

Name: _____

Chemistry 1410: Physical Chemistry I

Exam #2:

11:00-12:30 pm

- There are four questions worth a total of 250 points.
- Read all question first-answer the easiest first.
- Don't spend too much time on one question-if you get stuck move on.
- Justify any approximation you use.
- **Show all your work. No points will be given for answers without steps shown.**
- Good luck!

Cheat Sheet:

Fundamental Constants and factors:

Planck's constant	$h = 6.626 \times 10^{-34} \text{ Js}$
Boltzmann's constant	$k = 1.381 \times 10^{-23} \text{ JK}^{-1}$
Speed of light	$c = 2.998 \times 10^8 \text{ ms}^{-1}$
(Joule's to electron-volts)	$1\text{J} = 6.242 \times 10^{18} \text{ eV}$
Electronic charge	$e = -1.602177 \times 10^{-19} \text{ C}$
Mass of electron	$m_e = 9.1094 \times 10^{-31} \text{ kg}$
(amu to kg)	$1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$

Vibrational wavefunctions:

The wavefunctions are related to Hermite Polynomials, H_p .

$$\psi_p = A_p H_p e^{-\eta^2/2} \quad [1]$$

$$H_0 = 1; \quad H_1 = 2\eta; \quad [2]$$

Some wavefunctions are

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

Angular Momentum Operators

$$L_x = -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right)$$

$$L_y = -i\hbar \left(-\cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right)$$

$$L_z = -i\hbar \left(\frac{\partial}{\partial\phi} \right)$$

Grade:

Question 1 [50 points]

- (a) State Heisenberg's uncertainty principle. [10 points]
- (b) Consider two operators \hat{A} and \hat{B} . State the condition that allows you to determine whether the observables that correspond to \hat{A} and \hat{B} can be measured simultaneously to arbitrary precision. [10 points]
- (c) Describe and explain an experiment that demonstrates the x-component of magnetic moment (and therefore the x-component of angular momentum) and the z-component of magnetic moment (and therefore the z-component of angular momentum) cannot be measured simultaneously to arbitrary precision. [15 points]
- (e) The lifetime of an excited state of a molecule is τ . Write an equation that relates τ to the spread in the energy level. Draw a plot that illustrates the spread in the energy level. [15 points]

Question 2 [100 points]

(a) Consider the vibrational motion of a diatomic in a Harmonic Potential. Draw the Potential for this problem. On this plot draw the $n=2$ wavefunction (i.e. ψ_2) for the Harmonic Oscillator. Using dashed lines plot $\psi_2^* \psi_2$ on this diagram. Without any derivation -but clearly providing your reason – state what value you expect for $\langle x \rangle$. [20 points]

(b) Determine $\langle p_x \rangle$ for $n=2$ state of a quantum mechanical Harmonic Oscillator. You must show your work to get any credit. [20 points]

(c) The wavefunction of the quantum mechanical Harmonic oscillator are related to the Hermite polynomials, $H_n(\eta)$. Determine $H_4(\eta)$ and also $\psi_4(x)$ given that:

$$H_3 = 8\eta^3 - 12\eta \quad \text{and} \quad H_2 = 4\eta^2 - 2$$

Normalization of $\psi_4(x)$ is not required. [20 points]

(d) A rigid rotor exists in a state with a wavefunction of $\psi = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{-2i\phi}$. What is the value of the z-component of angular momentum? [20 points]

(e) An anharmonic diatomic exists in the $n=0$ vibrational and $l=2, m_l=2$ rotational state. Write an equation for the total energy of this state – include both vibrational and rotational terms. [20 points]

Question 3 [50 points]

(a) Both CO_2 and N_2 have zero dipole moments at equilibrium. However the asymmetric stretch in CO_2 is IR active while N_2 does not give an IR spectrum. Explain. [10 points]

(b) Explain why spontaneous emission does not exist in IR spectroscopy. [5 points]

(c) Radiation in the microwave region is used to monitor rotational levels in a rigid rotor. Comment on the existence of stimulated emission amongst rotational levels of the rigid rotor. [5 points]

(d) Consider the case of a quantum mechanical diatom which executes both vibrational and three-dimensional rotational motion. The potential for the vibrational motion is Harmonic. In this question you are asked to consider the case where the rotational fine structure is visible in the IR-spectra.

(i) Infra-red radiation is used to induce transitions between vibrational levels. Draw an energy level diagram. On this diagram indicate with solid lines the R-type transitions. Also indicate P-type transitions using dashed line. Draw and a spectrum and clearly label the P and R –type transitions. Make sure that relative features are clearly shown in you spectrum. [10 points]

(ii) Write down the selection rules for the P-type transitions [5 points]

(iii) Using the selection rules for P-type transitions and an equation that describes the energy of the relevant levels, derive an equation for the frequency of radiation required to create P-type transitions. [15 points]

Question 4 [50 points]

This problem examines the vibrational transition of an anharmonic oscillator – you can ignore the rotational fine structure. The fundamental IR transition for $^1\text{H}^{35}\text{Cl}$ occurs at 2886 cm^{-1} . The reduced mass for HCl is 1.627×10^{-27} . In class we considered HCl to be a Harmonic oscillator and we used this wavenumber to determine the force constant (478 Nm^{-1}). A more refined value may be calculated if we realize that HCl is an anharmonic oscillator. According to expectations overtone bands may also be generated and the first overtone occurs at 5668 cm^{-1} .

- (i) Write an equation for the energy of an anharmonic oscillator. The fundamental transition involves a $n=0 \rightarrow n=1$ transition while the first overtone involves a $n=0 \rightarrow n=2$ transition. Write two equations that relate the frequencies of the fundamental and first overtone transitions to the bond properties (i.e. D_e , ν_0). [10 points]
- (ii) With the two equations and the experimental values of the fundamental and overtone frequencies, determine ν_0 and from that an estimate of the force constant (k) of the bond. [20 points]
- (iii) With the two equations and the experimentally measured fundamental and overtone frequencies determine the D_e and the disassociation energy. [20 points]

