EXERCISES

A. Write the integral for the transition dipole moment (μ_{fi}) for a particle in a 1-D box being excited from n=3 to n=8. You do not need to solve the integral.

B. Using the selection rule, not calculus, determine if the transition in Exercise A allowed or forbidden. Would a transition from v=1 to v=8 be allowed for a harmonic oscillator?

C. Examine Table 1 at http://www2.chem.uic.edu/sneep/chem343/manuals/FTIR.pdf showing the vibrational modes of acetylene. Determine whether the following transitions are allowed or forbidden, treating these modes as harmonic oscillators
   i) symmetric C-H stretch in acetylene (v=0 to v=1)
   ii) asymmetric C-H stretch in acetylene (v=1 to v=2)
   iii) asymmetric C-H stretch in acetylene (v=0 to v=2)
   iv) asymmetric C-H stretch in acetylene (v=1 to v=0)
   v) C_2^- (v=0 to v=1)
   vi) C-H stretch in CH_3CH_2Cl (v=0 to v=1)

D. How many rotations and vibrational modes do each of the following molecules possess?
   i. O=C=S   **ii.** acetylene
   iii. ethylene (C_2H_4)   **iv.**   pentane (C_5H_{12})

E. A particle in a 1-D box transitions from state n to state n+1. Use algebra to show that the energy difference, ΔE, equal $h^2(2n+1)/8mL^2$

F.   Over the temperature range 223-400 K, the rate constant for the elementary reaction OH + CH_4 might be expressed as:

$$4.7 \times 10^{-13} \, e^{-1270/T} \, cm^3 \, molecule^{-1} \, sec^{-1}.$$

The tunneling correction, $\kappa = k_{obs}/k_{classical}$, is given by the table at right. Use Excel to plot lnk vs 1/T for both the observed rate constant (with tunneling, k_{obs}) and the hypothetical classical rate constant (without tunneling, $k_{classical}$) for 223 K $\leq$ T $\leq$ 400 K.

T (K)	κ
223	71.0
273	14.8
325	6.09
400	3.11

G.   Use the Wigner formula to compute the tunneling correction for the following set of conditions:
         a) $v^* = 500i \, cm^{-1}$, and T=200, 300, and 500 K
         b) $v^* = 1000i \, cm^{-1}$, and T=200, 300, and 500 K
Note: 1 $cm^{-1} = 1.9864 \times 10^{-23}$ Joules

H.   Which is bigger, D_e or D_0?

I.   The vibrational frequencies of acetylene are 612, 612, 730, 730, 1974, 3290, and 3374 cm^{-1}. What is the total zero-point energy of acetylene?

J. H_2 has a measured bond dissociation energy, D_0, of 435.99 kJ/mole. The vibrational frequency <u>corresponds to</u> (does not equal) 4341 cm^{-1}.

   a What is the value of D_e for H_2?   MW(H)= 1.007 g/mole

   b What is the value of D_0 for D_2?   MW(D)= 2.014 g/mole

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, **8th Edition**, by Peter Atkins and Julio De Paula. Numerical answers for the (b) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.   13.22-23

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, **9th Edition**, by Peter Atkins and Julio De Paula. Numerical answers for the (a) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.   12.23-24

PROBLEMS

1.a For parts A, B, and C of (the corrected version of) Question #3 on Homework #3, calculate the energy difference, ΔE, between the quantum number, n, of the particle and the state above it (n+1).

   Use the formula from Exercise E of **this** Homework.

1.b Consider the ratio $\Delta E/E_n$. Are the energy levels very close together compared to their values (nearly continuous and close to classical behavior) or relatively far apart (typical of quantum mechanical behavior)?

1.c Are these ratios reasonable in light of the dimensions of the box?

1.d What is the wavelength of the photon that would be needed to excite each system (parts A, B, and C of the corrected version of Question #3 on Homework #3) from n to n+1? What region of the spectrum are they in (infrared, visible, etc.)?

2.   For the SrH molecule treated as a harmonic oscillator :

$$\psi(v=0) = 1.83 \times 10^5 \text{ meters}^{-1/2} e^{-x^2/2\alpha^2}, \text{ where } \alpha = 1.68 \times 10^{-11} \text{ meters}$$
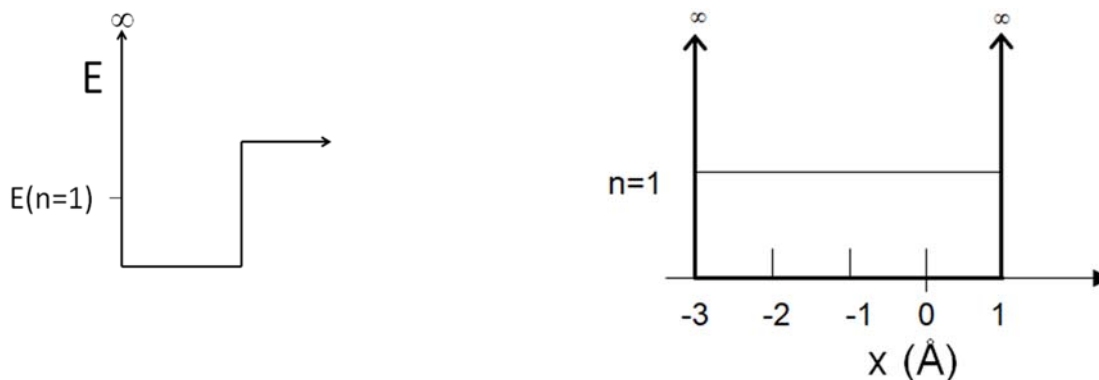
$$d\mu/dx = 5.0 \times 10^{-31} \text{ Coulombs}$$

Calculate the transition dipole moment for a transition from v=1 to v=0, given:

$$N_v = \left(\frac{1}{\alpha \pi^{1/2} 2^v v!}\right)^{1/2} \qquad \int_{-\infty}^{\infty} x^2 e^{-a^2 x^2} = \frac{\sqrt{\pi}}{2a^3}$$

NOTE: In this question Greek letter α (alpha) is highlighted, but a's are not.

3.a   Copy the figures below into your homework. Add to your copies of the figures a sketch of
the wavefunction of the n=1 state.

4.   A hydrogen transfer reaction with μ <u>corresponding to</u> (not equal to!) 1 g/mole. The
corresponding deuterium transfer reaction has with μ <u>corresponding to</u> 2 g/mole.

(By "corresponding to 1 g/mole", I am saying you need to change this value to the correct units
for μ).

For hydrogen transfer, ν^* corresponds to $1200i$ cm^{-1}.

4.a.   What is the value of ν^* for deuterium transfer?

4.b   Using Wigner tunneling to compute the tunneling correction, $\kappa(200)$, for deuterium transfer
at 200 K.

5. Consider the data in Exercise I

a. What is the energy difference between the states $(1, 0, 2, 0, 0, 0, 0)$ and $(0, 1, 0, 0, 2, 0, 1)$?

b. Compute D_e for the HCC-H bond, considering the data in Exercise I, and
   - D_0 for the HCC-H bond is 551.07 kJ/mole
   - the vibrational frequencies of HCC are 372, 372, 1841, and 3299 cm^{-1}