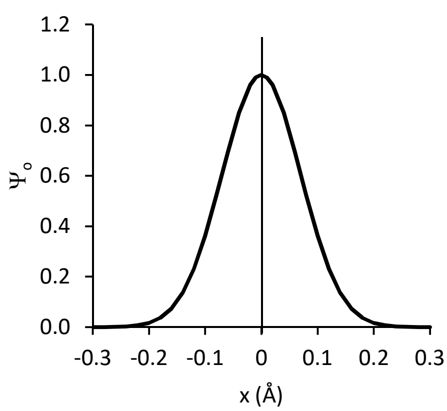
Chapter 24 Problems: The Quantum Mechanics of Rotation and Vibration

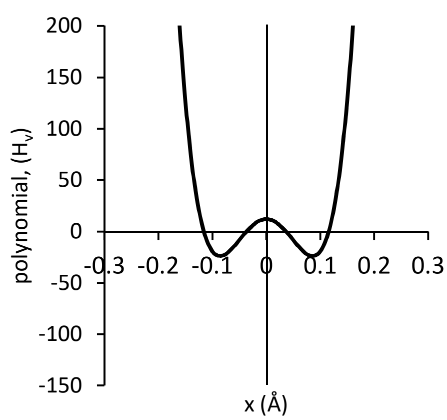
1. (a). How many nodes are in the $\upsilon = 3$ wave function for the harmonic oscillator? (b). How many angular nodes are in the $\ell = 3$, $m_\ell = 2$ wave function for the rigid rotor? (c). How many of the angular nodes for the $\ell = 3$, $m_\ell = 2$ rigid rotor include the z-axis? (d). Why are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

Answer: (a). The lowest energy state for the harmonic oscillator is for $\upsilon = 0$, which has no nodes. The number of nodes is therefore given by υ. For $\upsilon = 3$ there are three nodes. Reference to Figure 24.2.3b verifies the assignment.
(b). The total number of angular nodes for the rigid rotor is given by ℓ and the number of nodes that include the z-axis is m_ℓ. For $\ell = 3$ there are 3 total nodes.
(c). For $m_\ell = 2$, there are 2 nodes that include the z-axis. The spherical harmonics for this wave function have the same angular distribution as an atomic f-orbital.
(d). Nodes are important because they are a measure of the curvature of the wave function, which in turn determines the kinetic energy. The nodes that include the z-axis also determine the orientation of the angular momentum vector. For $m_\ell = \ell$, all the nodes include the z-axis and the angular momentum vector has its maximum projection on the z-axis. For $m_\ell = 0$, the angular momentum vector is perpendicular to the z-axis. The number of nodes that include the z-axis determines the spatial quantization.

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).

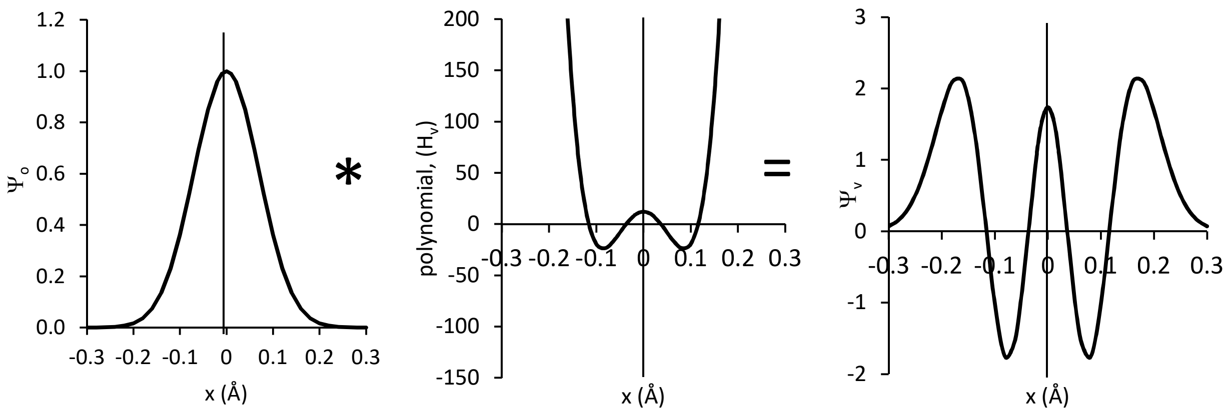


(b).

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.

Answer: The plan is to note that the excited state is the product of the ground state wave function and a polynomial. Also, note that v for the ground state is zero and there are no nodes for the ground state.

The ground state wave function determines the asymptotic form for the wave function at large r. The number of zeros for the polynomial determines the number of nodes for the excited state wave function. The number of nodes is equal to the quantum number, nodes = v. For this example, there are four nodes giving v = 4.



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?

Answer: The plan is to note that the fundamental vibration frequency is given by:
$\nu = (1/2\pi)\sqrt{k/\mu}$ with $\mu = [\mathcal{M}_1\mathcal{M}_2/(\mathcal{M}_1 + \mathcal{M}_2)](1/N_A)(1 \text{ kg}/1000 \text{ g})$. The units for the force constant are N m^{-1} and the reduced mass kg $molecule^{-1}$, or officially just kg.

(a). The wavenumber is converted to m^{-1} by $\tilde{\nu} = 2649.67 \text{ cm}^{-1}(100 \text{ cm}/1 \text{ m})$. The frequency-wavenumber conversion is given by solving $\nu\lambda = c$:

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \qquad \text{and} \qquad \nu = \tilde{\nu}c = 264967.\ \text{m}^{-1}(2.99792458\text{x}10^8 \text{m s}^{-1})$$
$$= 7.943511\text{x}10^{13} \text{ s}^{-1}$$

The reduced mass is given using isotope specific atomic masses:

$$\mu = \left(\frac{\mathcal{M}_1\mathcal{M}_2}{\mathcal{M}_1 + \mathcal{M}_2}\right)\frac{1}{N_A}(1 \text{ kg}/1000 \text{ g})$$
$$= \frac{1.0078250 \text{ g mol}^{-1}(78.918337 \text{ g mol}^{-1})}{1.0078250 \text{ g mol}^{-1} + 78.918337 \text{ g mol}^{-1}}\left(\frac{1}{6.0221367\text{x}10^{23} \text{ mol}^{-1}}\right)(1 \text{ kg}/1000 \text{ g})$$
$$= 1.652432\text{x}10^{-27}\text{kg}$$

The force constant and energy change for the transition are:

$$k = 4\pi^2\nu^2\mu = 4\pi^2(7.943511\text{x}10^{13} \text{ s}^{-1})^2(1.652432\text{x}10^{-27}\text{kg}) = 411.631 \text{ N m}^{-1}$$

$$\Delta E = h\nu(N_A)(1 \text{ kJ}/1000 \text{ J}) = hc\tilde{\nu}\, N_A\, (1 \text{ kJ}/1000 \text{ J})$$
$$= 6.626076\text{x}10^{-34} \text{ J s}(2.997925\text{x}10^8 \text{m s}^{-1})(264967.\ \text{m}^{-1})(6.0221367\text{x}10^{23} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})$$
$$= 31.6971 \text{ kJ mol}^{-1}$$

(b). The calculations are summarized in the table, below.

Molecule	ν (cm^{-1})	$\mathfrak{M}_1$ (g mol^{-1})	$\mathfrak{M}_2$ (g mol^{-1})	μ (kg)	k (N m^{-1})	ΔE (J)	ΔE (kJ mol^{-1})
$^1H^{79}Br$	2649.67	1.0078250	78.918337	1.6524x10^{-27}	411.631	5.263x10^{-20}	31.6971
$^1H^{35}Cl$	2989.74	1.0078250	34.9688527	1.6267x10^{-27}	515.90	5.939x10^{-20}	35.765

(c). Because HCl has the larger force constant, HCl has the stronger bond. The reason is often ascribed to the larger atomic radius for Br atoms compared to Cl, which gives a longer bond for HBr.

4. Normalize the wave function for the ground state of the harmonic oscillator, $\Psi_o = N\, e^{-\frac{1}{2}\alpha^2x^2}$ (without using Eq. 24.2.22).

Answer: The plan is to use the normalization integral, $\int_{-\infty}^{\infty} \Psi^*\Psi\, dx = 1$, to find the normalization constant N.

Remember that $(e^x)^2 = e^{2x}$. Substitution of the wave function into the normalization integral gives:

$$N^2 \int_{-\infty}^{\infty} e^{-\alpha^2x^2}\, dx = 1 \qquad \text{with} \quad \alpha^2 = m\omega_o/\hbar$$

This integrand is even about x = 0. Using the table in the Appendix: $\int_0^{\infty} e^{-ax^2}\, dx = \frac{1}{2}(\pi/a)^{1/2}$:

$$N^2\, 2\int_0^{\infty} e^{-\alpha^2x^2}\, dx = N^2 (\pi/\alpha^2)^{1/2} = 1$$

Solving for the normalization constant gives: $N = \left(\frac{\alpha^2}{\pi}\right)^{1/4} = \left(\frac{m\omega_o}{\pi\hbar}\right)^{1/4}$

The complete wave function is then: $\Psi_o = \left(\frac{\alpha^2}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha^2x^2} = \left(\frac{m\omega_o}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega_o}{2\hbar}x^2}$

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

Answer: The plan is to note that the position operator is just "multiply by x", $\hat{x} = x$, and the momentum operator is $\hat{p} = \hbar/i\, (d/dx)$. The expectation values are then:

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} \Psi_o^*\, x\, \Psi_o\, dx}{\int_{-\infty}^{\infty} \Psi_o^*\, \Psi_o\, dx} \qquad \text{and} \qquad \langle p\rangle = \frac{\int_{-\infty}^{\infty} \Psi_o^*\, \frac{\hbar}{i}\left(\frac{d}{dx}\right) \Psi_o\, dx}{\int_{-\infty}^{\infty} \Psi_o^*\, \Psi_o\, dx}$$

Since the harmonic oscillator wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, $N = (\alpha^2/\pi)^{1/4}$, giving $\int_{-\infty}^{\infty} \Psi_o^2\, dx = 1$.

The expectation value of the position, using a normalized wave function, is:

$$<x> = \int_{-\infty}^{\infty} \Psi_o^* \, x \, \Psi_o \, dx = N^2 \int_{-\infty}^{\infty} e^{-½ \alpha^2 x^2} \, x \, e^{-½ \alpha^2 x^2} \, dx$$

The integrand is a product of functions, so the order is immaterial:

$$<x> = N^2 \int_{-\infty}^{\infty} \underset{\substack{\uparrow \\ \textit{odd}}}{x} \quad \underset{\substack{\uparrow \\ \textit{even}}}{e^{-\alpha^2 x^2}} \, dx$$

The integrand is the product of an odd and an even function over all space, which gives an integral of zero: <x> = 0.

The expectation value of the momentum, using a normalized wave function, is:

$$<p> = \int_{-\infty}^{\infty} \Psi_o^* \frac{\hbar}{i} \left(\frac{d}{dx}\right) \Psi_o \, dx = \frac{\hbar}{i} N^2 \int_{-\infty}^{\infty} e^{-½ \alpha^2 x^2} \left(\frac{d}{dx}\right) e^{-½ \alpha^2 x^2} \, dx$$

The derivative is:

$$\left(\frac{d}{dx}\right) e^{-½ \alpha^2 x^2} = -\alpha^2 x \, e^{-½ \alpha^2 x^2}$$

Substitution of the derivative into the integral gives:

$$<p> = -\frac{\hbar}{i} N^2 \alpha^2 \int_{-\infty}^{\infty} x \, e^{-\alpha^2 x^2} \, dx$$

Once again, the integrand is the product of an odd and an even function over all space, which gives an integral of zero: <p> = 0.

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

Answer: The plan is to note that we must find the expectation value of the potential energy operator, $\hat{V} = ½ \, kx^2$. Since the harmonic oscillator wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, $N = (\alpha^2/\pi)^{¼}$, giving $\int_{-\infty}^{\infty} \Psi_o^2 \, dx = 1$.

The expectation value of the potential energy is:

$$<V> = \int_{-\infty}^{\infty} \Psi_o^* \, ½ \, kx^2 \, \Psi_o \, dx = ½ \, k \, N^2 \int_{-\infty}^{\infty} e^{-½ \alpha^2 x^2} \, x^2 \, e^{-½ \alpha^2 x^2} \, dx$$

The integrand is a product of functions, so the order is immaterial. Noting that the integrand is an even function of x gives:

$$<V> = ½ \, k \, N^2 \, 2 \int_{0}^{\infty} x^2 \, e^{-\alpha^2 x^2} \, dx$$

Using the integral table in the Appendix: $\int_0^\infty x^2 e^{-ax^2} \, dx = (1/4a) \, (\pi/a)^{½}$:

$$<V> = ½ \, k \, N^2 \, 2 \left(\frac{1}{4\alpha^2}\right) \left(\frac{\pi}{\alpha^2}\right)^{½}$$

Substitution of the normalization constant, $N = (\alpha^2/\pi)^{1/4}$, into the last equation gives:

$$<V> = \tfrac{1}{2}\, k \left(\frac{\alpha^2}{\pi}\right)^{1/2} 2 \left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{1/2} = k\left(\frac{1}{4\alpha^2}\right)$$

The force constant and α^2 are related through Eq. 24.2.11; with $\alpha^2 = (mk)^{1/2}/\hbar$:

$$<V> = \frac{k}{4}\frac{\hbar}{(mk)^{1/2}} = \frac{\hbar}{4}\left(\frac{k}{m}\right)^{1/2} = \frac{\hbar\omega_o}{4}$$

where $\omega_o = (k/m)^{1/2}$. The total energy of the harmonic oscillator in the ground state is $E = \hbar\omega_o/2$. The average potential energy is, then, one-half of the total energy: $<E_k> = \tfrac{1}{2} E$. Since $E = <E_k> + <V>$, the average potential and kinetic energies are equal, $<E_k> = <V>$. This result is a specific example of the **Virial Theorem**. If the potential is in the form of a power law, $V(x) = k\, x^n$, then the average potential and kinetic energy are related by:

$$2 <E_k> = n <V>$$

For the harmonic oscillator, $n = 2$, which gives $<E_k> = <V>$ by the Virial Theorem, as shown by this problem.

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

Answer: The plan is to note that we must find the expectation value of the kinetic energy operator, $\hat{E}_k = -(\hbar^2/2m)\, d^2/dx^2$. Since the harmonic oscillator wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, $N = (\alpha^2/\pi)^{1/4}$, giving $\int_{-\infty}^{\infty} \Psi_o^2\, dx = 1$.
The expectation value of the kinetic energy is:

$$<E_k> = \int_{-\infty}^{\infty} \Psi_o^* \left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}\right)\right] \Psi_o\, dx = -\frac{\hbar^2}{2m} N^2 \int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha^2 x^2} \left(\frac{d^2}{dx^2}\right) e^{-\frac{1}{2}\alpha^2 x^2}\, dx$$

with: $\left(\frac{d}{dx}\right) e^{-\frac{1}{2}\alpha^2 x^2} = -\alpha^2 x\, e^{-\frac{1}{2}\alpha^2 x^2}$ and $\left(\frac{d^2}{dx^2}\right) e^{-\frac{1}{2}\alpha^2 x^2} = (\alpha^4 x^2 - \alpha^2)\, e^{-\frac{1}{2}\alpha^2 x^2}$

Substituting in the second derivative gives:

$$<E_k> = -\frac{\hbar^2}{2m} N^2 \int_{-\infty}^{\infty} (\alpha^4 x^2 - \alpha^2)\, e^{-\alpha^2 x^2}\, dx$$

Separating the integral into two terms and noting that the integrand for each integral is even gives:

$$<E_k> = -\frac{\hbar^2}{2m} N^2\, 2\left[\alpha^4 \int_0^{\infty} x^2\, e^{-\alpha^2 x^2}\, dx - \alpha^2 \int_0^{\infty} e^{-\alpha^2 x^2}\, dx\right]$$

Using the table in the Appendix: $\int_0^{\infty} e^{-ax^2}\, dx = \tfrac{1}{2}(\pi/a)^{1/2}$ and $\int_0^{\infty} x^2 e^{-ax^2}\, dx = (1/4a)\,(\pi/a)^{1/2}$:

$$\langle E_k \rangle = -\frac{\hbar^2}{2m} N^2\, 2\left[\alpha^4\left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{1/2} - \alpha^2\left(\frac{1}{2}\right)\left(\frac{\pi}{\alpha^2}\right)^{1/2}\right] = -\frac{\hbar^2}{2m} N^2\, 2\alpha^2\left(\frac{\pi}{\alpha^2}\right)^{1/2}\left[\left(\frac{1}{4}\right)-\left(\frac{1}{2}\right)\right]$$

Substitution of the normalization constant, $N = (\alpha^2/\pi)^{1/4}$, Eq. 24.2.13, into the last equation gives:

$$\langle E_k \rangle = -\frac{\hbar^2}{2m}\left(\frac{\alpha^2}{\pi}\right)^{1/2} 2\alpha^2\left(\frac{\pi}{\alpha^2}\right)^{1/2}\left[-\frac{1}{4}\right] = \frac{1}{2}\left(\frac{\hbar^2\alpha^2}{2m}\right)$$

The total energy of the harmonic oscillator in the ground state is $E = \hbar^2\alpha^2/2m$. The average kinetic energy is, then, one-half of the total energy: $\langle E_k \rangle = \frac{1}{2} E$. Since $E = \langle E_k \rangle + \langle V \rangle$, the potential and kinetic energies are equal, $\langle E_k \rangle = \langle V \rangle$. This result is a specific example of the **Virial Theorem**. If the potential is in the form of a power law, $V(x) = k\, x^n$, then the average potential and kinetic energy are related by:

$$2 \langle E_k \rangle = n \langle V \rangle$$

For the harmonic oscillator, $n = 2$, which gives $\langle E_k \rangle = \langle V \rangle$, as shown by this problem.

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 $\langle x \rangle = 0$ and $\langle p \rangle = 0$, which are established by symmetry.]

Answer: The plan is to note that since $\langle x \rangle = 0$ and $\langle p \rangle = 0$, then $\sigma_x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} = (\langle x^2 \rangle)^{1/2}$ and $\sigma_p = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2} = (\langle p^2 \rangle)^{1/2}$. Note that the momentum operator is $\hat{p} = \hbar/i\, (d/dx)$.

Since the harmonic oscillator wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, $N = (\alpha^2/\pi)^{1/4}$, giving $\int_{-\infty}^{\infty} \Psi_o^2\, dx = 1$.The expectation value of x^2 is then (see also Problem 6):

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \Psi_o^*\, x^2\, \Psi_o\, dx = N^2 \int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha^2 x^2}\, x^2\, e^{-\frac{1}{2}\alpha^2 x^2}\, dx$$

The integrand is a product of functions, so the order is immaterial. Noting that the integrand is an even function of x gives:

$$\langle x^2 \rangle = N^2\, 2 \int_0^{\infty} x^2\, e^{-\alpha^2 x^2}\, dx$$

Using the integral table in the Appendix: $\int_0^{\infty} x^2 e^{-ax^2}\, dx = (1/4a)\,(\pi/a)^{1/2}$:

$$\langle x^2 \rangle = N^2\, 2\left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{1/2}$$

Substitution of the normalization constant, $N = (\alpha^2/\pi)^{1/4}$, into the last equation gives:

$$\langle x^2 \rangle = \left(\frac{\alpha^2}{\pi}\right)^{1/2} 2\left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{1/2} = \left(\frac{1}{2\alpha^2}\right)$$

The operator, $\hat{p}^2 = \hat{p}\,\hat{p} = -\,\hbar^2\,(d^2/dx^2)$, involves a derivative, so the order of operation is important, giving for the expectation value of $\hat{p}^2$ (see also Problem 7):

$$<p^2> = \int_{-\infty}^{\infty} \Psi_o^* \left(-\hbar^2\frac{d^2}{dx^2}\right) \Psi_o\,dx = -\,\hbar^2\,N^2 \int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha^2x^2} \left(\frac{d^2}{dx^2}\right) e^{-\frac{1}{2}\alpha^2x^2}\,dx$$

with: $\left(\frac{d}{dx}\right) e^{-\frac{1}{2}\alpha^2x^2} = -\,\alpha^2x\,e^{-\frac{1}{2}\alpha^2x^2}$ and $\left(\frac{d^2}{dx^2}\right) e^{-\frac{1}{2}\alpha^2x^2} = (\alpha^4x^2 - \alpha^2)\,e^{-\frac{1}{2}\alpha^2x^2}$

Substituting in the second derivative gives:

$$< p^2> = -\,\hbar^2\,N^2 \int_{-\infty}^{\infty} (\alpha^4x^2 - \alpha^2)\,e^{-\alpha^2x^2}\,dx$$

Separating the integral into two terms and noting that the integrand for each integral is even gives:

$$< p^2> = -\,\hbar^2\,N^2\,2\left[\alpha^4\int_0^{\infty} x^2\,e^{-\alpha^2x^2}\,dx - \alpha^2\int_0^{\infty} e^{-\alpha^2x^2}\,dx\right]$$

Using the table in the Appendix: $\int_0^\infty e^{-ax^2}\,dx = \frac{1}{2}\,(\pi/a)^{\frac{1}{2}}$ and $\int_0^\infty x^2e^{-ax^2}\,dx = (1/4a)\,(\pi/a)^{\frac{1}{2}}$:

$$< p^2> = -\,\hbar^2\,N^2\,2\left[\alpha^4\left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{\frac{1}{2}} - \alpha^2\left(\frac{1}{2}\right)\left(\frac{\pi}{\alpha^2}\right)^{\frac{1}{2}}\right] = -\,\hbar^2\,N^2\,2\alpha^2\left(\frac{\pi}{\alpha^2}\right)^{\frac{1}{2}}\left[\left(\frac{1}{4}\right) - \left(\frac{1}{2}\right)\right]$$

Substitution of the normalization constant, $N = (\alpha^2/\pi)^{\frac{1}{4}}$, into the last equation gives:

$$< p^2> = -\,\hbar^2\left(\frac{\alpha^2}{\pi}\right)^{\frac{1}{2}} 2\alpha^2\left(\frac{\pi}{\alpha^2}\right)^{\frac{1}{2}}\left[-\frac{1}{4}\right] = \frac{1}{2}\,\hbar^2\alpha^2$$

The product of the variances is then: $\sigma_x^2\,\sigma_p^2 = \left(\frac{1}{2\alpha^2}\right)\left(\frac{1}{2}\,\hbar^2\alpha^2\right) = \frac{\hbar^2}{4}$

which is consistent with the Heisenberg uncertainty principle, $\sigma_x\,\sigma_p \geq \hbar/2$.

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).

Answer: The ground state and the general form for the wave functions of the harmonic oscillator are:

$$\Psi_o = \left(\frac{\alpha^2}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha^2x^2} \qquad\qquad \Psi_v = N_v\,H_v\,e^{-\frac{1}{2}\alpha^2x^2}$$

The recursion relationship is: $H_{v+1} = 2y\,H_v - 2v\,H_{v-1}$, and the first Hermite polynomial, upon which all the others are based is $H_o = 1$. Building up from H_o gives:

$$H_1 = 2y\,H_o = 2y$$
$$H_2 = 2y\,H_1 - 2(1)\,H_o = 2y\,(2y) - 2(1)(1) = 4y^2 - 2$$
$$H_3 = 2y\,H_2 - 2(2)\,H_1 = 2y(4y^2 - 2) - 2(2)(2y) = 8y^3 - 12y$$
$$H_4 = 2y\,H_3 - 2(3)\,H_2 = 2y(8y^3 - 12y) - 2(3)(4y^2 - 2) = 16y^4 - 48y^2 + 12$$

The normalization integral, using the change in variables $y = \alpha x$, $dy/dx = \alpha$, and $dx = dy/\alpha$, gives:

$$N_v^2\,(1/\alpha) \int_{-\infty}^{\infty} H_v\, e^{-\frac{1}{2} y^2}\, H_v\, e^{-\frac{1}{2} y^2}\, dy = 1$$

The standard form of the integral, using Eq. 24.2.99% with v' = v, is:

$$\int_{-\infty}^{\infty} H_v\, e^{-\frac{1}{2} y^2}\, H_v\, e^{-\frac{1}{2} y^2}\, dy = \pi^{\frac{1}{2}}\, 2^v\, v! \qquad \text{giving} \qquad N_v^2\,(1/\alpha)(\pi^{\frac{1}{2}}\, 2^v\, v!) = 1$$

The normalization constant is then $N_v = (\alpha/(\pi^{\frac{1}{2}}\, 2^v\, v!))^{\frac{1}{2}}$. Explicitly, the normalization for the first four excited state levels is:

$$N_1 = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^1\, 1!}\right)^{\frac{1}{2}} = \left(\frac{\alpha^2}{4\pi}\right)^{\frac{1}{4}} \qquad N_2 = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^2\, 2!}\right)^{\frac{1}{2}} = \frac{1}{2}\left(\frac{\alpha^2}{4\pi}\right)^{\frac{1}{4}}$$

$$N_3 = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^3\, 3!}\right)^{\frac{1}{2}} = \frac{1}{2}\left(\frac{\alpha^2}{144\pi}\right)^{\frac{1}{4}} \qquad N_4 = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^4\, 4!}\right)^{\frac{1}{2}} = \frac{1}{8}\left(\frac{\alpha^2}{36\pi}\right)^{\frac{1}{4}}$$

The final wavefunctions are:

$$\Psi_1 = \left(\frac{\alpha^2}{4\pi}\right)^{\frac{1}{4}} (2\alpha x)\, e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\Psi_2 = \frac{1}{2}\left(\frac{\alpha^2}{4\pi}\right)^{\frac{1}{4}} (4\alpha^2 x^2 - 2)\, e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\Psi_3 = \frac{1}{2}\left(\frac{\alpha^2}{144\pi}\right)^{\frac{1}{4}} (8\alpha^3 x^3 - 12\alpha x)\, e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\Psi_4 = \frac{1}{8}\left(\frac{\alpha^2}{36\pi}\right)^{\frac{1}{4}} (16\alpha^4 x^4 - 48\alpha^2 x^2 + 12)\, e^{-\frac{1}{2}\alpha^2 x^2}$$

<u>10</u>. 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.]

Answer: The plan is to show that $\int_0^{2\pi} \Psi_{m_\ell'}^{*} \Psi_{m_\ell}\, d\phi = 0$ with $m_{\ell'} \neq m_\ell$.

The integral to test for orthogonality is:

$$\int_0^{2\pi} \Psi_{m_\ell'}^{*} \Psi_{m_\ell}\, d\phi = a^2 \int_0^{2\pi} e^{-i\, m_{\ell'}\, \phi}\, e^{i\, m_\ell\, \phi}\, d\phi = a^2 \int_0^{2\pi} e^{i\,(m_\ell - m_{\ell'})\phi}\, d\phi$$

with $m_{\ell'} \neq m_\ell$. Using the Euler identity for the complex exponential gives:

$$\int_0^{2\pi} \Psi_{m_\ell'}^{*} \Psi_{m_\ell}\, d\phi = a^2 \int_0^{2\pi} \cos[(m_\ell - m_{\ell'})\phi]\, d\phi + i\, a^2 \int_0^{2\pi} \sin[(m_\ell - m_{\ell'})\phi]\, d\phi$$

However, $(m_\ell - m_{\ell'})$ is an integer. Let $n = (m_\ell - m_{\ell'})$ with $n \neq 0$, which gives:

$$\int_0^{2\pi} \cos n\phi\, d\phi = \sin n\phi\Big|_0^{2\pi} = 0 \qquad \text{and} \qquad \int_0^{2\pi} \sin n\phi\, d\phi = -\cos n\phi\Big|_0^{2\pi} = -[1 - 1] = 0$$

Substitution of these standard integrals into the orthogonality integral gives $\int_0^{2\pi} \Psi_{m_\ell'}^{*} \Psi_{m_\ell}\, d\phi = 0$.

11. Show that the wave function $\Psi(\phi) = a\, e^{im_\ell\phi}$ 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?

Answer: The plan is to note that the Hamiltonian for the 2D-rigid rotor is a function of the azimuthal angle ϕ through $\hat{\mathcal{H}} = -\,\hbar^2/2I\,(d^2/d\phi^2)$.
The derivatives are:

$$\frac{d\, e^{im_\ell\phi}}{d\phi} = i\, m_\ell\, e^{im_\ell\phi} \qquad \text{and} \qquad \frac{d^2 e^{im_\ell\phi}}{d\phi^2} = (i\, m_\ell)^2\, e^{im_\ell\phi} = -\, m_\ell^2\, e^{im_\ell\phi}$$

The Schrödinger equation is then: $\hat{\mathcal{H}}\Psi = -\dfrac{\hbar^2}{2I}\dfrac{d^2\, a\, e^{im_\ell\phi}}{d\phi^2} = \dfrac{\hbar^2 m_\ell^2}{2I}\, a\, e^{im_\ell\phi} = \dfrac{\hbar^2 m_\ell^2}{2I}\,\Psi$

This final result shows that the wave function is an eigenfunction of the Hamiltonian. The eigenvalue corresponding to the Hamiltonian is the energy:

$$E = \frac{\hbar^2 m_\ell^2}{2I}$$

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

Answer: The plan is to show that $-\,\hbar^2\,\Lambda^2\,\Psi = c\,\Psi$, with c a constant. For multi-step derivatives, order is important; remember to work from right to left. We can anticipate that since $\cos\theta$ is the spherical harmonic $Y_{1,0}$ without normalization, the constant will be $|L|^2 = \hbar^2\,\ell(\ell + 1)$, with $\ell = 1$.

The first step is to note that: $\Lambda^2 = \dfrac{1}{\sin^2\theta}\left(\dfrac{\partial^2}{\partial\phi^2}\right) + \left(\dfrac{1}{\sin\theta}\right)\left(\dfrac{\partial}{\partial\theta}\sin\theta\,\dfrac{\partial}{\partial\theta}\right)$

The wave function is not a function of ϕ, so $(\partial^2\cos\theta/\partial\phi^2)_\theta = 0$. The remaining derivatives are:

$$\begin{aligned}
\Lambda^2\cos\theta &= \left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}\sin\theta\,\frac{\partial}{\partial\theta}\right)\cos\theta \\
&= \left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}(-\sin^2\theta)\right) \\
&= -\left(\frac{1}{\sin\theta}\right)(2\sin\theta\cos\theta) \\
&= -\,2\cos\theta
\end{aligned}$$

The square of the total angular momentum operating on the wave function is then:

$$-\,\hbar^2\,\Lambda^2\cos\theta = 2\hbar^2\cos\theta$$

This last result shows that $\cos\theta$ is an eigenfunction. The eigenvalue for the total angular momentum operator squared is then $|L|^2 = 2\hbar^2$. This result agrees with Eq. 24.5.34 since $\ell = 1$ for $Y_{1,0}$ and then $|L|^2 = \hbar^2\,\ell(\ell+1) = 2\hbar^2$.

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

Answer: The plan is to note that normalization requires $\int \Psi^*\Psi\, d\tau = 1$, where the integral is over all space and the volume element is $d\tau = \sin\theta\, d\theta\, d\phi$ for the rigid-rotor.
Note that $Y_{1,0}$ is real, so that $Y^*_{1,0} = Y_{1,0}$. The normalization integral is given by:

$$\int_0^\pi\int_0^{2\pi} Y^2_{1,0}\sin\theta\, d\theta\, d\phi = N^2\int_0^{2\pi} d\phi \int_0^\pi \cos^2\theta \sin\theta\, d\theta = 1$$

Integral tables give: $\int_0^\pi \cos^2(ax)\sin(ax)\,dx = -(1/3a)\cos^3(ax)$. In this case a = 1:

$$\int_0^\pi \cos^2\theta\sin\theta\, d\theta = -(1/3)\cos^3(\theta)\Big|_0^\pi = -(1/3)\,[\cos^3(\pi) - \cos^3(0)] = 2/3$$

The integral over the azimuthal angle is $\int_0^{2\pi} d\phi = 2\pi$:

$$N^2\int_0^{2\pi} d\phi\int_0^\pi \cos^2\theta\sin\theta\, d\theta = N^2\,(2\pi)(2/3) = 1 \qquad \text{and}\quad N = \left(\frac{3}{4\pi}\right)^{1/2}$$

The normalized spherical harmonic is then $Y_{1,0} = (3/4\pi)^{1/2}\cos\theta$.

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

Answer: The plan is to note that $Y_{0,0} = (1/4\pi)^{1/2}$ and $Y_{1,0} = (3/4\pi)^{1/2}\cos\theta$. Orthogonality requires $\int \Psi^*\Psi\, d\tau = 0$, where the integral is over all space and the volume element is $d\tau = \sin\theta\, d\theta\, d\phi$ for the rigid-rotor.
Note that these particular spherical harmonics are real, so that $Y^*_{0,0} = Y_{0,0}$. The orthogonality integral is given by:

$$\int_0^\pi\int_0^{2\pi} Y_{0,0}\,Y_{1,0}\sin\theta\, d\theta\, d\phi = (1/4\pi)^{1/2}\,(3/4\pi)^{1/2}\int_0^{2\pi} d\phi\int_0^\pi \cos\theta\sin\theta\, d\theta = 0$$

because integral tables give $\int_0^\pi \cos(ax)\sin(ax)\,dx = (1/2a)\sin^2(ax)\Big|_0^\pi = 0$.

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

Answer: The plan is to note that $Y_{1,0} = (3/4\pi)^{1/2}\cos\theta$ and $Y_{1,1} = (3/8\pi)^{1/2}\sin\theta\, e^{i\phi}$. Orthogonality requires $\int \Psi^*\Psi\, d\tau = 0$, where the integral is over all space and the volume element is $d\tau = \sin\theta\, d\theta\, d\phi$ for the rigid-rotor.
Note that $Y_{1,0}$ is real, so that $Y^*_{1,0} = Y_{1,0}$. The orthogonality integral is given by:

$$\int_0^{\pi}\int_0^{2\pi} Y_{1,0}\, Y_{1,0} \sin\theta\, d\theta\, d\phi = (3/4\pi)^{½} (3/8\pi)^{½} \int_0^{2\pi} e^{i\phi}\, d\phi \int_0^{\pi} \cos\theta \sin^2\theta\, d\theta = 0$$

because integral tables give $\int_0^{\pi} \cos(ax) \sin^2(ax)\, dx = (1/3a) \sin^3(ax)\big|_0^{\pi} = 0$.

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 ħ.

Answer: For $\ell = 2$ the magnitude of the angular momentum is: $|L| = \hbar \sqrt{\ell(\ell+1)} = \sqrt{6}\, \hbar$
The z-axis projection of the angular momentum is: $L_z = m_\ell \hbar = \hbar$.

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.

Answer: The plan is to use Eq. 24.5.43 converted to wave numbers, with J as the quantum number for the lower state: $\Delta E/hc = \tilde{\nu} = 2\, \tilde{B}\, (J + 1)$.
The reduced mass is given using isotope specific atomic masses:

$$\mu = \left(\frac{\mathfrak{M}_1 \mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2}\right) \frac{1}{N_A} (1\ \text{kg}/1000\ \text{g})$$
$$= \frac{12.000000\ \text{g mol}^{-1}(15.994915\ \text{g mol}^{-1})}{12.000000\ \text{g mol}^{-1} + 15.994915\ \text{g mol}^{-1}} \left(\frac{1}{6.0221367\text{x}10^{23}\ \text{mol}^{-1}}\right) (1\ \text{kg}/1000\ \text{g})$$
$$= 1.1385010\text{x}10^{-26}\ \text{kg}$$

Note that 1 Å = $1\text{x}10^{-10}$ m. The moment of inertia and rotational constant are:

$$I = \mu r^2 = 1.138501\text{x}10^{-26}\ \text{kg}(1.1282\text{x}10^{-10}\ \text{m})^2 = 1.44912\text{x}10^{-46}\ \text{kg m}^2$$
$$\tilde{B} = \frac{\hbar}{4\pi I c} = \frac{1.054573\text{x}10^{-34}\ \text{J s}}{4\pi(1.44912\text{x}10^{-46}\ \text{kg m}^2)(2.997925\text{x}10^{8}\ \text{m s}^{-1})} = 193.170\ \text{m}^{-1}$$
$$\tilde{B} = 193.170\ \text{m}^{-1}\ (1\ \text{m}/100\ \text{cm}) = 1.93170\ \text{cm}^{-1}$$

The transition energy using Eq. 24.5.43 is: $\Delta E/hc = \tilde{\nu} = 2\, \tilde{B}\, (J + 1) = 2\tilde{B} = 3.86341\ \text{cm}^{-1}$

The transition frequency is given by:

$$\nu = c/\lambda = \tilde{\nu} c = 3.86341\ \text{cm}^{-1}(2.997925\text{x}10^{8}\ \text{m s}^{-1})(100\ \text{cm}/1\text{m}) = 1.15822\text{x}10^{11}\ \text{s}^{-1}$$
$$\nu = 1.15822\text{x}10^{11}\ \text{s}^{-1}\ (1\ \text{GHz}/1\text{x}10^{9}\text{s}^{-1}) = 115.82\ \text{GHz}$$

This transition is one of the prominent lines observed in interstellar space using radio telescopes.

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.

Answer: The plan is to note that $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$, Eq. 23. 7.10. The operators are given by Eqs. 24.5.19. Note that the partial derivative with respect to x is taken with y and z constant. In addition using the Euler criterion, mixed partials are equal, Eq. 9.1.6. So for example:

$$\frac{\partial}{\partial x} z \frac{\partial}{\partial y} = z \frac{\partial}{\partial x}\frac{\partial}{\partial y} \qquad \text{and} \qquad \frac{\partial}{\partial y}\frac{\partial}{\partial x} = \frac{\partial}{\partial x}\frac{\partial}{\partial y}$$

Note also that multiplicative operators commute, yx = xy. The commutator is then:

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$$

$$= -\hbar^2\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]$$

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

Canceling the common factors, in xy and z^2, and using the product rule for the z-derivative gives:

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

Then $(\partial z/\partial z) = 1$ and canceling common factors gives:

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

The x and y components of the angular momentum cannot both be determined simultaneously with arbitrary precision.

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

Answer: The plan is to note that $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$, Eq. 23. 7.10. The operators are given by Eqs. 24.5.20-24.5.21. Note that the partial derivative with respect to θ is taken with ϕ constant.

From $[\hat{L}^2,\hat{L}_z] = \hat{L}^2\,\hat{L}_z - \hat{L}_z\,\hat{L}^2$, consider the first term and second term separately. Note that the ϕ derivative is done with θ held constant. The terms in θ are constants for the ϕ derivative and can factor in and out, for example:

$$\frac{\partial}{\partial\phi}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\frac{\partial}{\partial\phi} \qquad 1$$

The first term in the commutator is:

$$\hat{L}^2\,\hat{L}_z = -\frac{\hbar^3}{i}\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]\left(\frac{\partial}{\partial\phi}\right) \qquad 2$$

$$= -\frac{\hbar^3}{i}\left[\frac{1}{\sin^2\theta}\frac{\partial^3}{\partial\phi^3} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\frac{\partial}{\partial\phi}\right] \qquad 3$$

The second term in the commutator has the opposite order for the operators:

$$\hat{L}_z\,\hat{L}^2 = -\frac{\hbar^3}{i}\left(\frac{\partial}{\partial\phi}\right)\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] \qquad 4$$

Using Eq. 1 gives:

$$\hat{L}_z\,\hat{L}^2 = -\frac{\hbar^3}{i}\left[\frac{1}{\sin^2\theta}\frac{\partial^3}{\partial\phi^3} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\frac{\partial}{\partial\phi}\right] \qquad 5$$

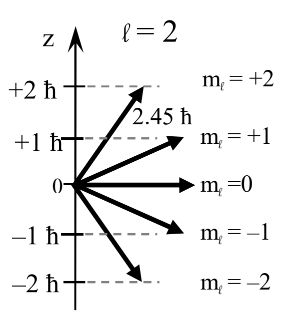
Note that Eqs. 3 and 5 are identical, so that $[\hat{L}^2,\hat{L}_z] = \hat{L}^2\,\hat{L}_z - \hat{L}_z\,\hat{L}^2 = 0$.

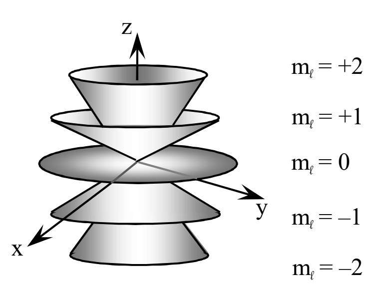
<u>20</u>. Why is $[\hat{L}^2,\hat{L}_z] = 0$ significant?

Answer: The <u>energy</u> of the system is given by $E_\ell = L^2/2I$. The eigenvalue of $\hat{L}^2$ is $L^2 = \hbar^2\,\ell(\ell + 1)$, which upon taking the square root gives the <u>magnitude</u> of the total angular momentum, $|L|$. The eigenvalue of $\hat{L}_z$ is $\ell_z = \hbar m_\ell$, which determines the <u>orientation</u> of the angular momentum vector. The vanishing commutator means that both L^2 and ℓ_z can be specified simultaneously to arbitrary precision. The total energy, the magnitude of the angular momentum, and the orientation with respect to the z-axis can all be specified exactly at the same time. The energy, angular momentum, and spatial orientation are all quantized. However, the spherical harmonics are not eigenfunctions of the two remaining projections, $\hat{L}_x$ and $\hat{L}_y$. Instead, these components give zero expectation values and the uncertainties span the range of ϕ.

<u>21</u>. Draw the angular momentum vector diagrams for $\ell = 2$ angular momentum states.

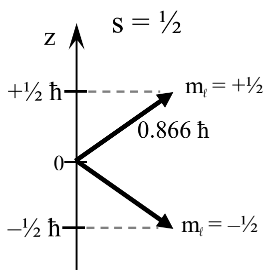
Answer: The magnitude of the angular momentum for $\ell = 2$ is $|L| = \sqrt{6}\,\hbar = 2.45\,\hbar$, Problem 16. For $\ell = 2$ the magnetic quantum number can be m_ℓ = -2, -1, 0, 1, 2, giving five precession cones:

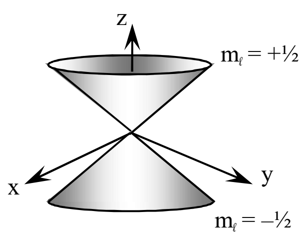




<u>22</u>. Draw the angular momentum vector diagram for a single electron or proton, s = ½.

Answer: The magnitude of the angular momentum for s = ½ is $|S| = \sqrt{3/4}\ \hbar = 0.866\ \hbar$. For s = ½ the magnetic quantum number can be $m_\ell = -½, ½$, giving two precession cones:





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 $I = {}^3/_2$. Give the possible values for the quantum number for the z-axis projection of the angular momentum.

Answer: The quantum number for the z-axis projection of the angular momentum is the magnetic quantum number, which for nuclei is called m_I. Starting from $m_I = -{}^3/_2$ in unit steps gives four m_I states: $m_I = (-{}^3/_2, -{}^1/_2, +{}^1/_2, +{}^3/_2)$. The angular momentum vector diagram has four precession cones.

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.)

Answer: The quantum number for the z-axis projection of the angular momentum is the magnetic quantum number, which for nuclei is called m_I. Starting from $m_I = -{}^5/_2$ in unit steps gives six m_I states: $m_I = (-{}^5/_2, -{}^3/_2, -{}^1/_2, +{}^1/_2, +{}^3/_2, +{}^5/_2)$. The angular momentum vector diagram has six precession cones.

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

Answer: The plan is to follow Example 24.7.2. We need to show that $[\hat{A},\hat{A}^-] = k\,\hat{A}^-$, Eq. 24.7.1.
The harmonic oscillator Hamiltonian is given by eq. 24.7.14: $\hat{\mathcal{H}} = \hat{\mathcal{H}}^-\hat{\mathcal{H}}^+ - 1$. The commutator is then:

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

$$= \hat{\mathcal{H}}^-\hat{\mathcal{H}}^+\hat{\mathcal{H}}^- - \hat{\mathcal{H}}^- - \hat{\mathcal{H}}^-\hat{\mathcal{H}}^-\hat{\mathcal{H}}^+ + \hat{\mathcal{H}}^-$$

Canceling the terms in just $\hat{\mathcal{H}}^-$ and factoring out the common term in $-\hat{\mathcal{H}}^-$ from the left gives:

$$= -\hat{\mathcal{H}}^- (\hat{\mathcal{H}}^-\hat{\mathcal{H}}^+ - \hat{\mathcal{H}}^+\hat{\mathcal{H}}^-) = -\hat{\mathcal{H}}^- [\hat{\mathcal{H}}^-,\hat{\mathcal{H}}^+]$$

Substituting for the commutator from Eq. 24.7.13 gives:

$$[\hat{\mathcal{H}},\hat{\mathcal{H}}^-] = -2\,\hat{\mathcal{H}}^- \qquad 24.7.14$$

The final result corresponds to k = -2, so $\hat{\mathcal{H}}^-$ is a lowering operator.

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

Answer: The plan is to operate on Ψ_2 with $\hat{\mathcal{H}}^+$, which defined by Eq. 24.7.12. See Example 24.7.3.

The next excited state is determined by:

$$\hat{\mathcal{H}}^+\Psi_2 = \left(y - \frac{d}{dy}\right)(4y^2 - 2)\, e^{-y^2/2} = 4y^3\, e^{-y^2/2} - 2y\, e^{-y^2/2} - \frac{d}{dy}\, 4y^2\, e^{-y^2/2} + 2\frac{d}{dy}\, e^{-y^2/2}$$

Using the product rule:

$$\hat{\mathcal{H}}^+\Psi_2 = 4y^3\, e^{-y^2/2} - 2y\, e^{-y^2/2} - 4y^2 \frac{d}{dy}\, e^{-y^2/2} - e^{-y^2/2}\frac{d}{dy}\, 4y^2 + 2(-y)\, e^{-y^2/2}$$

$$= 4y^3\, e^{-y^2/2} - 2y\, e^{-y^2/2} - 4y^2(-y)\, e^{-y^2/2} - 8\, y\, e^{-y^2/2} + 2(-y)\, e^{-y^2/2}$$

$$= (8y^3 - 12y)\, e^{-y^2/2}$$

The result is as expected from Table 24.1.1. Even though ladder operators are more abstract than directly solving the Hermite equation, ladder operators are computationally much simpler to use.

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 $\Psi_o = e^{-y^2/2}$.

Answer: The plan is to substitute in the lowering operator, Eq. 24.7.11, separate variables, and complete the integral, just as we did for chemical kinetics problems. This process is straight forward because the lowering operator involves only a first derivative.

Substituting in the definition of the lowering operator gives:

$$\hat{\mathcal{H}}^-\,\Psi_o = \left(y - \frac{d}{dy}\right)\Psi_o = 0$$

Adding $y\Psi_o$ to both sides of the last equation and then multiplying by -1 gives:

$$\frac{d}{dy}\,\Psi_o = -\,y\,\Psi_o$$

Separating variables gives: $\frac{1}{\Psi_o} d\Psi_o = -y\,dy$

The integrals give: $\int \frac{1}{\Psi_o} d\Psi_o = -\int y\,dy$ or $\ln \Psi_o = -\frac{y^2}{2}$

Exponentiation of both sides of the last equation gives: $\Psi_o = e^{-y^2/2}$
The result agrees with un-normalized form of Eq. 24.2.18.

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: $\hat{L}_x \sin\theta\, e^{-i\phi} = \hbar \cos\theta\, (\cos\phi + i \sin\phi)\, e^{-i\phi}$

(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: $\hat{L}^+ Y_{1,-1} = (\hat{L}_x + i\,\hat{L}_y)\sin\theta\, e^{-i\phi} = 2\hbar\cos\theta = 2\hbar\, Y_{1,0}$

Answer: The plan is to note that $\hat{L}^+$, $\hat{L}_x$, and $\hat{L}_y$ are given by Eqs. 24.5.20 and 24.7.18.
(a). Making the substitutions in spherical polar coordinates without normalization:

$$\hat{L}^+ Y_{1,-1} = (\hat{L}_x + i\,\hat{L}_y) \sin\theta\, e^{-i\phi} \qquad 1$$

(b). We consider the two terms separately to decrease confusion. Using Eqs. 24.5.20 for $\hat{L}_x$:

$$\hat{L}_x \sin\theta\, e^{-i\phi} = \frac{\hbar}{i}\left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\sin\theta\, e^{-i\phi} \qquad 2$$

$$= \frac{\hbar}{i}\big(-\sin\phi\cos\theta - \cot\theta\sin\theta\cos\phi\,(-i)\big)\, e^{-i\phi} \qquad 3$$

However, $\cot\theta = \cos\theta/\sin\theta$ giving:

$$\hat{L}_x \sin\theta\, e^{-i\phi} = \frac{\hbar}{i}(-\sin\phi\cos\theta + i\cos\theta\cos\phi)\, e^{-i\phi} \qquad 4$$

$$= \hbar\cos\theta\,(\cos\phi + i\sin\phi)\, e^{-i\phi} \qquad 5$$

(c). The Euler Identity gives $e^{i\phi} = (\cos\phi + i\sin\phi)$ and $e^{i\phi}\, e^{-i\phi} = 1$:

$$\hat{L}_x \sin\theta\, e^{-i\phi} = \hbar\cos\theta \qquad 6$$

(d). Now for the second term in Eq. 1 for the raising operator:

$$i\,\hat{L}_y \sin\theta\, e^{-i\phi} = i\,\frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\sin\theta\, e^{-i\phi} \qquad 7$$

$$i\,\hat{L}_y \sin\theta\, e^{-i\phi} = \hbar\,(\cos\theta\cos\phi - \cot\theta\sin\theta\sin\phi\,(-i))\, e^{-i\phi} \qquad 8$$

Once again, $\cot\theta = \cos\theta/\sin\theta$, $e^{i\phi} =$, and $e^{i\phi}\, e^{-i\phi} = 1$, giving:

$$i\,\hat{L}_y \sin\theta\, e^{-i\phi} = \hbar\,(\cos\theta\cos\phi - \cos\theta\sin\phi\,(-i))\, e^{-i\phi} \qquad 9$$
$$= \hbar\cos\theta\,(\cos\phi + i\sin\phi)\, e^{-i\phi} \qquad 10$$
$$= \hbar\cos\theta \qquad 11$$

(e). The sum of the two terms, Eqs. 6 and 11, gives the final result:

$$(\hat{L}_x + i\,\hat{L}_y)\sin\theta\, e^{-i\phi} = 2\hbar\cos\theta \qquad 12$$

where $Y_{1,0} = \cos\theta$, without the normalization:

$$(\hat{L}_x + i\,\hat{L}_y)\sin\theta\, e^{-i\phi} = 2\hbar\, Y_{1,0} \qquad 13$$

The raising operator raises $Y_{1,1}$ to $Y_{1,0}$, multiplied by a constant. The constant is resolved by normalization to give the final form for $Y_{1,0}$.

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.)

Answer: From the defintitions of the lowering and raising operators:

$$\hat{L}^-\hat{L}^+ = (\hat{L}_x - i\,\hat{L}_y)(\hat{L}_x + i\,\hat{L}_y) = \hat{L}_x^2 + i\hat{L}_x\,\hat{L}_y - i\,\hat{L}_y\,\hat{L}_x + \hat{L}_y^2$$

which, with the defintition of the commutator, rearranges to give:

$$\hat{L}^-\hat{L}^+ = \hat{L}_x^2 + \hat{L}_y^2 + i[\hat{L}_x, \hat{L}_y]$$

Using Eqs. 24.6.1 for the commutator gives the final result: $\hat{L}^-\hat{L}^+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$

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 $\Psi_{m_{max}}$ is zero, since there is no state with higher m_ℓ:

$$\hat{L}^+\,\Psi_{m_{max}} = 0$$

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

$$\hat{L}^-\hat{L}^+\,\Psi_{m_{max}} = 0$$

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 $\hat{L}^2\,\Psi_{m_{max}}$.
(b). Compare with the general eigenvalue equation $\hat{L}^2\,\Psi_{m_{max}} = L^2\,\Psi_{m_{max}}$ 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:

$$\hat{L}^2\,\Psi_{m_\ell} = \hbar^2\,\ell(\ell+1)\,\Psi_{m_\ell}$$

Answer: (a). Substituting $\hat{L}^-\hat{L}^+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$ into $\hat{L}^-\hat{L}^+\,\Psi_{m_{max}} = 0$ gives:

$$\hat{L}^-\hat{L}^+\,\Psi_{m_{max}} = (\hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z)\,\Psi_{m_{max}} = 0$$

Rearranging the last relationship gives the square of the angular momentum as:

$$\hat{L}^2\,\Psi_{m_{max}} = \hat{L}_z^2\,\Psi_{m_{max}} + \hbar\hat{L}_z\,\Psi_{m_{max}}$$

Given that $\hat{L}_z\,\Psi_{m_\ell} = m_\ell\hbar\,\Psi_{m_\ell}$:

$$\hat{L}^2\,\Psi_{m_{max}} = (m_\ell\,\hbar)^2\,\Psi_{m_{max}} + \hbar(\,m_\ell\hbar)\,\Psi_{m_{max}}$$
$$\hat{L}^2\,\Psi_{m_{max}} = \hbar^2\,(m_{max}^2 + m_{max})\,\Psi_{m_{max}} = \hbar^2\,m_{max}(m_{max}+1)\,\Psi_{m_{max}}$$

(b). Comparison with the general eigenvalue equation $\hat{L}^2\,\Psi_{m_{max}} = L^2\,\Psi_{m_{max}}$ gives:

$$L^2 = \hbar^2\,m_{max}(m_{max}+1) \qquad \text{and} \quad |L| = \hbar\,\sqrt{m_{max}(m_{max}+1)}$$

(c). We showed in Eq. 24.7.27 that m_ℓ increases in unit steps until the z-axis projection is bigger than the magnitude of the angular momentum, so that $m_\ell\hbar < \hbar\,\sqrt{m_{max}(m_{max}+1)}$. The total angular momentum is completely determined by m_{max}, while $m_\ell = 0, \pm1, \ldots, \pm\, m_{max}$. Renaming $m_{max} = \ell$ gives the final result:

$$\hat{L}^2\,\Psi_{m_{max}} = \hbar^2\,\ell(\ell+1)\,\Psi_{m_{max}} \qquad\qquad m_\ell = 0, \pm1, \ldots, \pm\,\ell$$

Since the raising operator doesn't change the magnitude of the angular momentum, Eq. 24.7.21, the preceding equation must then hold for all values of m_ℓ:

$$\hat{L}^2\,\Psi_{m_\ell} = \hbar^2\,\ell(\ell+1)\,\Psi_{m_\ell}$$