

Chem 249 Problem Set 4

R. Corn

Winter 2018

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. Consider the NMR spectrum of a deuterium atom, which has a nuclear spin I of 1.

a) In an external magnetic field, the deuterium has an energy of

$$E = -\hbar\omega_0 M_I$$

where M_I is the quantum number for I_z , the component of the nuclear spin in the direction of the magnetic field. Draw an energy level diagram for the atom in a magnetic field. Be sure to label the states and any energy level splittings.

b) Draw the NMR spectrum you would expect to see. Label the frequencies of any peaks in the spectrum.

c) A perturbation added to the system changes the energy levels such that

$$E = -\hbar\omega_0 M_I + \hbar b M_I^2$$

where b is a constant that is much less than ω_0 . Draw a modified energy level diagram and a new NMR spectrum.

2. This problem looks at j coupling in proton NMR. Consider a molecule that contains

two inequivalent protons, e.g. $\text{CHCl}_2\text{CHBr}_2$.

2.1) 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, naturally, 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?

2.2) The magnitude of \mathbf{I}_{tot} is related to the magnitudes of \mathbf{I}_A and \mathbf{I}_B and the dot product $\mathbf{I}_A \cdot \mathbf{I}_B$:

$$|\mathbf{I}_{\text{tot}}|^2 = |\mathbf{I}_A|^2 + |\mathbf{I}_B|^2 + 2\mathbf{I}_A \cdot \mathbf{I}_B$$

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

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

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

If $\omega_A = \omega_B$ (e.g., $\text{CHCl}_2\text{CHCl}_2$), the energy eigenstates for the two spin system are given by:

$$\begin{aligned} |1\rangle &= |aa\rangle \\ |2\rangle &= 1/2 [|ab\rangle + |ba\rangle] \\ |3\rangle &= 1/2 [|ab\rangle - |ba\rangle] \\ |4\rangle &= |bb\rangle \end{aligned}$$

where $|aa\rangle = |a_A\rangle|a_B\rangle$, etc. Eigenstates 1,2 and 4 have $I_{\text{tot}} = 1$; eigenstate 3 has $I_{\text{tot}} = 0$. Where do these eigenstates come from? What are the energies for these four states? What does the NMR spectrum look like?

2.4) Using FIRST ORDER perturbation theory, find the energy levels for the case when $\omega_A \neq \omega_B$ (e.g., $\text{CHBr}_2\text{CHCl}_2$).

2.5) Using matrix diagonalization, find the EXACT solutions for the energy levels for the case $\omega_A \neq \omega_B$ (e.g., $\text{CHBr}_2\text{CHCl}_2$).

From the Child Handouts on Local Modes:

3.1) 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).

3.2) 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 Handouts #1 and #2). The model Hamiltonian (Eq 3 in Handout #1) is said to only mix state $|n_a, n_b\rangle$ with states $|n_a+1, n_b-1\rangle$ and $|n_a-1, n_b+1\rangle$. Please show/explain why this is the case.

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