Homework Assignment 3; New Due Date 01/25/10

1) The exact ground state energy for a particle in a box is \( E_1 = \frac{\hbar^2}{8mL^2} \). And the exact wave function is \( \psi_1(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \). Consider an approximate particle in the box wave function: \( \psi_1(x) = x(L - x) \).

a) Show that the approximate wave function satisfies the boundary conditions.

Solution: \( \psi_1(0) = 0(L - 0) = 0 \) and \( \psi_1(L) = x(L - L) = 0 \)

b) There is a mathematical method called the Variational Method, that allows calculation of the energy using an approximate wave function, assuming the wave function fits the boundary conditions. The equation for the energy is:

\[
E = \frac{\int_0^L \psi(x) \hat{H} \psi(x) dx}{\int_0^L \psi^2(x) dx}
\]

where \( \hat{H} \) is the Hamiltonian operator for the particle in the box. Calculate the energy using the approximate wave function.

Solution:

\[
E = \frac{\int_0^L \psi(x) \hat{H} \psi(x) dx}{\int_0^L \psi^2(x) dx} = \frac{-\frac{\hbar^2}{2m} \int_0^L x(L - x) \frac{d^2}{dx^2} [xL - x^2] dx}{\int_0^L (xL - x^2)^2 dx}
\]

\[
= \frac{\hbar^2}{m} \int_0^L (xL - x^2) dx = \frac{\hbar^2}{m} \left( \frac{L^3}{2} - \frac{L^3}{3} \right) = \frac{\hbar^2}{m} \left( \frac{L^3}{6} \right)
\]

\[
= \frac{\hbar^2}{m} \left( \frac{L^3}{6} \right) = \frac{\hbar^2}{m} \frac{L^3}{6} = \frac{\hbar^2}{m} \frac{L^3}{6} \approx 0.127 \times \frac{\hbar^2}{mL^2} = \frac{\hbar^2}{mL^2} \frac{5}{7.89mL^2}
\]
c) According to the Variational Method, the more the approximate wave function resembles the real wave function, the closer the energy matches the real energy. Graph the approximate wave function and the real particle-in-the-box wave function. How different are the energies? Calculate the percent difference.

For the purpose of doing the graph let \( L = 1 \). Then the real wave function for \( n = 1 \) is
\[
\psi_{1,\text{real}}(x) = \sqrt{2} \sin \pi x
\]
and the trial wave function is
\[
\psi_{1,\text{trial}}(x) = x(1 - x)
\]

The graph is:

Here I have normalized the wave functions to be equal in amplitude at the maximum \( x = L/2 \). This is a good idea because the trial wave function is not normalized. The normalization is necessary because otherwise the trial wave function is not valid. When this is done the plot above results and we find the wave functions have a relative difference of 4.1%, approximately. Not a bad guess.

2) Generally the quantization of translational motion is not significant for atoms because of their mass. However, this conclusion depends upon the size of the space to which the atoms are confined. Zeolites are structures with small cubic pores with edge length 1 nm. Calculate the energy of a \( \text{H}_2 \) molecule confined to a zeolite pore, assuming \( n_x = n_y = n_z = 10 \). Compare this energy to \( k_B T \) assuming \( T = 300 \)K. Are quantization effects important in this case?

Solution:
\[
E = \frac{\hbar^2}{8ML^2} \left( n_x^2 + n_y^2 + n_z^2 \right) = \frac{\left( 6.63 \times 10^{-34} \text{Js} \right)^2 \left( 6.02 \times 10^{23} \text{mol}^{-1} \right)}{8 \left( 0.002 \text{kg mol}^{-1} \right) \left( 1.00 \times 10^{-10} \text{m} \right)^2} \left( 10^2 + 10^2 + 10^2 \right)
\]
\[
= \frac{\left( 44.0 \times 10^{-38} \text{J}^2 s^2 \right) \left( 6.02 \times 10^{23} \text{mol}^{-1} \right)}{\left( 0.016 \text{kg mol}^{-1} \right) \left( 1.00 \times 10^{-18} \text{m}^2 \right)} \times 300 = 4.97 \times 10^{6} \text{J} = 4.97 \times 10^{-21} \text{J}
\]
Now \( k_bT = \left(1.38 \times 10^{-23} \text{ JK}^{-1}\right)(300\text{K}) = 4.14 \times 10^{-21} \text{J} \)

3) Carbon monoxide absorbs radiation at a wave number \( \tilde{\nu} = 2144 \text{cm}^{-1} \) because of its internal vibration.
   a) Calculate the vibrational energy level spacing for CO. Assume the vibration of CO can be modeled as a harmonic oscillation.
      Solution: Calculate the reduced mass for \(^{12}\text{C}^{16}\text{O}\) in kilograms.
      \[
      \mu = \frac{.012 \times .016}{.012 + .016} \frac{1}{6.04 \times 10^{23}} = 1.14 \times 10^{-26} \text{kg}
      \]
      Calculate the oscillator frequency for \(^{12}\text{C}^{16}\text{O}\).
      \[
      \nu = \frac{1}{2\pi} \sqrt{\frac{1.902 \times 10^3 \text{Nm}^{-1}}{1.14 \times 10^{-26} \text{kg}}} = 6.5 \times 10^{13} \text{s}^{-1}
      \]
      \[\Delta E = h\nu = 6.63 \times 10^{-34} \text{J} \cdot \text{s} \times 6.5 \times 10^{13} \text{s}^{-1} = 4.31 \times 10^{-20} \text{J}\]
   b) Calculate \(k_bT\) for \(T=300\text{K}\). Based on this value and your answer in part a, will CO vibrations be thermally excited at \(T=300\text{K}\)? Explain.
      \(k_bT = 1.38 \times 10^{-23} \text{ JK}^{-1} \times 300\text{K} = 4.14 \times 10^{-21} \text{J}\). \(k_bT \ll \Delta E\) so no.
   c) At what temperature will thermal excitation of CO vibrations become important?
      Solution: \(k_bT \gg \Delta E \Rightarrow T \gg \frac{\Delta E}{k_b} = \frac{4.31 \times 10^{-20} \text{J}}{1.38 \times 10^{-23} \text{ JK}^{-1}} = 3.12 \times 10^3 \text{K}\)
   d) Calculate the vibrational heat capacity of 1 mole of CO at the temperature calculated in part c. Assume first the expression for the vibrational heat capacity based on the equipartition theorem. Compare this result to the quantum expression for the heat capacity \(C_V\).
      The two values are comparable.
4) The fundamental vibration frequency of gaseous $^{14}\text{N}^{16}\text{O}$ is 1904 cm$^{-1}$.

a) Calculate the force constant using formula for a simple harmonic oscillator.

Solution: $\nu = \frac{V}{c} \Rightarrow \nu = c\bar{V} = \left(3 \times 10^{16} \text{ cm s}^{-1}\right)\left(1904\text{cm}^{-1}\right) = 5.71 \times 10^{13} \text{ s}^{-1}$

$$\mu = \frac{m_N m_O}{m_N + m_O} = \frac{1}{N_A} \frac{M_N M_O}{M_N + M_O}$$

$$= \frac{1}{6.02 \times 10^{23} \text{ mol}^{-1}} \left(0.014 \text{ kg} \right) \left(0.016 \text{ kg} \right) = 2.24 \times 10^{-27} \frac{\text{kg}}{0.181} = 1.24 \times 10^{-26} \text{ kg}$$

Now $\omega = 2\pi\nu = \sqrt{\frac{\kappa}{\mu}}$. Therefore $\omega^2 = 4\pi^2\nu^2 = \frac{\kappa}{\mu}$ and so $4\pi^2
\nu^2\mu = \kappa$

We obtain:

$$\kappa = 4\pi^2
\nu^2\mu = \left(6.28\right)^2 \left(5.71 \times 10^{13} \text{ s}^{-1}\right)^2 \left(1.24 \times 10^{-26} \text{ kg}\right)$$

$$= 1595 \text{kg s}^{-1} = 1595 \text{Nm}^{-1}$$

b) Using the force constant in part a, calculate the fundamental vibration frequency of gaseous $^{15}\text{N}^{16}\text{O}$.

$$\mu = \frac{m_N m_O}{m_N + m_O} = \frac{1}{N_A} \frac{M_N M_O}{M_N + M_O}$$

$$= \frac{1}{6.02 \times 10^{23} \text{ mol}^{-1}} \left(0.015 \text{ kg} \right) \left(0.016 \text{ kg} \right) = 2.40 \times 10^{-27} \frac{\text{kg}}{0.187} = 1.28 \times 10^{-26} \text{ kg}$$

$$\frac{\nu\left(^{15}\text{N}^{16}\text{O}\right)}{\nu\left(^{14}\text{N}^{16}\text{O}\right)} = \sqrt{\frac{\mu\left(^{14}\text{N}^{16}\text{O}\right)}{\mu\left(^{15}\text{N}^{16}\text{O}\right)}} \Rightarrow \nu\left(^{15}\text{N}^{16}\text{O}\right) = \nu\left(^{14}\text{N}^{16}\text{O}\right) \sqrt{\frac{\mu\left(^{15}\text{N}^{16}\text{O}\right)}{\mu\left(^{14}\text{N}^{16}\text{O}\right)}} = \left(1904\text{cm}^{-1}\right)\sqrt{\frac{1.24}{1.28}} = 1874\text{cm}^{-1}$$

c) When $^{14}\text{N}^{16}\text{O}$ is bound to hemoglobin the oxygen is anchored to the protein so its effective mass is much greater (i.e. essentially infinite) compared to the mass of the nitrogen atom. Using the force constant from part a, calculate the fundamental vibration frequency of NO bound to hemoglobin.

$$\mu \approx m_N = \frac{0.014 \text{ kgmol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 2.33 \times 10^{-26} \text{ kg}$$

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{\kappa}{\mu}} = \frac{1}{6.28} \frac{1}{3 \times 10^{10} \text{ cm s}^{-1}} \sqrt{\frac{1595 \text{ Nm}^{-1}}{2.33 \times 10^{-26} \text{ kg}}} = 1389 \text{cm}^{-1}$$

Or... $\nu\left(^{14}\text{N}\infty\right) = \nu\left(^{14}\text{N}^{16}\text{O}\right) \sqrt{\frac{\mu\left(^{14}\text{N}^{16}\text{O}\right)}{m_N}} = \left(1904\text{cm}^{-1}\right)\sqrt{\frac{1.24}{2.33}} = 1389\text{cm}^{-1}$
5) The vibrational frequency of $^{1}\text{H}^{35}\text{Cl}$ is $8.963 \times 10^{13}$ s$^{-1}$.

a) Calculate the bond force constant $\kappa$ and the reduced mass $\mu$.

$$
\mu = \frac{m_H m_C}{m_H + m_C} = \frac{1}{N_A} \frac{M_H M_C}{M_H + M_C} \\
= \frac{1}{6.02 \times 10^{23} \text{ mol}^{-1}} \left(0.001 \text{ kg}\right) \left(0.0355 \text{ kg}\right) = 3.55 \times 10^{-28} \text{ kg} = 1.61 \times 10^{-27} \text{ kg}
$$

As in Problem 4a...

$$
\kappa = 4\pi^2 \nu^2 \mu = (6.28)^2 \left(8.963 \times 10^{13} \text{ s}^{-1}\right)^2 \left(1.61 \times 10^{-27} \text{ kg}\right)
= 510 \text{ kg} \text{s}^{-1} = 510 \text{ Nm}^{-1}
$$

b) Assume $^{1}\text{H}^{35}\text{Cl}$ is in the n=0 quantized vibrational state. Calculate the average of the square of the vibrational amplitude about the equilibrium position $\langle x^2 \rangle$

$$
\langle x^2 \rangle = \frac{\langle q^2 \rangle}{\alpha} = \frac{1}{\alpha} \int_{-\infty}^{\infty} \psi_0(q)^2 q^2 \psi_0(q) dq = \frac{1}{\alpha} \int_{-\infty}^{\infty} q^2 \left(\frac{1}{\sqrt{\pi}}\right) e^{-q^2} dq = \frac{2}{\alpha \sqrt{\pi}} \int_{0}^{\infty} q^2 e^{-q^2} = \frac{1}{2\alpha}
$$

$$
\alpha = \frac{\mu \omega}{\hbar} = \frac{(2\pi)(8.963 \times 10^{13} \text{ s}^{-1})(1.61 \times 10^{-27} \text{ kg})}{1.06 \times 10^{-34} \text{ Js}} = 8.55 \times 10^{21} \text{ m}^{-2}
$$

\[\therefore \langle x^2 \rangle = \frac{1}{2\alpha} = \frac{1}{2} \left(\frac{2}{8.55 \times 10^{21} \text{ m}^{-2}}\right) = 5.85 \times 10^{-23} \text{ m}^{-2}\]

c) Use you results from parts a and b to calculate the average potential energy $\langle V(x) \rangle$.

$$
\langle V \rangle = \frac{\kappa}{2} \langle x^2 \rangle = \frac{510 \text{ Nm}^{-1}}{2} \left(5.85 \times 10^{-23} \text{ m}^{-2}\right) = 1.49 \times 10^{-20} \text{ J}
$$

d) Starting with the definition for the momentum operator for a one dimensional harmonic oscillator $\hat{p} = -i\hbar \frac{d}{dx}$, calculate the average squared momentum $\langle p^2 \rangle$ for $^{1}\text{H}^{35}\text{Cl}$ in the n=0 quantized vibrational state. Use this result and the results of part a to calculate the average kinetic energy $\langle K \rangle$ for $^{1}\text{H}^{35}\text{Cl}$ in the n=0 quantized vibrational state.
\[
\langle p^2 \rangle = -\hbar^2 \int_{-\infty}^{+\infty} \psi_0^* \frac{d^2 \psi_0}{dx^2} dx = -\hbar^2 \int_{-\infty}^{+\infty} \psi_0^* \frac{d^2 \psi_0}{dx^2} dx = -\hbar^2 \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{+\infty} e^{-\alpha x^2/2} \frac{d^2 e^{-\alpha x^2/2}}{dx^2} dx
\]

\[
= -\hbar^2 \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{+\infty} e^{-\alpha x^2/2} \left(-\alpha x e^{-\alpha x^2/2}\right) dx = -\hbar^2 \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{+\infty} e^{-\alpha x^2/2} \left(-\alpha e^{-\alpha x^2/2} + \alpha^2 x^2 e^{-\alpha x^2/2}\right) dx
\]

\[
= -2\hbar^2 \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{0}^{+\infty} \left(-\alpha e^{-\alpha x^2} + \alpha^2 x^2 e^{-\alpha x^2}\right) dx = \left(-2\hbar^2 \left( \frac{\alpha}{\pi} \right)^{1/2} \right) \left[-\alpha \sqrt{\frac{\pi}{4\alpha}} + \alpha^2 \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} \right]
\]

\[
= \left(-2\hbar^2 \left( \frac{\alpha}{\pi} \right)^{1/2} \right) \left[-\alpha \sqrt{\frac{\pi}{4\alpha}} + \alpha^2 \frac{1}{2} \sqrt{\frac{\pi}{4\alpha}} \right] = \left(2\hbar^2 \left( \frac{\alpha}{\pi} \right)^{1/2} \right) \left[\frac{\alpha}{4} \sqrt{\frac{\pi}{\alpha}} \right]
\]

\[
= \frac{\hbar^2 \alpha}{2} = \frac{\left(1.06 \times 10^{-34} \text{ Js}\right)^2 \left(8.55 \times 10^{-21} \text{ m}^{-2}\right)}{2} = 4.80 \times 10^{-47} \text{ kg}^2 \text{ m}^2 \text{ s}^{-2}
\]

\[
\langle K \rangle = \frac{\langle p^2 \rangle}{2\mu} = \frac{4.80 \times 10^{-47} \text{ kg}^2 \text{ m}^2 \text{ s}^{-2}}{2 \left(1.61 \times 10^{-27} \text{ kg}\right)} = 1.49 \times 10^{-20} \text{ J}
\]

**e)** Based on the results of parts a-d, how are \( \langle V(x) \rangle \) and \( \langle K \rangle \) for a quantized harmonic oscillator related in general? Answer: \( \langle V \rangle = \langle K \rangle = \frac{E_n}{2} \)

6) The molecule \( ^{12}\text{C}^{16}\text{O} \) has a bond length of 1.13 Angstroms. Suppose that when \( ^{12}\text{C}^{16}\text{O} \) adsorbs onto the surface of a large protein it rotates as a quantized planar rigid rotor as described in Lecture 7.

**a)** Calculate the reduced mass and the moment of inertia \( I \) of \( ^{12}\text{C}^{16}\text{O} \).

Solution:
\[
\mu = \frac{m_c m_o}{m_c + m_o} = \frac{1}{N_A} \frac{M_c M_o}{M_c + M_o}
\]

\[
= \frac{1}{6.02 \times 10^{23} \text{ mol}^{-1}} \frac{0.012 \text{ kg}}{0.012 \text{ kg} + 0.016 \text{ kg}} = 1.92 \times 10^{-27} \text{ kg} = 1.14 \times 10^{-26} \text{ kg}
\]

\[
I = \mu R^2 = \left(1.14 \times 10^{-26} \text{ kg}\right) \left(1.13 \times 10^{-10} \text{ m}\right)^2 = 1.46 \times 10^{-46} \text{ kg} \text{ m}^2
\]

**b)** Assume \( ^{12}\text{C}^{16}\text{O} \) is in the \( k=2 \) rotational state. Calculate the average of the square of the angular momentum \( \langle L_z^2 \rangle \).

Solution: \( \langle L_z^2 \rangle = \hbar^2 k^2 = \left(1.06 \times 10^{-34} \text{ Js}\right)^2 \left(2^2\right) = 4.46 \times 10^{-68} \text{ J}^2 \text{ s}^2 \)

**c)** Use the results of parts a and b to calculate the energy of \( ^{12}\text{C}^{16}\text{O} \) in the \( k=2 \) state. Compare this value to the average rotational energy of a classic planar rigid rotor, assuming \( T=300\text{K} \). Are quantum effects important in this case?
Solution: \( E_k = \frac{\langle L_z^2 \rangle}{2I} = \frac{4.46 \times 10^{-68} J^2 s^2}{(2)(1.46 \times 10^{-40} \text{ kg m}^2)} = 1.53 \times 10^{-22} J \)

For a planar rigid rotor there is rotation in a single angular dimension. So by the equipartition theorem: \( \langle E_{\text{rotor}} \rangle = \frac{k_B T}{2} \left( \frac{1.38 \times 10^{-23} \text{ JK}^{-1}}{300 \text{ K}} \right) = 2.07 \times 10^{-21} J \)

The classic energy is about ten times that of k=2 state. Quantum effects are small.

7) The molecule \(^{12}\text{C}^{16}\text{O}\) has a bond force constant of \( \kappa = 1860 \text{ Nm}^{-1} \).

a) Calculate the vibrational zero point energy of this molecule.

Solution: the zero point energy is \( E_{n=0} = \frac{\hbar \omega}{2} = \frac{\hbar \omega}{2} \)

We need \( \omega \), which is given by \( \omega = \sqrt{\frac{\kappa}{\mu}} = \sqrt{\frac{1860 \text{ Nm}^{-1}}{1.14 \times 10^{-26} \text{ kg}}} = 4.04 \times 10^{14} \text{ s}^{-1} \)

where the reduced mass for CO was obtained from problem 6a.

\[ E_{n=0} = \frac{\hbar \omega}{2} = \frac{(1.06 \times 10^{-34} \text{ Js}) (4.04 \times 10^{14} \text{ S}^{-1})}{2} = 2.14 \times 10^{-20} J \]

b) If this amount of energy were converted to kinetic energy, how fast would the molecule be moving?

Solution: We set the translational kinetic energy equal to the zero point energy:

\[ \frac{mv^2}{2} = E_{n=0} \quad \text{where} \quad m = \frac{0.012 \text{ kg} + 0.016 \text{ kg}}{6.02 \times 10^{23}} = 4.65 \times 10^{-26} \text{ kg} \]

Note: Many students were concerned about whether to use the mass of CO or the reduced mass. This concern originates in uncertainty about whether the kinetic energy mentioned is associated with the translational motion of the entire CO molecule or the vibrational motion of the CO bond. If the former is intended the mass \( m \) is required. If the latter is intended the reduced mass \( \mu \) is required. The perceived ambiguity is resolved however in the next part which asks you to compare the computed velocity to the velocity predicted by the kinetic theory of gases. The kinetic theory of gases relates the translational motion of molecules to their macroscopic physical properties. The equation below is for translational motion and is derived from the equipartition statement:

\[ \frac{m \langle v^2 \rangle}{2} = \frac{3k_B T}{2} \quad \Rightarrow \quad \langle v^2 \rangle = \frac{3k_B T}{m} \]

Using

\[ m \ldots v = \sqrt{\frac{2E_{n=0}}{m}} = \sqrt{\frac{(2)(2.14 \times 10^{-20} J)}{4.65 \times 10^{-26} \text{ kg}}} = \sqrt{\frac{4.28 \times 10^{-20} J}{4.65 \times 10^{-26} \text{ kg}}} = 0.96 \times 10^3 \text{ ms}^{-1} = 960 \text{ ms}^{-1} \]

c) Compare your result in b to the average speed derived from the kinetic theory of gases:
\[ v_{\text{ave}} = \sqrt{\frac{3k_B T}{m}} \text{ where } T=300\text{K}. \]

Solution:

\[ v_{\text{ave}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{(3)(1.38 \times 10^{-23}\text{JK}^{-1})(300\text{K})}{4.65 \times 10^{-26}\text{kg}}} = \sqrt{\frac{1.24 \times 10^{-20}\text{J}}{4.65 \times 10^{-26}\text{kg}}} = 0.516 \times 10^3\text{ms}^{-1} = 516\text{ms}^{-1} \]

Note the classical prediction has the molecule moving slower than would occur if the zero-point energy were converted to kinetic energy. This results because for vibrational motions quantum effects like the zero point energy are larger than \( k_B T \).