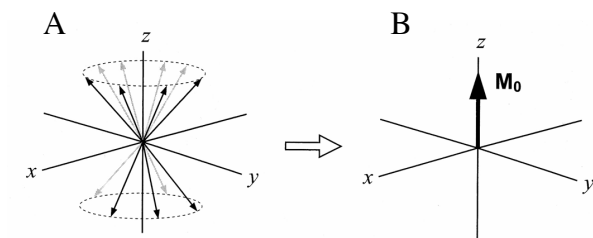


Exam 1: CHEM/BCMB 4190/6190/8189 (142 points) Thursday, 9 September, 2021

1). At thermal equilibrium, the microscopic view of an ensemble of spins in a magnetic field can be illustrated by individual magnetic dipoles precessing about the axis corresponding to the magnetic field (B_0) direction (z-axis), as shown in the figure (panel A). Here M_0 (panel B) represents the macroscopic, bulk, or net magnetization of the nuclear ensemble.



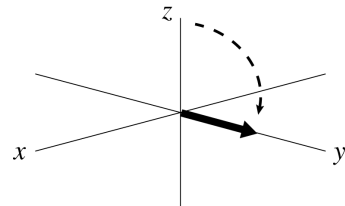
a. Considering only the macroscopic, bulk magnetization vector M_0 (i.e., panel B), draw a figure that shows the end result of application of a 180° electromagnetic pulse to the M_0 vector shown in panel B. (2 points)

b. For spin $\frac{1}{2}$ nuclei, the symbols N_α and N_β are used to represent the numbers of nuclei in the α and β states, respectively.

-Describe quantitatively the relationship between N_α and N_β in panel B above. Include in your description how the relationship between N_α and N_β contributes to M_0 .

-Then, describe in detail the quantitative relationship between N_α and N_β immediately after the 180° pulse is applied (as in your answer to 'a', above). Please do *not* use any equations copied from those at the end of this exam in your answer. (4 points)

c. In the *rotating* frame of reference, if a 90° pulse is applied along the x axis to \mathbf{M}_0 (panel B above), and if the reference frequency is assumed to be equal to the Larmor frequency of the nucleus in question, \mathbf{M}_0 is rotated cleanly into the transverse plane and lies along the y -axis, as shown (right). Because the reference frequency is equal to the Larmor frequency, there is no precession of the \mathbf{M}_0



vector about the z -axis during or after the pulse. Describe the situation in the *laboratory* frame of reference. Assume that initially the bulk magnetization vector is as shown in panel B above. Then, describe both qualitatively and quantitatively the motion of this vector with time during the 90° pulse. Assume the 90° pulse width is $5\ \mu\text{s}$ (microseconds) and that the Larmor frequency is 400 MHz. You will have to perform at least one calculation and show your work to receive credit for the quantitative explanation. **(6 points)**

d. For an ensemble of a particular spin $\frac{1}{2}$ nucleus, explain why simply equalizing the numbers of nuclei in α and β states ($N_\alpha = N_\beta$) is not the same as saturation of a resonance. **(4 points)**

2). You are going to perform a ^1H NMR experiment. You want the 90° pulse width to be $5\ \mu\text{s}$.

a). Please explain how you would experimentally ensure that the 90° pulse width was $5\ \mu\text{s}$. You will have to explain for credit. **(4 points)**

b). If the 90° pulse width is $5\ \mu\text{s}$, what is the 360° pulse width? Estimate the 360° pulse width and explain your rationale for credit. **(2 points)**

3). You record a ^{13}C NMR spectrum of your compound using 2000 scans and find that the signal-to-noise is 10 times higher than you need. In the future, how many scans will you acquire for similar samples in order to decrease the signal-to-noise by a factor of 10? You must do a calculation and show your work for credit. **(4 points)**

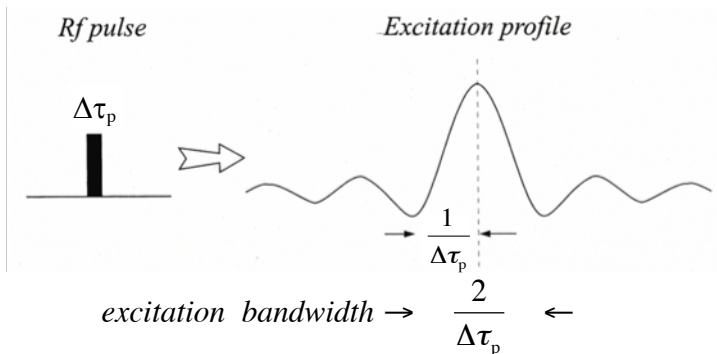
4). For nuclei with non-zero spin (the spin angular momentum quantum number, I , is not zero), in a magnetic field, degenerate (energetically equivalent) nuclear spin states for such nuclei split into nondegenerate (energetically nonequivalent) states called Zeeman levels or Zeeman states.

a. What values for the magnetic quantum number, m , do two nuclei have in common if one has a spin angular momentum quantum number, I , of 3 and the other has a spin angular quantum number of $3/2$? You must explain your answer for credit. **(4 points)**

b. If the spin angular quantum number for a nucleus is 3, what is the value of m for the state with energy $E = \gamma \hbar B_0$? You will have to justify your answer for credit. **(2 points)**

c. In a magnetic field (400 MHz), the energy difference between the lowest and highest energy states for a particular nucleus ($\gamma = 1.00 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$) is $4.956 \times 10^{-26} \text{ J}$. What is the spin angular momentum quantum number, I , for this nucleus? You will have to show your work or otherwise explain your answer for credit. **(6 points)**

5). The excitation profile for a short, high power electromagnetic radio frequency (“*rf*”) pulse is shown. The dashed line represents the frequency at which the *rf* pulse is applied (the carrier or reference frequency). The effective range of frequencies that can be excited extends from the excitation maximum (carrier frequency) to the first minima on either side of the sinc ($\sin x/x$) function that describes the profile. This effective range, or “excitation bandwidth” is therefore $2/\Delta\tau_p$, where $\Delta\tau_p$ is the pulse length.



a. A particular compound shows two signals in a normal ^1H NMR spectrum. These two signals are separated by 1 ppm (400 Hz using a 400 MHz magnet). You would like to selectively excite one of these two signals, without exciting the other, so that the spectrum you obtain would show only one signal. Please explain (with words, no equations) how you would do this. **(4 points)**

b. If the NMR instrument you are using has a 400 MHz magnet, calculate the pulse width of the excitation pulse necessary for the selective ^1H excitation experiment in ‘a’ (note: for a 400 MHz magnet, 1 ppm is 400 Hz). **(6 points)**

c. Calculate the field strength (B_1) of the applied electromagnetic *rf* pulse required to provide a 90° ($\pi/2$ radians) pulse angle for the ^1H pulse in 'b'. **(4 points)**

d. If this pulse were applied at the Larmor frequency of a particular ^{13}C nucleus, calculate what the pulse angle would be for this ^{13}C nucleus? **(4 points)**

e. For an electromagnetic pulse applied for approximately $10\ \mu\text{s}$ (at the Larmor frequency of a particular NMR active nucleus), the pulse angle is 90 degrees ($\pi/2$ radians), and the field strength of the applied electromagnetic pulse (B_1) is 0.0015 Tesla. What is the likely identity of the nucleus? You must do a calculation and justify your answer quantitatively for credit. **(4 points)**

6). a. Using no more than two complete sentences, and no equations or diagrams, explain what is meant by the “Ernst angle” as it applies to NMR spectroscopy. **(4 points)**

b. What is the Ernst angle for a case where the spin-lattice relaxation time is 5 s, the acquisition time is 2 s, and the relaxation delay d_1 is 3 s? You will need to do a calculation, show your work, and calculate and show an answer for credit. **(4 points)**

c. For a certain class of molecules, typical ^1H NMR spectra are acquired with acquisition times (AQ) on the order of $3T_2^*$, which usually allows for nearly complete decay of transverse relaxation between scans. Also, for these molecules, $T_1 \approx T_2$, and for well-shimmed magnets, $T_2^* \approx T_2$. Given these facts, what can you say about the magnitude of the optimal pulse angle for most typical ^1H NMR spectra for these molecules? **(4 points)**

7). Using complete sentences only, and without using any symbols, equations, drawings, etc., explain the concept of “directional quantization” as it relates to NMR spectroscopy. **(6 points)**

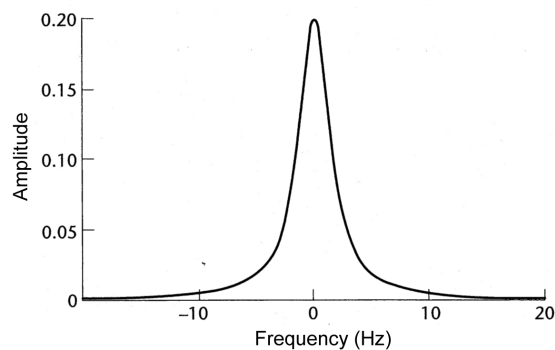
8). At equilibrium, for a given nucleus, the magnitude of the bulk magnetization, aligned along the $+z$ axis (M_z) is equal to M_0 ($M_z = M_0$).

a. Immediately following a 180° pulse, what is the magnitude of M_z in terms of M_0 ? **(4 points)**

b. Following the 180° pulse, how long will it take before $M_z = 0$, assuming $T_1 = 5$ s? You must show your work, do a calculation and calculate a result for credit. **(4 points)**

9). The natural lineshapes of signals in frequency domain NMR spectra are termed Lorentzian, resulting from the Fourier transforms of exponentially decaying signals. This is exemplified by the signal shown (right). The equation describing the lineshape is:

$$\text{amplitude} = \frac{2T_2^*}{1 + 4\pi^2(T_2^*)^2(\nu_L - \nu)^2}$$

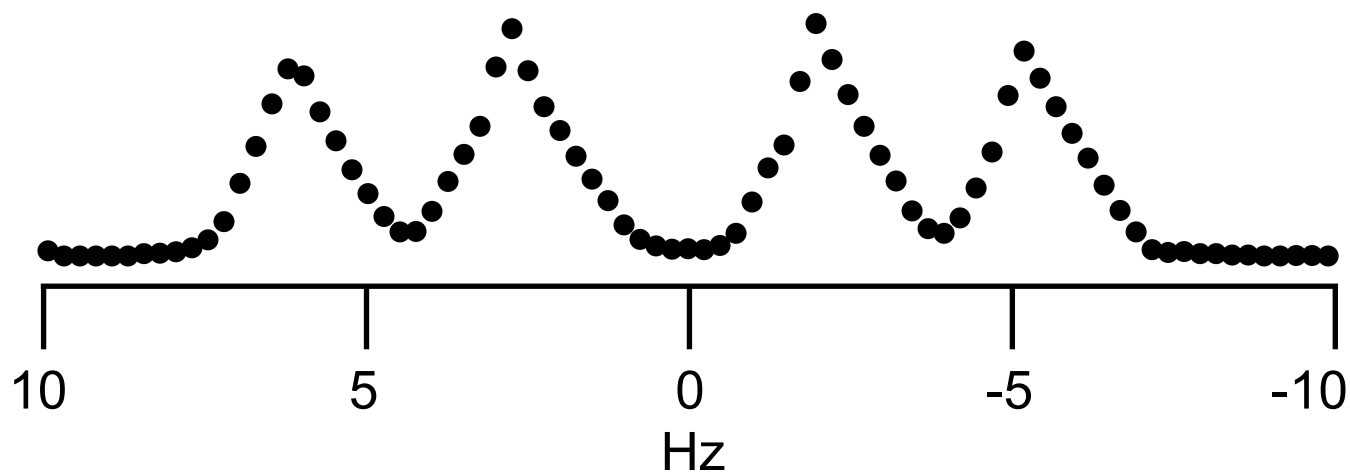


For the signal shown (right), the Larmor frequency is assumed equal to zero ($\nu_L = 0$). The maximum intensity (amplitude) of the signal, which occurs when $\nu = \nu_L = 0$, is 0.2.

a. Calculate the value of the observed transverse relaxation time constant, T_2^* , for this signal. (4 points)

b. Using the equation above, calculate the width of the signal shown above at half its maximum intensity ($\Delta\nu_{1/2}$). (8 points)

10). Shown (below) is an expansion of one signal (split into four peaks) in a ^1H NMR spectrum.

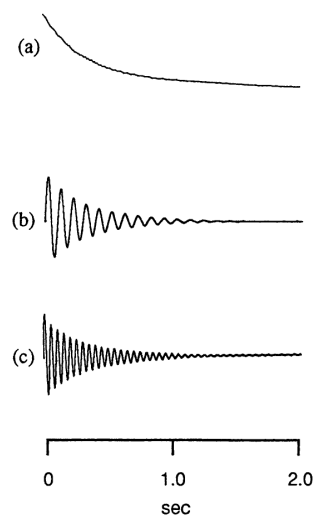


a. Determine the digital resolution of the spectrum shown above. You will have to clearly justify your answer for credit. **(4 points)**

b. What acquisition time was used to record the spectrum? You will have to show your work for credit. **(2 points)**

11). The FIDs for three ^1H NMR spectra of CHCl_3 are shown (right). They were all acquired with the same NMR instrument/magnet, and with identical sweep widths, acquisition times and numbers of points.

a. Why are the frequencies of the signals different. (4 points).



b. Why is there no cosine/sine modulation of the signal in 'a'? (4 points)

12). Two isotopes of a newly discovered element, ^{297}Zz and ^{299}Zz , are both NMR active. The natural abundance of ^{297}Zz is 18%, and the natural abundance of ^{299}Zz is 7%. For ^{297}Zz the spin quantum (I) number is 2. The ratio of the natural NMR sensitivity for ^{297}Zz is approximately 122.5 times larger than the sensitivity of the NMR signal for ^{299}Zz at natural isotopic abundance. The gyromagnetic ratio for ^{297}Zz is five times larger than the gyromagnetic ratio for ^{299}Zz . What is the spin quantum number for ^{299}Zz ? You will have to show your work for credit or otherwise justify your response. **(6 points)**

Name _____

13). Using complete sentences, and no equations, diagrams or symbols, explain in detail what is meant by *longitudinal relaxation* in NMR. A complete answer will address both the microscopic and macroscopic. **(8 points)**

Name _____

14). The spectra shown (right) were both acquired on the same compound. The inset for spectrum 'b' is a magnification of the small signal between the two large ones.

a. Please explain thoroughly the differences between these two spectra and the origins of those differences. **(6 points)**



b. Assuming that the spectrum in 'a' is the correct spectrum, what changes should be made to the acquisition parameters used to acquire spectrum 'b' before re-acquisition such that the resulting spectrum will be the same as the spectrum in 'a'? **(2 points)**

15). Figure 2.11 and its caption from the book “High-Resolution NMR Techniques in Organic Chemistry” are shown (right). The figure shows an NMR signal decaying as a function of time (the FID). The second sentence, “The signal fades as the nuclear spins relax back towards thermal equilibrium”, is true. However, the following sentence can also be true; “The signal can completely fade away without significant relaxation of the nuclear spin populations back to their thermal equilibrium values.” Please explain. **(8 points)**

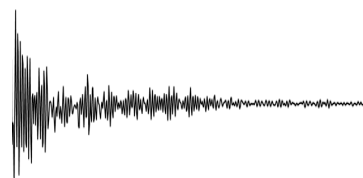


Figure 2.11. The detected NMR response, a Free Induction Decay (FID). The signal fades as the nuclear spins relax back towards thermal equilibrium.

Name _____

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You may find some of the information below useful:

Table 1-1.

Properties of some nuclides of importance in NMR spectroscopy.

Nuclide	Spin I	Electric quadrupole moment ^{a)} [eQ] [10^{-28} m^2]	Natural abundance) [%]	Relative sensitivity ^{b)}	Gyromagnetic ratio $\gamma^a)$ [$10^7 \text{ rad T}^{-1} \text{ s}^{-1}$]	NMR frequency [MHz] ^{b)} ($B_0 = 2.3488 \text{ T}$)
^1H	1/2	—	99.985	1.00	26.7519	100.0
^2H	1	2.87×10^{-3}	0.015	9.65×10^3	4.1066	15.351
$^3\text{H}^c)$	1/2	—	—	1.21	28.5350	106.664
^6Li	1	-6.4×10^{-4}	7.42	8.5×10^{-3}	3.9371	14.716
^{10}B	3	8.5×10^{-2}	19.58	1.99×10^{-2}	2.8747	10.746
^{11}B	3/2	4.1×10^{-2}	80.42	0.17	8.5847	32.084
^{12}C	0	—	98.9	—	—	—
^{13}C	1/2	—	1.108	1.59×10^{-2}	6.7283	25.144
^{14}N	1	1.67×10^{-2}	99.63	1.01×10^{-3}	1.9338	7.224
^{15}N	1/2	—	0.37	1.04×10^{-3}	-2.7126	10.133
^{16}O	0	—	99.96	—	—	—
^{17}O	5/2	-2.6×10^{-2}	0.037	2.91×10^{-2}	-3.6280	13.557
^{19}F	1/2	—	100	0.83	25.1815	94.077
^{23}Na	3/2	0.1	100	9.25×10^{-2}	7.0704	26.451
^{25}Mg	5/2	0.22	10.13	2.67×10^{-3}	-1.6389	6.1195
^{29}Si	1/2	—	4.70	7.84×10^{-3}	-5.3190	19.865
^{31}P	1/2	—	100	6.63×10^{-2}	10.8394	40.481
^{39}K	3/2	5.5×10^{-2}	93.1	5.08×10^{-4}	1.2499	4.667
^{43}Ca	7/2	-5.0×10^{-2}	0.145	6.40×10^{-3}	-1.8028	6.728
^{57}Fe	1/2	—	2.19	3.37×10^{-5}	0.8687	3.231
^{59}Co	7/2	0.42	100	0.28	6.3015	23.614
^{119}Sn	1/2	—	8.58	5.18×10^{-2}	-10.0318	37.272
^{133}Cs	7/2	-3.0×10^{-3}	100	4.74×10^{-2}	3.5339	13.117
^{195}Pt	1/2	—	33.8	9.94×10^{-3}	5.8383	21.499

B_0 (Tesla, T)	Resonance frequencies (MHz)	
	^1H	^{13}C
9.4	400	100.6
11.74	500	125.7
14.09	600	150.9
18.79	800	201.2

$$\gamma_{^1\text{H}} = 26.7519 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{10}\text{B}} = 2.8747 \times 10^7 \text{ rad/T/s}, I = 3$$

$$\gamma_{^{11}\text{B}} = 8.5847 \times 10^7 \text{ rad/T/s}, I = 3/2$$

$$\gamma_{^{13}\text{C}} = 6.7283 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{15}\text{N}} = -2.7126 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{17}\text{O}} = -3.6280 \times 10^7 \text{ rad/T/s}, I = 5/2$$

You may find some of the following information or equations useful:

$$k_B = 1.381 \times 10^{-23} \text{ J/K}$$

$$\text{Avagadro's number} = 6.02214179 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\hbar = h/(2\pi)$$

$$P = \hbar \sqrt{I(I+1)}$$

$$P_z = m\hbar$$

$$\mu = \gamma P = \hbar \gamma \sqrt{I(I+1)}$$

$$\text{for } m = \frac{1}{2}, \cos(\theta) = \frac{m\hbar}{\hbar \sqrt{I(I+1)}} = \frac{m}{\sqrt{I(I+1)}}$$

$$\pi/2 \text{ radians} = 90^\circ$$

$$M_0 = \frac{N\gamma^2 \hbar^2 B_0 I(I+1)}{3k_B T}$$

$$B_2 = \frac{\Delta \nu \sqrt{J^2 - J_r^2}}{J_r} = \frac{J \Delta \nu}{J_r}$$

$$\varepsilon \propto dM/dt = \gamma M_0 B = \frac{N\gamma^3 \hbar^2 B_0^2 I(I+1)}{3k_B T}$$

$$\Delta \nu = \nu_{BS} - \nu_0 = \frac{B_2^2}{2(\Delta B)} = \frac{B_2^2}{2(\nu_0 - \nu_i)}$$

$$S/N \propto NS^{1/2} \text{ (signal-to-noise improves with (number of scans)}^{1/2})$$

$$m = (-I, -I+1, \dots, I-1, I)$$

$$\Theta = \gamma B_1 \tau_p$$

$$E = -\mu_z B_0 = -m\gamma \hbar B_0$$

$$\frac{N_\beta}{N_\alpha} \approx 1 - \left(\frac{\gamma \hbar B_0}{k_B T} \right)$$

$$\Delta E = \mu_z B_0 = \gamma \hbar B_0 = h\nu_L = h\nu_1$$

$$B_{eff} = B_0(1 - \sigma)$$

$$\nu_L = |\gamma/(2\pi)| B_0 = \omega_0/(2\pi)$$

$$\nu_L = \frac{\gamma}{2\pi} (1 - \sigma) B_0$$

$$\omega_0 = \gamma B_0$$

$$\Delta \delta = \frac{\Delta \nu}{\text{observe frequency}} \times 10^6$$

$$SW = 1/(2DW) = \text{Nyquist frequency } (\nu_{NQ})/2$$

$$M_y = M_0 e^{-t/T_2^*}$$

$$AQ = DW * TD$$

$$M_z = M_0 (1 - e^{-t/T_1})$$

$$DR = 2SW/TD = 1/AQ$$

$$M_z = M_0 (1 - 2e^{-t/T_1})$$

$$(TD \equiv NP)$$

$$\Delta \nu_{1/2} = \frac{1}{\pi T_2^*}$$

$$\cos \alpha_{\text{Ernst}} = e^{-((d_1 + AQ)/T_1)}$$

$$\pi/2 \text{ radians} = 90^\circ$$

$$\frac{1}{T_2^*} = \frac{\gamma \Delta B_0}{2} + \frac{1}{T_2} \quad \frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2(B_0)}$$

$$t_{\text{zero}} = T_1 \ln(2)$$

$$1 + \gamma_A/\gamma_X \quad 1 - \gamma_A/\gamma_X$$

$$\eta = \gamma_a / (2\gamma_x)$$

$$\text{multiplicity} = 2nI + 1$$

$$I = (1 + \eta) I_0$$

$$\Theta = 2\pi J \tau$$

$$I \propto 1/r^6$$