

## Grade:

### Question 1 [80 points]

- (a) State the Heisenberg Uncertainty principle. [10 points]

IF YOU measure  $P_x$  to an accuracy  $\Delta P_x$ , and position,  $x$ , to an accuracy of  $\Delta x$  then

$$\Delta x \Delta P_x \geq \frac{\hbar}{2}$$

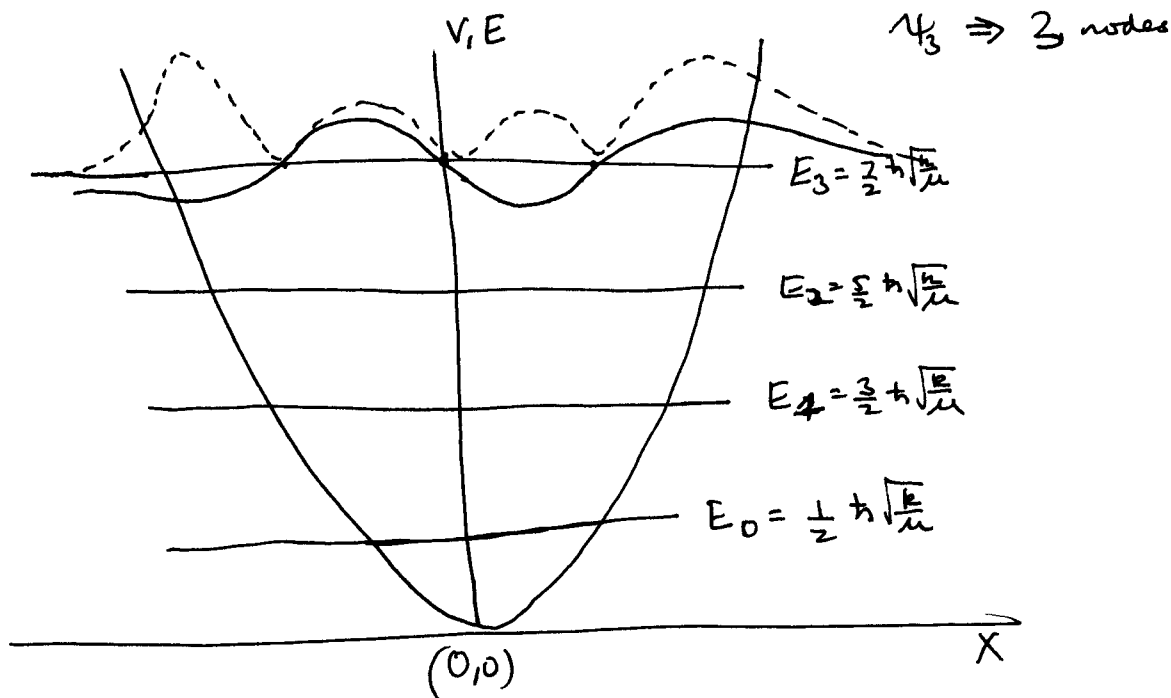
- (b) In class we saw that for three-dimensional rotation the z-component of angular momentum as well as the energy can be measured from the wavefunction. Without any derivations state the value of the commutator  $[\hat{l}_z, \hat{H}]$ ? [10 points]

$$[\hat{l}_z, \hat{H}] = 0$$

- (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 ~~first~~<sup>four</sup> three levels. Label the energy levels with equations that relate the energies to the fundamental properties such as the force constant 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  $\psi_3^* \psi_3$ . [10 points]



(iii) Without any derivations but clearly explaining your reasoning state the values of  $\langle x \rangle$  and  $\langle p_x \rangle$  in the  $n=3$  state.. [10 points]

$\langle x \rangle = 0$  ;  $\psi_3^* \psi_3$  is symmetric around  $x=0$ ;  
The average from the figure is 0.

$\langle p_x \rangle = 0$  ; With equal probability, you will measure either a positive  $p_x$  or the same magnitude of  $p_x$  but opposite sign. Thus  $\langle p_x \rangle = 0$

(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]

$$E_3 = \frac{7}{4} \cdot \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{1.35}{1+35} \times 1.661 \times 10^{-27} \text{ kg} = 1.615 \times 10^{-27} \text{ kg}$$

$$= 1.77 \times 10^{-19} \text{ J}$$

$$E_3 = \frac{6.626 \times 10^{-34} \text{ Js}}{2\pi} \sqrt{\frac{516}{1.615 \times 10^{-27}}}$$

$$= 1.043 \times 10^{-19} \text{ J}$$

Question 2 [100 points] 100

(a) The moment of inertia of  $^1\text{H}^{35}\text{Cl}$  is  $2.644 \times 10^{-47} \text{ kg.m}^2$ . An HCl molecule undergoing 3-D rigid rotation exists in a state which a wavefunction  $\psi = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$ .

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

$$\begin{aligned}
 & -\frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial \sin\theta}{\partial \theta} \frac{\partial \psi}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} e^{i\phi} \psi \right] \\
 &= -\frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial \sin\theta}{\partial \theta} \left(\frac{3}{8\pi}\right)^{1/2} \omega \theta e^{i\phi} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} \right] \\
 &= -\frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} (\omega^2\theta - \sin^2\theta) \left(\frac{3}{8\pi}\right)^{1/2} e^{i\phi} + \frac{1}{\sin^2\theta} (-1) \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} \right] \\
 &= -\frac{\hbar^2}{2\mu r^2 \sin^2\theta} \left[ \sin\theta (1 - 2\sin^2\theta) - \sin\theta \right] \left(\frac{3}{8\pi}\right)^{1/2} e^{i\phi} \\
 &= -\frac{\hbar^2}{2\mu r^2 \sin^2\theta} [-2\sin^3\theta] \left(\frac{3}{8\pi}\right)^{1/2} e^{i\phi} \\
 &= \frac{2\hbar^2}{2\mu r^2} \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} = \frac{2\hbar^2}{2\mu r^2} \psi
 \end{aligned}$$

Thus  $E = \frac{2\hbar^2}{2\mu r^2}$

(ii) By using the appropriate operator determine the value of the z-component of angular momentum. [20 points]

$$\begin{aligned}
 \hat{l}_z &= -i\hbar \frac{\partial}{\partial \phi} \\
 \hat{l}_z \psi &= -i\hbar \frac{\partial}{\partial \phi} \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} = -i\hbar \left(\frac{3}{8\pi}\right)^{1/2} (i) \sin\theta e^{i\phi} \\
 &= \hbar \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} = \hbar \psi
 \end{aligned}$$

Value of  $l_z = \hbar$

(iii) Based on your answer to parts (i) and (ii) determine the values of the  $l$  and  $m_l$  quantum numbers. [10 points]

$$E_l = \frac{l(l+1)\hbar^2}{2\mu r^2} = \frac{2\hbar^2}{2\mu r^2} \Rightarrow l(l+1) = 2 \quad \text{or} \quad \boxed{l=1}$$

$$\text{Value of } l_z \text{ is } m_l \hbar \Rightarrow m_l = 1$$

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

$$\hat{l}^2 \psi = l(l+1)\hbar^2 \psi$$

$$\text{Value of } l^2 \text{ is } l(l+1)\hbar^2 = 2\hbar^2$$

$$\text{Value of total angular momentum is } \sqrt{l(l+1)} \hbar = \sqrt{2} \hbar$$

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

$\psi$  is not an eigenfunction of  $\hat{l}_x$ . There is no information on  $l_x$ .

70  
Question 3 [70 points]

(a) Explain why spontaneous emission is very weak for vibrational spectroscopy. [10 points]

$\text{Rate} = N_n A_{nm}$   
 $\& A_{nm} = 6 \times 10^{-58} \times \nu_0^3 \times B_{nm}$   
 $(\nu_0^3)_{\text{max in IR}} \sim 10^{40}$   
 $\text{Thus } A_{nm} \sim 10^{-18} B_{nm} \quad [B_{nm} \text{ in } \text{O}(\text{C}1)]$   
 $\text{Thus Rate is very small.}$

(b) 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]

$\frac{N_1}{N_0} = e^{-(E_1 - E_0)/kT} \Rightarrow \text{smaller } E_1 - E_0 \text{ the larger } N_1 \text{ is.}$

$E_1 - E_0 = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$

Molecules with largest  $\mu$  has smallest  $E_1 - E_0$   
 $\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$

large  $\mu \Rightarrow$  smallest  $\frac{1}{\mu}$  which occurs when  $M_1 \& M_2$  are large.

Thus  $^{37}\text{Cl}_2$  has the largest  $\mu$ .  
 $\hookrightarrow$  hence the smallest  $(E_1 - E_0)$   
 $\hookrightarrow$  hence the largest  $N_1$

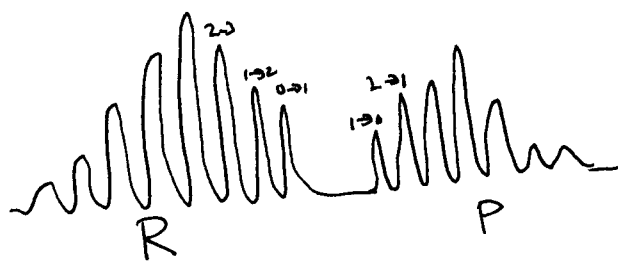
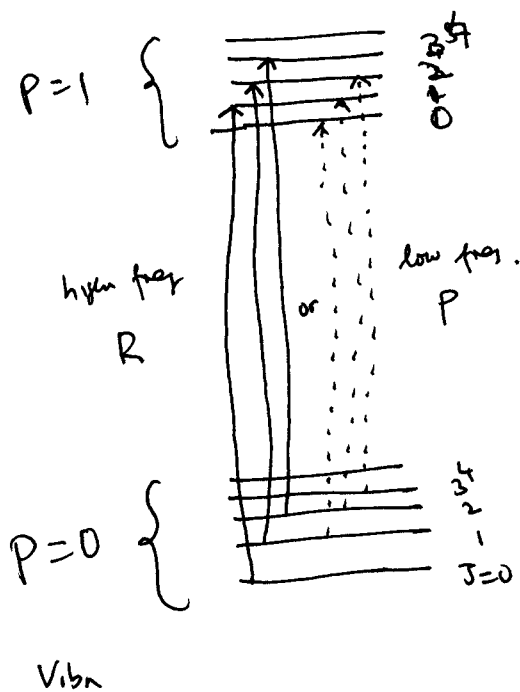
(c) Consider the case of a diatom executing vibrational and 3D-rotations. Infra-red radiation is used to induce transitions between vibrational levels. You are asked to consider the case where the rotational fine-structure is visible.

(i) Draw an energy level diagram. On the diagram clearly show the possible transitions. Draw a sample spectrum you might obtain at a low temperature – make sure to show relative features. [10 points]

(ii) If you wish to study the P-branch would you increase or decrease the temperature in order to ~~increase the intensity~~. Explain your answer. [10 points]

measure a large # of transitions

$$\Delta J = \pm 1, \Delta P = \pm 1, \Delta M = 0$$



ii)

As you increase temp you populate higher J state [  $T \rightarrow \infty$  all pop are equal ]  
 The intensity of P branch will increase & the # transitions also increases as more and more Rotn levels become populated.

(b) The value of B for  $^1\text{H}^{35}\text{Cl}$  is  $10.5909 \text{ cm}^{-1}$ . Determine the H-Cl bond length. [20 points]

$$B = \frac{h}{8\pi^2 \mu c r^2}$$

$$\begin{aligned} \Rightarrow r &= \sqrt{\frac{h}{8\pi^2 \mu B c}} \\ &= \sqrt{\frac{6.626 \times 10^{-34}}{8\pi^2 \cdot \frac{1 \times 35}{1+35} \cdot 1.661 \times 10^{-27} \cdot 10.5909 \cdot 3 \times 10^{10}}} \\ &= 1.224 \times 10^{-10} \text{ m} \end{aligned}$$