**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 ^1H-^1H AX spin system. Consider the spin-echo pulse sequence shown (right).

$$90°x \qquad 180°x$$

$$^1H \quad \blacksquare \quad \tau \quad \blacksquare \quad \tau$$
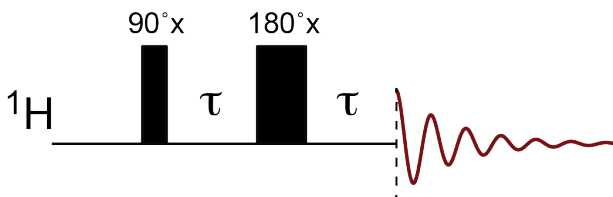
a) Using product operators, demonstrate the effect of the sequence on homonuclear coupling (AX, i.e. first order). You can ignore chemical shift evolution (the spin echo refocuses chemical shift evolution). You must show your work for credit. You must explain the results you get from the product operators and what they mean. (**10 points**)

b) Based on your results for part 'a' (above), consider the case where the delay τ 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**)

c) Based on your results for part 'a' (above), consider the case where the delay τ 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**)

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**)

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**)

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**)

c) If a 90° '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**)

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

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

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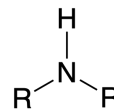
b) For the ^{15}N experiment, how many scans would it take to give the same signal-to-noise as just one scan of the ^1H experiment? You must do a calculation and show your work for credit. (**4 points**)

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

d) For the ^{1}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}H signal is 1400 Hz downfield of the carrier (reference) frequency. What is the chemical shift of the ^{1}H signal? (**4 points**)

e) For the compound shown in part 'a', the magnitude of the one-bond coupling constant between ^{1}H and ^{15}N ($^1J_{1H-15N}$) 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**)

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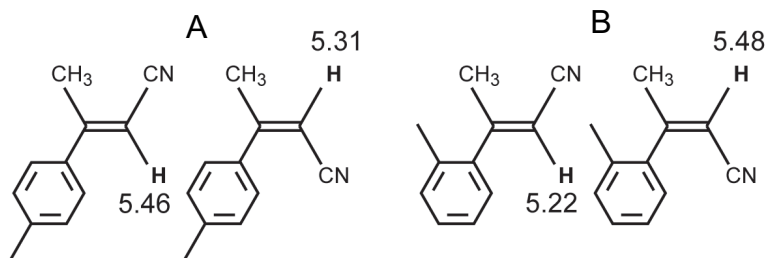
6) For ^1H-^1H, the value for the one-bond scalar coupling constant is 287 Hz. For ^1H-^2H, the coupling constant is 44 Hz, and for ^1H-^3H the coupling constant is 306 Hz. What is the gyromagnetic ratio for ^3H? You must do a calculation, calculate the value and otherwise explain your answer for credit.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

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**)
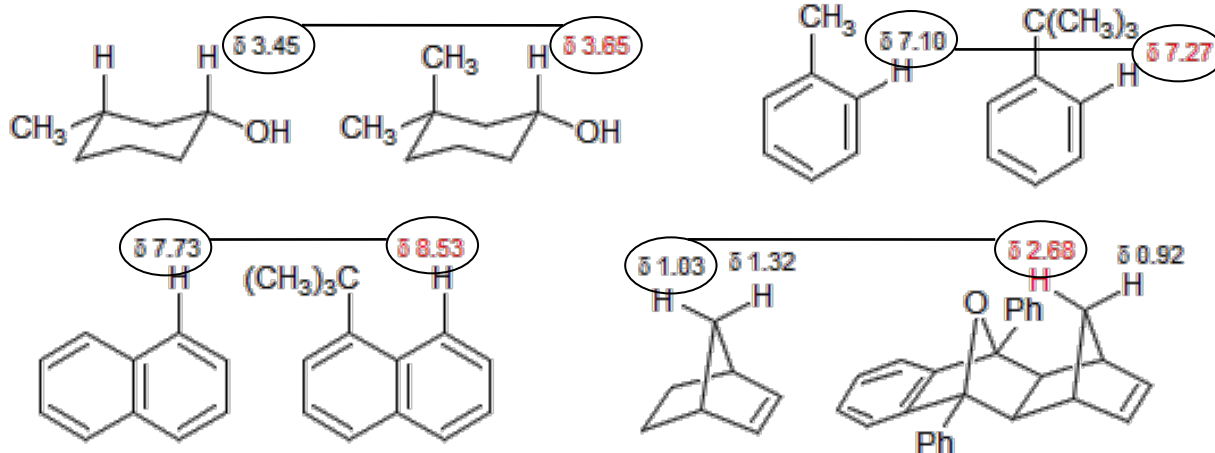
8) NMR signals decay with time exponentially according to the magnitude of the transverse relaxation rate, T_2^* ($e^{(-t/T2^*)}$). The linewidths of NMR signals are likewise dependent on transverse relaxation:

$$\Delta v_{1/2} = \frac{1}{(\pi T_2^*)} \ (in \ Hz)$$
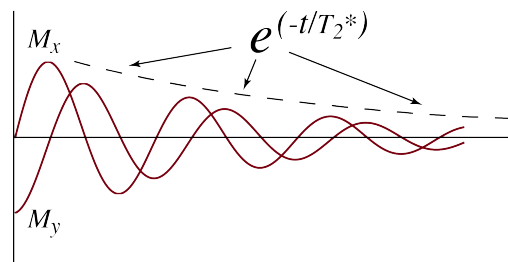
a) Often it is advantageous to use apodization/window functions to mathematically modify the signal (FID) in order to change the signal-to-noise or the resolution. The apodization function called the "matched filter" multiplies the FID by an exponential function that matches the exponential decay of the FID ($e^{(-t/T2^*)}$). 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**).

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**)

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

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

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**)

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

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**)

$$\hat{H} = -hv_A\hat{I}_{Az} - hv_X\hat{I}_{Xz} + hJ_{AX}\hat{I}_{Az}\hat{I}_{Xz}$$

12) The hydrogens labeled 'Hc' and 'Hd' have identical coupling constants with the bolded hydrogen labeled '**Ha**' ($^3J_{HcHa}=^3J_{HdHa}$).
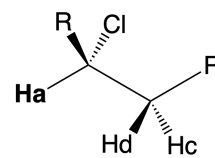
a) Hydrogens 'Hc' and 'Hd' are coupled to one another, so they could comprise either an 'AX', an 'A$_2$', or an 'AB' system. Which is it? You will have to provide a detailed explanation for credit. (**4 points**)

b) Please explain the differences between an A$_2$, AX, and AB spin systems. (**4 points**)

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

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