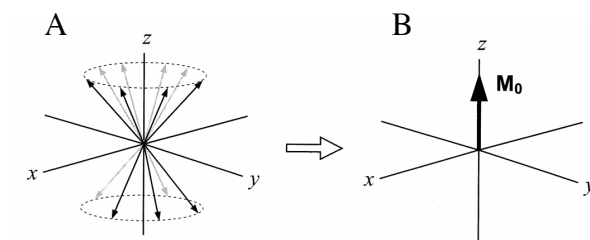
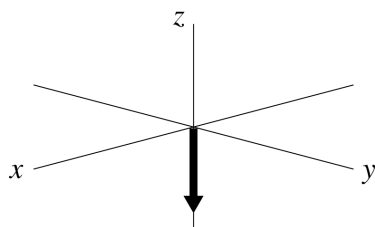


Exam 1: CHEM/BCMB 4190/6190/8189 (142 points) Thursday, 9 September, 2021

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)



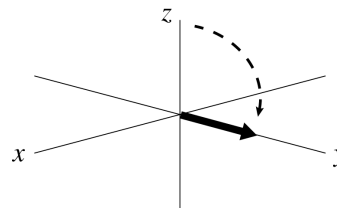
b. For spin $\frac{1}{2}$ nuclei, the symbols N_α and N_β are used to represent the numbers of nuclei in the α and β states, respectively.

-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 .

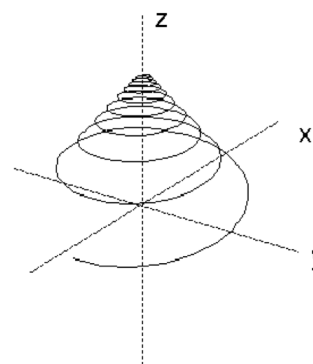
-Then, describe in detail the quantitative relationship between N_α and N_β immediately after the 180° pulse is applied (as in your answer to 'a', above). Please do *not* use any equations copied from those at the end of this exam in your answer. (4 points)

N_α and N_β represent the numbers of nuclei in the α and β states, and, therefore, represent the numbers of individual nuclear magnetic dipoles shown in panel 'A' above (α states are represented by nuclear dipoles pointed 'up' or along $+z$, and β states are represented by nuclear dipoles pointed 'down' or along $-z$). These individual magnetic dipoles are summed to give M_0 , thus, the relative values of N_α and N_β govern the magnitude of M_0 . After the 180° pulse, the values of N_α and N_β are exchanged relative to their equilibrium values, and the magnitude of the bulk magnetization vector along $-z$ after the pulse is essentially identical to its magnitude along $+z$ before the pulse.

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)**



Once the pulse begins, the bulk vector is moved away from the z -axis and precesses about z at its Larmor frequency. During the pulse, the vector continues to precess about z and it bends towards the transverse plane. After $5\ \mu\text{s}$, the entire vector is in the transverse plane, and continues to precess about z (and relax back to the initial state). At a Larmor frequency of 400 MHz, the vector will rotate about the z -axis 2000 times during the $5\ \mu\text{s}$ pulse (400,000,000 per second; 400 per μs ; 2000 in $5\ \mu\text{s}$). If we follow the tip of the vector during the pulse, it will sketch one-half of a hollow sphere with the flat side defining the transverse plane.



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)**

Saturation implies both equalizing the numbers of nuclei in α and β states AND randomization of the individual nuclear magnetic dipoles about the z -axis. A very long pulse applied, for instance, at the Larmor frequency of a particular spin $\frac{1}{2}$ nucleus, equalizes the numbers of ^1H nuclei in α and β states ($N_\alpha = N_\beta$) but does NOT create any phase coherence. In such a case, the individual magnetic dipoles of the nuclei are randomly distributed about the z -axis, and no net macroscopic magnetization exists either along z or in the transverse plane. The numbers of nuclei in α and β states can be equalized in other ways. For instance, if a 90° pulse is applied to the system at equilibrium, this will promote equalization of numbers of nuclei in α and β states, but will also create phase coherence so that a net macroscopic magnetization vector can be detected in the transverse plane.

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)**

We know that a 90° ($\pi/2$ radians) pulse gives the maximum signal amplitude. We also know that the pulse angle (Θ , in radians) is related to the gyromagnetic ratio (γ), the pulse length (τ_p) and the applied electromagnetic field strength (B_1 , or pulse amplitude) as shown:

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

Thus, in order to ensure that τ_p is $5\ \mu\text{s}$, the magnitude of the applied electromagnetic field strength (the pulse amplitude, B_1), must be adjusted to give a maximum signal with τ_p held constant at $5\ \mu\text{s}$. Typically, experimentally the value of τ_p is held constant at $5\ \mu\text{s}$, and the B_1 adjusted to a very small value such that a very small signal results. The value of B_1 is then systematically increased until the maximum signal is attained. This value of B_1 , that gives the maximum signal, is then the value that gives a 90° pulse when τ_p adjusted to $5\ \mu\text{s}$.

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)**

The 360° pulse width will be approximately four times the 90° pulse width, or approximately $20\ \mu\text{s}$.

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)**

Signal-to-noise (S/N) increases as the square root of the number of scans ($S/N \propto N^{1/2}$). In order to decrease S/N by $10\times$, you would have to acquire 10^2 or $100\times$ fewer scans. Because 2000 scans were used initially, $2000/100=20$ scans could be used next time for a $10\times$ S/N decrease.

$$\frac{10}{1} = \frac{\sqrt{2000}}{\sqrt{x}} \quad \sqrt{x} = \frac{\sqrt{2000}}{10} \quad x = \left(\frac{\sqrt{2000}}{10} \right)^2 = \frac{2000}{100} = 20$$

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)**

None. Magnetic quantum numbers range from I to $-I$ in increments of 1 ($I, I-1, I-2, \dots, -I$). So, values of m for nuclei with integral spin quantum numbers are integral (for $I=3$, they are 3, 2, 1, 0, -1, -2, -3) and values of m for nuclei with half-integral spin quantum numbers are half-integral (for $I=3/2$, they are $3/2, 1/2, -1/2, -3/2$).

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)**

In general, the energy, E , is described by the following equation:

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

If $m = -1$, then:

$$E = \gamma\hbar B_0$$

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)**

The energy between any two adjacent energy levels is:

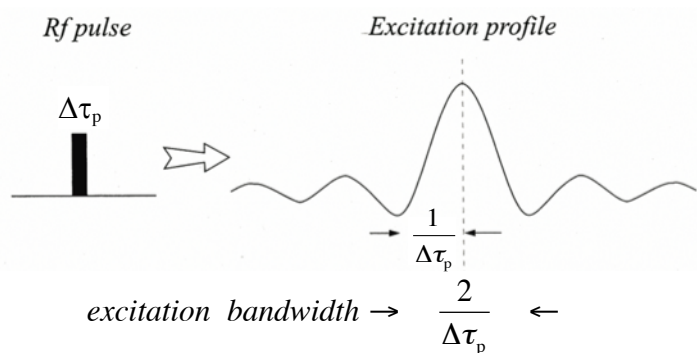
$$E = \gamma\hbar B_0$$

There are $(2I+1)$ levels, ranging from I to $-I$ ($I, I-1, I-2, \dots, -I$). So, the highest and lowest values of I are separated by $2I$ ($I - (-I) = 2I$). So, the energy between the highest and lowest energy levels is then:

$$E = (2I)\gamma\hbar B_0$$

$$E = (2I)\gamma\hbar B_0 \quad I = \frac{E}{2\gamma\hbar B_0} = \frac{4.956 \times 10^{-26} \text{ J}}{1.00 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1} \frac{6.626 \times 10^{-34} \text{ J s}}{\pi} 9.4 \text{ T}} = 2.5 = 5/2$$

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)**

The excitation profile is dependent on the width of the rf pulse (τ_p), as described in the figure above, with an excitation maximum at the carrier frequency and a minimum at a distance of $1/\Delta\tau_p$ from the carrier. Thus, in order to selectively excite only one of the signals, the carrier can be placed at the Larmor frequency of one and the pulse width adjusted such that the first excitation minimum occurs 1 ppm away, which is at the Larmor frequency of the other.

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)**

With a 400 MHz magnet, 1 ppm is equal to 400 Hz:

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

$$\Delta\nu = \frac{\Delta\delta \times \text{spectrometer frequency}}{10^6} = \frac{1 \times 400,000,000 \text{ Hz}}{10^6} = 400 \text{ Hz}$$

The pulse width, τ_p , is then adjusted so that $1/\tau_p = 400 \text{ Hz}$:

$$\frac{1}{\tau_p} = 400 \text{ Hz} \quad \tau_p = \frac{1}{400 \text{ Hz}} = 0.0025 \text{ s} = 2.5 \text{ ms}$$

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)**

The pulse angle (Θ , in radians) is related to the gyromagnetic ratio (γ), the pulse length (τ_p) and the applied electromagnetic field strength (B_1) as shown:

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

Thus, the field strength necessary to produce a 90° , 2.5 ms pulse is:

$$B_1 = \frac{\Theta}{\gamma \tau_p} = \frac{\frac{\pi}{2} \text{ rad}}{26.7519 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1} \times 0.0025 \text{ s}} = 2.35 \times 10^{-6} \text{ T}$$

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)**

As shown above, the pulse angle is dependent on the gyromagnetic ratio of the nucleus.

$$\frac{\Theta_{1\text{H}}}{\Theta_{^{13}\text{C}}} = \frac{\gamma_{1\text{H}} B_1 \tau_p}{\gamma_{^{13}\text{C}} B_1 \tau_p} = \frac{\gamma_{1\text{H}}}{\gamma_{^{13}\text{C}}} = \frac{26.7519 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}}{6.7283 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}} \approx \frac{4}{1}$$

So, compared to ^1H , the pulse angle for ^{13}C will be about 4 times smaller (about 22°).

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)**

Given the relationship between the pulse angle (Θ , in radians), the gyromagnetic ratio (γ), the pulse length (τ_p) and the applied electromagnetic field strength (B_1) described above in 'c', the gyromagnetic ratio of the nucleus that would respond to the pulse indicated above in the manner described is:

$$\gamma = \frac{\Theta}{B_1 \tau_p} = \frac{\frac{\pi}{2} \text{ rad}}{0.0015 \text{ T} \times 10 \times 10^{-6} \text{ s}} = 10.47 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$$

According to the table at the end of the exam, this could correspond to either ^{31}P or perhaps ^{119}Sn .

- 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)

In an NMR experiment where multiple scans are collected and averaged, the pulse angle that gives maximum signal-to-noise in a given amount of time is called the Ernst angle.

- 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)

$$\cos \alpha_{\text{Ernst}} = e^{-((d_1 + AQ)/T_1)} = e^{-((3+2)/5)} = e^{-1} = 0.367879 \quad \alpha_{\text{Ernst}} = 68.4^\circ$$

- 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)

The above facts, therefore, argue that typical acquisition times are $3T_1$. Thus, $d_1 + AQ$ is at least $3T_1$. According to Ernst, therefore,

$$\cos \alpha_{\text{Ernst}} = e^{-((d_1 + AQ)/T_1)} \quad \alpha_{\text{Ernst}} = \cos^{-1}[e^{-((d_1 + AQ)/T_1)}] \quad \alpha_{\text{Ernst}} > \cos^{-1}[e^{-(3)}] = 87^\circ$$

This suggests that the optimal pulse angle for most of these types of experiments is nearly 90° . This is the expected result. In this case, because $T_1 \approx T_2$, when the signal has decayed due to T_2 relaxation, the equilibrium populations of spin states (N_α and N_β for spin $1/2$) have also returned to their equilibrium values (T_1). So, after $3T_2^$, T_1 relaxation is also complete, so 90° pulses can be used and will give maximum signal-to-noise.*

- 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)**

Directional quantization refers to the behavior of a nucleus in a magnetic field. For a nucleus with a nuclear magnetic moment (spin quantum number not equal to zero), in a magnetic field the angular momentum vector or magnetic dipole vector of the nucleus will orient in a particular direction. Its z component (aligned along the direction of the field) will be an integral or half-integral multiple of a constant, with the number of orientations determined by the spin quantum number. Thus, rather than a continuum of orientations, the number of orientations and direction of the orientation are quantized.

- 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)**

The 180° pulse inverts the bulk magnetization vector to the -z axis. So, immediately after the pulse (no significant relaxation has occurred), $M_z = -M_0$. Or, formally, we assume that the relaxation process is first order:

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

The “2” reflects the fact that the equilibrium magnetization was inverted (+z to -z axis) before the return to equilibrium was begun. When $t = 0$ (immediately following the 180° pulse):

$$M_z = M_0(1 - 2e^{-t/T_1}) = M_0(1 - 2e^{-0}) = M_0(1 - 2) = -M_0$$

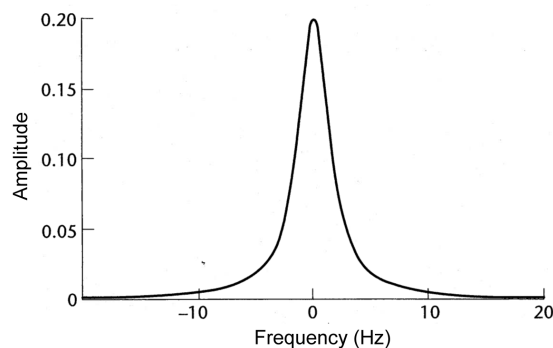
- b. Following the 180° pulse, how long will it take before $M_z = 0$, assuming $T_1 = 5$ s? You must show your work, do a calculation and calculate a result for credit. **(4 points)**

$$M_z = M_0(1 - 2e^{-t/T_1}) \quad 0 = M_0(1 - 2e^{-t/T_1}) = M_0 - M_0 2e^{-t/T_1} \quad M_0 = M_0 2e^{-t/T_1}$$

$$\frac{1}{2} = e^{-t/T_1} \quad \ln\left(\frac{1}{2}\right) = -t / T_1 \quad t = T_1 \ln(2) = 5 \times (0.693) = 3.47 \text{ s}$$

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)

At zero frequency ($\nu = 0$) the amplitude is equal to 0.2, and $\nu_L - \nu = 0$. Thus:

$$0.2 = \frac{2T_2^*}{1 + 4\pi^2(T_2^*)^2(0 - 0)^2} = 2T_2^* \quad T_2^* = 0.1 \text{ s}$$

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

The maximum intensity of the signal is 0.2, thus half the maximum is 0.1. Because we know the value of T_2^ (part 'a'), we can calculate the frequency when the intensity is equal to 0.1:*

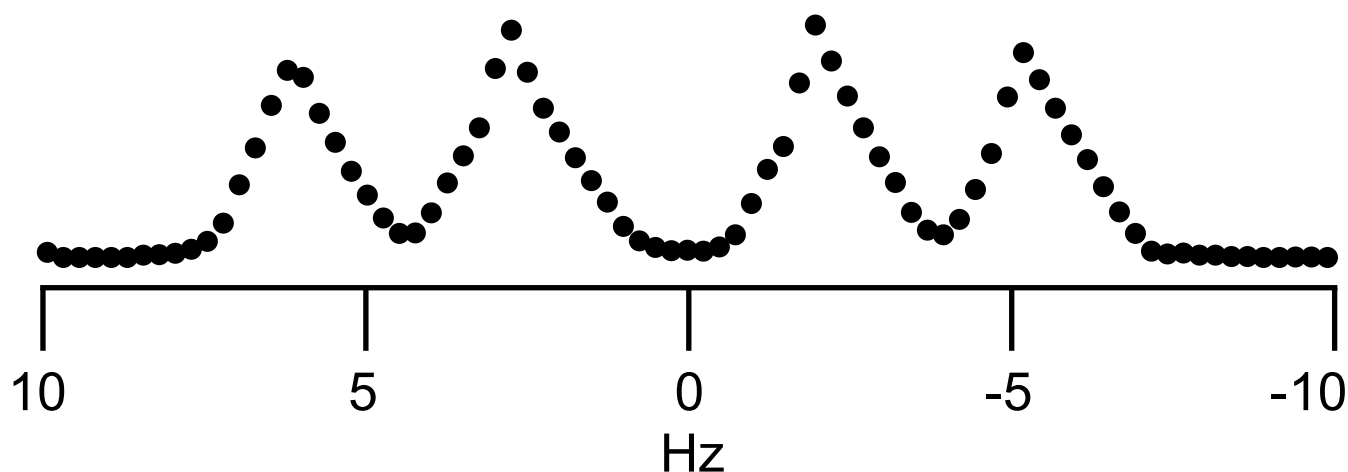
$$0.1 = \frac{2T_2^*}{1 + 4\pi^2(T_2^*)^2(\nu_L - \nu)^2} = \frac{2 \times 0.1}{1 + 4\pi^2(0.1)^2(0 - \nu)^2} = \frac{0.2}{1 + 0.394784(0 - \nu)^2}$$

$$0.1 = \frac{0.2}{1 + 0.394784(-\nu)^2} \quad 1 + 0.394784(-\nu)^2 = \frac{0.2}{0.1} = 2 \quad (-\nu)^2 = \frac{1}{0.394784}$$

$$\nu = \pm \sqrt{\frac{1}{0.394784}} \quad \nu = \pm 1.59 \text{ Hz}$$

*This frequency represents the difference from zero. So, the **width** of the signal (at half-height, $\Delta\nu_{1/2}$), is then twice this frequency difference ($1.59 \times 2 = 3.18$).*

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)**

Digital resolution is Hz per data point, or Hz/pt. There are approximately 80 points that describe the 20 Hz region. Therefore, the digital resolution is $20/80$ or 0.25 Hz/pt .

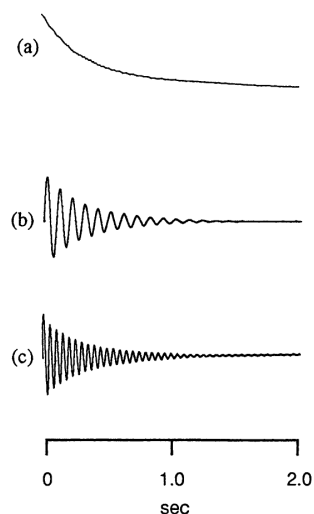
b. What acquisition time was used to record the spectrum? You will have to show your work for credit. **(2 points)**

Acquisition time is the inverse of digital resolution. Therefore, the acquisition time is 4 s.

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).

The frequencies of the signals in NMR spectra are differences from a reference (carrier) frequency. Thus, the carrier frequency was different for each spectrum.



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

This signal was acquired with the carrier frequency exactly the same as the Larmor frequency. Thus, the frequency difference is zero, so the apparent frequency is zero.

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)**

Sensitivity is proportional to the electromotive force (ε) induced in the receiver coil by the bulk magnetic moment. The magnitude of ε is proportional to the rate of change in the magnetic moment ($\varepsilon \propto dM/dt = \gamma M_0 B_0$).

$$\frac{\varepsilon_{297\text{Zz}}}{\varepsilon_{299\text{Zz}}} = \frac{\frac{N_{297\text{Zz}} \gamma_{297\text{Zz}}^3 \hbar^2 B_0^2 I_{297\text{Zz}} (I_{297\text{Zz}} + 1)}{3k_B T}}{\frac{N_{299\text{Zz}} \gamma_{299\text{Zz}}^3 \hbar^2 B_0^2 I_{299\text{Zz}} (I_{299\text{Zz}} + 1)}{3k_B T}} = \frac{N_{297\text{Zz}} \gamma_{297\text{Zz}}^3 I_{297\text{Zz}} (I_{297\text{Zz}} + 1)}{N_{299\text{Zz}} \gamma_{299\text{Zz}}^3 I_{299\text{Zz}} (I_{299\text{Zz}} + 1)}$$

$$122.5 \approx \frac{18 \times 5^3 \times 2(2+1)}{7 \times 1^3 \times I_{299\text{Zz}} (I_{299\text{Zz}} + 1)} \quad I_{299\text{Zz}} (I_{299\text{Zz}} + 1) = \frac{18 \times 5^3 \times 2(2+1)}{7 \times 1^3 \times 122.5}$$

$$I_{299\text{Zz}} (I_{299\text{Zz}} + 1) \approx \frac{18 \times 5^3 \times 2(2+1)}{7 \times 1^3 \times 122.5} = 15.74 \quad \frac{7}{2} \left(\frac{7}{2} + 1 \right) = 15.75$$

The spin quantum number is therefore 7/2.

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)**

For a given nuclear ensemble at thermal equilibrium in a static magnetic field, the nuclear dipoles (magnetic moments) that define the ensemble for a particular nucleus ($I \neq 0$, and we will assume $I = 1/2$) are oriented at a defined angle with respect to the static magnetic field, so that the longitudinal (+z and -z) components are known. For spin $1/2$ nuclei, a slight excess of dipoles aligned with the magnetic field (+z) produces a bulk, or net, macroscopic magnetization vector oriented along +z. The individual dipoles are, however, distributed randomly about the longitudinal (+z or -z) axes, so that there is no net magnetization in any particular direction in the x-y (transverse) plane. An electromagnetic pulse creates a torque on the macroscopic magnetization vector, tilting it towards the transverse (x-y) plane, and producing a finite macroscopic magnetization in the x-y plane (transverse magnetization). Microscopically, the populations of nuclei aligned with (α states for spin $1/2$ nuclei) and against (β states) the static magnetic field are perturbed relative to the equilibrium populations by absorption of energy from the pulse. In order to return to thermal equilibrium, the system must lose energy, which leads to re-establishment of the equilibrium populations of α and β states, and re-establishment of the bulk magnetization along the longitudinal axis in the +z direction. This return to thermal equilibrium via enthalpic processes that release absorbed energy from the ensemble of spins to the surroundings, and that promotes recovery of magnetization that re-establishes longitudinal components, is called longitudinal relaxation.

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)



The spectrum in 'a' was collected with a proper spectral width (SW), where the spectral window included all of the signals. Stated another way, the sampling frequency was fast enough so that the largest frequency differences between signals could be observed. All signals appear in the spectrum with the same phase and at the correct frequencies.

The spectrum in 'b' was collected with a spectral width set inappropriately so that the rightmost signal in 'a' is folded or aliased in spectrum 'b', with an apparent frequency between that of the other two signals. This aliased/folded signal is also out of phase with respect to the other signals. Stated another way, the sampling frequency was not fast enough to properly digitize a signal corresponding to the largest frequency difference in the spectrum.

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)

Increase the spectral width (SW).

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)

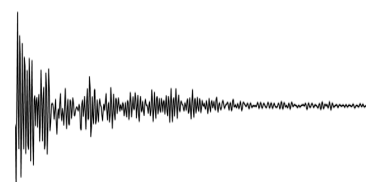


Figure 2.11. The detected NMR response, a Free Induction Decay (FID). The signal fades as the nuclear spins relax back towards thermal equilibrium.

Following a pulse, the populations of nuclei in the various spin states (for instance, α and β spin states for spin $\frac{1}{2}$ nuclei) are perturbed from their equilibrium values and phase coherence is established between individual spins (the individual nuclear dipole vectors are no longer randomly oriented about the B_0 field, $+z$, axis). These produce a bulk magnetization vector component in the transverse plane. The amplitude of the observed signal is dependent on the magnitude of this vector component. As “the nuclear spins relax back towards thermal equilibrium” (i.e. as T_1 relaxation occurs), the equilibrium spin populations are re-established, leading to a smaller component of the bulk magnetization in the transverse plane and a smaller signal (“the signal fades”). However, if T_2 relaxation is very fast (T_2^ is short) compared to T_1 relaxation (if $T_2^* \ll T_1$) then phase coherence is lost very quickly, meaning the individual nuclear dipoles become randomly oriented about $+z$ and there is no bulk magnetization in the transverse plane. Because the amplitude of the signal is dependent on the magnitude of the bulk magnetization vector in the transverse plane, there will be no signal remaining (“the signal can completely fade away”) before there is significant T_1 relaxation (the T_1 time period is long, i.e. before there is “significant relaxation of the nuclear spins back towards thermal equilibrium”, or before the populations of α and β spin states return to their equilibrium values). Another way of stating this is that T_2 relaxation can be faster (and even much faster) than T_1 relaxation, but T_1 relaxation cannot be faster than T_2 relaxation (i.e. $T_1 \geq T_2$)*

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:

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

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

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

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

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

$$P_z = m\hbar$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\omega_0 = \gamma B_0$$

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

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

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

$$AQ = DW * TD$$

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

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

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

$$(TD \equiv NP)$$

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

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

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

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

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

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

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

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

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

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

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