Chem 249 Problem Set 4
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Basic Quantum Theory and Energy Levels in Spectroscopy

- Spin (Angular Momentum) Systems
- Time Independent Perturbation Theory
- Perturbed Spin 1/2 Systems
- Singlet - Triplet Spin Coupling

Handouts:

1. QM1: Basic Equations
2. QM2: Time Independent Perturbation Theory

Additional Readings:

1. Atkins, Quantum Mechanics
2. Cohen-Tannoudji, Quantum Mechanics
3. Schiff, Quantum Mechanics

Problems:

1. This problem looks at J coupling in proton NMR. Consider a molecule that contains two inequivalent protons, e.g. $CHCl_2CHBr_2$.

1.1) The protons in this molecule have spins $\mathbf{I}_A$ and $\mathbf{I}_B$ with quantum numbers I_A and I_B that are both, of course, equal to 1/2. The two spins have unperturbed frequencies ω_A and ω_B. Like the angular momentum in an atom, they couple to form a total spin $\mathbf{I}_{tot}$. What values can the quantum number I_{tot} take?

1.2) The magnitude of I_{tot} is related to the magnitudes of $\mathbf{I}_A$ and $\mathbf{I}_B$ and the dot product $\mathbf{I}_A \bullet \mathbf{I}_B$:

$$\left|\mathbf{I}_{tot}\right|^2 = \left|\mathbf{I}_A\right|^2 + \left|\mathbf{I}_B\right|^2 + 2\mathbf{I}_A \bullet \mathbf{I}_B$$

Find the value of $\mathbf{I}_A \bullet \mathbf{I}_B$ for the two possible values of I_{tot}.

1.3) Consider the total Hamiltonian of the system for the case of spin-spin coupling:

$$H = -\omega_A I_Z^A - \omega_B I_Z^B + \frac{J}{\hbar}\mathbf{I}_A \bullet \mathbf{I}_B$$

If $\omega_A = \omega_B$ (e.g., $CHCl_2CHCl_2$), the energy eigenstates for this two spin system can be given by:

|1> = |++>
|2> = 1/2 [|+-> + |-+>]
|3> = 1/2 [|+-> - |-+>]
|4> = |-->

where |++> = $|+_A>|+_B>$, etc. Eigenstates 1,2 and 4 have $I_{tot} = 1$; Eigenstate 3 has $I_{tot} =0$. Where do these eigenstates come from? What are the energies for these four states? What does the NMR spectrum look like?

1.4) Using FIRST ORDER perturbation theory, find the energy levels for the case when $\omega_A \neq \omega_B$ (e.g., $CHBr_2CHCl_2$).

1.5) Using matrix diagonalization, find the EXACT solutions for the energy levels for the case $\omega_A \neq \omega_B$ (e.g., $CHBr_2CHCl_2$).

2) This problem is about local vs. normal modes as described in the Child papers #1 and 2 on the website.

2.1) Bond vibrations of the form X-H are highly anharmonic. A local mode picture has been suggested for the XH stretches in H_2X which uses a Morse Potential. What is a Morse Potential, and what are its eigenvalues? (Hint: see section 10.9 in Atkins).

2.2) In the local mode approximation with molecules of the form H_2X, the two fundamental modes are given by symmetric and antisymmetric combinations of local modes (See Child papers #1 and #2). The model Hamiltonian (Eq 3 in Child paper #1) is said to only mix state $|n_a, n_b>$ with states $|n_a+1, n_b-1>$ and $|n_a-1, n_b+1>$. Please show/explain why this is the case.

2.3) The coupled local mode Hamiltonian predicts splittings for the fundamentals and overtones as shown in Figure 3 of Child paper #1. Figure 3 contains the anharmonic term ωx and the coupling strength parameter lambda, which is given in Eqns 5 and 6. Please explain the figure and use Child paper #2 to explain where lambda comes from.

2.4) Please explain Figure 4 of Child paper #1, and what it is useful for. Why is the x-axis $(2/\pi)*\arctan(\lambda/\omega x)$?