1) We learned that the Hamiltonian for the quantized harmonic oscillator is
\[ \hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{\kappa x^2}{2}. \]
You can obtain the general expression for the energy, i.e. \( E_n = \hbar \omega \left(n + \frac{1}{2}\right) \), for \( n = 0, 1, 2, \ldots \) by solving Schrodinger’s equation \( \hat{H} \psi(x) = E \psi(x) \).

The quartic oscillator which has the Hamiltonian \( \hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{\kappa x^4}{2} \). Note the quartic oscillator differs from the harmonic oscillator by having the potential energy depend upon \( x^4 \) instead of \( x^2 \).

a) A trial \( n=0 \) wave function for the quartic oscillator is \( \psi_0(x) = \left( \frac{\alpha}{\sqrt{\pi}} \right)^{1/2} e^{-\alpha x^2} \), where \( \alpha \) is a constant, and the energy for the quartic oscillator is
\[ \langle E \rangle = \frac{\int_{-\infty}^{\infty} \psi_0(x) \hat{H} \psi_0(x) dx}{\int_{-\infty}^{\infty} \psi_0^2(x) dx} = \frac{3}{4} \frac{\kappa}{\alpha^2} + \frac{\hbar^2}{4\mu} \alpha \]

Determine the value of \( \alpha \) that minimizes the energy in part a. That is, using your expression for \( \langle E \rangle \) from part a, set \( \frac{\partial \langle E \rangle}{\partial \alpha} = 0 \) and solve for \( \alpha \). Is the ground state energy of the quartic oscillator greater than, less than, or equal to the ground state energy of the harmonic oscillator? Assume the spring constants and reduces masses of the two oscillators are equal.

\[ \langle E \rangle = \frac{3}{4} \frac{\kappa}{\alpha^2} + \frac{\hbar^2}{4\mu} \alpha \]

\[ \frac{\partial \langle E \rangle}{\partial \alpha} = 0 = -\frac{6\kappa}{4\alpha^3} + \frac{\hbar^2}{4\mu} \Rightarrow \frac{1}{\alpha^3} = \frac{\hbar^2}{6\kappa \mu} \Rightarrow \alpha = \left( \frac{6\kappa \mu}{\hbar^2} \right)^{1/3} \]
\[
\langle E \rangle = \frac{3\kappa}{4} \left( \frac{\hbar^2}{6\kappa \mu} \right)^{2/3} + \frac{\hbar^2}{4\mu} \left( \frac{6\kappa \mu}{\hbar^2} \right)^{1/3} = \frac{3}{4} \left( \frac{\hbar^2}{6\kappa \mu} \right)^{2/3} + \frac{1}{4} \left( \frac{6\hbar^6 \kappa \mu}{\hbar^2 \mu^4} \right)^{1/3}
\]

\[
= \frac{3}{4} \left( \frac{\hbar^2}{6\mu} \right)^{1/2} \left( \frac{\hbar^2}{6\mu} \right)^{1/2} + \frac{1}{4} \left( \frac{6\hbar^6 \kappa}{\mu^2} \right)^{1/3} = \frac{3}{4} \left( \frac{\hbar^2}{6\mu^2} \right)^{1/3} + \frac{1}{4} \left( \frac{36\hbar^4 \kappa}{\mu^2} \right)^{1/3}
\]

\[
= \frac{3}{4} \left( \frac{\hbar^2}{6\mu^2} \right)^{1/3} + \frac{3.30}{4} \left( \frac{\hbar^2}{6\mu^2} \right)^{1/3} = 6.3 \left( \frac{\hbar^2}{6\mu^2} \right)^{1/3}
\]

There are several ways to proceed. You could select arbitrary constants for \( \kappa \) and \( \mu \), but one could also select realistic numbers typical for diatomics. Let’s try realistic numbers first using \(^1\text{H}^{35}\text{Cl}\) as a typical diatomic. For \(^1\text{H}^{35}\text{C} \kappa = 481 \text{Nm}^{-1} \). The reduced mass is:

\[
\mu = \frac{m_H m_{\text{Cl}}}{m_H + m_{\text{Cl}}} = \frac{M_H M_{\text{Cl}} N_A}{(M_H + M_{\text{Cl}}) N_A} = \frac{M_H M_{\text{Cl}}}{(M_H + M_{\text{Cl}}) N_A} = \frac{0.001 \text{kg mol}^{-1}}{(0.037 \text{kg mol}^{-1})(6.02 \times 10^{23} \text{mol}^{-1})} = 1.62 \times 10^{-27} \text{ kg}
\]

Then

\[
\langle E \rangle = \frac{6.3}{4} \left( \frac{\hbar^2}{6\mu^2} \right)^{1/3} = 1.58 \left( \frac{1.05 \times 10^{-34} \text{ Js}^4}{6(1.62 \times 10^{-27} \text{ kg})^2} \right)^{1/3} = 1.58 \left( \frac{1.22 \times 10^{-16} \text{ Js}^4}{6(2.62 \times 10^{-25} \text{ kg}^2)} \right)^{1/3}
\]

\[
= 1.58 \left( \frac{5.87 \times 10^{-14} \text{ Js}^3}{1.57 \times 10^{-33}} \right)^{1/3} = 1.58 \left( 3.73 \times 10^{-8} \right)^{1/3} J = 2.45 \times 10^{-27} J
\]

For a harmonic oscillator:

\[
E = \frac{h \omega}{2} = \frac{1}{2} \sqrt{\frac{\hbar^2 \kappa}{\mu}} = 0.5 \left( \frac{1.05 \times 10^{-34} \text{ Js}^2}{1.62 \times 10^{-27} \text{ kg}} \right)^{1/2} = 32.7 \times 10^{-40} \text{ J}^2 = 5.72 \times 10^{-20} J
\]

b) Using your ground state wave function from part a, calculate \( \langle x^2 \rangle \) for the ground state of the quartic oscillator. How does this compare to \( \langle x^2 \rangle \) for a harmonic oscillator in the ground state? Explain.

Solution: Note there was a minor typo in this problem. It does not affect the procedure nor the answer. The wave function should have been: \( \psi_0(x) = \left( \frac{\alpha^2}{\pi} \right)^{1/4} e^{-\alpha^2 x^2/2} \)
Instead of $\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2} e^{-ax^2}$. The solution we show uses the wave function given. The result is still correct.

$$
\langle x^2 \rangle = \left\langle \frac{\alpha}{\sqrt{\pi}} \right\rangle \int_{-\infty}^{\infty} x^2 e^{-2ax^2} \, dx = \frac{1}{8\alpha} \sqrt{\frac{\pi}{4a}} = \frac{1}{8} \left(\frac{6\kappa\mu}{\hbar^2}\right)^{1/3}
$$

$\langle x^2 \rangle$ will be smaller for the quartic oscillator than for the harmonic oscillator because the $x^4$ potential is steeper than the $x^2$ potential.

2) Carbon monoxide $^{12}$C$^{16}$O has a bond length of 112.8 pm. In this problem we will first assume the rotation of CO in the gas phase can be treated classically and then we will compare the classical energy of rotation to the quantum mechanical rigid rotor model. In this problem, neglect the vibration of the C-O bond.

a) Assuming the rotation of $^{12}$C$^{16}$O can be treated classically, use the equipartition principle to calculate the average rotational energy per molecule at $T=300K$.

Solution: This rotation changes two angles $\theta$ and $\varphi$ so there are two degrees of freedom. So the average rotational energy is

$$
\langle E_{rot} \rangle = 2 \left(\frac{k_B T}{2}\right) = k_B T = \left(1.38 \times 10^{-23} \text{JK}^{-1}\right)(300K) = 4.14 \times 10^{-21} \text{J}
$$

b) Assume that the rotation of $^{12}$C$^{16}$O in the gas phase can be treated using the quantum mechanical rigid rotor model. Determine the quantum state $\ell$ that corresponds to the average energy calculated in part a. What is the degeneracy of this state?

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

$$
\mu = \frac{0.012 \text{kgmol}^{-1} \times 0.016 \text{kgmol}^{-1}}{0.012 \text{kgmol}^{-1} + 0.016 \text{kgmol}^{-1}} \frac{1}{6.023 \times 10^{23} \text{mol}^{-1}} = 1.92 \times 10^{-26} \text{kg}
$$

$$
I = \mu R^2 = \left(1.14 \times 10^{-26} \text{kg}\right) \left(112.8 \times 10^{-12} \text{m}\right)^2 = \left(1.14 \times 10^{-26} \text{kg}\right) \left(1.27 \times 10^{-20} \text{m}^2\right) = 1.45 \times 10^{-46} \text{kgm}^2
$$
\[
E_{\text{rot}} = \frac{\hbar^2}{2I} \ell (\ell + 1) = \langle E_{\text{rot}} \rangle = k_B T
\]
\[
\ell (\ell + 1) = 2I k_B T \hbar^2 = \frac{(2)(1.45 \times 10^{-46} \text{kgm}^2)(4.14 \times 10^{-21} J)}{(1.05 \times 10^{-34} \text{Js})^2}
\]
Then
\[
= \frac{1.20 \times 10^{-66} \text{kg}^2 \text{m}^4 \text{s}^{-2}}{1.10 \times 10^{-68} \text{kg}^2 \text{m}^4 \text{s}^{-2}} = 1.09 \times 10^2
\]
\[
\therefore \ell^2 + \ell - 109 = 0 \Rightarrow \ell = \frac{-1 + \sqrt{1 - (4)(-109)}}{2} = 9.95 \approx 10
\]
The degeneracy is \(2\ell + 1 = 2(10) + 1 = 21\)

c) Assume that the \(^{12}\text{C}^{16}\text{O}\) molecule adsorbs from the gas phase onto a flat surface where its subsequent motion can be treated using the quantum mechanical planar rigid rotor model. Assuming the temperature on the surface is still \(T=300\text{K}\), determine the average classical rotational energy per molecule and also determine the quantum state that corresponds to this energy.

The molecule rotates in a plane so there is one dof and
\[
\langle E_{\text{rot}} \rangle = \left(\frac{k_B T}{2}\right) = (1.38 \times 10^{-23} \text{JK}^{-1})(300\text{K})/2 = 2.07 \times 10^{-21} J
\]
\[
E_{\text{rot}} = \frac{\hbar^2 m^2}{2I} = \frac{k_B T}{2}
\]
\[
m^2 = \frac{2I k_B T}{\hbar^2} = \frac{I k_B T}{\hbar^2} \left(\frac{1.45 \times 10^{-46} \text{kgm}^2}{(1.05 \times 10^{-34} \text{Js})^2}\right)
\]
\[
= \frac{6.00 \times 10^{-67}}{1.10 \times 10^{-68}} = 54.5 \Rightarrow m = \sqrt{54.5} = \pm 7.38 \approx \pm 7
\]

d) Using your result from part b, calculate the energy level spacing between the \(\ell\) and \(\ell + 1\) rotational states. Similarly, using your result from part c calculate the energy level spacing for the plane rigid rotator. From these energy level spacings, compare the importance of quantum effects in the rotation of \(^{12}\text{C}^{16}\text{O}\) in the gas phase versus on the surface.

For a rigid rotor the energy level spacing is
\[
\Delta E_{\text{rot}} = \frac{\hbar^2}{2I} (2\ell + 2) = \frac{(1.05 \times 10^{-34} \text{Js})^2}{(2)(1.45 \times 10^{-46} \text{kgm}^2)}(2 \times 10 + 2) = 8.36 \times 10^{-22} J
\]
For a plane rigid rotator:
\[
\Delta E_{\text{rot}} = \frac{\hbar^2}{2I} (2m + 1) = \frac{(1.05 \times 10^{-34} \text{Js})^2}{(2)(1.45 \times 10^{-46} \text{kgm}^2)}(2 \times 7 + 1) = 5.70 \times 10^{-22} J
\]
Both energy level spacings are about 1/5 to 1/8 the value of \( k_B T \). So quantum effects for rotational motions are not as important as in vibrational motions but are more important than in translational motions.

3) Assume \(^1\text{H}^{35}\text{Cl}\) can be treated as a quantum mechanical rigid rotor. The H-Cl bond length is 0.127 nm.

a) Suppose wave function associated with the rotational state of HCl is \( Y_{\ell,0}(\theta, \phi) \), i.e. \( \ell = 2, m=0 \). Calculate the rotational energy, the total angular momentum, and the \( z \) component of the angular momentum.

\[
\mu = \frac{1}{N_A} \frac{M_H M_{Cl}}{M_H + M_{Cl}} = \frac{1}{6.02 \times 10^{23} \text{mol}^{-1}} \left( \frac{0.001 \text{kgmol}^{-1}}{0.001 \text{kgmol}^{-1} + 0.035 \text{kgmol}^{-1}} \right) = \frac{1}{0.036 \text{kgmol}^{-1}} = 1.62 \times 10^{-27} \text{kg}
\]

\[
I = \mu R^2 = (1.62 \times 10^{-27} \text{kg}) \left( 0.127 \times 10^{-9} \text{m} \right)^2 = 2.61 \times 10^{-47} \text{kgm}^2
\]

\[
E = \frac{\hbar^2}{2I} (\ell + 1) = \frac{\hbar^2}{2 \mu R^2} (\ell + 1) = \left( \frac{1.05 \times 10^{-34} \text{Js}}{2} \right) \left( \frac{2.61 \times 10^{-47} \text{kgm}^2}{(2)(2+1)} \right) = 1.27 \times 10^{-21} \text{J}
\]

\[
L = \hbar \sqrt{\ell (\ell + 1)} = \left( 1.05 \times 10^{-34} \text{Js} \right) (6)^{1/2} = 2.57 \times 10^{-34} \text{Js}
\]

\[
L_z = m \hbar = (0) \hbar = 0
\]

b) Using this wave function, calculate the probability that the rigid rotor occurs within the surface of the sphere defined by \( \phi=0 \) and \( \phi=\pi/2 \) and \( \theta=0 \) and \( \theta=\pi/2 \). Give a geometric explanation of your result.

\[
Y_{20}(\theta, \phi) = \Theta_{20}(\theta) \Phi_0(\phi) = \sqrt{\frac{5}{16\pi}} \left( 3 \cos^2 \theta - 1 \right) \frac{1}{\sqrt{2\pi}}
\]

\[
P_{20}(\theta, \phi) = \int_0^{\pi/2} d\phi \int_0^{\pi/2} d\theta \sin \theta Y_{20}^2(\theta, \phi)
\]

\[
= \left( \frac{5}{16\pi} \right) \int_0^{\pi/2} d\phi \int_0^{\pi/2} d\theta \sin \theta \left( 3 \cos^2 \theta - 1 \right)^2
\]

\[
= \left( \frac{5}{16\pi} \right) \left( \frac{\pi}{2} \right) \int_0^{\pi/2} d\theta \sin \theta \left( 9 \cos^4 \theta - 6 \cos^2 \theta + 1 \right) = \frac{5}{32} \left( -9 \cos^5 \frac{\theta}{5} + 6 \cos^3 \frac{\theta}{3} - \cos \theta \right) \bigg|_0^{\pi/2}
\]

\[
= \frac{5}{32} \left( 9 - 2 + 1 \right) \bigg|_0^{\pi/2} = \frac{5}{32} \times \frac{4}{5} = \frac{1}{8}
\]
The volume in question is an octant, one eighth of the unit sphere volume.

4) Consider the hydrogen atomic wave function $\psi_{3,2,0}(r, \theta, \varphi) = R_{3,2}(r) Y_{2,0}(\theta, \varphi)$

a) Write out the individual, normalized radial and angular wave functions $R_{3,2}(r)$ and $Y_{2,0}(\theta, \varphi)$. Confirm that each is normalized. For the radial wave function consult the text and/or notes. For the angular wave function you can consult the notes.

Solution: We have already proven that $Y_{2,0}(\theta, \varphi)$ is normalized in problem 3.

The radial is normalized as shown below…

$$\int_0^{\infty} r^2 R_{32}^2(r) dr = \left( \frac{4}{81\sqrt{30}} \right)^2 \left( \frac{1}{a_0} \right)^7 \int_0^{\infty} r^6 e^{-2r/3a_0} dr$$

$$= \left( \frac{4}{81\sqrt{30}} \right)^2 \left( \frac{1}{a_0} \right)^7 \left( \frac{3a_0}{2} \right)^6 6!$$

$$= \left( \frac{2^4}{9^4(30)} \right)^7 \left( \frac{3}{2} \right)^6 6! = \left( \frac{2^4}{3^86^5} \right)^7 \left( \frac{3}{2} \right)^6 6! = \left( \frac{1}{3} \right)^7 \left( \frac{1}{2^5} \right) \times 4 \times 3 \times 2 = 1$$

b) Calculate the probability of the electron occurring between $\varphi=0$ and $\varphi=\pi/4$. Solve this problem by performing the appropriate integral. Confirm your answer with a simple geometric argument. See problem 2d.

Solution: By now this is clear…as long as the angular wave function is normalized, the angular limits determine the probability. Just set up the integral as in problem 2d…with appropriate limit changes…

$$\int_0^{\frac{\pi}{4}} \int_0^\varphi r^2 \theta Y_{2,0}^2(\theta, \varphi) d\theta \sin \theta d\varphi = \frac{\pi}{4} \left( \frac{5}{16\pi} \right)^7 \int_0^{\frac{\pi}{4}} d\theta \sin \theta \left( 3\cos^2 \theta - 1 \right)^2$$

$$= \left( \frac{5}{64} \right)^7 \int_0^{\frac{\pi}{4}} d\theta \sin \theta \left( 9\cos^4 \theta - 6\cos^2 \theta + 1 \right) = \left( \frac{5}{64} \right)^7 \left[ -\frac{9\cos^5 \theta}{5} \right]_0^{\frac{\pi}{4}} + \frac{6\cos^3 \theta}{3} \left[ \cos \theta \right]_0^{\frac{\pi}{4}}$$

$$= \left( \frac{5}{64} \right)^7 \left[ \frac{18}{5} - 4 + 2 \right] = \left( \frac{5}{64} \right)^7 \left[ \frac{18}{5} - 2 \right] = \left( \frac{5}{64} \right)^7 \left( \frac{8}{5} \right) = \frac{1}{8}$$

Again, the $\varphi$ range is $0$ to $\pi/4$ which is $1/8$ the total range.

C) Repeat the calculation in b but now let the electron be located between $\varphi=0$ and $\varphi=\pi/4$ and $\theta=0$ and $\pi/2$. Does the value of the integral correspond to a geometric analysis?

Solution: we already know the answer…the $\varphi$ range is $1/8$ the full range and the $\theta$ range is half. So the probability is $1/16$. Easy to show using the Problem 2d integral…
\[
\int_0^{\pi/4} d\varphi \int_0^{\pi/2} d\theta \sin \theta Y_{2,0}^2 (\theta, \varphi) = \frac{\pi}{4} \left( \frac{5}{16\pi} \right)^{\pi/2} \int_0^{\pi/2} d\theta \sin \theta (3\cos^2 \theta - 1)^2
\]
\[
= \left( \frac{5}{64} \right) \left[ -\frac{9\cos^{5\pi/2}}{5} + \frac{6\cos^3 \theta}{3} \right]_{0}^{\pi/2} - \cos \theta_{\pi/2}^{\pi/2}
\]
\[
= \left( \frac{5}{64} \right) \left[ \frac{9}{5} - 2 + 1 \right] = \left( \frac{5}{64} \right) \left[ \frac{9}{5} - 1 \right] = \left( \frac{5}{64} \right) \left( \frac{4}{5} \right) = \frac{1}{16}
\]

4) The Virial Theorem of Mechanics states that given a potential energy of the form 
\[ V(r) = ar^n \] where \( a \) is a constant and \( n \) is a positive or negative integer, the average potential energy \( \langle V \rangle \) is related to the average kinetic energy \( \langle K \rangle \) as
\[ 2 \langle K \rangle = n \langle V \rangle. \]

a) For an electron in the ground energy state of hydrogen, calculate the average kinetic energy and the average momentum squared, i.e. \( \langle p^2 \rangle \). Hint: Use the fact that for all \( n \), \( \langle K \rangle + \langle V \rangle = E_n \).

Solution: For \( H \), \( V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \), therefore \( 2 \langle K \rangle = -\langle V \rangle \) and so
\[ \langle K \rangle + \langle V \rangle = \langle K \rangle - 2\langle K \rangle = E_n = -\frac{R_H}{n^2} \]
\[ \therefore \langle K \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{R_H}{1} \Rightarrow \langle p^2 \rangle = 2mR_H = (2)(9.11 \times 10^{-31} \text{kg})(2.18 \times 10^{-18} \text{J}) 
\]
\[ = (2)(9.11 \times 10^{-31} \text{kg})(2.18 \times 10^{-18} \text{J}) = 3.97 \times 10^{-48} \text{kg}^2 \text{m}^2 \text{s}^{-2} \]

b) Using the hint from part a, calculate the average potential energy of an electron in the ground energy state of hydrogen and calculate the average of \( 1/r \), i.e. \( \langle \frac{1}{r} \rangle \).

\[ \langle K \rangle + \langle V \rangle = -\frac{\langle V \rangle}{2} + \frac{\langle V \rangle}{2} = E_n \]
\[ \therefore \langle V \rangle = 2E_n = 2R_H = (2)(2.18 \times 10^{-18} \text{J}) = 4.36 \times 10^{-18} \text{J} \]
\[ \langle V \rangle = \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{r} \right) = \left( \frac{4.36 \times 10^{-18} \text{J}}{4\pi(4.36 \times 10^{-18} \text{J})} \right) \frac{8.85 \times 10^{-12} \text{C}^2 \text{J}^{-1} \text{m}^{-1}}{(1.60 \times 10^{-19} \text{C})^2} 
\]
\[ = (4\pi)(4.36 \times 10^{-18} \text{J}) \frac{8.85 \times 10^{-12} \text{C}^2 \text{J}^{-1} \text{m}^{-1}}{(1.60 \times 10^{-19} \text{C})^2} 
\]
\[ = 1.89 \times 10^{10} \text{m}^{-1} \]
c) Using the wave function expression for the 1s electron in hydrogen, calculate $\langle r \rangle$.

How close is $\frac{1}{\langle r \rangle}$ to $\left\langle \frac{1}{r} \right\rangle$?

$$\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^2 e^{-r/a_0} \, dr = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-r/a_0} \, dr = \frac{4 \times 3!}{a_0^3} \left( \frac{a_0}{2} \right)^4$$

$$= \frac{3a_0}{2} = (1.5)(0.529 \times 10^{-10} \text{ m}) = 7.93 \times 10^{-11} \text{ m}$$

$$\frac{1}{\langle r \rangle} = \frac{1}{7.93 \times 10^{-11} \text{ m}} = 1.26 \times 10^{10} \text{ m}^{-1} \neq \left\langle \frac{1}{r} \right\rangle$$