = \langle\hat{L}_y\rangle = 0$. The subsequent angular momentum vectors lie on a cone with fixed height, $\hbar m_\ell$, Figure 24.6.1b.

(a).   (b).   (c).
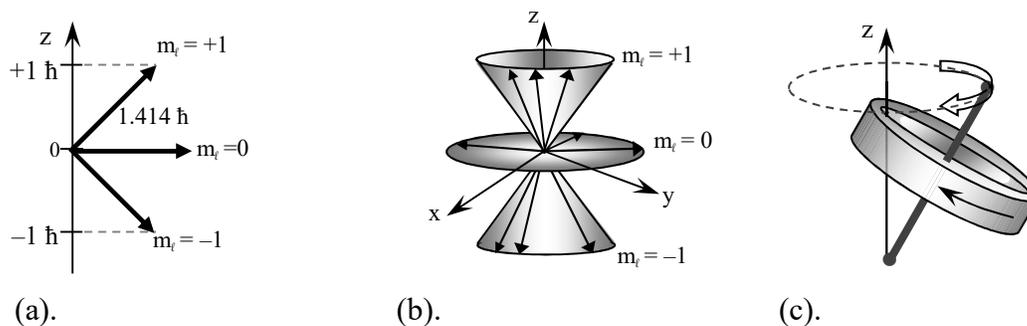
Figure 24.6.1: (a). Angular momentum vector diagram for $\ell = 1$, for single observations. (b). Only the magnitude and the z-axis projection can be determined precisely, so repeated observations lie on precession cones with fixed projections on the z-axis. (c). Precession is the classical analogy for the x- and y-projection uncertainty.

   The classical analogy to the uncertainty in the x- and y- directions is precession. A spinning gyroscope that is tilted with respect to the z-axis, as defined by the gravitational field, precesses about the z-axis. Electron and nuclear precession are a useful model for understanding magnetic resonance spectroscopy.

24.7 Ladder Operators Simplify Finding Quantum States

Solving the harmonic oscillator and rigid rotor Schrödinger equations is a bit complicated. We stated above, without proof, that the energy of the harmonic oscillator is $E_\upsilon = h\nu_o(\upsilon + \frac{1}{2})$, with the quantum number increasing in unit steps. We also stated that the quantum number for the z-axis projection of the angular momentum, m_ℓ, ranges from $-\ell$ to $+\ell$ in unit steps. The restriction of unit changes in m_ℓ determines the degeneracy of a given ℓ state. In this section, we derive these relationships. **Ladder operators** simplify the process. A ladder operator has the property:

$$[\hat{A},\hat{A}^{\pm}] = k\,\hat{A}^{\pm} \qquad\qquad 24.7.1$$

where $\hat{A}$ is general operator, k a constant, and $\hat{A}^{\pm}$ is either a **raising operator**, $\hat{A}^{+}$, or a **lowering operator**, $\hat{A}^{-}$. Consider an eigenfunction of the operator $\hat{A}$:

$$\hat{A}\ \Psi_\upsilon = \varepsilon_\upsilon\ \Psi_\upsilon \qquad\qquad 24.7.2$$

Because $\hat{A}$ and $\hat{A}^{\pm}$ don't commute, Ψ_υ cannot be an eigenfunction of $\hat{A}^{\pm}$. Let the result of the action of $\hat{A}^{\pm}$ on Ψ_υ give the new function Φ:

$$\hat{A}^{\pm}\ \Psi_\upsilon \equiv \Phi \qquad\qquad 24.7.3$$

However, the new function is still an eigenfunction of $\hat{A}$. To prove that the new function Φ is an eigenfunction of $\hat{A}$, let $\hat{A}$ act on Φ and then use the definition of Φ from Eq. 24.7.3:

$$\hat{A}\ \Phi = \hat{A}\hat{A}^{\pm}\ \Psi_\upsilon \qquad\qquad 24.7.4$$

The commutator, Eq. 24.7.1, can be expanded to solve for $\hat{A}\hat{A}^{\pm}$, giving:

$$[\hat{A},\hat{A}^{\pm}] = \hat{A}\hat{A}^{\pm} - \hat{A}^{\pm}\hat{A} = k\hat{A}^{\pm} \qquad\text{or}\qquad \hat{A}\hat{A}^{\pm} = \hat{A}^{\pm}\hat{A} + k\hat{A}^{\pm} \qquad 24.7.5$$

Substituting this last result into Eq. 24.7.4 gives:

$$\hat{A}\ \Phi = \hat{A}^{\pm}\hat{A}\ \Psi_\upsilon + k\hat{A}^{\pm}\ \Psi_\upsilon \qquad\qquad 24.7.6$$

However, using the fact that Ψ_υ is an eigenfunction of $\hat{A}$ from Eq. 24.7.2 gives:

$$\hat{A}\ \Phi = \hat{A}^{\pm}\ \varepsilon_\upsilon\Psi_\upsilon + k\hat{A}^{\pm}\ \Psi_\upsilon = (\varepsilon_\upsilon + k)\ \hat{A}^{\pm}\ \Psi_\upsilon = (\varepsilon_\upsilon + k)\ \Phi \qquad 24.7.7$$

where the last substitution uses the definition of Φ from Eq. 24.7.3. The last expression shows that the new function is an eigenfunction of $\hat{A}$ with eigenvalue $(\varepsilon_\upsilon + k)$. In many applications, the operator $\hat{A}$ is the Hamiltonian, $\hat{\mathcal{H}}$. Then if k is positive, the new function $\hat{A}^{+}\ \Psi_\upsilon$ is the eigenfunction with the next higher energy. If k is negative, $\hat{A}^{-}\ \Psi_\upsilon$ is the eigenfunction with the next lower energy. $\hat{A}^{+}$ raises Ψ_υ to the next highest energy level and $\hat{A}^{-}$ lowers Ψ_υ to the next lower energy level. Repeated application of $\hat{A}^{+}$ generates a ladder of quantum states; $\hat{A}^{+}$ moves up a rung of the ladder and $\hat{A}^{-}$ moves down a rung. However, the lowering operator acting on the lowest energy state gives zero: for example for the harmonic oscillator $\hat{A}^{-}\ \Psi_o = 0$, since there is no state with lower energy. The harmonic oscillator is a good example.

Harmonic Oscillator Excited States Can be Generated Using Ladder Operators: The harmonic oscillator Hamiltonian in dimensionless form is given by Eq. 24.3.6. This Hamiltonian can be factored into two terms using the relationship:

$$\left(y + \frac{d}{dy}\right)\left(y - \frac{d}{dy}\right) = y^2 - y\frac{d}{dy} + \frac{d}{dy}y - \frac{d^2}{dy^2} = y^2 - \frac{d^2}{dy^2} + \left[\frac{d}{dy}, y\right]$$

24.7.8

The commutator is $[d/dy, y] = 1$. Solving for the harmonic oscillator Hamiltonian gives:

$$\hat{\mathcal{H}} = -\frac{d^2}{dy^2} + y^2 = \left(y + \frac{d}{dy}\right)\left(y - \frac{d}{dy}\right) - 1$$

24.7.9

Substitution of this last equation into the Schrödinger equation for the Harmonic oscillator, Eq. 24.3.6, gives:

$$\left(y + \frac{d}{dy}\right)\left(y - \frac{d}{dy}\right)\Psi_\upsilon = (\varepsilon_\upsilon + 1)\,\Psi_\upsilon$$

24.7.10

The power of this relationship is that the Hamiltonian factors into the product of a lowering and raising operator:

$$\hat{\mathcal{H}}^- = \left(y + \frac{d}{dy}\right)$$
(lowering)   24.7.11

$$\hat{\mathcal{H}}^+ = \left(y - \frac{d}{dy}\right)$$
(raising)   24.7.12

We can interpret Eq. 24.7.10 in the following way. Starting with Ψ_υ, $\hat{\mathcal{H}}^+$ moves up one energy level and then $\hat{\mathcal{H}}^-$ moves back down to give the original wave function.

Example 24.7.1: *Commutator for $\hat{\mathcal{H}}^-$ and $\hat{\mathcal{H}}^+$*
Find the commutator $[\hat{\mathcal{H}}^-, \hat{\mathcal{H}}^+]$.

Answer: Using Eqs. 24.7.11 and 24.7.12, the commutator expands to give:

$$[\hat{\mathcal{H}}^-, \hat{\mathcal{H}}^+] = \left(y + \frac{d}{dy}\right)\left(y - \frac{d}{dy}\right) - \left(y - \frac{d}{dy}\right)\left(y + \frac{d}{dy}\right)$$
$$= y^2 - y\frac{d}{dy} + \frac{d}{dy}y - \frac{d^2}{dy^2} - y^2 - y\frac{d}{dy} + \frac{d}{dy}y + \frac{d^2}{dy^2}$$

Canceling terms and using $[d/dy, y] = 1$ gives;

$$[\hat{\mathcal{H}}^-, \hat{\mathcal{H}}^+] = 2\left(\frac{d}{dy}y - y\frac{d}{dy}\right) = 2\left[\frac{d}{dy}, y\right] = 2$$

24.7.13

Example 24.7.2: *Raising Operator for the Harmonic Oscillator*
Show that the operator defined in Eq. 24.7.12 is a raising operator.

Answer: We need to show that $[\hat{A}, \hat{A}^+] = k\,\hat{A}^+$, Eq. 24.7.1. The harmonic oscillator Hamiltonian can be written in terms of the lowering and raising operators by substituting Eqs. 24.7.11 and 24.7.12 into Eq. 24.7.9 to give:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^- \hat{\mathcal{H}}^+ - 1 \qquad\qquad 24.7.14$$

The commutator is then:

$$\begin{aligned}
[\hat{\mathcal{H}},\hat{\mathcal{H}}^+] &= (\hat{\mathcal{H}}^- \hat{\mathcal{H}}^+ - 1)\,\hat{\mathcal{H}}^+ - \hat{\mathcal{H}}^+(\hat{\mathcal{H}}^- \hat{\mathcal{H}}^+ - 1) \\
&= \hat{\mathcal{H}}^- \hat{\mathcal{H}}^+\,\hat{\mathcal{H}}^+ - \hat{\mathcal{H}}^+ - \hat{\mathcal{H}}^+\hat{\mathcal{H}}^-\hat{\mathcal{H}}^+ + \hat{\mathcal{H}}^+ \\
&= (\hat{\mathcal{H}}^- \hat{\mathcal{H}}^+ - \hat{\mathcal{H}}^+\hat{\mathcal{H}}^-)\,\hat{\mathcal{H}}^+ = [\hat{\mathcal{H}}^-,\hat{\mathcal{H}}^+]\,\hat{\mathcal{H}}^+
\end{aligned}$$

Substituting for the commutator from Eq. 24.7.13 gives:

$$[\hat{\mathcal{H}},\hat{\mathcal{H}}^+] = 2\,\hat{\mathcal{H}}^+ \qquad\qquad 24.7.15$$

The final result corresponds to k = 2, so $\hat{\mathcal{H}}^+$ is a raising operator. A good practice problem is to show that $\hat{\mathcal{H}}^-$ is a lowering operator.

A ladder of states is generated by repeated action of $\hat{\mathcal{H}}^+$ on the ground state wave function, Ψ_o. The excited states are given by $\Psi_1 = \hat{\mathcal{H}}^+ \Psi_o$, $\Psi_2 = \hat{\mathcal{H}}^+ \Psi_1$, …. Using Eq. 24.7.7 with the Hamiltonian operator and k = 2 from Eq. 24.7.15, the eigenvalues generate the series:

$$\begin{aligned}
\hat{\mathcal{H}}\Psi_1 &= (\varepsilon_o + k)\,\Psi_1 = (\varepsilon_o + 2)\,\Psi_1 \\
\hat{\mathcal{H}}\Psi_2 &= (\varepsilon_1 + k)\,\Psi_2 = (\varepsilon_o + 2 + 2)\,\Psi_2 \\
\hat{\mathcal{H}}\Psi_3 &= (\varepsilon_2 + k)\,\Psi_3 = (\varepsilon_o + 2 + 2 + 2)\,\Psi_3 \quad …. \\
\hat{\mathcal{H}}\Psi_\upsilon &= (\varepsilon_{\upsilon\text{-}1} + k)\,\Psi_\upsilon = (\varepsilon_o + 2\upsilon)\,\Psi_\upsilon \qquad 24.7.16
\end{aligned}$$

The eigenvalues, $\varepsilon_\upsilon = (\varepsilon_o + 2\upsilon)$, are for the dimensionless Hamiltonian. In dimensionless units, the ground state eigenvalue is $\varepsilon_o = 1$. In joules the ground state energy is $E_o = \tfrac{1}{2} h\nu_o$. Working back to the original units by using $\varepsilon_o = 1$, Eqs. 24.3.3 and $E_o = \tfrac{1}{2} h\nu_o$ gives:

$$E_\upsilon = E_o\,\varepsilon_\upsilon = \tfrac{1}{2} h\nu_o\,(1 + 2\upsilon) = h\nu_o(\upsilon + \tfrac{1}{2}) \qquad 24.7.17$$

which proves that the harmonic oscillator quantum number, υ, increases in unit steps. The advantage of using ladder operators is that we didn't need to solve the full explicit differential equation. Ladder operators can also be used to generate the explicit wave functions.

Exercise 24.7.3: *Generating the Hermite polynomials Using Ladder Operators*
The ground state wave function for the harmonic oscillator in unnormalized, dimensionless form is $\Psi_o = e^{-y^2/2}$, Eq. 24.2.18. Use the harmonic oscillator raising operator to find the first two excited states of the harmonic oscillator.

Answer: The first excited state is given using Eq. 24.7.12:

$$\Psi_1 = \hat{\mathcal{H}}^+ \Psi_o = \left(y - \frac{d}{dy}\right) e^{-y^2/2} = y\,e^{-y^2/2} - (-y)\,e^{-y^2/2} = 2y\,e^{-y^2/2}$$

Comparison with Table 24.1.1 with $\upsilon = 1$ shows the same result, $H_1 = 2y$. For the next excited state:

$$\Psi_2 = \hat{\mathcal{H}}^+ \Psi_1 = \left(y - \frac{d}{dy}\right) 2y\, e^{-y^2/2} = 2y^2\, e^{-y^2/2} - 2\frac{d}{dy}\, y\, e^{-y^2/2}$$

Using the product rule for the last term results in:

$$\Psi_2 = \hat{\mathcal{H}}^+ \Psi_1 = \left(y - \frac{d}{dy}\right) 2y\, e^{-y^2/2} = 2y^2\, e^{-y^2/2} - 2y(-y)\, e^{-y^2/2} - 2\, e^{-y^2/2}$$

$$= (4y^2 - 2)\, e^{-y^2/2}$$

Comparison with Table 24.1.1 with $\upsilon = 2$ shows the same result, $H_1 = 4y^2 - 2$.

For Angular Momentum, the Values for m_ℓ can be Determined Using Ladder Operators: The lowering and raising operators for the z-axis projection of the angular momentum are given by:

$$\hat{L}^- = \hat{L}_x - i\,\hat{L}_y \qquad \text{(lowering)} \qquad \text{and} \qquad \hat{L}^+ = \hat{L}_x + i\,\hat{L}_y \qquad \text{(raising)} \qquad 24.7.18$$

The commutation relationships are:

$$[\hat{L}_z, \hat{L}^-] = -\hbar\hat{L}^- \qquad\qquad [\hat{L}_z, \hat{L}^+] = \hbar\hat{L}^+ \qquad\qquad 24.7.19$$
$$[\hat{L}^+, \hat{L}^-] = 2\hbar\hat{L}_z \qquad\qquad 24.7.20$$
$$[\hat{L}^2, \hat{L}^\pm] = 0 \qquad\qquad 24.7.21$$

Eqs. 24.7.19 show that $\hat{L}^-$ is a lowering operator for $\hat{L}_z$ with $k = -\hbar$ and $\hat{L}^+$ is a raising operator with $k = \hbar$. Eq. 24.7.21 shows that the raising and lowering operators don't change the total angular momentum; ℓ remains constant. The wave functions are eigenfunctions of $\hat{L}_z$ with quantum number m_ℓ:

$$\hat{L}_z \Psi_{m_\ell} = m_\ell \hbar\, \Psi_{m_\ell} \qquad\qquad 24.7.22$$

For a given m_ℓ value, we can find the adjacent state of higher quantum number using the raising operator:

$$\hat{L}^+ \Psi_{m_\ell} \equiv \Phi \qquad\qquad 24.7.23$$

What is the eigenvalue for this new state? The z-axis projection eigenvalue is given by $\hat{L}_z$ acting on the new wave function:

$$\hat{L}_z \Phi = \hat{L}_z \hat{L}^+ \Psi_{m_\ell} \qquad\qquad 24.7.24$$

Expanding the commutator in Eq. 24.7.19, allows us to solve for $\hat{L}_z\hat{L}^+$ to give:

$$[\hat{L}_z, \hat{L}^+] = \hat{L}_z\hat{L}^+ - \hat{L}^+\hat{L}_z = \hbar\hat{L}^+$$
$$\hat{L}_z\hat{L}^+ = \hat{L}^+\hat{L}_z + \hbar\hat{L}^+ \qquad\qquad 24.7.25$$

Substituting this last relationship into Eq. 24.7.24 gives:

$$\hat{L}_z \Phi = (\hat{L}^+\hat{L}_z + \hbar\hat{L}^+)\Psi_{m_\ell} = \hat{L}^+\hat{L}_z\Psi_{m_\ell} + \hbar\hat{L}^+\, \Psi_{m_\ell} \qquad\qquad 24.7.26$$

However, using the fact that Ψ_{m_ℓ} is an eigenfunction of $\hat{L}_z$ from Eq. 24.7.22, in the first term of the last equation, gives:

$$\hat{L}_z \Phi = \hat{L}^+ m_\ell \hbar\ \Psi_{m_\ell} + \hbar\hat{L}^+ \Psi_{m_\ell} = (m_\ell \hbar + \hbar)\hat{L}^+ \Psi_{m_\ell} = (m_\ell + 1)\hbar\Phi \qquad\qquad 24.7.27$$

The new wave function has quantum number $(m_\ell + 1)$, proving that m_ℓ increases in unit steps. Since the projection of the angular momentum on the z-axis cannot exceed the total angular momentum, m_ℓ must have a minimum and maximum value. For half-integer ℓ, typical series include examples $(-\frac{1}{2}, +\frac{1}{2})$ and $(-\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2})$, with unit steps. For integer ℓ, typical series include examples $(-1, 0, +1)$ and $(-2, -1, 0, +1, +2)$, again with unit steps. In either case the degeneracy is $2\ell + 1$.

   The use of ladder operators allows us to generate the spectrum of the quantum solutions without explicitly needing to use Hermite polynomials or spherical harmonics. Reference to Eqs. 24.7.1 and 24.7.7 shows that commutation relationships allow us to derive the landscape of solutions to the Schrödinger equation, in addition to determining uncertainty relationships.

24.8 Summary – Looking Ahead

   The ground state wave function of the harmonic oscillator approaches zero gradually for large extension, tunneling beyond the classical turning points. The excited states are a product of a Hermite polynomial with the asymptotic form of the ground state. The order of the Hermite polynomial is the vibrational quantum number and is equal to the number of nodes in the wave function. The Hermite polynomial based harmonic oscillator wave functions are a complete orthonormal set that describe the vibrational states of a molecule. In molecules larger than diatomics, each normal mode can be modeled as an independent harmonic oscillator. The harmonic oscillator has a zero point energy. At absolute zero K, all normal modes have vibrational energy.

   Spherical harmonics describe how waves "wrap" around the origin for spherical motion. Spherical harmonics are the normal modes of a sphere. Geologists and atmospheric scientists decompose the motions of the earth, the oceans, and the atmosphere into spherical harmonic components to discuss the interactions of the geosphere and the atmosphere. Acoustic engineers use spherical harmonics to discuss sound patterns. The spherical harmonics are also a complete orthonormal set of wave functions that describe angular momentum states. Linear motion can be decomposed into a superposition of Hermite polynomial based vibrational states, and angular motion can be decomposed into a superposition of spherical harmonics. Angular momentum has quantized energies and quantized spatial orientations. Rotation has no zero point energy; at absolute zero K all rotational energy is zero. The theory of angular momentum is universally applicable to spinning molecules, electrons spinning around the nucleus of atoms, and the intrinsic spin of elementary particles and atomic nuclei.

   In the next two chapters we use the theory of angular momentum to determine the electronic states for atoms and molecules. In subsequent chapters we use the rigid rotor and harmonic oscillator as models for molecular rotation and vibration spectroscopy.

   At this point we should take a moment to reflect on the amazing differences between the macroscopic and microscopic worlds. The macroscopic world is chaotic and unsymmetrical. The macroscopic world presents a seemingly endless array of variety and complexity. The microscopic world of individual molecules, on the other hand, is very orderly and described remarkably simply. The motion of molecules is governed by a few quantum numbers, which are

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applicable for all types of molecules, no matter how complex. The quantum numbers are for translation (n_x, n_y, and n_z), for rotation (J and m_J), and vibration (υ for each normal mode). The wave functions for vibration and rotation have simple symmetries and shapes, which are governed by the number of nodes. One of the most interesting questions is how the amazing simplicity of the microscopic world of molecules translates into the rich and varied complexity that we experience in our lives.

24.8 Addendum: Integrals in Multiple Dimensions and Spherical Polar Coordinates

The volume of a rectangular box of side lengths a, b, and c can be determined using the integral over x, y, and z:

$$V = \int_0^a \int_0^b \int_0^c dx \, dy \, dz \qquad\qquad 24.8.1$$

A visual interpretation of this triple integral is that we are adding the infinitesimal volumes, dx dy dz, within the box, Figure 24.8.1a. The integrand is "1", which is independent of x, y, and z. The triple integral then factors into the product of the three one-dimensional integrals:

$$V = \int_0^a dx \int_0^b dy \int_0^c dz = abc \qquad\qquad 24.8.2$$

The volume is then just the product of the side lengths as expected.

(a). (b).
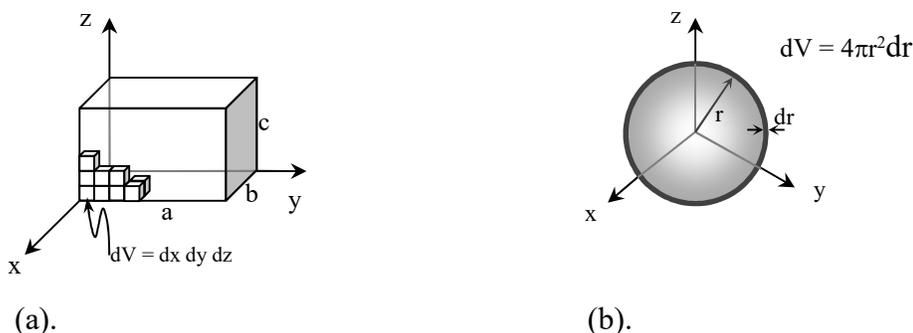
Figure 24.8.1: (a). The sum of the infinitesimal volumes, dV = dx dy dz, inside the box gives the total volume. (b). The area of a thin annular region from r to r + dr.

The infinitesimal, dx dy dz, is the volume of an infinitesimal box, giving the **volume element** in three Cartesian dimensions as:

$$d\tau = dx \, dy \, dz \qquad\qquad 24.8.3$$

Example 24.8.1: *3D-Integrals in Cartesian Coordinates*

Normalize the 3D-particle in a box wave function: $\Psi(x,y,z) = N \sin \dfrac{n_x \pi x}{a} \sin \dfrac{n_y \pi y}{b} \sin \dfrac{n_z \pi z}{c}$

Answer: The normalization integral is:

$$\int_0^a \int_0^b \int_0^c \underbrace{N^2 \sin^2 \frac{n_x \pi x}{a} \sin^2 \frac{n_y \pi y}{b} \sin^2 \frac{n_z \pi z}{c}}_{\Psi^2} \underbrace{dx\, dy\, dz}_{\text{volume element, } d\tau} = 1$$

The integral factors into three one-dimensional terms:

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

The one-dimensional integrals are given by Eq. 23.4.15:

$$N^2 \left(\frac{a}{2}\right)\left(\frac{b}{2}\right)\left(\frac{c}{2}\right) = N^2 \left(\frac{abc}{8}\right) = 1 \qquad \text{or} \qquad N = \left(\frac{8}{abc}\right)^{1/2}$$

Luckily, for our purposes in this course, the integrals almost always factor into three one-dimensional terms.

The volume element in spherical polar coordinates is given by Eq. 24.5.15. Integrals using spherical polar coordinates simplify problems in spherical systems. For example, the total surface area of a sphere of radius r_o is the integral over all θ and ϕ at fixed radius. The integrand factors into products of terms of only one variable, so the integral factors into the product of two one-dimensional integrals.:

$$\int_0^\pi \int_0^{2\pi} r_o^2 \sin\theta\, d\theta\, d\phi = r_o^2 \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = 4\pi\, r_o^2 \qquad (r_o = \text{constant}) \qquad 24.8.4$$

The integrals over θ and ϕ are given by Eq. 24.5.16. The total solid angle in a sphere is 4π radians, Eq. 24.5.17. The volume of a sphere of radius r_o is given by the integral over r from 0 to r_o and over all angles:

$$V = \int_0^{r_o} \int_0^\pi \int_0^{2\pi} r^2 \sin\theta\, dr\, d\theta\, d\phi = \int_0^{r_o} r^2\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = \frac{4}{3} \pi r_o^3 \qquad 24.8.5$$

The volume of a sphere is difficult to find without spherical polar coordinates. The volume of a thin annular region of a sphere from r to r + dr is given by the integral over all angles:

$$dV = \int_0^\pi \int_0^{2\pi} r^2 \sin\theta\, dr\, d\theta\, d\phi = 4\pi r^2\, dr \qquad 24.8.6$$

which is the surface area multiplied by the thickness of the "shell." This annular area, which is like a thin "onion skin," will be used in finding the size of atoms, Figure 24.8.1b.

Example 24.8.3: *3D-Integrals in Spherical Polar Coordinates*
Normalize the ground state of the hydrogen atom, which is given by: $\Psi(r) = N\, e^{-Zr/a_o}$.

Answer: The normalization integral is given by:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \underbrace{N^2\, e^{-2Zr/a_o}}_{\Psi^2}\ \underbrace{r^2 \sin\theta\ dr\ d\theta\ d\phi}_{\text{volume element, } d\tau} = 1$$

Notice that the volume element $d\tau = r^2 \sin\theta\ dr\ d\theta\ d\phi$ is substituted as a "package", you need the full volume element. Once again the integrand factors into a product of one-dimensional terms:

$$N^2 \int_0^\infty e^{-2Zr/a_o}\, r^2\, dr \int_0^\pi \sin\theta\ d\theta \int_0^{2\pi} d\phi = 1$$

The angular integrals give 4π: $\quad 4\pi\, N^2 \int_0^\infty e^{-2Zr/a_o}\, r^2\, dr = 1$

Integral tables list $\displaystyle\int_0^\infty x^n\, e^{-ax}\, dx = \frac{n!}{a^{n+1}}$ giving the normalization integral as:

$$4\pi\, N^2 \frac{2}{(2Z/a_o)^3} = 1 \qquad\qquad \text{or}\quad N = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2}$$

as given in Eq. 23.3.16.

Chapter Summary

1. The center of mass of a diatomic molecule is determined from $m_1 r_1 = m_2 r_2$, where r_1 is the distance from mass m_1 to the center of mass, r_2 is the distance from mass m_2 to the center of mass, and the bond length is $r = r_1 + r_2$.

2. The distances to the center of mass are mass weighted fractions of the full bond length.

$$r_1 = \frac{m_2}{m_1 + m_2}\, r \qquad\qquad \text{and} \qquad r_2 = \frac{m_1}{m_1 + m_2}\, r$$

3. The reduced mass of the diatomic molecule is: $\mu \equiv \dfrac{m_1 m_2}{m_1 + m_2}$

4. The kinetic energy of a diatomic molecule is: $E_k = \frac{1}{2}\,\mu \left(\dfrac{dx}{dt}\right)^2$

5. The fundamental vibration frequency for a diatomic harmonic oscillator is:

$$\nu_o = \frac{1}{2\pi}\sqrt{k/\mu} \qquad\qquad \text{or in radians} \qquad \omega_o = 2\pi\nu_o \qquad \omega_o = \sqrt{k/\mu}$$

6. The potential energy operator and Schrödiner equation for the harmonic oscillator are:

$$\hat{V}(x) = \frac{1}{2}\, kx^2 \qquad\qquad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi + \frac{1}{2}\, kx^2\, \Psi = E\Psi$$

7. The ground state of the harmonic oscillator is a Gaussian function: $\Psi_o(x) = N_o\, e^{-\frac{1}{2}\alpha^2 x^2}$, with:

$$\alpha^2 = \frac{\sqrt{mk}}{\hbar} = \frac{m}{\hbar}\sqrt{k/m} = \frac{m\omega_o}{\hbar} \qquad\qquad \text{and normalization}\quad N_o = \left(\frac{\alpha^2}{\pi}\right)^{1/4}$$

8. The energy of the ground state is given by: $E_o = \hbar^2\alpha^2/2m = \frac{1}{2}\,\hbar\omega_o = \frac{1}{2}\, h\nu_o$

9. The energy levels for the harmonic oscillator with quantum number $\upsilon = 0, 1, 2, \ldots, \infty$ are:

$$E_\upsilon = h\nu_o(\upsilon + \tfrac{1}{2})$$

10. The harmonic oscillator energy states are equally spaced: $\Delta E = E_{\upsilon+1} - E_\upsilon = h\nu_o$

11. The bond force constant with $\tilde{\nu}_o$ in wave numbers is: $k = 4\pi^2\tilde{\nu}_o^2 c^2\mu$

12. Excited state wave functions are built from the ground state wave function by multiplying the ground state wave function by a polynomial, $\Psi_\upsilon(x) = $ (polynomial) $\Psi_o(x)$. The polynomial is chosen to have the number of zeros equal to the number of nodes.

13. With $y = \alpha x$, the harmonic oscillator wave functions are $\Psi_\upsilon(y) = N_\upsilon H_\upsilon(y)\, e^{-\frac{1}{2}y^2}$, where $H_\upsilon(y)$ are the Hermite polynomials of order $\upsilon = $ number of nodes. The normalization is:

$$N_\upsilon = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^\upsilon\, \upsilon!}\right)^{\frac{1}{2}}$$

14. The $H_\upsilon(y)$ are the solutions of the Hermite equation: $\dfrac{d^2 H_\upsilon}{dy^2} - 2y\dfrac{dH_\upsilon}{dy} + 2\upsilon\, H_\upsilon = 0$

15. The $H_\upsilon(y)$ are generated using a recursion relationship: $H_{\upsilon+1} = 2y\, H_\upsilon - 2\upsilon\, H_{\upsilon-1}$

16. For orthonormality: $\int_{-\infty}^{\infty} H_{\upsilon'}\, e^{-\frac{1}{2}y^2}\, H_\upsilon\, e^{-\frac{1}{2}y^2}\, dy = \pi^{\frac{1}{2}}\, 2^\upsilon\, \upsilon!$ if $\upsilon' \neq \upsilon$ and $= 0$ if $\upsilon' = \upsilon$.

17. The dimensionless form of the harmonic oscillator Schrödinger equation with $y = \alpha x$ is:

$$-\frac{d^2}{dy^2}\,\Psi_\upsilon + y^2\,\Psi_\upsilon = \varepsilon_\upsilon\,\Psi_\upsilon \qquad\qquad \text{with}\quad \varepsilon_\upsilon = \frac{E_\upsilon}{E_o}$$

18. The angular momentum for rotation is a plane is $L = I\omega$ and the kinetic energy is $E_k = L^2/2I$. The angular velocity is $\omega = d\phi/dt$. The moment of inertia for a single mass at distance r from the origin is $I = mr^2$, for a diatomic molecule is $I = \mu r^2$, and for a linear molecule $I = \Sigma\, m_i\, r_i^2$.

19. The rigid rotor approximation assumes that the bond lengths and angles in the molecule are fixed and independent of the rotational state of the molecule.

20. The Schrödinger equation for rotation in a plane is: $-\dfrac{\hbar^2}{2I}\left(\dfrac{\partial^2\Psi}{\partial\phi^2}\right) = E_{m_\ell}\Psi_{m_\ell} \qquad \Psi_{m_\ell} = a\, e^{im_\ell\phi}$

21. The magnetic quantum number varies in unit steps and gives the number of angular nodes that include the z-axis: $m_\ell = 0, \pm1, \pm2, \pm3, \ldots$

22. Ψ_{m_ℓ} is also an eigenfunction of the z-component of the angular momentum:

$$\hat{L}_z\,\Psi_{m_\ell} = \frac{\hbar}{i}\frac{\partial\Psi_{m_\ell}}{\partial\phi} = \hbar m_\ell\Psi_{m_\ell} \qquad\qquad \text{with}\quad L_z = \hbar m_\ell$$

23. The spherical polar coordinate system is given by the transformations with $0 \leq r \leq \infty$, $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$, and $r = \sqrt{x^2 + y^2 + z^2}$:

$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

24. The volume element in spherical polar coordinates is: $d\tau = r^2\sin\theta\, dr\, d\theta\, d\phi$

25. The operators for the components of the total angular momentum are:

$$\hat{L}_x = (\hat{y}\,\hat{p}_z - \hat{z}\,\hat{p}_y) = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \qquad\qquad \hat{L}_x = \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = (\hat{z}\,\hat{p}_x - \hat{x}\,\hat{p}_z) = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \qquad\qquad \hat{L}_y = \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = (\hat{x}\,\hat{p}_y - \hat{x}\,\hat{p}_x) = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \qquad\qquad \hat{L}_z = \frac{\hbar}{i}\left(\frac{\partial}{\partial\phi}\right)$$

26. The square of the total angular momentum operator is: $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\Lambda^2$ with:

$$\Lambda^2 = \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) + \left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) \qquad\qquad \text{(curvature in } \theta \text{ and } \phi)$$

27. The 3-dimensional Schrödinger equation in spherical polar coordinates is:

$$-\frac{\hbar^2}{2m}\nabla^2\,\Psi + \hat{V}(x,y,z) = E\,\Psi \qquad\qquad \text{with the curvature: } \nabla^2 = \frac{1}{r}\left(\frac{\partial^2}{\partial r^2}\right)r + \left(\frac{1}{r^2}\right)\Lambda^2$$

28. The eigenfunctions of the total angular momentum squared are the spherical harmonics:

$$\hat{L}^2\,Y_{\ell,m_\ell} = L^2\,Y_{\ell,m_\ell} \qquad\qquad -\hbar^2\,\Lambda^2 Y_{\ell,m_\ell} = \hbar^2\,\ell\,(\ell+1)\,Y_{\ell,m_\ell}$$

29. The square of the total angular momentum for Y_{ℓ,m_ℓ} is $L^2 = \hbar^2\,\ell\,(\ell+1)$ with magnitude:

$$|L| = \hbar\sqrt{\ell\,(\ell+1)}$$

30. The rigid rotor corresponds to motion in θ and ϕ on the surface of a sphere, with fixed r and no potential energy: $-\dfrac{\hbar^2}{2I}\Lambda^2\,Y_{\ell,m_\ell} = E_\ell\,Y_{\ell,m_\ell}$ and $E_\ell = \dfrac{\hbar^2}{2I}\ell\,(\ell+1)$

31. The Y_{ℓ,m_ℓ} are also eigenfunctions of the z-axis projection of the angular momentum:

$$\hat{L}_z\,Y_{\ell,m_\ell} = \frac{\hbar}{i}\frac{\partial Y_{\ell,m_\ell}}{\partial\phi} = \hbar m_\ell\,Y_{\ell,m_\ell} \qquad\qquad L_z = \hbar m_\ell$$

32. The total number of angular nodes is ℓ. The number of angular nodes that include the z-axis is m_ℓ. The number of angular nodes that include the z-axis cannot exceed the total number of nodes, so the restrictions on the quantum numbers are: $\ell = 0, 1, 2, \ldots$ and $m_\ell = 0, \pm1, \ldots, \pm\ell$

33. The degeneracy is: $g_\ell = 2\ell + 1$

34. For rotating linear molecule:

$$E_J = \frac{\hbar^2}{2I}J(J+1) \quad J = 0, 1, 2, \ldots \text{ and } m_J = 0, \pm1, \ldots, \pm J \qquad g_J = 2J+1$$

35. In wave numbers, the energy levels are called the rotational term values, $\tilde{F}_J$, where $\tilde{B}$ is the rotational constant in wave numbers:

$$\tilde{F}_J = \frac{E_J}{hc} = \tilde{B}\,J(J+1) \qquad\qquad \text{with } \tilde{B} = \frac{\hbar}{4\pi Ic}$$

36. In joules, $E_J = \tilde{B}hc\,J\,(J+1)$ and the energy difference between adjacent energy levels is:

$$\Delta E = E_{J+1} - E_J = \tilde{B}hc[(J+1)(J+1+1) - J(J+1)] = 2\tilde{B}hc(J+1) \qquad \text{with J for the lower level}$$

37. Angular momentum for elementary particles is called intrinsic angular momentum or spin.

38. For a spin ½ particle the wave functions are α for spin up and β for spin down with angular momentum magnitude: $|S| = \hbar \sqrt{s(s+1)} = \hbar \sqrt{½(½+1)}$ and $m_s = \pm½$:

$\hat{S}^2 \alpha = \hbar^2 s(s+1) \alpha$ $S_z \alpha = +½ \hbar \alpha$

$\hat{S}^2 \beta = \hbar^2 s(s+1) \beta$ $S_z \beta = -½ \hbar \beta$

39. The spin quantum numbers of the electron, proton and neutron are s = ½.

40. For photons, s = 1. However, since a photon travels at the speed of light, $m_s = -1, +1$ only.

41. The x and y components of the angular momentum cannot be determined simultaneously to arbitrary precision, because $\hat{L}_x$ and $\hat{L}_y$ do not commute. The commutation relationships are:

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

$[\hat{L}^2, \hat{L}_x] = 0$ $[\hat{L}^2, \hat{L}_y] = 0$ $[\hat{L}^2, \hat{L}_z] = 0$

42. Angular momentum vectors are drawn as vector diagrams. The projection on the z-axis is less than the length, $|L| = \hbar \sqrt{\ell(\ell+1)}$, so the vector must be tilted with respect to the z-axis.

43. Angular momentum is quantized in space, by a fixed orientation with respect to the z-axis. The restricted value for the orientation is called spatial quantization.

44. Only $\hat{L}^2$ and one of the projections can be determined precisely simultaneously. If L^2 and L_z are known precisely from the quantum numbers ℓ and m_ℓ, then repeated observations have different projections on the x- and y-axes and $\langle \hat{L}_x \rangle = \langle \hat{L}_y \rangle = 0$. The angular momentum vectors lie on a precession cone with fixed height, $L_z = \hbar m_\ell$.

45. A ladder operator has the property: $[\hat{A}, \hat{A}^\pm] = k \hat{A}^\pm$, where $\hat{A}$ is general operator, k is a constant, and $\hat{A}^\pm$ is either a raising operator, $\hat{A}^+$, or a lowering operator, $\hat{A}^-$.

46. Because $\hat{A}$ and $\hat{A}^\pm$ don't commute, Ψ_υ cannot be an eigenfunction of $\hat{A}^\pm$.

47. If k is positive, $\hat{A}^+ \Psi_\upsilon$ is the eigenfunction with the next higher eigenvalue. If k is negative, $\hat{A}^- \Psi_\upsilon$ is the eigenfunction with the next lower eigenvalue: $\hat{A}\hat{A}^\pm \Psi_\upsilon = (\varepsilon_\upsilon + k) \hat{A}^\pm \Psi_\upsilon$

48. The lowering and raising operators for the harmonic oscillator are:

$$\hat{\mathcal{H}}^- = \left(y + \frac{d}{dy} \right) \qquad \hat{\mathcal{H}}^+ = \left(y - \frac{d}{dy} \right)$$

with $[\hat{\mathcal{H}}^-, \hat{\mathcal{H}}^+] = 2$ $[\hat{\mathcal{H}}, \hat{\mathcal{H}}^+] = 2 \hat{\mathcal{H}}^+$ $[\hat{\mathcal{H}}, \hat{\mathcal{H}}^-] = -2 \hat{\mathcal{H}}^-$

49. The lowering and raising operators for the z-axis projection of the angular momentum are: $\hat{L}^- = \hat{L}_x - i \hat{L}_y$ and $\hat{L}^+ = \hat{L}_x + i \hat{L}_y$. The commutation relationships are:

$[\hat{L}_z, \hat{L}^-] = -\hbar \hat{L}^-$ $[\hat{L}_z, \hat{L}^+] = \hbar \hat{L}^+$ $[\hat{L}^+, \hat{L}^-] = 2\hbar \hat{L}_z$ $[\hat{L}^2, \hat{L}^\pm] = 0$

50. The z-projection angular momentum raising and lowering operators don't change the total angular momentum; ℓ remains constant.

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Further Reading

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Problems: The Quantum Mechanics of Rotation and Vibration

1. (a). How many nodes are in the $\upsilon = 3$ wave function for the harmonic oscillator? (b). How many angular nodes are in the $\ell = 3$, $m_\ell = 2$ wave function for the rigid rotor? (c). How many of the angular nodes for the $\ell = 3$, $m_\ell = 2$ rigid rotor include the z-axis? (d). Why are the nodes important?

2. Multiply the harmonic oscillator ground state wave function, Figure P24.1a, by the polynomial, Figure P24.1b, to give the excited state wave function. Sketch the excited state wave function. What is the quantum number for this wave function?

(a).   (b).
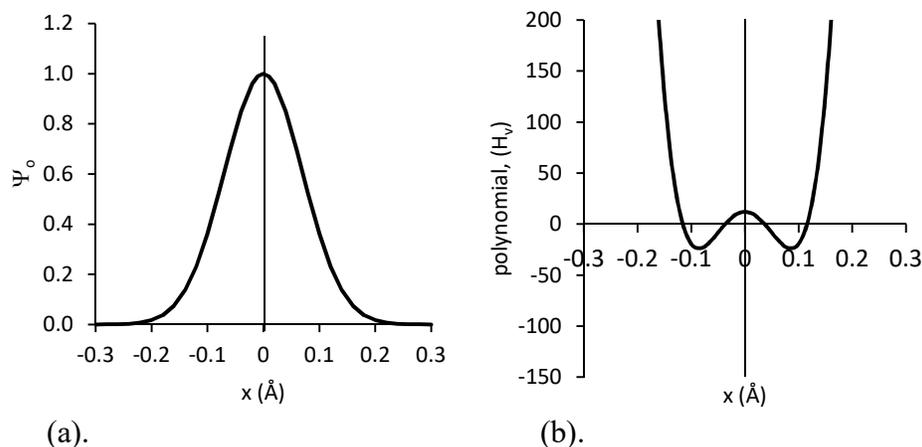
Figure P24.1: (a) The ground state for the harmonic oscillator. (b). The polynomial used to generate an excited state of the harmonic oscillator. The polynomial is a Hermite polynomial.

3. (a). The fundamental vibration frequency for $^1H^{79}Br$ is 2649.67 cm^{-1}. Calculate the force constant. Calculate the energy for the transition in kJ mol^{-1}. (b). The force constant for the vibration in $^1H^{35}Cl$ is 515.90 N m^{-1}. Calculate the vibration frequency in cm^{-1}. Calculate the energy for the transition in kJ mol^{-1}. (c). Which has a stronger bond, and why?

4. Normalize the wave function for the ground state of the harmonic oscillator, $\Psi_o = N\, e^{-\frac{1}{2}\alpha^2 x^2}$

5. Find the expectation values for the position and momentum of the ground state of the harmonic oscillator.

6. Find the expectation value of the potential energy for the ground state of the harmonic oscillator.

7. Find the expectation value of the kinetic energy for the ground state of the harmonic oscillator.

8. Show that the ground state of the harmonic oscillator is consistent with the Heisenberg uncertainty principle. [Hint: Calculate the standard deviations of the position and momentum. However, you don't need to prove that $<x> = 0$ and $<p> = 0$, which are given by symmetry.]

9. Use the recursion relationship for Hermite polynomials to generate the first four excited state wave functions for the harmonic oscillator (H_1 to H_4).

10. Confirm that wavefunctions for a 2D-rigid rotor (particle-in-a-ring) are orthogonal. [Hint: the wave functions are $\psi(\phi) = a\, e^{i\,m_\ell\,\phi}$ with different m_ℓ.]

11. Show that the wave function $\Psi(\phi) = a\, e^{i m_\ell \phi}$ is an eigenfunction of the Hamiltonian for the rigid-rotor in the x-y plane, where $\hat{\mathcal{H}} = -\hbar^2/2I\,(d^2/d\phi^2)$. What is the energy for this wavefunction?

12. Show that $\Psi(\theta) = \cos\theta$ is an eigenfunction of the square of the total angular momentum operator, where: (total angular momentum operator)$^2 = \hat{L}^2 = -\hbar^2\,\Lambda^2$.

13. Normalize $Y_{1,0} = N\cos\theta$.

14. Show that the rigid-rotor wave functions $Y_{0,0}$ and $Y_{1,0}$ are orthogonal.

15. Show that the rigid-rotor wave functions $Y_{1,0}$ and $Y_{1,1}$ are orthogonal.

16. Give the magnitude of the total angular momentum and the z-axis projection of the angular momentum for an $\ell = 2$, $m_\ell = 1$ state of a rigid rotor. Give your answers in multiples of $\hbar$.

17. Give the transition energy, in wave numbers, for the $J = 0$ to $J = 1$ transition in carbon monoxide. Find the transition frequency in GHz. Use the most abundant isotopes, $^{12}C\equiv^{16}O$, with the bond length 1.1282 Å.

18. Show that $[\hat{L}_x, \hat{L}_y] = i\hbar\,\hat{L}_z$. This problem is best done using the operators expressed in Cartesian coordinates.

19. Show that $[\hat{L}^2, \hat{L}_z] = 0$. This problem is best done using the operators expressed in spherical polar coordinates.

20. Why is $[\hat{L}^2, \hat{L}_z] = 0$ significant?

21. Draw the angular momentum vector diagrams for $\ell = 2$ angular momentum states.

22. Draw the angular momentum vector diagram for a single electron or proton, $s = \frac{1}{2}$.

23. The spins of the protons and neutrons combine to give the overall spin of a nucleus. The details depend on the quantum structure of the nucleus and can result in half-integer or integer overall spin. The nucleus of ^{35}Cl has a spin of $I = \frac{3}{2}$. Give the possible values for the quantum number for the z-axis projection of the angular momentum.

24. The nucleus of ^{105}Pd has a spin of $I = {}^5/_2$. Give the possible values for the quantum number for the z-axis projection of the angular momentum. (The NMR resonance frequency for ^{105}Pd is 22.9 MHz on a 500 MHz NMR.)

25. Show that the operator $\hat{\mathcal{H}}^- = \left(y + \dfrac{d}{dy}\right)$ is a lowering operator for the z-axis projection angular momentum quantum states.

26. Use the raising operator for the harmonic oscillator to find Ψ_3 from $\Psi_2 = (4y^2 - 2)\, e^{-y^2/2}$.

27. The lowering operator acting on the lowest energy state gives zero. For the harmonic oscillator $\hat{\mathcal{H}}^- \Psi_o = 0$, since there is no state with lower energy. Integrate $\hat{\mathcal{H}}^- \Psi_o = 0$ to show that the un-normalized ground state wave function of the harmonic oscillator is $\Psi_o = e^{-y^2/2}$.

28. Show that the z-projection angular momentum raising operator acting on $Y_{1,-1}$ gives $Y_{1,0}$. Use the un-normalized form of the wave functions, $Y_{1,-1} = \sin\theta\, e^{-i\phi}$ and $Y_{1,0} = \cos\theta$. Do this problem in the following steps.
   (a). Show that: $\hat{L}^+ Y_{1,-1} = (\hat{L}_x + i\,\hat{L}_y) \sin\theta\, e^{-i\phi}$
   (b). Using $\cot\theta = \cos\theta/\sin\theta$, show that: $\quad \hat{L}_x \sin\theta\, e^{-i\phi} = \hbar \cos\theta\,(\cos\phi + i\sin\phi)\, e^{-i\phi}$
   (c). Using the Euler Identity, $e^{i\phi} = (\cos\phi + i\sin\phi)$, show that: $\hat{L}_x \sin\theta\, e^{-i\phi} = \hbar \cos\theta$
   (d). Show that: $i\,\hat{L}_y \sin\theta\, e^{-i\phi} = \hbar \cos\theta\,(\cos\phi + i\sin\phi)\, e^{-i\phi} = \hbar \cos\theta$
   (e). Finally show that: $\hat{L}^+ Y_{1,-1} = (\hat{L}_x + i\,\hat{L}_y) \sin\theta\, e^{-i\phi} = 2\hbar \cos\theta = 2\hbar\, Y_{1,0}$

29. Show that $\hat{L}^-\hat{L}^+ = \hat{L}_x^2 + \hat{L}_y^2 + i[\hat{L}_x, \hat{L}_y] = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$. (This expression is used in the next problem to find the eigenvalue for the total angular momentum.)

30. Given $\hat{L}_z\Psi_{m_\ell} = m_\ell \hbar\, \Psi_{m_\ell}$, prove that $\hat{L}^2\, \Psi_{m_\ell} = \hbar^2\, \ell(\ell + 1)\, \Psi_{m_\ell}$, using the following steps.
   (a). Since the z-axis projection of the angular momentum can't be larger than the total angular momentum, there must be a maximum value of m_ℓ for a given total angular momentum. Let that value be m_{max}. The result for the raising operator acting on Ψ_{mmax} is zero, since there is no state with higher m_ℓ:

$$\hat{L}^+ \Psi_{mmax} = 0$$

The subsequent application of the lowering operator must also give zero:

$$\hat{L}^-\hat{L}^+ \Psi_{mmax} = 0$$

Given that $\hat{L}^-\hat{L}^+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\,\hat{L}_z$, which was proved in the last problem, solve for $\hat{L}^2\, \Psi_{mmax}$.
   (b). Compare with the general eigenvalue equation $\hat{L}^2\, \Psi_{mmax} = L^2\, \Psi_{mmax}$ to find the eigenvalue L^2 and the magnitude of the angular momentum $|L|$, in terms of m_{max}.
   (c). Notice that the total angular momentum is not a function of m_ℓ, but only the maximum value m_{max}. In other words, the total angular momentum is completely determined by m_{max}. Show that renaming $m_{max} = \ell$ gives the final result:
$$\hat{L}^2\, \Psi_{m_\ell} = \hbar^2\, \ell(\ell + 1)\, \Psi_{m_\ell}$$