

Name: Jshara

**Chemistry 1410: Physical Chemistry I**  
**Exam #2:**

11:00 am -12:30 pm

- There are two questions worth a total of 250 points and a bonus question worth 50 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,  $H_p$ .

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

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

Recursion Relationship:  $H_{n+1} = 2\eta H_n - 2nH_{n-1}$

Some wavefunctions are

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

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

Angular Momentum Operators

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

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

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

The Hamiltonian for 3D rigid rotor is:

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2} \left( \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right)$$

Grade:

Question 1 [130 points]

(a) State the Heisenberg Uncertainty principle in words. [10 points]  
 If the position of a particle is measured to an accuracy of  $\Delta x$ , then the accuracy to which the x-component of momentum is measured ( $\Delta P_x$ ) must be greater than or equal to  $\frac{h}{2\Delta x}$ ; i.e.

$$\Delta x \Delta p_x \geq \frac{h}{2}$$

(10)

(c) For 1-D translational motion, determine whether the x-component of momentum and Kinetic Energy can be measured simultaneously. Use an arbitrary function,  $f(x)$ , to set up and solve the problem. [20 points]

$$\hat{T} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad \hat{P}_x = -i\hbar \frac{\partial}{\partial x}$$

$$[\hat{T}, \hat{P}_x] = \left( \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \left( -i\hbar \frac{\partial}{\partial x} \right) f(x) - \left[ -i\hbar \frac{\partial}{\partial x} \left( \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) f(x) \right]$$

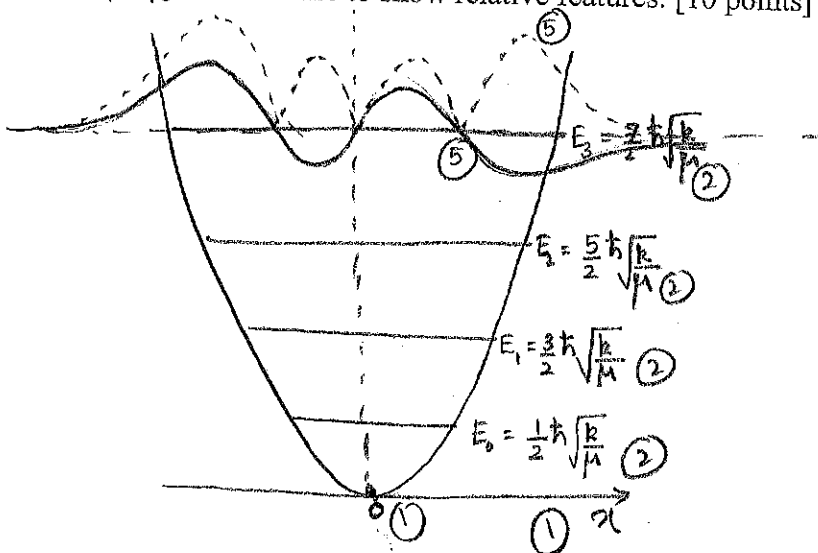
$$= \left[ +\frac{i\hbar^3}{2m} \frac{\partial^3}{\partial x^3} - \frac{i\hbar^3}{2m} \frac{\partial^3}{\partial x^3} \right] f(x) = 0$$

\(\therefore\) They can be measured simultaneously.

(c) Consider the vibrational motion of a diatomic in a simple Harmonic Potential

(i) Draw the Potential versus position plot. Clearly label the axes as well as the origin. On the plot draw the energies of the lowest four levels. Label the energy levels with equations that relate the energies to the fundamental properties such as the force constant and the reduced mass of the molecule. [10 points]

(ii) On the plot draw  $\psi_3$ . (ie the wavefunction for  $p=3$  state). Using dashed line plot  $\psi_3^* \psi_3$ . Make sure to show relative features. [10 points]



$$x = x_{eq} - \gamma$$

(iii) Without any derivations but clearly explaining your reasoning state the values of  $\langle x \rangle$  and  $\langle p_x \rangle$  in the  $p=3$  state. [20 points]

$$\langle x \rangle = 0 ; \int \psi_3^* \psi_3 \text{ is symmetric around } x=0, \text{ hence the average of } \psi_3^* \psi_3 \text{ is "0" } (10)$$

$$\langle P_x \rangle = 0 ; \int \psi_3^* \psi_3 \text{ is symmetric and measures positive and negative momentum values of same magnitude. } \therefore \text{Average is "0" } (10)$$

(iv) The force constant of  $^1\text{H}^{35}\text{Cl}$  is  $516 \text{ Nm}^{-1}$ . Determine the value of  $E_3$  (assume that the motion is simple Harmonic). [20 points]

$$E_3 = \frac{7}{2} \hbar \sqrt{\frac{k}{\mu}} (6) ; \mu = \frac{1 \times 35}{1+35} \times 1.661 \times 10^{-27} \text{ kg} (6)$$

$$= 1.615 \times 10^{-27} \text{ kg} (6)$$

$$E_3 = \frac{7}{2} \frac{h}{2\pi} \sqrt{\frac{516}{1.615 \times 10^{-27}}} (6)$$

$$= 2.09 \times 10^{-19} \text{ J} (2)$$

(d) Explain why spontaneous emission is very weak for vibrational spectroscopy. You should explain your answer by being as quantitative as possible. [20 points]

$$\frac{A_{mn}}{B_{mn}} = 6 \times 10^{-56} \nu_{mn}^3 \quad (5)$$

$$\nu_{mn}^3 \text{ at maximum} \approx 10^{39}$$

$$\text{Thus, } \frac{A_{mn}}{B_{mn}} \text{ at maximum } \nu_{mn}^3 \text{ be } \sim 6 \times 10^{-56} \times 10^{39} \\ \sim 6 \times 10^{-19} \quad (5)$$

$A_{mn}$  is very small. (5)

$\therefore$  The rate of spontaneous emission  $\Rightarrow N_n A_{mn}$  is small (5)

(e) For which species will the  $p=1$  vibrational level have a greater population at thermal equilibrium: (a)  $^{35}\text{Cl}_2$ , (b)  $^{35}\text{Cl}^{37}\text{Cl}$ ; (c)  $^{37}\text{Cl}_2$ . No calculations are necessary but you must carefully explain your reasoning. [20 points]

$$N_1 = N_0 e^{-\Delta E/kT} \quad (3) \quad ; \quad \Delta E = (E_1 - E_0) = h \sqrt{\frac{k}{\mu}} \quad (2)$$

The larger the  $\mu$  is smaller the  $\Delta E$  is, the larger the  $N_1$  is. (5)

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (5)$$

$$\left. \begin{aligned} M_{^{37}\text{Cl}_2} &> M_{^{37}\text{Cl}^{35}\text{Cl}} > M_{^{35}\text{Cl}_2} \\ N_1(^{37}\text{Cl}_2) &> N_1(^{37}\text{Cl}^{35}\text{Cl}) > N_1(^{35}\text{Cl}_2) \end{aligned} \right\} (5)$$

## Question 2 [100 points]

(a) The moment of inertia of  $^1\text{H}^{35}\text{Cl}$  is  $2.644 \times 10^{-47} \text{ kg}\cdot\text{m}^2$ . An HCl molecule undergoing

3-D rigid rotation exists in a state which a wavefunction  $\psi = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$ .

(i) Substitute this wavefunction into the Schrodinger's Equation to derive an equation for the total energy. [30 points]

$$\Psi = A \cos\theta \quad ; \quad A = \left(\frac{3}{4\pi}\right)^{1/2}$$

$$= \frac{-\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} A \cos\theta + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} A \cos\theta \right] \quad (5)$$

$$= \frac{-\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta (-A \sin\theta) \right] \quad (5)$$

$$= + \frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} 2A \sin^2\theta \right] \quad (15)$$

$$= + \frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} 2A \sin\theta \cos\theta \right] \quad (5)$$

$$= \underbrace{\frac{\hbar^2}{2\mu r^2}}_E \underbrace{2A \cos\theta}_\Psi = \frac{2\hbar^2}{2\mu r^2} \Psi = E\Psi \quad (5)$$

$$\therefore E = \frac{2\hbar^2}{2\mu r^2} \quad (5)$$

(ii) By using the appropriate operator determine the value of the z-component of angular momentum. [30 points]

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \phi} \quad (10)$$

$$\hat{l}_z \psi = -i\hbar \frac{\partial}{\partial \phi} A \cos \theta = 0 \quad (10)$$

$$\hat{l}_z = 0 \quad (10)$$

(iii) Based on your answer to parts (i) and (ii) determine the values of the l and m<sub>l</sub> quantum numbers. [20 points]

$$l_z = m_l \hbar = 0 \quad ; \quad \therefore m_l = 0 \quad (5)$$

$$E = \frac{l(l+1)\hbar^2}{2\mu r^2} = \frac{2\hbar^2}{2\mu r^2} \quad (3)$$

$$l(l+1) = 2 \quad (3)$$

$$l = 1 \quad (2)$$

$$l = 1, m_l = 0$$

(iv) Based on your answer to part (iii) write down the value of total angular momentum? [20 points]

$$\text{Total angular momentum} = \sqrt{l(l+1)} \hbar \quad (10)$$

$$= \sqrt{2} \hbar \quad (10)$$

(v) What is the x-component of angular momentum in this state? [20 points]

$\psi$  is not an eigenfunction of  $\hat{l}_x$ .  $\therefore$  No information about the x-component of angular momentum is obtained. (10)

### Bonus Question [50 points]

(a) Consider the case of selection rules in IR spectroscopy. We saw that at the core selection rules depend on the nature of the potential and on the way the dipole moment changes with vibrational mode. Assume that the variation of the molecular electric dipole moment with  $q$  is given by:

$$\mu = \mu_0 + \kappa_1 \eta + \kappa_2 \eta^2$$

where  $\mu_0$ ,  $\kappa_1$  and  $\kappa_2$  are constants. Determine the IR selection rules for this vibrational mode.

$$\begin{aligned}
 I &= \int \Psi_n^* \hat{\mu} \Psi_m \, d\eta \\
 &= \int \Psi_n^* (\mu_0 + \kappa_1 \eta + \kappa_2 \eta^2) \Psi_m \, d\eta \quad (5) \\
 &= \mu_0 \int \Psi_n^* \Psi_m \, d\eta + \kappa_1 \int \Psi_n^* \eta \Psi_m \, d\eta + \kappa_2 \int \Psi_n^* \eta^2 \Psi_m \, d\eta \quad (5) \\
 &= \kappa_1 A_n A_m \int H_n \eta H_m e^{-\eta^2} \, d\eta + \kappa_2 A_n A_m \int (\eta H_n)(\eta H_m) e^{-\eta^2} \, d\eta \quad (5) \\
 &= \kappa_1 A_n A_m \left[ \underbrace{\frac{1}{2} \int H_n H_{m+1} e^{-\eta^2} \, d\eta}_{\text{non zero when } n=m+1} + m \underbrace{\int H_n H_{m-1} e^{-\eta^2} \, d\eta}_{\text{non zero when } n=m-1} \right] \rightarrow \left\{ \begin{array}{l} n-m = \pm 1 \end{array} \right. \\
 &\quad + \kappa_2 A_n A_m \left[ \int \left\{ \frac{1}{2} (H_{n+1}) + n H_{n-1} \right\} \left\{ \frac{1}{2} (H_{m+1}) + m H_{m-1} \right\} e^{-\eta^2} \, d\eta \right] \\
 &= \kappa_1 A_n A_m \left[ \frac{1}{2} \int H_n H_{m+1} e^{-\eta^2} \, d\eta + m \int H_n H_{m-1} e^{-\eta^2} \, d\eta \right] \left\{ \begin{array}{l} n-m = \pm 1 \end{array} \right. \\
 &\quad + \kappa_2 A_n A_m \left[ \frac{1}{4} \int H_{n+1} H_{m+1} e^{-\eta^2} \, d\eta + \frac{1}{2} m \int H_{n+1} H_{m-1} e^{-\eta^2} \, d\eta + \frac{1}{2} n \int H_{n-1} H_{m+1} e^{-\eta^2} \, d\eta + nm \int H_{n-1} H_{m-1} e^{-\eta^2} \, d\eta \right] \\
 &\quad \begin{array}{ll} \text{non zero,} & \text{non zero} \\ n+1 = m+1 & n+1 = m-1 \\ n-m = 0 & n-m = -2 \end{array} \quad \begin{array}{ll} \text{non zero} & \text{non zero} \\ n-1 = m+1 & n-1 = m-1 \\ n-m = +2 & n-m = 0 \end{array} \\
 \therefore \Delta P = n-m = 0, \pm 1, \pm 2 \quad (5)
 \end{aligned}$$