Chem 249 Problem Set 5
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The Zeeman Effect in Hydrogen and Sodium
Rabi Vectors and Feynman Paper
The Vibrational Spectroscopy of Water

1. Gas Phase Spectra

Isotopic Substitution
Vibrational-Rotational Lines
Coriolis Coupling
Born-Oppenheimer Approximation
Atmospheric Water
Water Lines in Sunspots

2. Hydrogen Bonding

Liquid Phase Spectrum
Homogeneous vs Inhomogeneous Broadening
Hole Burning
Fermi Resonance
Isotopic Dilution
Ice Spectrum
Water in Stoichiometric Hydrates
Surface Water
Water in Salt Solutions
Time Resolved Studies

3. Low Frequency Motions

Far IR spectrum
Librations vs Free Rotation
Correlation Functions

Handouts:

Lande g factor handout
Water Handouts 1-4
Feynman Paper
CT Zeeman Complement Handout
For fun: XRF Handout, Mars Rover Handout

Problems:

NOTE: PLEASE DO PROBLEM 1 AND THEN EITHER PROBLEM 2 OR PROBLEM 3. (YOU CAN DO BOTH 2 AND 3 IF YOU'D LIKE EXTRA CREDIT)

1. Sodium Doublet and the Zeeman Effect

1.1) We are going to model the Sodium D-Line transition ([Ne]3s^1 → {Ne]3p^1) with the Hydrogen 1s-2p transition as described in the CT handouts. Please write down (a) the Hamiltonian matrix, (b) the Energy Levels, (c) the Energy Level Diagram with allowed transitions, and (d) the spectrum you'd expect to see for the following model systems:

i) $H = H_0$
ii) $H = H_0 + W_Z$
iii) $H = H_0 + W_{SO}$
iv) $H = H_0 + W_Z + W_{SO}$ where ($W_Z >> W_{SO}$)
v) $H = H_0 + W_{SO} + W_Z$ where ($W_{SO} >> W_Z$)

Please See the C-T Complement DXII (pdf file on the website) for definitions of H_0, W_{SO} and W_Z.

1.2) Pieter Zeeman won the Nobel Prize in Physics in 1902 for the splitting of the Sodium D line spectrum of Na in a magnetic field. Which of the five cases in 1.1 applies best describes his measurements?

2. Density Matrix Description of Absorption: Rabi Oscillations

Please see the Feynman Paper and Rabi Paper PDFs as well as the Density Matrix PDF for more information.

Consider a generalized TLS with States |1> and |2>:

$H_0|1\rangle = (\hbar\omega_0/2)\,|1\rangle$
$H_0|2\rangle = -(\hbar\omega_0/2)\,|2\rangle$

The 2x2 density matrix for this system ρ is given by:

ρ11	ρ12
ρ21	ρ22

2.1 If we create the density matrix for a state |ψ> given by:

$|\psi\rangle = a(t)|1\rangle + b(t)|2\rangle$ (a and b can be complex) what are values of the four density matrix elements of $|\psi\rangle\langle\psi|$ in terms of a(t) and b(t)?

2.2 Equation 2 of the Feynman paper defines a vector in real space $\mathbf{r} = r_1\mathbf{i} + r_2\mathbf{j} + r_3\mathbf{k}$. What are the values of r_1, r_2 and r_3 in terms of the density matrix elements? State in words what r_3 is in terms of state populations.

2.3 We now want to examine the time evolution of ρ under the influence of the Hamiltonian $H = H_0 + V(t)$, where the matrix V(t) is given by:

0	$-\mu E(t)$
$-\mu E(t)$	0

where μ is the real transition dipole moment element $\langle 1|\mu|2\rangle$ and $E(t) = E_0 \cos(\omega t)$ is the externally applied electromagnetic E field. The Feynman paper defines another vector in real space $\boldsymbol{\omega} = \omega_1\mathbf{i} + \omega_2\mathbf{j} + \omega_3\mathbf{k}$, where $\omega_1=-2\mu E(t)/\hbar$, $\omega_2=0$ and $\omega_3= \omega_0$.

Using the Heisenberg equation of motion for $\rho(t)$:

$$d\rho/dt = (-i/\hbar)[H(t), \rho(t)]$$

prove that the Equation 4 in the Feynman paper is true:

$$d\mathbf{r}/dt = \boldsymbol{\omega} \times \mathbf{r}$$

(This was a brilliant realization by Feynman).

2.4 Equation 4 describes the rotation of the vector **r** in time. Please show that the equations of motion of **r** when $E(t) = 0$ is just a rotation about the z-axis at a frequency ω_0. (Hint: see the Rabi Paper or a physics textbook on mechanics).

2.5 If we choose new x and y axes that are rotating at the frequency ω (this is called the rotating frame), then $E_0 \cos(\omega t)$ looks stationary and the $\boldsymbol{\omega}$ is transformed as described by Feynman on pg. 51 above Eqn 14 (the rotating axes are **I** and **II**). Use the new $\boldsymbol{\omega}$ and Eqn 4 to derive an equation for the vector **r**(t) (all three components) when when $\omega = \omega_0$. (Hint: Feyman gives you two of the answers in Eqn 14).

2.6 Draw a picture like Fig. 1 to show what happens to the vector **r**(t) for the case when when $\omega = \omega_0$. Feynman calls Ω the "driving torque." Is Ω the Rabi Frequency? What is happening to the populations $\rho_{11}(t)$ and $\rho_{22}(t)$?

3. The Vibrational Spectroscopy of Water

Please use the four water papers on the website as well as other papers/reference materials that exist on the web for these problems.

3.1) The traditional normal mode theory as applied to the water molecule H_2O predicts 3N-6=3 harmonic vibrations, two OH stretches and one bend. Please write down the symmetries of these three vibrations, their gas phase frequencies, and sketch the normal modes. Why are the two stretches at different frequencies in the harmonic approximation?

3.2) Write down the three vibrations, gas phase frequencies and sketch the normal coordinates for the molecule HDO.

3.3) In the liquid and solid phase, the frequency of the OH stretch decreases significantly due to Hydrogen bonding. Find the frequencies of the OH stretch of HDO dilute in D_2O (you can do the OD stretch of HDO dilute in H_2O instead if you like) in liquid water or ice and compare it percentage-wise with the gas phase frequency. Then try and find overtone spectra (just the first overtone is sufficient) of the OH stretch in HDO and calculate the anharmonicity constants in liquid water or ice. How do they compare with the gas phase values?

3.4) Water has an intense absorption in the far IR in both gas and condensed phase – it's even been seen in sunspots on the surface of the Sun(!).
a) What motions are these absorptions due to in the gas phase?
b) The liquid far IR spectrum can be related to the dipole moment correlation function, obtained either by a model or a full molecular dynamics simulation. What's a dipole moment correlation function, and how is it related to the vibrational spectrum?
(Hint: see, for example, McQuarrie "Statistical Mechanics")

3.5) Hole burning spectroscopy is a method to explore inhomogenous broadening in solid samples. (a) Please find an exemplary paper that uses of hole burning spectroscopy in a glass and explain what is learned from the measurements. (b) Please look at Water Paper 4 which describes hole burning in ice, and explain what is learned about the structure of ice from those measurements.