Ch126
Winter Quarter - 2024
Problem Set 2
Due: 25 January, 2024

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1. (10 points) Consider the ^{14} N nucleus with spin $I = 1$. The gyromagnetic ratio for ^{14} N is $\gamma_{\mathrm{N}} = 1.9337798 \times 10^7$ radians s $^{-1}$ T^{-1}.

a. Determined the energies of all nuclear spin sublevels for a free ^{14} N nucleus in a 10 T magnetic field.

1.1

Since the spin is $I = 1$, there will be three sublevels, $m_I = -1, 0, 1$. The energy of each sublevel is given by:

$$E = -\gamma_N B_0 m_I \tag{1}$$

So the energies are:

$$E = -1.9337798 \times 10^8 \text{ rad} \cdot \text{s}^{-1} \cdot 10 \text{ T} \cdot m_I \tag{2}$$

My script gives:

$$E_{-1} = 1.933 \times 10^8 J \tag{3}$$
$$E_0 = 0 \tag{4}$$
$$E_1 = -1.933 \times 10^8 J \tag{5}$$

b. Determine the differences in populations (in ppm) among all sublevels at 295 K in the 10 T magnetic field.

1.2

We want to use the equation:

$$P_j = \frac{N_j}{N_T} = \frac{\Omega_j e^{-\beta E_j}}{\sum_{j=1}^{3} \Omega_j e^{-\beta E_j}} \tag{6}$$

where each state has no degenerates in the presence of the magnetic field and $\beta = \frac{1}{kT}$. We can calculate the partition function as:

$$Q = \sum_{j=1}^{3} \Omega_j e^{-\beta E_j} = e^{-\beta E_{-1}} + e^{-\beta E_1} + 1 \tag{7}$$

c. Determine the resonance frequencies for all allowed transitions among nuclear sublevels.

2. (5 points) On a certain NMR spectrometer a proton signal has a chemical shift of 5ppm, corresponding to a frequency range of 3kHz. What is the operating frequency of the spectrometer and what is the approximate magnetic field strength?

3. (5 points) Calculate the magnetic field strength required for ^{19} F $(\mathrm{I} = 1/2, \gamma_{\mathrm{F}} = 2.516233 \times 10^8$ radians s $^{-1}$ $\mathrm{T}^{-1})$ and $^{13}\mathrm{C}\,(\mathrm{I} = 1/2, \gamma_{\mathrm{C}} = 6.728286 \times 10^7$ radians $^{-1}$ $\mathrm{T}^{-1})$ resonances in a 500MHz spectrometer.

4. (5 points) Consider a two-proton spin system in which the two protons are equivalent. If the two protons are equivalent, then they are indistinguishable, and quantum mechanics requires that the wavefunction for the system is either symmetric or antisymmetric with respect to exchange of identical particles. Write down all possible orthonormal wavefunctions for this two-proton system where:

$$|\alpha(j)\rangle = |\psi_j(1/2, 1/2)\rangle \quad \text{and} \quad |\beta(j)\rangle = |\psi_j(1/2, -1/2)\rangle$$

6. (15 points) Assume the zero-order Hamiltonian for this spin system in a magnetic field directed along the z-axis of magnitude B_0 is:

$$\widehat{H}^0 = -\gamma_H B_0 (1 - \sigma_A) \left(\hat{I}_{z1} + \hat{I}_{z2} \right)$$

where σ_A is the chemical shift parameter for the two equivalent protons. The perturbation Hamiltonian is:

$$\widehat{H}' = \frac{hJ_{AA}}{\hbar^2} \hat{I}_1 \cdot \hat{I}_2$$

where J_{AA} is the spin-spin coupling constant between the two protons. Using the wavefunctions from problem 5 , determined the zero-order energies and first order corrections to the energies of all four states.

7. (5 points) Using the wavefunctions from the problem 5 , identify all of the allowed NMR transitions among them. How many lines do you expect to see in the proton NMR spectrum of this system?