

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

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.

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

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

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

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.

d. (3 Points) Describe what happens to Δp and Δx as the box gets longer.

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 (cm^{-1})	83.32	104.13	124.73	145.37	165.89	186.23	206.60	226.86
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b. (3 Points) Based on your fit of the data, was our assumption that centrifugal distortion could be ignored a valid one? Explain.

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., H-³⁵Cl and H-³⁷Cl), 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.

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.

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, β is the Bohr magneton ($0.46686 \text{ cm}^{-1} \cdot \text{T}^{-1}$, where $1 \text{ T} = 10^4 \text{ G}$), 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 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.

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?

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.

d. (5 Points) Often EPR spectroscopists will refer to EPR transitions by an effective g value (g_{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_{eff} for each of the transitions that you found in part c?