

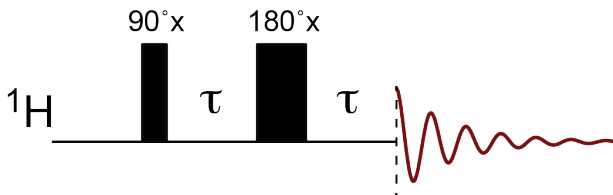
**Midterm Exam: CHEM/BCMB 8190 (112 points) Friday, 28 February, 2020**

**INSTRUCTIONS:** You will have 90 minutes to work on this exam. You can use any notes or books that you bring with you to assist you in answering the questions. You cannot leave the examination room to retrieve additional notes or books. You can use a computer for the purpose of accessing course notes that you have downloaded, or books that you have downloaded. You can only access the internet to access our course website or course textbooks. You must have a handheld calculator.

**Please write your answers on this exam in the space provided.** Make certain to write your name on the exam. Please do not detach any pages from the exam (leave it stapled and intact). *If a question asks for a calculation, simply 'setting up' the calculation or writing down an equation is not adequate. You must complete the calculation for credit.* There is a table at the end of the exam with information you may find useful.

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1) Assume you have a  $^1\text{H}$ - $^1\text{H}$  AX spin system. Consider the spin-echo pulse sequence shown (right).



a) Using product operators, demonstrate the effect of the sequence on homonuclear coupling (AX, i.e. first order). You can ignore chemical shift evolution (the spin echo refocuses chemical shift evolution). You must show your work for credit. You must explain the results you get from the product operators and what they mean. **(10 points)**

$$I_{1z} + I_{2z} \xrightarrow{\pi/2 I_{1x} \pi/2 I_{2x}} -I_{1y} - I_{2y}$$

$$\xrightarrow{2\pi J_{1,2} I_{1z} I_{2z} \tau} -I_{1y} \cos(\pi J_{1,2} \tau) + 2I_{1x} I_{2z} \sin(\pi J_{1,2} \tau) - I_{2y} \cos(\pi J_{1,2} \tau) + 2I_{1z} I_{2x} \sin(\pi J_{1,2} \tau)$$

$$\xrightarrow{\pi I_{1x} \pi I_{2x}} I_{1y} \cos(\pi J_{1,2} \tau) - 2I_{1x} I_{2z} \sin(\pi J_{1,2} \tau) + I_{2y} \cos(\pi J_{1,2} \tau) - 2I_{1z} I_{2x} \sin(\pi J_{1,2} \tau)$$

$$\xrightarrow{2\pi J_{1,2} I_{1z} I_{2z} \tau} I_{1y} \cos^2(\pi J_{1,2} \tau) - 2I_{1x} I_{2z} \cos(\pi J_{1,2} \tau) \sin(\pi J_{1,2} \tau)$$

$$- 2I_{1x} I_{2z} \cos(\pi J_{1,2} \tau) \sin(\pi J_{1,2} \tau) - I_{1y} \sin^2(\pi J_{1,2} \tau)$$

$$+ I_{2y} \cos^2(\pi J_{1,2} \tau) - 2I_{1z} I_{2x} \cos(\pi J_{1,2} \tau) \sin(\pi J_{1,2} \tau)$$

$$- 2I_{1z} I_{2x} \cos(\pi J_{1,2} \tau) \sin(\pi J_{1,2} \tau) - I_{2y} \sin^2(\pi J_{1,2} \tau)$$

At this point the trigonometric identities that help to simplify the result are:

$$\cos^2(a) - \sin^2(a) = \cos(2a) \quad \cos(a) \sin(a) + \cos(a) \sin(a) = 2 \cos(a) \sin(a) = \sin(2a)$$

$$= I_{1y} \cos(2\pi J_{1,2} \tau) - 2I_{1x} I_{2z} \sin(2\pi J_{1,2} \tau) + I_{2y} \cos(2\pi J_{1,2} \tau) - 2I_{1z} I_{2x} \sin(2\pi J_{1,2} \tau)$$

The results shown that for each spin the doublet is a mix of in-phase ( $I_{1y}$ ) and antiphase ( $2I_{1x}I_{2z}$ ) magnetization. Thus, with an arbitrary value of the  $\tau$  delay, homonuclear coupling is not refocused. Modulation is by coupling constant ( $J_{1,2}$ ) only, as is expected, because chemical shift is refocused in this experiment.

**b)** Based on your results for part 'a' (above), consider the case where the delay  $\tau$  is equal to  $1/(4J_{1,2})$ . Please explain how this affects your answer to part 'a', and what the meaning of the result is in terms of the magnetization vectors for the nuclei (this may require comparison to your answer to part 'c'). **(6 points)**

*When the  $\tau$  delay is equal to  $1/(4J_{1,2})$ ,  $2\pi J_{1,2}\tau$  reduces to  $\pi/2$  or  $90^\circ$ . So, the cosine terms go to '0', and the sine terms go to '1'. Thus, the result is then:*

$$-2I_{1x}I_{2z} - 2I_{1z}I_{2x}$$

*This represents antiphase 'x' magnetization for both spin 1 and spin 2. So, as the magnetization evolves during acquisition, the signal from each nucleus will consist of an antiphase doublet.*

**c)** Based on your results for part 'a' (above), consider the case where the delay  $\tau$  is equal to  $1/(2J_{AX})$ . Please explain how this affects your answer to part 'a', and what the meaning of the result is in terms of the magnetization vectors for the nuclei (this may require comparison to your answer to part 'b'). **(6 points)**

*When the  $\tau$  delay is equal to  $1/(2J_{1,2})$ ,  $2\pi J_{1,2}\tau$  reduces to  $\pi$  or  $180^\circ$ . So, the cosine terms go to '-1', and the sine terms go to '0'. Thus, the result is then:*

$$-I_{1y} - I_{2y}$$

*This represents pure in phase 'y' magnetization for both spin 1 and spin 2. So, as the magnetization evolves during acquisition, the signal from each nucleus will consist of an in phase doublet*

2) Determine the expectation value for the magnitude of the bulk magnetization along 'y' ( $M_y$ ) at thermal equilibrium. You should use the equilibrium deviation density matrix (single spin basis set) and the correct matrix representation for the 'y' magnetization operator. You must do a calculation and explain your result for credit. **(8 points)**

$$\hat{\sigma}_{eq} = \frac{1}{2} \begin{bmatrix} \gamma \hbar B_0 / (2k_B T) & 0 \\ 0 & -\gamma \hbar B_0 / (2k_B T) \end{bmatrix} \quad \hat{\mu}_y = \gamma \hbar \hat{I}_y = \frac{\gamma \hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$\begin{aligned} M_{y,eq} &= N \text{Tr}\{\hat{\sigma}_{eq}[\hat{\mu}_y]\} = N \text{Tr}\left\{\frac{1}{2} \begin{bmatrix} \gamma \hbar B_0 / (2k_B T) & 0 \\ 0 & -\gamma \hbar B_0 / (2k_B T) \end{bmatrix} \frac{\gamma \hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\right\} \\ &= N \text{Tr}\left\{\frac{\gamma \hbar}{4} \begin{bmatrix} \gamma \hbar B_0 / (2k_B T) & 0 \\ 0 & -\gamma \hbar B_0 / (2k_B T) \end{bmatrix} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\right\} \\ &= N \text{Tr}\left\{\frac{\gamma \hbar}{4} \begin{bmatrix} 0 & -i\gamma \hbar B_0 / (2k_B T) \\ -i\gamma \hbar B_0 / (2k_B T) & 0 \end{bmatrix}\right\} = 0 \quad (\text{trace} = 0) \end{aligned}$$

*So, the calculation shows the expected result. At thermal equilibrium there is no net/bulk transverse magnetization on 'y' (or 'x').*

3) Using the product operator formalism, the result of subjecting 'y' magnetization on spin '1' to an rf pulse along the 'x' axis is shown below:

$$I_{1y} \xrightarrow{\omega_1 t I_x} I_{1y} \cos(\omega_1 t) + I_{1z} \sin(\omega_1 t)$$

a) Write down the product operator expression for subjecting 'z' magnetization on spin '2' to an rf pulse along the 'x' axis. (4 points)

$$I_{2z} \xrightarrow{\omega_1 t I_x} I_{2z} \cos(\omega_1 t) - I_{2y} \sin(\omega_1 t)$$

b) Derive the product operator that describes an rf pulse along the 'x' axis on antiphase '1y,2z' magnetization ( $2I_{1y}I_{2z}$ ). (6 points)

*This is easily derived by multiplying together the results of the two operations shown above ('x' pulse on '1y' and 'x' pulse on '2z'):*

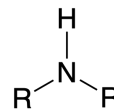
$$\begin{aligned} 2I_{1y}I_{2z} &\xrightarrow{\omega_1 t I_x} 2[(I_{1y} \cos(\omega_1 t) + I_{1z} \sin(\omega_1 t))(I_{2z} \cos(\omega_1 t) - I_{2y} \sin(\omega_1 t))] \\ &= 2[(I_{1y} \cos(\omega_1 t))(I_{2z} \cos(\omega_1 t)) + (I_{1z} \sin(\omega_1 t))(I_{2z} \cos(\omega_1 t)) \\ &\quad - (I_{1y} \cos(\omega_1 t))(I_{2y} \sin(\omega_1 t)) - (I_{1z} \sin(\omega_1 t))(I_{2y} \sin(\omega_1 t))] \\ &= 2I_{1y}I_{2z}\cos^2(\omega_1 t) + 2I_{1z}I_{2z}\sin(\omega_1 t)\cos(\omega_1 t) \\ &\quad - 2I_{1y}I_{2y}\sin(\omega_1 t)\cos(\omega_1 t) - 2I_{1z}I_{2y}\sin^2(\omega_1 t) \\ &= 2I_{1y}I_{2z}\cos^2(\omega_1 t) + (2I_{1z}I_{2z} - 2I_{1y}I_{2y})\sin(\omega_1 t)\cos(\omega_1 t) - 2I_{1z}I_{2y}\sin^2(\omega_1 t) \end{aligned}$$

c) If a  $90^\circ$  'x' pulse is used, what is then the result when this pulse is applied on the antiphase '1y,2z' magnetization ( $2I_{1y}I_{2z}$ )? (4 points)

*If a  $90^\circ$  'x' pulse is used, all of the cosine terms go to zero, and only the final term survives. Because  $\sin^2(\omega_1 t) = 1$ , the result is simply  $-2I_{1z}I_{2y}$ . This is the result shown in the product operator transformation table.*

4) For  $^1\text{H}$ , the natural isotopic abundance is essentially 100%, and the gyromagnetic ratio for  $^1\text{H}$  is  $26.7519 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ . For  $^{15}\text{N}$ , the natural isotopic abundance is about 0.37% and the gyromagnetic ratio is  $-2.7126 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ .

a) For a compound such as that shown (right), with one  $^1\text{H}$  nucleus and one  $^{15}\text{N}$  nucleus, what would be the ratio of the signal intensity (relative sensitivity) for a  $^1\text{H}$  NMR experiment compared to a  $^{15}\text{N}$  NMR experiment at natural isotopic abundance? You must do a calculation and show your work for credit. (4 points)



*Sensitivity is proportional to the magnitude of the signal (emf) induced in the coil:*

$$emf = \gamma B_0 M_0 = N \gamma^3 B_0^2 \hbar I(I+1) / (3k_B T)$$

$$\frac{emf(^1\text{H})}{emf(^{15}\text{N})} = \frac{100\%(26.7519)^3}{0.37\%(2.7126)^3} = 2.592417 \times 10^5$$

*So, the  $^1\text{H}$  experiment is  $2.59 \times 10^5$  times more sensitive than the  $^{15}\text{N}$  experiment.*

b) For the  $^{15}\text{N}$  experiment, how many scans would it take to give the same signal-to-noise as just one scan of the  $^1\text{H}$  experiment? You must do a calculation and show your work for credit. (4 points)

*Signal-to-noise (S/N) is proportional to the square root of the number of scans (NS):*

$$\frac{S/N}{S/N} = \frac{\sqrt{NS}}{\sqrt{NS}} \quad \frac{2.592417 \times 10^5}{1} = \frac{\sqrt{NS}}{\sqrt{1}} \quad \sqrt{NS} = 2.592417 \times 10^5 \quad NS = 6.72 \times 10^{10}$$

*So, in order to get the same S/N in the  $^{15}\text{N}$  experiment as one scan in the  $^1\text{H}$  experiment,  $6.72 \times 10^{10}$  scans would be needed.*

c) Using a 14.1 Tesla magnet, the resonance frequency of  $^1\text{H}$  is about 600 MHz. What is the resonance frequency of  $^{15}\text{N}$ ? **(4 points)**

*The Larmor frequency is proportional to the gyromagnetic ratio ( $\gamma$ ), so:*

$$\nu_L = \gamma B_0 / (2\pi) \quad \nu_{^{15}\text{N}} = \nu_{^1\text{H}} \frac{\gamma_{^{15}\text{N}}}{\gamma_{^1\text{H}}} = 600 \frac{2.7126}{26.7519} = 60.8 \text{ MHz}$$

*So, the  $^{15}\text{N}$  resonance frequency is about 60.8 MHz.*

d) For the  $^1\text{H}$  NMR spectrum of the compound shown in 'a', collected using an NMR instrument with a 14.1 Tesla magnet, the carrier (reference) frequency was set to 4.76 ppm. The  $^1\text{H}$  signal is 1400 Hz downfield of the carrier (reference) frequency. What is the chemical shift of the  $^1\text{H}$  signal? **(4 points)**

*The chemical shift difference of the signal from the reference/carrier is:*

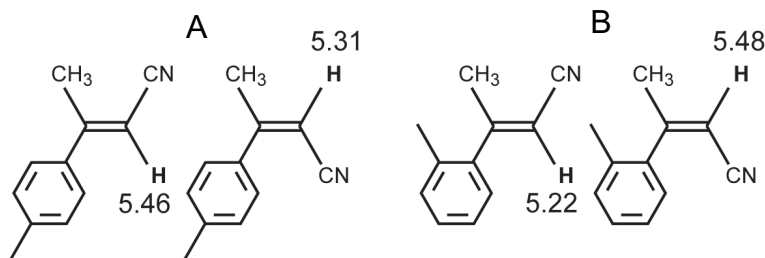
$$\delta_i = \frac{\nu_i - \nu_{\text{ref}}}{\nu_{\text{ref}}} \times 10^6 = \frac{1400 \text{ Hz}}{600 \text{ MHz}} \times 10^6 = 2.33 \text{ ppm}$$

*The  $^1\text{H}$  signal is downfield from the reference, so the chemical shift of the  $^1\text{H}$  signal is  $4.76 + 2.33 = 7.09 \text{ ppm}$ .*

e) For the compound shown in part 'a', the magnitude of the one-bond coupling constant between  $^1\text{H}$  and  $^{15}\text{N}$  ( $^1J_{^1\text{H}-^{15}\text{N}}$ ) is about 92 Hz using a 14.1 Tesla (600 MHz) magnet. What is the magnitude of this coupling constant using a 21.1 Tesla (900 MHz) magnet? **(4 points)**

*Still 92 Hz. Scalar coupling constants are independent of magnetic field strength.*

5) The chemical shifts (ppm) of the ethylenic hydrogens (bold) from the following styrene compounds 'A' and 'B' are shown. For each compound, there are two possible conformers, with the hydrogen and derivatized phenyl group either 'cis' or 'trans' to each other. For both compounds shown below (and both conformers of each compound), the atoms in the phenyl groups are drawn coplanar with the other atoms. However, this is incorrect for one of the compounds. For one of the compounds (either 'A' or 'B') the phenyl rings for both conformers are actually perpendicular to the plane of the other atoms. Based on the chemical shifts, decide which compound this is, and provide a detailed explanation of your answer based on the chemical shifts. **(6 points)**



The magnetic anisotropy of the phenyl ring is such that atoms coplanar with the ring are in the deshielding region (for instance, the hydrogens on the phenyl ring), and atoms above and below the plane are in the shielding region. Thus, if the phenyl ring were coplanar with the other atoms, then the 'cis' hydrogen would be more deshielded (because it is closer to the edge of the ring relative to the 'trans' isomer). This is what occurs for compound 'A', indicating that for the conformers of this compound the phenyl ring is coplanar. If the phenyl ring were rotated so that the plane of the ring is perpendicular to the other atoms, then the cis hydrogen would be oriented just above the plane of the ring. Thus, it would be in the shielding region, and it would be expected to be shifted upfield (relative to the 'trans' hydrogen). This is the case for compound 'B'. So, based on the chemical shifts, it is expected that for compound 'B', the planes of the derivatized phenyl rings are perpendicular to the other atoms.

From a chemistry perspective, most organic chemists would recognize the steric crowding/repulsion between the two methyl groups in 'B' when the ring is coplanar with the other atoms, which also supports the contention that the ring is perpendicular to the plane of the other atoms in 'B'.

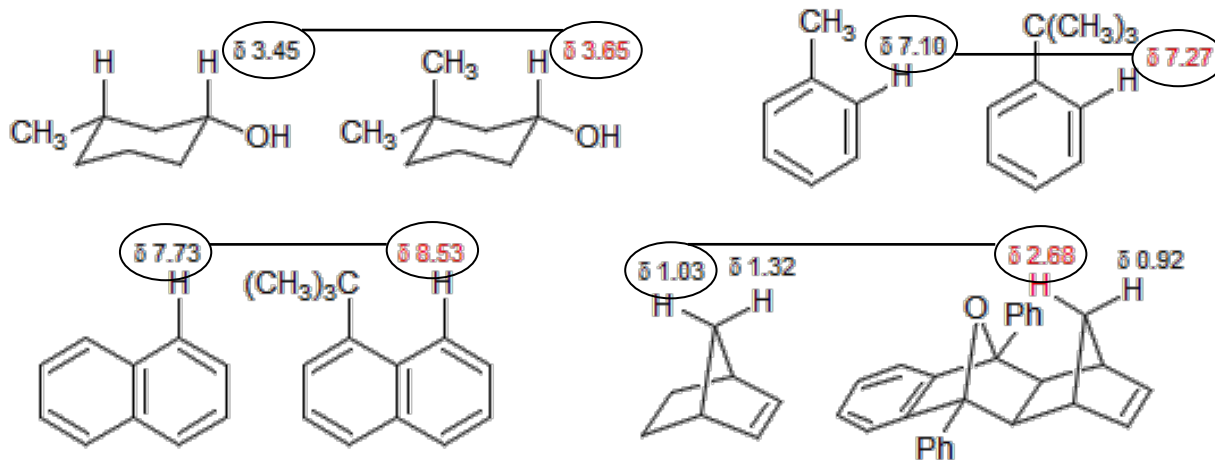


6) For  $^1\text{H}$ - $^1\text{H}$ , the value for the one-bond scalar coupling constant is 287 Hz. For  $^1\text{H}$ - $^2\text{H}$ , the coupling constant is 44 Hz, and for  $^1\text{H}$ - $^3\text{H}$  the coupling constant is 306 Hz. What is the gyromagnetic ratio for  $^3\text{H}$ ? You must do a calculation, calculate the value and otherwise explain your answer for credit. The gyromagnetic ratio for  $^1\text{H}$  is  $26.7159 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ . (6 points)

*The coupling constant scales with the gyromagnetic ratio:*

$$\frac{J_{1\text{H}-1\text{H}}}{J_{1\text{H}-3\text{H}}} = \frac{\gamma_{1\text{H}}}{\gamma_{3\text{H}}} \quad \frac{287}{306} = \frac{26.7159 \times 10^7}{\gamma_{3\text{H}}} \quad \gamma_{3\text{H}} = 26.7159 \times 10^7 \frac{306}{287} = 28.5 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$$

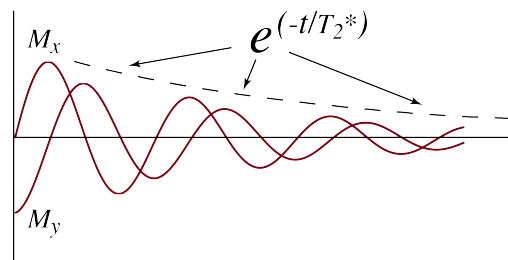
7) Below are pairs of molecules with the chemical shifts of pairs of hydrogen nuclei (circled, connected with horizontal line) compared. For each pair of circled shifts, one of the hydrogens is significantly deshielded relative to the other. Propose a simple explanation/generalization/hypothesis (one sentence), that applies to all four pairs of molecules, to explain why this is the case (this is not “magnetic anisotropy”). (6 points)



*This problem is courtesy of Professor Hans Reich (University of Wisconsin, <https://www.chem.wisc.edu/areas/reich/chem605/>). The simplest explanation is, apparently, steric crowding promotes deshielding.*

8) NMR signals decay with time exponentially according to the magnitude of the transverse relaxation rate,  $T_2^*$  ( $e^{(-t/T_2^*)}$ ). The linewidths of NMR signals are likewise dependent on transverse relaxation:

$$\Delta\nu_{1/2} = \frac{1}{(\pi T_2^*)} \text{ (in Hz)}$$



a) Often it is advantageous to use apodization/window functions to mathematically modify the signal (FID) in order to change the signal-to-noise or the resolution. The apodization function called the “matched filter” multiplies the FID by an exponential function that matches the exponential decay of the FID ( $e^{(-t/T_2^*)}$ ). If the linewidth of the signal (width at half the maximum height) is 1 Hz before application of the matched filter, what is the linewidth after application? You will have to perform a calculation, show your work, and otherwise explain your answer for credit. **(8 points)**.

*The exponential decay of the FID and the matched filter are described by the same function,  $e^{(-t/T_2^*)}$ . Multiplying them then gives the exponential describing the decay of the FID after application of the function:*

$$e^{(-t/T_2^*)} \times e^{(-t/T_2^*)} = e^{(-2t/T_2^*)}$$

*Thus, rather than decaying as  $1/T_2^*$ , the apodized decays as  $2/T_2^*$ . The linewidth of the signal is therefore dependent on  $2/T_2^*$ , so is twice as large as the original signal:*

$$\Delta\nu_{1/2} = \frac{2}{(\pi T_2^*)} \text{ (in Hz)}$$

*So, if the linewidth of the original signal was 1 Hz, the linewidth after apodization is 2 Hz.*

b) Application of the matched filter results in improved signal-to-noise. However, not all signals in a given spectrum will experience the same improvement. Please explain why. **(4 points)**

*The matched filter attempts to match the exponential decay of the FID. This decay is an average based on the  $T_2^*$  relaxation times of all of the nuclei contributing to the signal. Because  $T_2^*$  relaxation times of nuclei giving rise to signals with different resonance frequencies will typically not be identical, they will typically experience varying degrees of signal-to-noise improvement when the filter is applied.*

9) The rotation operators in matrix form for rotation about the y-axis are:

$$\hat{\mathbf{R}}_y = \begin{bmatrix} \cos(\omega_1 t/2) & -\sin(\omega_1 t/2) \\ \sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{bmatrix} \quad \hat{\mathbf{R}}_y^{-1} = \begin{bmatrix} \cos(\omega_1 t/2) & \sin(\omega_1 t/2) \\ -\sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{bmatrix}$$

Using these operators and the appropriate matrix operations, show the result of applying a 180° pulse along the y-axis on equilibrium (z) magnetization. You will have to show your work and explain/interpret the final result for credit. **(8 points)**

For a 180° ( $\pi$ ) pulse, the operators reduce to:

$$\hat{\mathbf{R}}_y = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \quad \hat{\mathbf{R}}_y^{-1} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$$

The equilibrium deviation density matrix is:

$$\hat{\sigma}_{eq} = \frac{1}{2} \begin{bmatrix} \gamma \hbar B_0 / 2k_B T & 0 \\ 0 & -\gamma \hbar B_0 / 2k_B T \end{bmatrix} \equiv \frac{1}{2} \begin{bmatrix} \delta & 0 \\ 0 & -\delta \end{bmatrix} \propto M_z(eq)$$

The rotation operation is as follows:

$$\hat{\sigma}(t) \hat{\mathbf{R}}_{y,\pi} \hat{\sigma}_{eq} \hat{\mathbf{R}}_{y,\pi}^{-1} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \frac{1}{2} \begin{bmatrix} \delta & 0 \\ 0 & -\delta \end{bmatrix} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & \delta \\ \delta & 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} -\delta & 0 \\ 0 & \delta \end{bmatrix} = \delta \frac{1}{2} \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$$

The matrix representation for the  $I_z$  and  $-I_z$  operators are:

$$\hat{I}_z = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad -\hat{I}_z = \frac{1}{2} \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$$

The result of the rotation operation gives  $\delta I_z$ . Thus, rotation of equilibrium z-magnetization 180° about the y-axis results in -z magnetization

**10)** Using the relationships between the lowering operator ( $\hat{I}_-$ ) and the  $\hat{I}_x$  and  $\hat{I}_y$  operators, show that  $\hat{I}_-|\alpha\rangle = \beta$ . You must show your work and otherwise explain your answer for credit. **(4 points)**

We know that  $\hat{I}_- = \hat{I}_x - i\hat{I}_y$ ,  $\hat{I}_x|\alpha\rangle = \frac{1}{2}\beta$ , and  $\hat{I}_y|\alpha\rangle = \frac{1}{2}i\beta$ . Thus:

$$\hat{I}_-|\alpha\rangle = \hat{I}_x|\alpha\rangle - i\hat{I}_y|\alpha\rangle = \frac{1}{2}\beta - i\left(\frac{1}{2}i\beta\right) = \frac{1}{2}\beta - (-1)\frac{1}{2}\beta = \frac{1}{2}\beta + \frac{1}{2}\beta = \beta$$

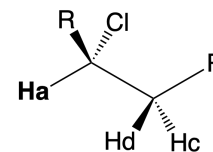
**11)** Using the Hamiltonian shown below (written in terms of frequencies) for a first order spin system ('A' and 'X'), solve for the expectation value for the  $\alpha\beta$  state (*NOT* the  $\beta\alpha$  state). Your final answer should be in terms of the resonance frequencies for 'A' and 'X' and the  $J_{AX}$  coupling constant. You must show your work/derivation and otherwise explain your answer for credit. **(6 points)**

$$\hat{H} = -h\nu_A\hat{I}_{Az} - h\nu_X\hat{I}_{Xz} + hJ_{AX}\hat{I}_{Az}\hat{I}_{Xz}$$

Recall,  $\hat{I}_z|\alpha\rangle = \frac{1}{2}\alpha$  and  $\hat{I}_z|\beta\rangle = -\frac{1}{2}\beta$ . Thus:

$$\begin{aligned} \langle \alpha\beta | \hat{H} | \alpha\beta \rangle &= \langle \alpha\beta | -h\nu_A\hat{I}_{Az} | \alpha\beta \rangle - \langle \alpha\beta | h\nu_X\hat{I}_{Xz} | \alpha\beta \rangle + \langle \alpha\beta | hJ_{AX}\hat{I}_{Az}\hat{I}_{Xz} | \alpha\beta \rangle \\ &= \langle \alpha\beta | -h\nu_A\frac{1}{2} | \alpha\beta \rangle - \langle \alpha\beta | -h\nu_X\frac{1}{2} | \alpha\beta \rangle - \langle \alpha\beta | hJ_{AX}\frac{1}{4} | \alpha\beta \rangle \\ &= -h\nu_A\frac{1}{2} \langle \alpha\beta | \alpha\beta \rangle + h\nu_X\frac{1}{2} \langle \alpha\beta | \alpha\beta \rangle - hJ_{AX}\frac{1}{4} \langle \alpha\beta | \alpha\beta \rangle \\ &= -h\nu_A\frac{1}{2} + h\nu_X\frac{1}{2} - hJ_{AX}\frac{1}{4} = -h(\nu_A - \nu_X)/2 - hJ_{AX}/4 \end{aligned}$$

12) The hydrogens labeled 'Hc' and 'Hd' have identical coupling constants with the bolded hydrogen labeled '**Ha**' ( $^3J_{\text{HcHa}} = ^3J_{\text{HdHa}}$ ).



a) Hydrogens 'Hc' and 'Hd' are coupled to one another, so they could comprise either an 'AX', an 'A<sub>2</sub>', or an 'AB' system. Which is it? You will have to provide a detailed explanation for credit. (4 points)

*An A<sub>2</sub> spin system is one in which two coupled nuclei have identical resonance frequencies, and not by coincidence. Hydrogens 'Hc' and 'Hd' are diastereotopic, so they could not have identical resonance frequencies (except perhaps by coincidence), so they could not comprise an 'A<sub>2</sub>' spin system. Whether these are an AB or AX system depends on their relative resonance frequencies, which we don't know, so we can't say which it is. The coupling constants mentioned in the question are irrelevant.*

b) Please explain the differences between an A<sub>2</sub>, AX, and AB spin systems. (4 points)

*All of these terms describe spin systems comprised of two coupled spins. An A<sub>2</sub> spin system is one where the two nuclei have identical resonance frequencies, and not by coincidence. These spin systems give rise to a single signal that has only one peak (a singlet). An AX system is one where the resonance frequency difference between the two nuclei is large compared to the coupling constant. Each nucleus gives rise to a single signal that is split into two peaks (doublets) by the other. The spectrum is first order, so the peaks in each doublet have identical intensities, and the resonance frequency is the average of the resonance frequencies of the peaks. The AB system is not first order, so the resonance frequencies of the two nuclei are similar with their difference on the same order as the coupling constant between them. Their spectra show second order characteristics.*

Name \_\_\_\_\_

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You may find some of the information in this table useful:

Nuclide	Spin $I$	Natural abundance (%)	Relative sensitivity	Gyromagnetic ratio, $\gamma$ ( $10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ )	NMR frequency (MHz @ $B_0 = 2.3488 \text{ T}$ )
$^1\text{H}$	1/2	99.985	1.00	26.7519	100
$^2\text{H}$	1	0.015	$9.65 \times 10^{-3}$	4.1066	15.351
$^3\text{H}$	1/2	~0	1.21	28.5350	106.664
$^{10}\text{B}$	3	19.58	$1.99 \times 10^{-2}$	2.8747	10.746
$^{11}\text{B}$	3/2	80.42	0.17	8.5847	32.084
$^{12}\text{C}$	0	98.9	-	-	-
$^{13}\text{C}$	1/2	1.108	$1.59 \times 10^{-2}$	6.7283	25.144
$^{14}\text{N}$	1	99.63	$1.01 \times 10^{-3}$	1.9338	7.224
$^{15}\text{N}$	1/2	0.37	$1.04 \times 10^{-3}$	-2.7126	10.133
$^{19}\text{F}$	1/2	100	0.83	25.1815	94.077
$^{31}\text{P}$	1/2	100	$6.63 \times 10^{-2}$	10.8394	40.481
$^{103}\text{Rh}$	1/2	100	$3.11 \times 10^{-5}$	-0.846	3.1474
$^{195}\text{Pt}$	1/2	33.8	$9.94 \times 10^{-3}$	5.8383	21.499