

**CHEM 325**  
**Spring 2009**  
**Take-Home Portion of Exam 1**

Name: \_\_\_\_\_

**Instructions**

Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't assess it and I will assume that you don't know it and will grade your work accordingly.

Show all work for full credit! Use complete sentences. Indicate what you are doing at important steps (you do not need to tell me about every mathematical manipulation you do). If you change your mind on a question, cross out the incorrect answer and clearly indicate your final answer. Better yet, write out your answers on scratch paper first and then transfer your final answers to this booklet.

There are **12** pages, **0** blank.

You may use your book to look up any needed physical constants, equations, etc. However, you may not work with anyone else, and you may not ask any other faculty members to help you with the specific questions given here. You may ask any chemistry faculty member for help on the concepts involved, and you may ask me anything you want.

You may use the back of any page as additional workspace. Please indicate that you have done so. You may also use extra pages, but please insert them near the relevant problem.

Problem	Possible Points	Points Received
1	16	
2	27	
3	25	
4	27	
Free	5	5
Total	100	
	Bonus	
	Grand Total	

1a. (7 Points) Derive a general equation, in terms of the quantum number,  $n$ , that describes the probability of finding a quantum mechanical particle in the middle third of a one-dimensional box

**The probability of finding a quantum mechanical particle is given by  $|\psi^* \psi|$  integrated over the region of interest. For a particle in the middle third of a box this becomes**

$$|\psi^* \psi| = \int_{L/3}^{2L/3} \left( -i \sqrt{\frac{2}{L}} \right) \sin\left(\frac{n\pi x}{L}\right) \left( i \sqrt{\frac{2}{L}} \right) \sin\left(\frac{n\pi x}{L}\right) dx$$

$$|\psi^* \psi| = \frac{2}{L} \int_{L/3}^{2L/3} \sin^2\left(\frac{n\pi x}{L}\right) dx = \left(\frac{2}{L}\right) \left[ \left( \frac{x}{2} - \frac{L}{8n\pi} \sin\left(\frac{2n\pi x}{L}\right) \right) \right]_{L/3}^{2L/3}$$

$$|\psi^* \psi| = \left(\frac{2}{L}\right) \left[ \frac{L}{3} - \frac{L}{8n\pi} \sin\left(\frac{4n\pi}{3}\right) - \frac{L}{6} + \frac{L}{8n\pi} \sin\left(\frac{2n\pi}{3}\right) \right]$$

$$|\psi^* \psi| = \left(\frac{2}{L}\right) \left[ \frac{L}{6} - \frac{L}{8n\pi} \left( \sin\left(\frac{4n\pi}{3}\right) - \sin\left(\frac{2n\pi}{3}\right) \right) \right] = \frac{1}{3} - \frac{1}{2n\pi} \left( \sin\left(\frac{4n\pi}{3}\right) - \sin\left(\frac{2n\pi}{3}\right) \right)$$

b. (4 Points) The classical probability of finding a particle in the region  $x$  to  $x + dx$  in a one-dimensional box of length  $L$  is  $dx/L$ . Derive the classical probability of finding the particle in the middle third of a one-dimensional box.

**For a classical particle the probability of finding it in the middle third of the box is**

$$p = \int_{L/3}^{2L/3} \frac{1}{L} dx = \frac{1}{L} \int_{L/3}^{2L/3} dx = \frac{1}{L} (x)_{L/3}^{2L/3} = \frac{1}{L} \left( \frac{2L}{3} - \frac{L}{3} \right) = \frac{1}{3}$$

c. (5 Points) Show that, as  $n \rightarrow \infty$ , the quantum mechanical answer becomes the same as the classical result.

**The sine portion of the expression  $|\psi^* \psi| = \frac{1}{3} - \frac{1}{2n\pi} \left( \sin\left(\frac{4n\pi}{3}\right) - \sin\left(\frac{2n\pi}{3}\right) \right)$  will become rapidly oscillating as  $n \rightarrow \infty$ , but this entire term will vanish because of the  $1/n$  which will go to 0 as  $n$  approaches  $\infty$ . Thus, this expression will simplify to  $1/3$  in the limit of large  $n$ , which is the classical result, as required by the Correspondence Principle.**

2a. (8 Points) Calculate  $\langle x \rangle$  and  $\langle x^2 \rangle$  for a quantum mechanical particle in a box.

**First determine  $\langle x \rangle$ .**

$$\langle x \rangle = \langle \psi | \hat{x} | \psi \rangle = \int_0^L \left( \frac{2}{L} \right) x \sin^2 \left( \frac{n\pi x}{L} \right) dx = \left( \frac{2}{L} \right) \left[ \left( \frac{x^2}{4} - \frac{x \sin\left(\frac{2n\pi x}{L}\right)}{\left(\frac{4n\pi}{L}\right)} - \frac{\cos\left(\frac{2n\pi x}{L}\right)}{8\left(\frac{n\pi}{L}\right)^2} \right) \right]_0^L$$

$$\langle x \rangle = \left( \frac{2}{L} \right) \left[ \frac{L^2}{4} - \frac{L \sin(2n\pi)}{\left(\frac{4n\pi}{L}\right)} - \frac{\cos(2n\pi)}{8\left(\frac{n\pi}{L}\right)^2} + \frac{\cos(0)}{8\left(\frac{n\pi}{L}\right)^2} \right] = \left( \frac{2}{L} \right) \left[ \frac{L^2}{4} \right] = \frac{L}{2}$$

**Now determine  $\langle x^2 \rangle$ .**

$$\langle x^2 \rangle = \langle \psi | \hat{x}^2 | \psi \rangle = \int_0^L \left( \frac{2}{L} \right) x^2 \sin^2 \left( \frac{n\pi x}{L} \right) dx$$

$$\langle x^2 \rangle = \left( \frac{2}{L} \right) \left[ \left( \frac{x^3}{6} - \left( \frac{x^2}{\left(\frac{4n\pi}{L}\right)} - \frac{1}{8\left(\frac{n\pi}{L}\right)^3} \right) \sin\left(\frac{2n\pi x}{L}\right) - \frac{x \cos\left(\frac{2n\pi x}{L}\right)}{4\left(\frac{n\pi}{L}\right)^2} \right) \right]_0^L$$

$$\langle x^2 \rangle = \left( \frac{2}{L} \right) \left[ \left( \frac{L^3}{6} - \frac{L}{4\left(\frac{n\pi}{L}\right)^2} \right) \right] = \left( \frac{2}{L} \right) \left[ \left( \frac{L^3}{6} - \frac{L^3}{4n^2\pi^2} \right) \right] = \left( \frac{L}{2n\pi} \right)^2 \left( \frac{4n^2\pi^2}{3} - 2 \right)$$

b. (8 Points) Calculate  $\langle p \rangle$  and  $\langle p^2 \rangle$  for a particle in a box.

**Determine  $\langle p \rangle$ .**

$$\langle p \rangle = \int_0^L -i \left( \sqrt{\frac{2}{L}} \right) \sin\left(\frac{n\pi x}{L}\right) \left( -i\hbar \frac{\partial}{\partial x} \right) i \left( \sqrt{\frac{2}{L}} \right) \sin\left(\frac{n\pi x}{L}\right) dx$$

$$\langle p \rangle = -\frac{2i\hbar}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \left( \frac{\partial \sin\left(\frac{n\pi x}{L}\right)}{\partial x} \right) dx = \left( -\frac{2i\hbar}{L} \right) \left( \frac{n\pi}{L} \right) \int_0^L \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx$$

$$\langle p \rangle = \left( -\frac{2n\pi i\hbar}{L^2} \right) \left( \frac{L}{2n\pi} \right) \left[ \left( \sin^2\left(\frac{n\pi x}{L}\right) \right) \Big|_0^L \right] = \left( -\frac{i\hbar}{L} \right) (\sin^2(n\pi)) = 0$$

**Since  $\sin(n\pi) = 0$  for all integer values of  $n$ , and  $n$  can only have integer values, this whole expression must equal 0.**

**Now determine  $\langle p^2 \rangle$ . The square of an operator is equivalent to performing the**

**operation twice, in this case  $\hat{p}^2 = i\hbar \frac{\partial}{\partial x} \left( i\hbar \frac{\partial}{\partial x} \right) = i^2 \hbar^2 \frac{\partial^2}{\partial x^2} = -\hbar^2 \frac{\partial^2}{\partial x^2}$ .**

$$\langle p^2 \rangle = \int_0^L -i \left( \sqrt{\frac{2}{L}} \right) \sin\left(\frac{n\pi x}{L}\right) \left( -\hbar^2 \frac{\partial^2}{\partial x^2} \right) \left( \sqrt{\frac{2}{L}} i \right) \sin\left(\frac{n\pi x}{L}\right) dx$$

**And since  $\frac{d^2 \sin(f)}{dx^2} = f' \frac{d \cos(f)}{dx} = -f'^2 \sin(f)$ , we can write**

$$\langle p^2 \rangle = \left( \frac{2\hbar^2}{L} \right) \int_0^L -\sin\left(\frac{n\pi x}{L}\right) \left( \frac{\partial^2 \sin\left(\frac{n\pi x}{L}\right)}{\partial x^2} \right) dx = \left( \frac{2\hbar^2}{L} \right) \left( \frac{n\pi}{L} \right)^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$\langle p^2 \rangle = \left( \frac{2n^2 \pi^2 \hbar^2}{L^3} \right) \left[ \left( x - \frac{L}{4n\pi} \sin\left(\frac{2n\pi x}{L}\right) \right) \Big|_0^L \right] = \left( \frac{2n^2 \pi^2 \hbar^2}{L^3} \right) \left[ \frac{L}{2} - \frac{L}{4n\pi} \sin(2n\pi) \right]$$

Once again we can use  $\sin(n\pi) = 0$  for all integer values of  $n$ , because  $n$  can only have integer values to give  $\langle p^2 \rangle = \frac{n^2 \pi^2 \hbar^2}{L^2}$ .

c. (8 Points) Using the definition of the uncertainty in a measured quantum mechanical property (i. e.,  $\Delta q = \left( \langle q^2 \rangle - \langle q \rangle^2 \right)^{1/2}$ ), derive an equation for  $\Delta p \Delta x$  for a particle in a box. Demonstrate that the Heisenberg Uncertainty Principle holds.

**Determine the uncertainties for  $p$  and  $x$ .**

$$\Delta p = \left( \langle p^2 \rangle - \langle p \rangle^2 \right)^{1/2} = \left( \frac{n^2 \pi^2 \hbar^2}{L^2} - 0 \right)^{1/2} = \frac{n\pi\hbar}{L}$$

$$\Delta x = \left( \langle x^2 \rangle - \langle x \rangle^2 \right)^{1/2} = \left( \left( \frac{L}{2n\pi} \right)^2 \left( \frac{4n^2 \pi^2}{3} - 2 \right) - \frac{L^2}{4} \right)^{1/2}$$

$$\Delta x = \left( \left( \frac{L^2}{3} - \frac{L^2}{2n^2 \pi^2} \right) - \frac{L^2}{4} \right)^{1/2} = \left( \frac{4L^2}{12} - \frac{L^2}{2n^2 \pi^2} - \frac{3L^2}{12} \right)^{1/2} = \left( \frac{L^2}{12} - \frac{L^2}{2n^2 \pi^2} \right)^{1/2}$$

$$\Delta x = \left( \frac{L^2}{12} - \frac{L^2}{2n^2 \pi^2} \right)^{1/2} = \left( \frac{L}{2n\pi} \right) \left( \frac{n^2 \pi^2}{3} - 2 \right)^{1/2}$$

**Now for the product of the uncertainties.**

$$\Delta p \Delta x = \left( \frac{n\pi\hbar}{L} \right) \left( \frac{L}{2n\pi} \right) \left( \frac{n^2 \pi^2}{3} - 2 \right)^{1/2} = \left( \frac{\hbar}{2} \right) \left( \frac{n^2 \pi^2}{3} - 2 \right)^{1/2}$$

Since  $\left( \frac{n^2 \pi^2}{3} - 2 \right)^{1/2} > 1$ , the product  $\left( \frac{\hbar}{2} \right) \left( \frac{n^2 \pi^2}{3} - 2 \right)^{1/2}$  must be greater than  $\frac{\hbar}{2}$ , as required by the Heisenberg Uncertainty Principle.

d. (3 Points) Describe what happens to  $\Delta p$  and  $\Delta x$  as the box gets longer.

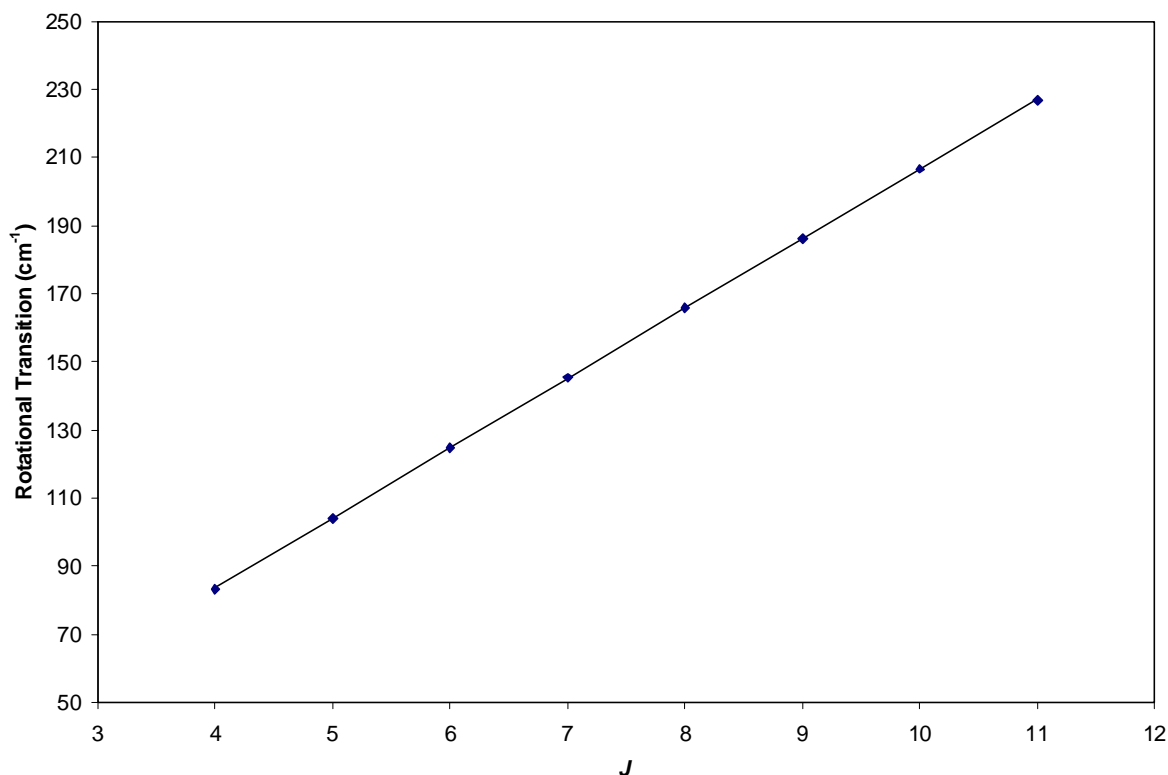
**As  $L$  gets bigger,  $\Delta x$  gets larger (the position becomes less well-defined) while  $\Delta p$  gets smaller (the momentum becomes more well-defined).**

3a. (8 Points) The peaks occurring in the far infrared portion of HCl's absorption spectrum arise from transitions between different rotational states of the molecule. The wavenumber at which each of these transitions occurs is listed below. From a best fit of these data, determine the value of  $B$  for HCl along with its uncertainty at 95% confidence. Prepare the appropriate graph of the data showing the best fit line through the data, and tape it in the space below. For this analysis ignore centrifugal distortion and note that the lowest transition does not start at  $J = 0$  (this means you need to determine what two  $J$  values are involved in each transition).

Wavenumber ( $\text{cm}^{-1}$ )	83.32	104.13	124.73	145.37	165.89	186.23	206.60	226.86
$J_{\text{initial}} \rightarrow J_{\text{final}}$	3 $\rightarrow$ 4	4 $\rightarrow$ 5	5 $\rightarrow$ 6	6 $\rightarrow$ 7	7 $\rightarrow$ 8	8 $\rightarrow$ 9	9 $\rightarrow$ 10	10 $\rightarrow$ 11

**In a pure rotation spectrum with no centrifugal distortion the peaks are separated by  $2B$ . The peaks here are separated by roughly  $21 \text{ cm}^{-1}$ , therefore  $2B$  must be about  $21 \text{ cm}^{-1}$  and there must be additional, unreported peaks at about  $62 \text{ cm}^{-1}$ ,  $41 \text{ cm}^{-1}$  and  $21 \text{ cm}^{-1}$ . The peak at about  $21 \text{ cm}^{-1}$ , as it is the lowest allowed rotational transition, must be the  $J = 0$  to  $J = 1$  transition. The remaining peaks can then be indexed as shown above.**

**The peak energies, in  $\text{cm}^{-1}$ , are given by the equation  $F(J) - F(J-1) = BJ$  (assuming that  $D_J = 0$ ). Thus a graph of wavenumber as a function of  $J$  (note that this is  $J$  for the final rotational state) gives a straight line with a slope of  $B$ , as shown below.**



**This gives  $2B$  equal to  $20.50 \pm 0.09 \text{ cm}^{-1}$  at 95% confidence (RMS error of the fit equals 0.2287). This means  $B$  equals  $10.25 \pm 0.04 \text{ cm}^{-1}$ , assuming that  $D_J$  is negligible.**

b. (3 Points) Based on your fit of the data, was our assumption that centrifugal distortion could be ignored a valid one? Explain.

**If  $D_J$  were not negligible, we would expect to see deviations from linearity. There are small deviations from linearity, thus  $D_J$  would be small, and our value of  $B$  should be relatively accurate. However, comparing our value to the accepted value of  $B$  (10.593  $\text{cm}^{-1}$  for  $^1\text{H}-^{35}\text{Cl}$ ) suggests that  $D_J$  is not negligible because the two values are not that close (although the presence of  $^1\text{H}-^{37}\text{Cl}$ , which we did not account for, would affect the measured value of  $B$  by shifting the peak that we've assumed is only due to  $^1\text{H}-^{35}\text{Cl}$  slightly from its true position).**

c. (6 Points) The instrument on which these data were obtained didn't have a sufficiently high resolution to distinguish between the different isotopomers of HCl arising from the different Cl isotopes (i. e.,  $\text{H}-^{35}\text{Cl}$  and  $\text{H}-^{37}\text{Cl}$ ), but it could distinguish between HCl and DCl. Calculate  $B$  for DCl and from it predict the wavenumber of the  $J=6$  to  $J=7$  transition for DCl.

**For a linear molecule  $I = \mu r^2$  and  $\mu = \frac{m_1 m_2}{m_1 + m_2}$ . Since the bond length should be**

**independent of isotopic substitution, we can use the H-Cl bond length (127.45 pm) for the D-Cl bond length. We were not able to distinguish between  $^1\text{H}-^{35}\text{Cl}$  and  $^1\text{H}-^{37}\text{Cl}$  in the original experiment, but we can just perform the calculation for the more abundant  $^{35}\text{Cl}$  isotope.**

**First calculate the reduced mass.**

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2.0140 \text{ amu})(34.96885 \text{ amu})}{2.0140 \text{ amu} + 34.96885 \text{ amu}} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)$$

$$\mu = \left( \frac{70.427_2}{36.9828_5} \text{ amu} \right) \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) = (1.9043_2 \text{ amu}) \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)$$

$$\mu = 3.1622_0 \times 10^{-27} \text{ kg}$$

**Now find  $B$ .**

$$B = \frac{\hbar}{4\pi c I} = \frac{\hbar}{4\pi c \mu r^2} = \frac{1.05457 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{4\pi (2.99792458 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}) (3.1622_0 \times 10^{-27} \text{ kg}) (127.45 \times 10^{-12} \text{ m})^2}$$

$$B = 5.4497 \text{ cm}^{-1}$$

*Note that the mass of D is about twice the mass of H, so it makes sense that  $B$  should go down by about half ( $\mu$  is twice as big for DCl than for HCl, and since it is in the denominator of the expression for  $B$ , it makes  $B$  half as big).*

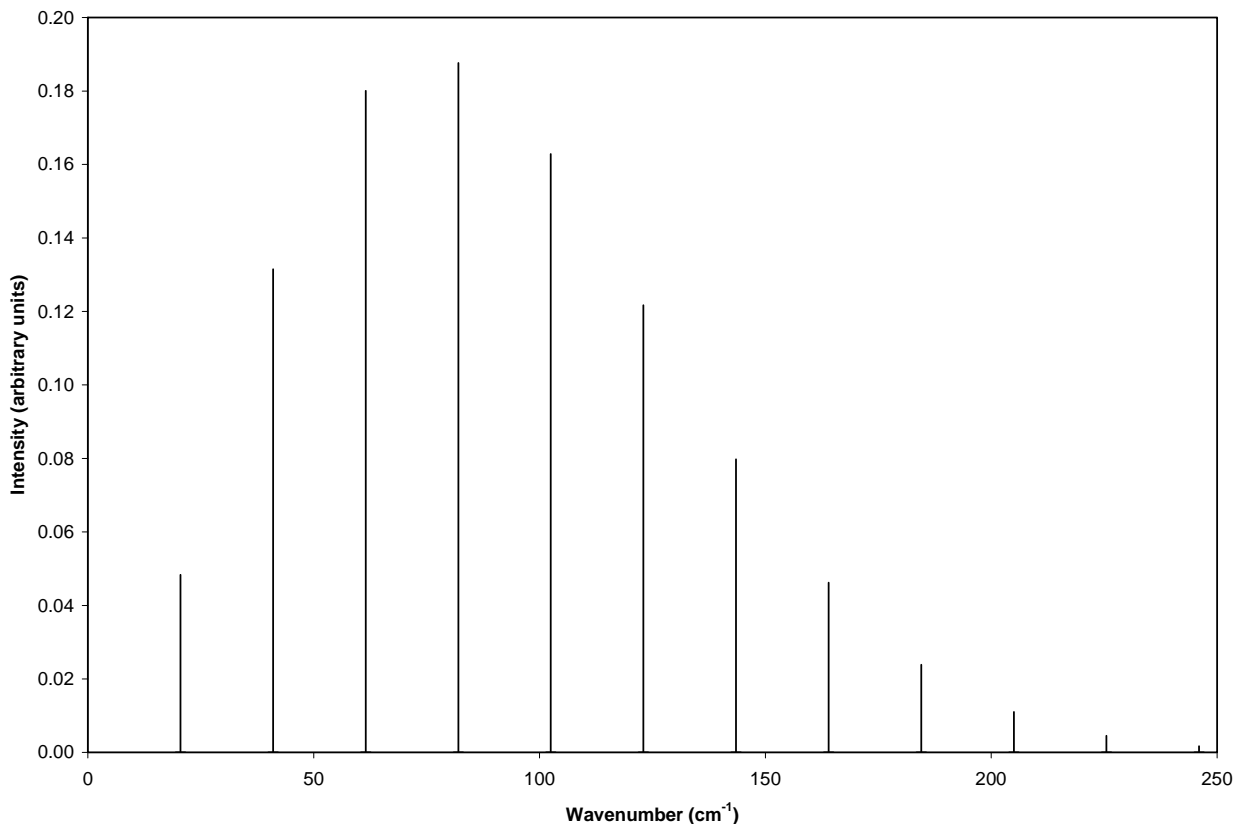
Starting from the equation  $F(J) = BJ(J+1) - D_J J^2(J+1)^2$ , and again assuming  $D_J$  is small, gives the expression  $F(J) - F(J-1) = 2BJ$ . The  $J = 6$  to  $J = 7$  transition can be found by substituting in

$$F(7) - F(6) = 2B(7) = 14B = 14(5.4497 \text{ cm}^{-1}) = 76.296 \text{ cm}^{-1}$$

*This transition was observed experimentally to occur at  $75.24 \text{ cm}^{-1}$ . Given the experimental uncertainty and that the unresolved peak due to  $^1\text{H}-^{37}\text{Cl}$ , which undoubtedly affected the reported measured peak position, the  $0.05 \text{ cm}^{-1}$  difference between observed and experimental is not too bad.*

d. (8 Points) The transitions listed in part *a* do not have the same intensity. Using your value of  $B$  for HCl and assuming that the intensity of a line depends only on the population of the lower state, create a simulation of the HCl rotational absorption spectrum (intensity as a function of wavenumber) at 300.0 K showing the twelve lowest energy transitions. Assume a Boltzmann population distribution and don't forget the degeneracies. Note that you will want to include more than twelve states in your Boltzmann analysis to be sure that you have the correct populations for the states of interest. Helpful hint: use a spreadsheet.

**With  $B = 10.25 \text{ cm}^{-1}$ , the following simulated rotational spectrum of HCl may be produced, assuming a Boltzmann distribution at 300.0 K.**



4. One of the Hamiltonians that is used in the quantum mechanical treatment of electron paramagnetic resonance (EPR) spectroscopy (and NMR, too) is given below. In this expression  $S$  is the total spin quantum number,  $\beta$  is the Bohr magneton ( $0.46686 \text{ cm}^{-1} \cdot \text{T}^{-1}$ ,  $1 \text{ T} = 10^4 \text{ G}$ ), the  $H_x$ ,  $H_y$  and  $H_z$  are the magnetic field strength along the molecule's different axes,  $g_{\parallel}$  and  $g_{\perp}$  are called the Landé  $g$  factors and are related to how the molecule responds to the magnetic field,  $D$  is the axial zero-field splitting parameter, and  $\hat{S}_x$ ,  $\hat{S}_y$  and  $\hat{S}_z$  are the three spin operators for the different orientations of the magnetic field relative to the molecular axes.

$$\hat{H} = g_{\parallel} \beta H_z \hat{S}_z + g_{\perp} \beta (H_x \hat{S}_x + H_y \hat{S}_y) + D \left[ \hat{S}_z^2 - \frac{1}{3} S(S+1) \right]$$

Here is how each of the spin operators are defined and how they work.

$$\hat{S}_z |S, M_S\rangle = M_S |S, M_S\rangle$$

When  $\hat{S}_z$  operates on a wavefunction defined by the total and one of the allowed  $M_S$  values, it simply returns the original wavefunction times  $M_S$  (e. g.,  $\hat{S}_z \left| \frac{1}{2}, +\frac{1}{2} \right\rangle = +\frac{1}{2} \left| \frac{1}{2}, +\frac{1}{2} \right\rangle$ ).

The operators  $\hat{S}_x$  and  $\hat{S}_y$  are a bit more complicated and are written in terms of the raising ( $\hat{S}_+$ ) and lowering operators ( $\hat{S}_-$ ) as follows:

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \qquad \hat{S}_- = \hat{S}_x - i\hat{S}_y$$

$$\hat{S}_+ |S, M_S\rangle = [S(S+1) - M_S(M_S+1)]^{1/2} |S, M_S+1\rangle$$

$$\hat{S}_- |S, M_S\rangle = [S(S+1) - M_S(M_S-1)]^{1/2} |S, M_S-1\rangle$$

Note that if a particular operator raises or lowers  $M_S$  to a forbidden value, then the result is 0. For example if  $S = 1/2$ , then the only allowed values of  $M_S$  are  $+1/2$  and  $-1/2$ , but if we apply  $\hat{S}_+$  to the wavefunction  $\left| \frac{1}{2}, +\frac{1}{2} \right\rangle$  (i. e.,  $\hat{S}_+ \left| \frac{1}{2}, +\frac{1}{2} \right\rangle$ ) the result would be

$$\hat{S}_+ \left| \frac{1}{2}, +\frac{1}{2} \right\rangle = \left[ \frac{1}{2} \left( \frac{1}{2} + 1 \right) - \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right]^{1/2} \left| \frac{1}{2}, +\frac{3}{2} \right\rangle. \text{ But, this is impossible since } M_S \neq +3/2 \text{ when } S = 1/2. \text{ Therefore } \hat{S}_+ \left| \frac{1}{2}, +\frac{1}{2} \right\rangle = 0 \left| \frac{1}{2}, +\frac{1}{2} \right\rangle.$$

For this problem we will consider a system with  $S = 1$  (a spin triplet), which means that the allowed values of  $M_S$  are +1, 0 and -1 and we will write the orthonormal wavefunctions as  $|1,+1\rangle$ ,  $|1,0\rangle$  and  $|1,-1\rangle$ .

The matrix representation of the Hamiltonian when  $D = 0$  and the molecule is aligned so that the magnetic field is along the molecule's z axis ( $H_x = H_y = 0$ ) is given below. Note that each matrix element corresponds to an integral that may be written  $\langle S', M_S' | \hat{H} | S, M_S \rangle$ . For example, the entry in the row labeled  $\langle 1,+1 |$  under the column labeled  $|1,-1\rangle$  is the result of  $\langle 1,+1 | \hat{H} | 1,-1 \rangle$ . Helpful hint: be sure that you can reproduce this matrix before working the rest of the problem!

$$\begin{array}{l} \langle 1,+1 | \\ \langle 1,0 | \\ \langle 1,-1 | \end{array} \begin{bmatrix} |1,+1\rangle & |1,0\rangle & |1,-1\rangle \\ \hline g_{\parallel} \beta H_z & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -g_{\parallel} \beta H_z \end{bmatrix}$$

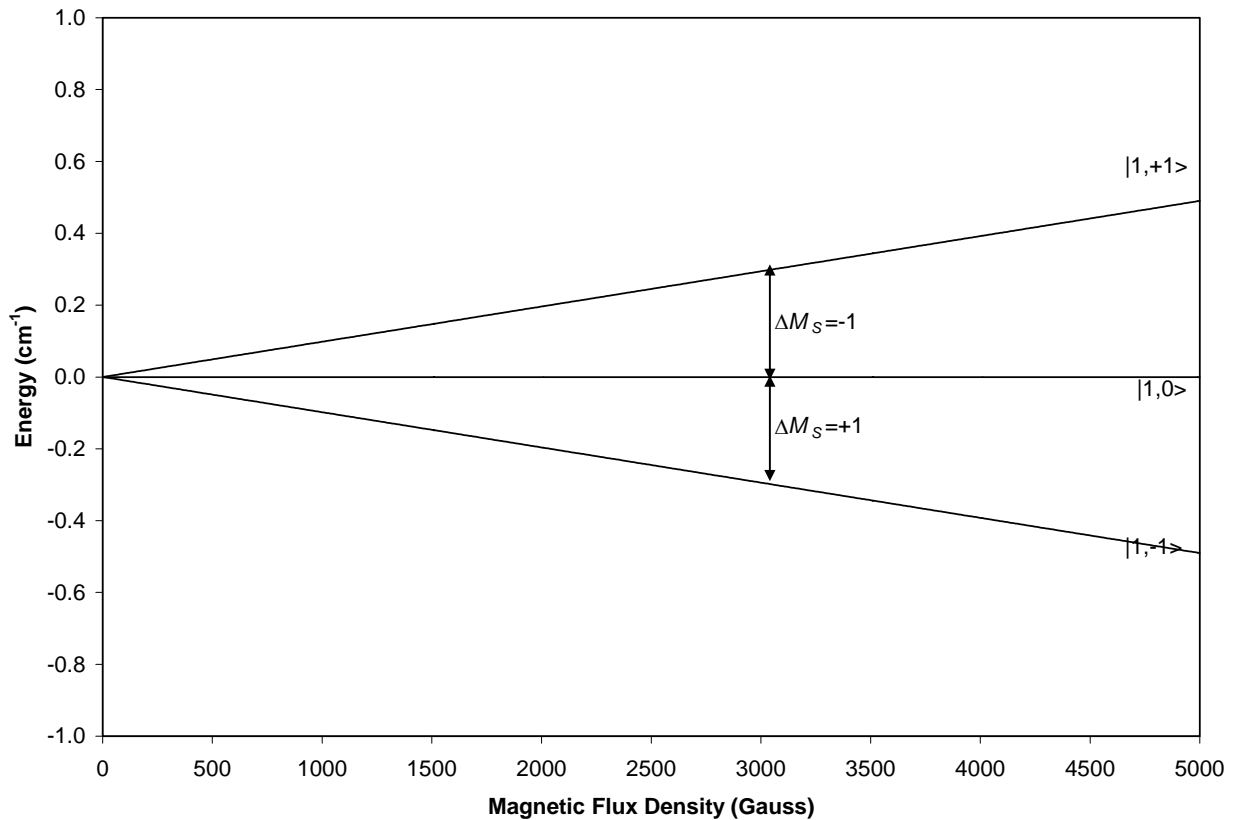
a. (7 Points) Diagonalize this matrix to solve for the energies of each state. Prepare a graph of the energy of each state (in  $\text{cm}^{-1}$ ) as a function of the applied magnetic field in gauss (0 - 5000 G). Label the states with the appropriate wavefunction (i. e.,  $|1,+1\rangle$ ,  $|1,0\rangle$  or  $|1,-1\rangle$ ). Take  $g_{\parallel} = 2.10$  ( $g_{\perp}$  won't enter into the problem). The selection rule for EPR spectroscopy is  $\Delta M_S = \pm 1$ ; indicate the two allowed EPR transitions on your graph. Tape the graph in the space below.

**We are only considering  $\hat{S}_z$ , which does not change  $M_S$ . Therefore, any integral of the type  $\langle S, M_S' | \hat{H} | S, M_S \rangle$  where  $M_S' \neq M_S$  will equal 0 and the only non-zero values will appear along the diagonal. For example,**

$$\langle 1,+1 | \hat{H} | 1,+1 \rangle = \langle 1,+1 | (g_{\parallel} \beta H_z \hat{S}_z | 1,+1 \rangle) = \langle 1,+1 | (+1) g_{\parallel} \beta H_z | 1,+1 \rangle = g_{\parallel} \beta H_z \langle 1,+1 | 1,+1 \rangle = g_{\parallel} \beta H_z$$

$$\langle 1,+1 | \hat{H} | 1,-1 \rangle = \langle 1,+1 | (g_{\parallel} \beta H_z \hat{S}_z | 1,-1 \rangle) = \langle 1,+1 | (-1) g_{\parallel} \beta H_z | 1,-1 \rangle = g_{\parallel} \beta H_z \langle 1,+1 | 1,-1 \rangle = 0$$

**The resulting matrix is thus diagonal and the matrix elements correspond to the energy of each state (i. e.,  $E_{|1,+1\rangle} = g_{\parallel} \beta H_z$ ,  $E_{|1,0\rangle} = 0$  and  $E_{|1,-1\rangle} = -g_{\parallel} \beta H_z$ ).**



b. (10 Points) Now create the matrix with  $D \neq 0$  (keep  $H_x = H_y = 0$ ). Diagonalize the matrix to solve for the energies of each state and prepare a graph like the one for part a (let  $g_{\parallel} = 2.10$  again and set  $D = 0.15 \text{ cm}^{-1}$ ) and tape it in the space below. Again indicate the two allowed transitions and label the states. Why is the parameter  $D$  called zero-field splitting parameter?

**Adding  $D$  to the analysis will not change the fact that the only non-zero matrix elements are along the diagonal (the term containing  $D$  only has  $\hat{S}_z$  in it), but the matrix elements themselves change.**

**We first write out the Hamiltonian operator and distribute the ket through the expression (note that, since  $S = 1$  for all of the states,  $\frac{1}{3}S(S+1) = \frac{2}{3}$ ). It can then be evaluated term by term (note that since  $g_{\parallel}$ ,  $\beta$ ,  $D$  and  $H_z$  are all constants they remain unchanged during the operation by  $\hat{S}_z$ ).**

$$\langle 1,+1 | \hat{H} | 1,+1 \rangle = \langle 1,+1 | \left( g_{\parallel} \beta H_z \hat{S}_z | 1,+1 \rangle + D \hat{S}_z^2 | 1,+1 \rangle - \frac{2}{3} D | 1,+1 \rangle \right)$$

$$\langle 1,+1 | \hat{H} | 1,+1 \rangle = \langle 1,+1 | \left( g_{\parallel} \beta H_z | 1,+1 \rangle + D | 1,+1 \rangle - \frac{2}{3} D | 1,+1 \rangle \right)$$

$$\langle 1,+1|\hat{H}|1,+1\rangle = \langle 1,+1|\left(g_{\parallel}\beta H_z + \frac{1}{3}D\right)|1,+1\rangle$$

Since  $\left(g_{\parallel}\beta H_z + \frac{1}{3}D\right)$  is a constant, it can be factored out to give (recall that the wavefunctions are orthonormal)

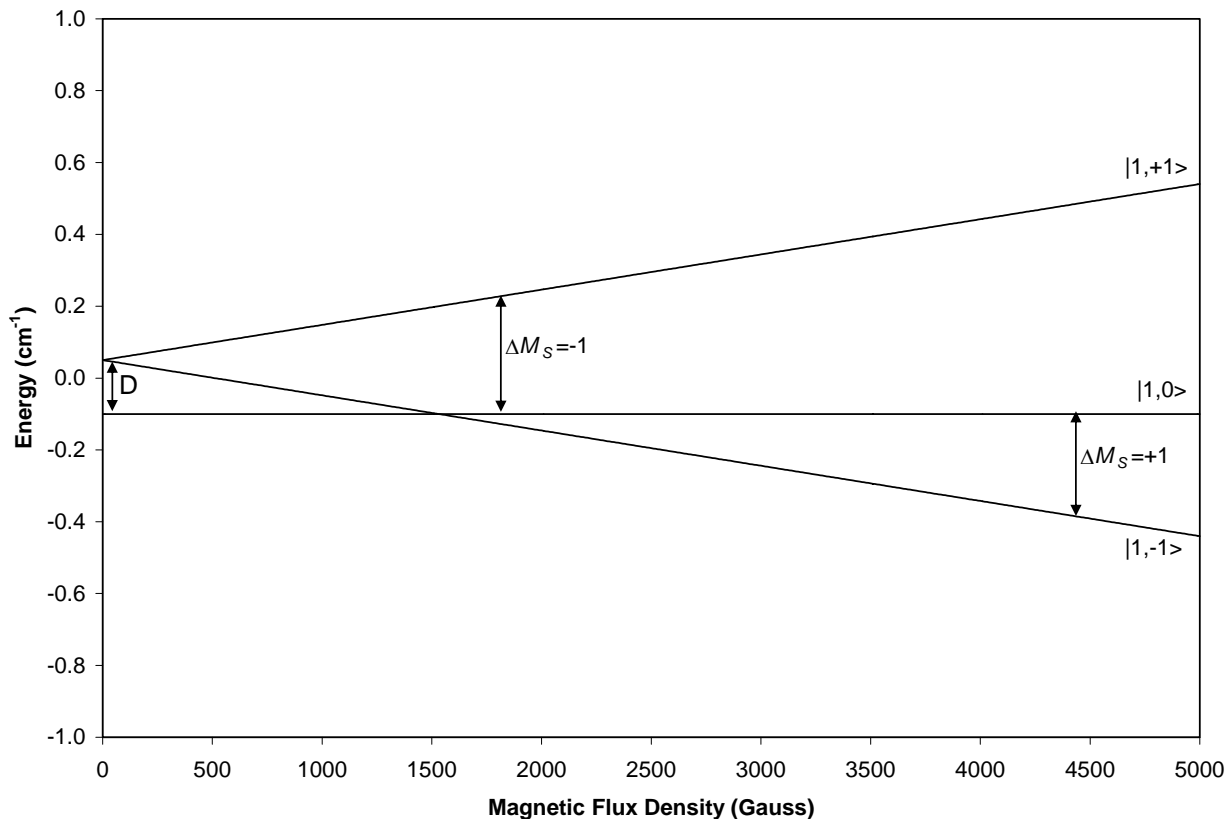
$$\langle 1,+1|\hat{H}|1,+1\rangle = \left(g_{\parallel}\beta H_z + \frac{1}{3}D\right)\langle 1,+1|1,+1\rangle = g_{\parallel}\beta H_z + \frac{1}{3}D$$

By similar methods we can also find

$$\langle 1,0|\hat{H}|1,0\rangle = -\frac{2}{3}D$$

$$\langle 1,-1|\hat{H}|1,-1\rangle = -g_{\parallel}\beta H_z + \frac{1}{3}D$$

Graphing these gives the following graph. Note how  $D$  moves the  $|1,\pm 1\rangle$  states away from the  $|1,0\rangle$  state in energy when there is no field (unlike what we saw in part a), and this is why it is one of the zero-field splitting parameters.



c. (5 Points) In EPR spectroscopy the frequency of light (microwaves) is held constant while the field is swept (usually from 0 to 5000 G). Given  $g_{\parallel} = 2.10$  and  $D = 0.15 \text{ cm}^{-1}$ , at what field strength will the two allowed transitions occur if the frequency of incident light is 9.27 GHz? Hint: you have equations describing the energy of the states as a function of field which form a system of simultaneous equations and you know the Bohr frequency condition.

**The  $\Delta M_S = +1$  transition occurs at an energy of**

$$E_{|1,+1\rangle} - E_{|1,0\rangle} = g_{\parallel}\beta H_z + \frac{1}{3}D - \left(-\frac{2}{3}D\right) = D + g_{\parallel}\beta H_z$$

$$E_{|1,+1\rangle} - E_{|1,0\rangle} = h\nu \text{ (the Bohr frequency condition)}$$

$$D + g_{\parallel}\beta H_z = h\nu$$

$$H_z = \frac{h\nu - D}{g_{\parallel}\beta} = \frac{(6.62608 \times 10^{-34} \text{ J}\cdot\text{s})(9.27 \times 10^9 \text{ s}^{-1}) \left( \frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}} \right) - 0.15 \text{ cm}^{-1}}{(2.10) \left( 0.46686 \text{ cm}^{-1} \cdot \text{T}^{-1} \right) \left( \frac{1 \text{ T}}{1 \times 10^4 \text{ G}} \right)}$$

$$H_z = \frac{0.309_2 \text{ cm}^{-1} - 0.15 \text{ cm}^{-1}}{9.80_4 \times 10^{-5} \text{ cm}^{-1} \cdot \text{G}^{-1}} = \frac{0.15_92 \text{ cm}^{-1}}{9.80_4 \times 10^{-5} \text{ cm}^{-1} \cdot \text{G}^{-1}} = 1.6_{23} \times 10^3 \text{ G}$$

**The  $\Delta M_S = -1$  transition occurs at an energy of**

$$E_{|1,0\rangle} - E_{|1,-1\rangle} = -\frac{2}{3}D - \left(-g_{\parallel}\beta H_z + \frac{1}{3}D\right) = g_{\parallel}\beta H_z - D$$

$$g_{\parallel}\beta H_z - D = h\nu$$

$$H_z = \frac{h\nu + D}{g_{\parallel}\beta} = \frac{(6.62608 \times 10^{-34} \text{ J}\cdot\text{s})(9.27 \times 10^9 \text{ s}^{-1}) \left( \frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}} \right) + 0.15 \text{ cm}^{-1}}{(2.10) \left( 0.46686 \text{ cm}^{-1} \cdot \text{T}^{-1} \right) \left( \frac{1 \text{ T}}{1 \times 10^4 \text{ G}} \right)}$$

$$H_z = \frac{0.309_2 \text{ cm}^{-1} + 0.15 \text{ cm}^{-1}}{9.80_4 \times 10^{-5} \text{ cm}^{-1} \cdot \text{G}^{-1}} = \frac{0.45_92 \text{ cm}^{-1}}{9.80_4 \times 10^{-5} \text{ cm}^{-1} \cdot \text{G}^{-1}} = 4.6_{83} \times 10^3 \text{ G}$$

d. (5 Points) Often EPR spectroscopists will refer to EPR transitions by an effective  $g$  value ( $g_{\text{eff}}$ ), which they obtain from the field at which a transition occurs and assuming that  $g_{\text{eff}}\beta H = h\nu$ .

What are the  $g_{\text{eff}}$  for each of the transitions that you found in part c?

**Solve  $g_{\text{eff}}\beta H = h\nu$  for  $g_{\text{eff}}$ .**

$$g_{\text{eff}} = \frac{h\nu}{\beta H}$$

**For the transition at  $1.6_{23}\times 10^3$  G,**

$$g_{\text{eff}} = \frac{h\nu}{\beta H} = \frac{(6.62608 \times 10^{-34} \text{ J}\cdot\text{s})(9.27 \times 10^9 \text{ s}^{-1})\left(\frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}}\right)}{(0.46686 \text{ cm}^{-1} \cdot \text{T}^{-1})\left(\frac{1 \text{ T}}{1 \times 10^4 \text{ G}}\right)(1.6_{23} \times 10^3 \text{ G})} = 4.1$$

**and for the transition at  $4.6_{83}\times 10^3$  G,**

$$g_{\text{eff}} = \frac{h\nu}{\beta H} = \frac{(6.62608 \times 10^{-34} \text{ J}\cdot\text{s})(9.27 \times 10^9 \text{ s}^{-1})\left(\frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}}\right)}{(0.46686 \text{ cm}^{-1} \cdot \text{T}^{-1})\left(\frac{1 \text{ T}}{1 \times 10^4 \text{ G}}\right)(4.6_{83} \times 10^3 \text{ G})} = 1.4$$

*Note how the effective  $g$  values are very different than the actual  $g_{\parallel}$  value and that two different  $g_{\text{eff}}$  values arise from a single  $g_{\parallel}$  because of the presence of a zero-field splitting.*