FCH 361 **Homework #4** **Spring 2020**

EXERCISES

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, 8^{th} **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.

9.1 9.5 9.7
9.8 -10
9.15 Also, what is the vibrational frequency, ν, of Cl_2, and the energy separation of adjacent energy levels?

Problem 9.2

Answer to 9.15 $\nu = 1.7 \times 10^{13}$ sec^{-1} and $\Delta E = 1.12 \times 10^{-20}$ Joules

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The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, 9^{th} **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.

8.1 8.6 -7
8.9-11
8.17 Also, what is the vibrational frequency, ν, of N_2, and the energy separation of adjacent energy levels?

Problem 8.2

Answer to 8.17 $\nu = 7.1 \times 10^{13}$ sec^{-1} and $\Delta E = 4.68 \times 10^{-20}$ Joules

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A. Consider a 2-D box with $L_1=\sqrt{3}\ L_2$. Verify that the (8,3) and (4,5) states are degenerate.

B. For an electron in a 3-D box with L_1, L_2, L_3 = 3.0, 1.0, and 5.0 Angstroms, compute the energy of the state n_1, n_2, n_3 = 3, 5, 1 and the state n_1, n_2, n_3 = 1, 3, 5. Why is the energy of the first state larger than the energy of the second state?

C. Compute the reduced mass, μ, of the molecules O_2 and HBr in kg/molecule.
For a molecule, A-A (like O_2), how does μ relate to the mass of an individual atom (m_A)?
For a diatomic molecule, A-B, where $m_B \gg m_A$ (like HBr), how does μ relate to m_A?

D. Given a harmonic oscillator with:
i) $k = 300$ kg/sec^2 and $\mu = 5.0 \times 10^{-26}$ kg, what is ν?
ii) $\mu = 1.0 \times 10^{-26}$ kg and $\nu = 5.0 \times 10^{13}$ sec^{-1}, what is k?

E. For light with $\tilde{\nu} = 1000$ cm^{-1}, what is the frequency and wavelength of a photon?

F. What are the energies of the v=0, v=1, and v=2 states of a harmonic oscillator with $\nu = 2.0 \times 10^{14}$ sec^{-1} ? What is the energy gap between v=0 and v=1? Between v=1 and v=2? What is the frequency of the photon absorbed when the harmonic oscillator is excited from v=0 to v=1?

G. H_2 and D_2 have the same force constant, as isotopologues must. If H_2 (as a harmonic oscillator) has $\nu = 1.31944 \times 10^{14}$ sec^{-1}, ($\tilde{\nu} = 4401.21$ cm^{-1}) what is ν for D_2? For this question only, use https://physics.nist.gov/cgi-bin/Compositions/stand_alone.pl for the exact isotopic masses and pay attention to significant figures.

H. Write the integral corresponding to the quantities below and simplify as much as possible. Also, for the ones marked with a *, determine the value of the quantity using logic (not calculus). For harmonic oscillators, look up the expression for the Hermite polynomial but write the normalization constant as N_v.

H.i* The probability of finding a particle on the left-hand side of the n=5 state of a 1-D box.

H.ii* The probability of finding a particle at $x \leq 0$ for the v=1 state of a harmonic oscillator.

H.iii The expectation value of x^2 for a particle in the n=2 state of a 1-D box of length L.

H.iv.* The expectation value of p_x for a particle in the n=3 state of a 1-D box of length L. Evaluate the derivative inside the integral!

H.vi.* The expectation value of x for the v=0 state of a harmonic oscillator.

I. Use the formula search (https://webbook.nist.gov/chemistry/form-ser/) on the NIST Chemistry WebBook to look up $\tilde{\nu}$ of the **ground** (X) state of O_2, O_2^+, and O_2^-.

See the video on Blackboard for how to find this information on that site.

NOTE: this website uses ω_e for $\tilde{\nu}$, which is what I am asking for.

J. Use calculus to determine the probability of finding a particle between 0 and L/2 in the n=3 state of a 1-D box. Recall $\int \sin^2(ax)dx = \frac{x}{2} - \frac{1}{4a}\sin(2ax)$

PROBLEMS

1. Consider an electron in the n = 3 state of a 1-D box with length $L = 1.0 \times 10^{-9}$ meters

a) Use logic to determine the values of $\langle x \rangle$ and $\langle p_x \rangle$. EXPLAIN!

b) Use the relationship between kinetic energy and momentum to calculate $\langle p_x^2 \rangle$.

c) Using the values of $\langle p_x \rangle$ and $\langle p_x^2 \rangle$, compute Δp_x.

d) Use the Heisenberg Uncertainty Principle to compute the minimum value of $\langle x^2 \rangle$.

2. State <u>as specifically as possible</u> the <u>identity</u> of the quantities being calculated in (a) - (d) and EXPLAIN your logic. (Is this an expectation value or a probability? For a 1-D box or harmonic oscillator? For what state?)

a) $$-\left(\frac{2}{L}\right)\left(\frac{h}{2\pi i}\right)^2\left(\frac{5\pi}{L}\right)^2\int_{x=0}^{L}\sin^2\left(\frac{5\pi x}{L}\right)dx$$

b) $$\left(\frac{2}{L}\right)\int_{x=0}^{L}x\sin^2\left(\frac{4\pi x}{L}\right)dx$$

c) $$\int_0^{\infty}\left(N_0 e^{-x^2/2\alpha^2}\right)^2 dx$$

d) $$\int_{-\infty}^{\infty}N_1\frac{2x}{\alpha}e^{-x^2/2\alpha^2}\,x\,N_1\frac{2x}{\alpha}e^{-x^2/2\alpha^2}dx$$

e) Use logic and/or a sketch to determine the value of the integral in (b).

3. For the 2-D box in Exercise A, find one other pair of states (other than (8,3) and (4,5)) that have the same energy as each other. Show your work (which might be mostly trial and error)! You can use a spreadsheet for this, but if you do, turn in a printout of all your calculations.

4. Consider the HF molecule with $\tilde{\nu} = 4138\ \text{cm}^{-1}$. Calculate:

a. the force constant of HF

b. the zero-point energy level of HF and DF.

c. When HF goes from v = 3 to v = 0, is a photon absorbed or emitted?

d. calculate the wavelength and frequency of the photon in part c.

5. Use calculus to determine the expectation value of x for the following wavefunction:
$\psi(x) = (2.236 \times 10^{25}\ \text{meters}^{5/2})x^2$ between 0 and 1.000×10^{-10} meters; $\psi(x)=0$ elsewhere.