Exam 1: CHEM/BCMB 4190/6190/8189 (136 points) Thursday, 8 September, 2022

1). There are two contributors to the NMR relaxation parameter T_2^*. Please identify these contributors and their origins, and how they contribute, microscopically, to relaxation in the transverse plane. (**8 points**)

2). The Larmor frequency for ^1H is 400 MHz in a magnet with a magnetic field strength of 9.4 T. What would be the magnetic field strength of a magnet that would make the Larmor frequency of this nucleus 900 MHz? (**4 points**)

3). For a compound with a single ^{1}H nucleus (i.e. CHCl$_3$), following a 90° ^{1}H pulse along the +*x*-axis, the bulk ^{1}H magnetization vector lies along the *y* axis in the transverse plane, as shown in 'A' below. In the *rotating frame*, after a short time, the bulk magnetization vector has moved to the position shown in 'B', and after an additional short time has moved to the position shown in 'C'. The magnitude of the *y* component of the bulk magnetization vector, **M**$_y$, as a function of time in the rotating frame (i.e. the FID), is plotted below (below, right). The decay in amplitude due to relaxation is ignored.
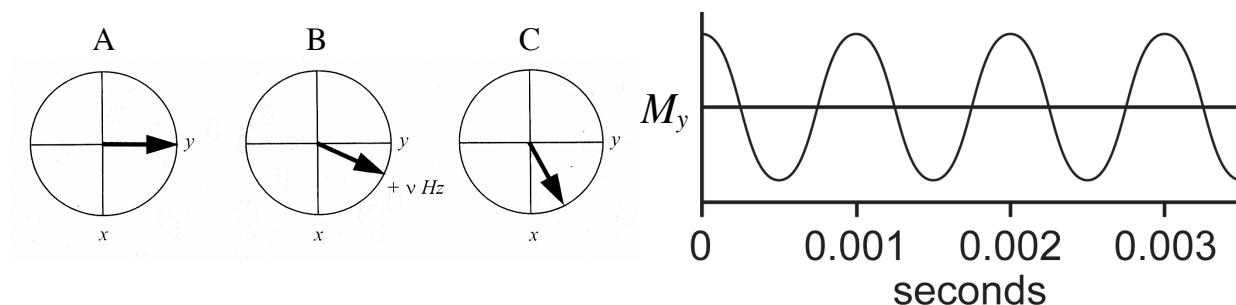

a. What is the frequency in the rotating frame for this ^{1}H nucleus? You must do a calculation and get an answer for credit. (**4 points**)

b. The rotating frame frequency for a nucleus is determined from other frequencies. Please state what these are and exactly how the rotating frequency is calculated? (**4 points**)

c. The figure (above, right) shows the magnitude of **M**$_y$ for this nucleus plotted as a function of time. On the same graph, plot **M**$_x$ for this nucleus versus time. (**4 points**)

4). Shown (right) is the time-domain ^1H NMR data acquired for a particular compound that has only a single ^1H nucleus (for instance, $CHCl_3$).
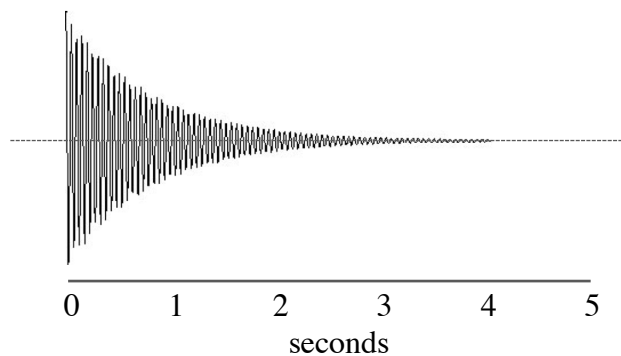
a. Estimate T_2 for this ^1H nucleus. For credit, you must do a calculation, get an answer, and your rationale must be clear. You must clearly describe any assumptions or approximations you make. (**6 points**)

b. What is T_1 for this ^1H nucleus? Please explain for credit. (**6 points**)

5). For a sample containing a molecule with a single ^1H nucleus (i.e. $CHCl_3$), you are given a finite, limited amount of time to acquire a one-dimensional ^1H NMR spectrum of the sample.

$$d_1 \qquad AQ$$
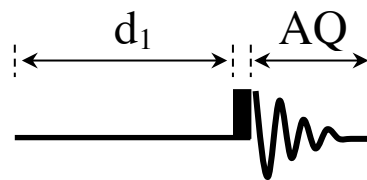
a. You have only about 1 minute to acquire data, and you decide to set d_1 to 1 second. What should the pulse angle be to give maximum signal-to-noise. Assume the acquisition time (AQ) is 2 s, the T_1 for the ^1H nucleus is 5 s, and the width of the pulse is only a few microseconds. (**4 points**)

b. 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 typical small and medium sized organic 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 typical organic molecules? (**4 points**)

6). Explain why, for an ensemble of spin ½ nuclei at thermal equilibrium, there is a net, bulk, macroscopic magnetization vector (M_0) along the *z*-axis, and in the *+z* direction, but there is no net macroscopic magnetization along either the *x*-axis, the *y*-axis, or anywhere in the *x-y* plane. (**8 points**)

7). The thermodynamics of T_1 and T_2^* processes are much different. One of these process is purely entropic and the other is purely enthalpic. Please explain which is which and why. (**8 points**)

8). For an electromagnetic pulse applied for 10 μs (at the Larmor frequency for a particular ^{1}H nucleus), the pulse angle is 90 degrees ($\pi/2$ radians). Calculate the strength (in Tesla) of this pulse? (**6 points**)

9). Define "Larmor frequency" as it applies to NMR. Use complete sentences and no symbols, equations or drawings. (**4 points**)

10). You record an ^{13}C NMR spectrum of your compound using 1000 scans. You realize that you need to improve the sensitivity (signal-to-noise) by 4-fold. How many scans will be required to record a spectrum with 4 times the signal-to-noise? **(4 points)**

11). For nuclei that possess a magnetic moment, discrete energy levels (Zeeman levels/states) are occupied in the presence of a magnetic field.

a. What is the value of the spin angular momentum quantum number, **I**, for a particular nucleus that has six Zeeman levels? For full credit you will have to explain your reasoning. **(4 points)**

b. If the magnetic quantum number, **m**, for one of the Zeeman energy levels for a particular nucleus is -2, what is the energy of this Zeeman energy level. **(2 points)**

c. If the magnetic quantum number, **m**, for one of the Zeeman energy levels for a particular nucleus is -2, what is the spin angular momentum quantum number for this nucleus? Please explain. **(4 points)**

12). A simple pulse sequence for collecting a 1D NMR spectrum is shown (right). Following a delay (d₁), a 90° pulse is applied along the *x*-axis. After the pulse, the data are acquired for a time (indicated by the decaying sinusoidal line) and stored in the computer. The data consist of amplitude of the acquired signal as a function of time. As a function of time following the pulse, the amplitude of the signal decays until it reaches zero amplitude, or nearly zero (what's left is noise).

$90°$x

d_1 FID
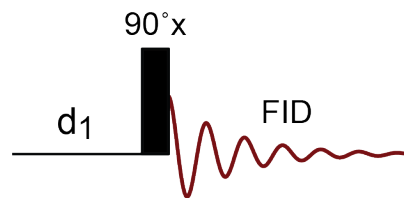
a). In the course notes, it states that the oscillating signal decays as a function of time, "as the phase coherence between the precessing magnetic dipoles (vectors) is lost". Please explain what is meant by the time-dependent loss of phase coherence between the precessing magnetic dipoles. (**6 points**)

b). Following the pulse, what else changes (besides the distribution of the vectors about the *z*-axis? Then, what happens as a function of time? (**6 points**)

13). If we directly compare ^{1}H spins and ^{2}H spins:

a. Calculate the ratio of the bulk/macroscopic magnetization ($M_{0\ 1H}/M_{0\ 2H}$) produced for equal numbers of ^{1}H and ^{2}H nuclei? **(6 points)**

b. Calculate how the sensitivities of the NMR signals compare for ^{1}H and ^{2}H spins? **(6 points)**

c. Fill in the blank: ^{2}H, ^{10}B, ^{11}B, ^{25}Mg, and ^{133}Cs are collectively referred to as _____ nuclei by NMR spectroscopists. **(2 points)**

14). For a sample of $CHCl_3$, you apply a very long (seconds), low power pulse at the ^1H frequency of the single ^1H nucleus in the molecule. Immediately after this pulse, you apply a normal, high power 90° pulse at the same frequency and then record the FID. Sketch what you would expect the FID to look like. Also, sketch the spectrum you would expect to observe following Fourier transformation of the FID. You must thoroughly explain your answers for credit. (**6 points**).

15). You acquired a ^1H NMR spectrum of your sample. The spectral width (SW) was 6000.00 Hz. The acquisition time (AQ) was 2.0 seconds.

a. When the FID was digitized, how many points were collected/sampled? (**4 points**)

b. If more points had been sampled, would the digital resolution improve or worsen. You will have to explain your answer for credit. (**4 points**)

16). In NMR, for an experiment using a single pulse (i.e. a 'one scan' experiment), the maximum signal-to-noise is obtained if the pulse is a 90° pulse.

a. Explain why a 90° pulse gives the maximum signal-to-noise for a one scan experiment. (**6 points**)

b. Explain why it is often advantages to use shorter pulses (i.e., pulses shorter than 90°) if the amount of time available to perform an NMR experiment is limited. (**6 points**)

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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 γ[a] $[10^7\ rad\ T^{-1}\ s^{-1}]$	NMR frequency [MHz][b] ($B_0 = 2.3488$ 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
^3H[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

$\gamma_{1H} = 26.7519 \times 10^7$ rad/T/s, $I = 1/2$ $\gamma_{13C} = 6.7283 \times 10^7$ rad/T/s, $I = 1/2$

$\gamma_{10B} = 2.8747 \times 10^7$ rad/T/s, $I = 3$ $\gamma_{15N} = -2.7126 \times 10^7$ rad/T/s, $I = 1/2$

$\gamma_{11B} = 8.5847 \times 10^7$ rad/T/s, $I = 3/2$ $\gamma_{17O} = -3.6280 \times 10^7$ rad/T/s, $I = 5/2$

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

$k_B = 1.381 \times 10^{-23}$ J/K $\qquad$ Avagadro's number $= 6.02214179 \times 10^{23}$ mol^{-1}

$h = 6.626 \times 10^{-34}$ Js $\qquad \hbar = h/(2\pi)$

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

$\mu = \gamma P = \hbar\gamma\sqrt{I(I+1)} \qquad$ for $m = \frac{1}{2}, \cos(\theta) = \frac{m\hbar}{\hbar\sqrt{I(I+1)}} = \frac{m}{\sqrt{I(I+1)}}$

$\pi/2$ radians $= 90°$

$$M_0 = \frac{N\gamma^2\hbar^2 B_0 I(I+1)}{3k_B T} \qquad\qquad B_2 = \frac{\Delta v\sqrt{J^2-J_r^2}}{Jr} = \frac{J\Delta v}{Jr}$$

$$\varepsilon \propto dM/dt = \gamma M_0 B = \frac{N\gamma^3\hbar^2 B_0^2 I(I+1)}{3k_B T} \qquad \Delta v = v_{BS} - v_0 = \frac{B_2^2}{2(\Delta B)} = \frac{B_2^2}{2(v_0-v_i)}$$

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

$m = (-I, -I+1, -I+2,\ldots, I) \qquad (2I+1)$

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

$\Delta E = \mu_z B_0 = \gamma\hbar B_0 = h v_L = h v_1$

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

$\omega_0 = \gamma B_0$

$\Delta\delta = \dfrac{\Delta v}{\text{observe frequency}} \times 10^6$

$M_y = M_0 e^{-t/T_2^*}$
$M_z = M_0(1 - e^{-t/T_1})$
$M_z = M_0(1 - 2e^{-t/T_1})$

$\Delta v_{1/2} = \dfrac{1}{\pi T_2^*}$

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

$t_{zero} = T_1\ln(2)$
$\eta = \gamma_a/(2\gamma_x)$
$I = (1 + \eta)I_0$
$I \propto 1/r^6$

$\Theta = \gamma B_1 \tau_p$

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

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

$v_L = \dfrac{\gamma}{2\pi}(1-\sigma)B_0$

SW$=1/(2$DW$)=$Nyquist frequency $(v_{NQ})/2$
AQ$=$DW$*$TD
DR$=2$SW/TD$=1/$AQ
(TD$\equiv$NP)

$\cos\alpha_{Ernst} = e^{-((d_1 + AQ)/T_1)}$
$\pi/2$ radians $= 90°$

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

multiplicity$=2nI + 1$
$\Theta=2\pi J\tau$