

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

1

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

a. Determine 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:

$$E = -\gamma_{\text{N}} B_0 m_I \quad (1)$$

So the energies are:

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

Additionally, we have to multiply by \hbar to get the energy in Joules. My script gives:

$$E_{-1} = 2.04 \times 10^{-26} \text{ J} \quad (3)$$

$$E_0 = 0 \quad (4)$$

$$E_1 = -2.04 \times 10^{-26} \text{ J} \quad (5)$$

See the part c code for the script.

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:

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

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:

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

So the populations are:

$$N_{-1} = e^{-\beta E_{-1}} \times 10^{-6} ppm = \quad (8)$$

With the script I get:

$$N_{-1} = 0.999994993009271 ppm \quad (9)$$

$$N_0 = 1.0 ppm \quad (10)$$

$$N_1 = 1.00000500701580 ppm \quad (11)$$

So the differences in population are:

$$N_{-1} - N_0 = -5.01 \times 10^{-6} ppm \quad (12)$$

$$N_{-1} - N_1 = -1.00 \times 10^{-5} ppm \quad (13)$$

$$N_0 - N_1 = -5.01 \times 10^{-6} ppm \quad (14)$$

$$(15)$$

Changing the order of the above merely changes the sign of the difference.

```
1 import sympy as sp
2
3 # Constants
4 gamma_N = 1.9337798 * 10**7 # Gyromagnetic ratio in radians
   s^-1 T^-1
5 B0 = 10 # Magnetic field strength in Tesla
6 k_B = 1.380649e-23 # Boltzmann's constant in J/K
7 T = 295 # Temperature in Kelvin
8
```

```

9 # Magnetic quantum numbers and energies
10 m_I_values = [-1, 0, 1]
11 energies = [-gamma_N * B0 * m_I for m_I in m_I_values] #
    frequency for each m_I
12 # convert this to energies by multiplying by the reduced
    Planck's constant
13 rpc = 1.0545718e-34 # reduced Planck's constant in J s
14 energies = [rpc * f for f in energies]
15
16 # Beta (\beta = 1/(k_B * T))
17 beta = 1 / (k_B * T)
18
19 # get the population for each m_I in ppm
20 N_j = [sp.exp(-beta * E) * 10**(-6) for E in energies] #
    Correctly use list comprehension
21
22 # take all of the different differences between the
    populations
23 for i in range(len(N_j)):
24     for j in range(i + 1, len(N_j)):
25         print("N_{0} - N_{1} = {2:.2e} ppm".format(i, j, (N_j
            [i] - N_j[j]).evalf()))

```

1.3

c. Determine the resonance frequencies for all allowed transitions among nuclear sublevels. The three frequencies arise from the three energy levels. The frequencies are:

$$\nu_{m_I=-1 \rightarrow m_I=0} = \frac{E_{-1} - E_0}{h} = 30.8 \text{ MHz} \quad (16)$$

$$\nu_{m_I=0 \rightarrow m_I=1} = \frac{E_0 - E_1}{h} = 30.8 \text{ MHz} \quad (17)$$

$$\nu_{m_I=-1 \rightarrow m_I=1} = \frac{E_{-1} - E_1}{h} = 61.6 \text{ MHz} \quad (18)$$

```

1 import sympy as sp
2
3 # Constants
4 gamma_N = 1.9337798 * 10**7 # Gyromagnetic ratio in radians
    s^-1 T^-1
5 B0 = 10 # Magnetic field strength in Tesla
6

```

```

7 # Magnetic quantum numbers
8 m_I_values = [-1, 0, 1]
9
10 # reduced Planck's constant value
11 hbar = 6.62607004 * 10**-34 / (2 * sp.pi)
12
13 # Calculating the energy for each m_I
14 energies = [-gamma_N * B0 * m_I * hbar for m_I in m_I_values]
15
16 for m_I, energy in zip(m_I_values, energies):
17     energy_float = float(energy.evalf()) # Convert the Sympy
18     # expression to a float
19     print("m_I = {0}, E = {1:.2e} J".format(m_I, energy_float))
20
21 for m, e in zip(m_I_values, energies):
22     # if the m_Is are different, calculate the transition
23     # energy
24     if m_I != m:
25         transition_energy = energy - e
26         # divide by plancks constant and not hbar because
27         # we want the frequency
28         transition_frequency = transition_energy /
29         (6.62607004 * 10**-34)
30         transition_frequency_float = float(
31         transition_frequency.evalf())
32         print("m_I = {0} -> m = {1}, f = {2:.2e} Hz".
33         format(m_I, m, transition_frequency_float))

```

2. (15 points) Consider a two-proton spin system in which the shielding constants for the two protons (σ_1, σ_2) differ by 1.2×10^{-7} , and in which the coupling constant between the two spins is 5 Hz. Sketch the NMR spectra, including relative intensities, that you would expect for this spin system using spectrometers operating at the following frequencies: (a) 60MHz; (b) 270MHz; and (c) 500MHz. (See the lecture notes for expressions describing the intensities of the resonances).

2

3. (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? The chemical shift is given by the equation:

$$\delta_H = \frac{\nu - \nu_{ref}}{\nu_{ref}} \times 10^6 ppm \quad (19)$$

So we can solve for the frequency:

$$\nu_{ref} = \frac{\nu - \nu_{ref}}{\delta_H \times 10^{-6}} \quad (20)$$

My script gives:

$$\nu_{ref} = 600 MHz \quad (21)$$

$$(22)$$

So the magnetic field strength is:

$$B_0 = \frac{2\pi\nu_{ref}}{\gamma_H} \quad (23)$$

My script gives:

$$B_0 = 14.1 T \quad (24)$$

```

1 import sympy as sp
2
3 # Constants
4 # Gyromagnetic ratio in radians s^-1 T^-1 for a proton
5 gamma_H = 2.6752219 * 10**8
6
7 # Given values
8 delta_ppm = 5 # Chemical shift in ppm
9 delta_hz = 3 * 10**3 # Frequency range corresponding to
   chemical shift in Hz
10
11 # Calculation
12 # Rearrange the chemical shift formula to solve for nu_0
   (operating frequency)
13 nu_0 = sp.Symbol('nu_0')
14 nu = nu_0 + delta_hz
15 operating_frequency_equation = sp.Eq(delta_ppm, ((nu -
   nu_0) / nu_0) * 10**6)

```

```

16 operating_frequency_solution = sp.solve(
    operating_frequency_equation, nu_0)
17
18 # Calculate the magnetic field strength using the
    corrected formula
19 B = sp.Symbol('B')
20 magnetic_field_equation = sp.Eq(2 * sp.pi *
    operating_frequency_solution[0], gamma_H * B)
21 magnetic_field_strength = sp.solve(
    magnetic_field_equation, B)
22
23 # print with units
24 print("Operating frequency: {0:.2e} Hz".format(float(
    operating_frequency_solution[0].evalf()))))
25 print("Magnetic field strength: {0:.2e} T".format(float(
    magnetic_field_strength[0].evalf()))))

```

4. (5 points) Calculate the magnetic field strength required for ^{19}F ($I = 1/2, \gamma_{\text{F}} = 2.516233 \times 10^8 \text{ radians s}^{-1} \text{ T}^{-1}$) and ^{13}C ($I = 1/2, \gamma_{\text{C}} = 6.728286 \times 10^7 \text{ radians s}^{-1} \text{ T}^{-1}$) resonances in a 500MHz spectrometer. I get:

$$B_0^{\text{F}} = 12.5T \quad (25)$$

$$B_0^{\text{C}} = 46.7T \quad (26)$$

```

1 import sympy as sp
2
3 # Constants
4 # Gyromagnetic ratios in radians s^-1 T^-1 for 19F and 13
    C
5 gamma_F = 2.516233 * 10**8 # 19F
6 gamma_C = 6.728286 * 10**7 # 13C
7 nu_0 = 500 * 10**6 # 500 MHz in Hz
8
9 # Calculation for 19F
10 B_F = sp.Symbol('B_F')
11 magnetic_field_equation_F = sp.Eq(2 * sp.pi * nu_0,
    gamma_F * B_F)
12 magnetic_field_strength_F = sp.solve(
    magnetic_field_equation_F, B_F)
13
14 # Calculation for 13C
15 B_C = sp.Symbol('B_C')
16 magnetic_field_equation_C = sp.Eq(2 * sp.pi * nu_0,
    gamma_C * B_C)

```

```

17 magnetic_field_strength_C = sp.solve(
    magnetic_field_equation_C, B_C)
18
19 # print with units
20 print("Magnetic field strength for 19F: {0:.2e} T".format
    (float(magnetic_field_strength_F[0].evalf()))))
21 print("Magnetic field strength for 13C: {0:.2e} T".format
    (float(magnetic_field_strength_C[0].evalf()))))

```

5. (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:

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

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

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

where J_{AA} is the spin-spin coupling constant between the two protons. Using the wavefunctions from problem 5, determine 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?