

Problem Set #1, CHEM/BCMB 4190/6190/8189

1). Which of the following statements are *True*, *False*, or *Possibly True*, for the hypothetical element X?

- a. The ground state spin is $I=0$ for $^{52}_{24}\text{X}$.
- b. The ground state spin is $I=0$ for $^{70}_{31}\text{X}$.
- c. The ground state spin is $I=1/2$ for $^{45}_{21}\text{X}$.
- d. The ground state spin is $I=1$ for $^{48}_{22}\text{X}$.
- e. The ground state spin is $I=1/2$ for $^{29}_{14}\text{X}$.

- a. *True*: both the mass number and the atomic number are even. Therefore, $I=0$.
- b. *False*: the mass number is even and the atomic number is odd. Therefore, I is integral and non-zero.
- c. *Possibly True*: the mass number is odd, therefore the spin is half-integral (might be $1/2$, might also be $3/2$ or $5/2$, etc.).
- d. *False*: both the mass number and the atomic number are even. Therefore, $I=0$.
- e. *Possibly True*: same rationale as 'c'.

2). The resonance/precession frequency of a ^1H nucleus (ν_{1H}) in a 14.09 T (Tesla) magnet is 600.0 MHz.

- a. What is the resonance frequency of a ^{13}C nucleus ($\nu_{^{13}\text{C}}$) in the same magnet? ($\gamma_{\text{1H}} = 26.7519 \times 10^7 \text{ rad/Ts}$, $\gamma_{^{13}\text{C}} = 6.7283 \times 10^7 \text{ rad/Ts}$).
- b. What is the resonance frequency of the ^1H nucleus in a 11.74 T magnet?

a.

$$\nu_{\text{1H}} = \left| \frac{\gamma_{\text{1H}}}{2\pi} \right| B_0 \text{ and } \nu_{^{13}\text{C}} = \left| \frac{\gamma_{^{13}\text{C}}}{2\pi} \right| B_0, \text{ therefore}$$

$$\frac{\nu_{\text{1H}}}{\nu_{^{13}\text{C}}} = \frac{600.0 \text{ MHz}}{\nu_{^{13}\text{C}}} = \frac{\left| \frac{\gamma_{\text{1H}}}{2\pi} \right| B_0}{\left| \frac{\gamma_{^{13}\text{C}}}{2\pi} \right| B_0} = \frac{\left| \gamma_{\text{1H}} \right|}{\left| \gamma_{^{13}\text{C}} \right|} = \frac{26.7519 \times 10^7}{6.7283 \times 10^7}$$

$$\nu_{^{13}\text{C}} = 150.9 \text{ MHz}$$

b.

$$\frac{\nu_{\text{1H}, 14.09 \text{ T}}}{\nu_{\text{1H}, 11.74 \text{ T}}} = \frac{600.0 \text{ MHz}}{\nu_{\text{1H}, 11.74 \text{ T}}} = \frac{\left| \frac{\gamma_{\text{1H}}}{2\pi} \right| 14.09}{\left| \frac{\gamma_{\text{1H}}}{2\pi} \right| 11.74} = \frac{14.09}{11.74}$$

$$\nu_{\text{1H}, 11.74 \text{ T}} = 499.9 \text{ MHz} \approx 500 \text{ MHz}$$

- 3). How does the magnitude of the bulk/macroscopic magnetization compare for:
- ^1H and ^{13}C spins?
 - ^1H and ^{13}C spins at natural abundance (assume the natural abundance of ^1H is 100% and ^{13}C is 1.11%)?
 - ^1H and ^{17}O spins?
- ($\gamma_{1\text{H}} = 26.7519 \times 10^7 \text{ rad/Ts}$, $\gamma_{13\text{C}} = 6.7283 \times 10^7 \text{ rad/Ts}$, $\gamma_{17\text{O}} = -3.6280 \times 10^7 \text{ rad/Ts}$)

a.

$$M_0 = \frac{N\gamma^2\hbar^2B_0I(I+1)}{3k_B T} \quad (\text{"h" here is "h-bar", Planck's constant divided by } 2\pi)$$

$$\frac{M_{0\text{H}}}{M_{0\text{13C}}} = \frac{\frac{N\gamma_{1\text{H}}^2\hbar^2B_0I_{1\text{H}}(I_{1\text{H}}+1)}{3k_B T}}{\frac{N\gamma_{13\text{C}}^2\hbar^2B_0I_{13\text{C}}(I_{13\text{C}}+1)}{3k_B T}} = \frac{\gamma_{1\text{H}}^2}{\gamma_{13\text{C}}^2} = \frac{(26.7519 \times 10^7 \text{ rad/Ts})^2}{(6.7283 \times 10^7 \text{ rad/Ts})^2} = 15.809 \quad \text{So, the bulk}$$

magnetization is about 16 times as large for ^1H compared to ^{13}C , or ^{13}C magnetization is about 6.3% that of ^1H .

b.

$$\frac{M_{0\text{H}}}{M_{0\text{13C}}} = \frac{\frac{N\gamma_{1\text{H}}^2\hbar^2B_0I_{1\text{H}}(I_{1\text{H}}+1)}{3k_B T}}{\frac{N\gamma_{13\text{C}}^2\hbar^2B_0I_{13\text{C}}(I_{13\text{C}}+1)}{3k_B T}} = \frac{(100) \gamma_{1\text{H}}^2}{(1.11) \gamma_{13\text{C}}^2} = \frac{(100) (26.7519 \times 10^7 \text{ rad/Ts})^2}{(1.11) (6.7283 \times 10^7 \text{ rad/Ts})^2} = 1424$$

So, the bulk magnetization is about 1424 times as large for ^1H compared to ^{13}C at natural abundance, or ^{13}C magnetization is about 0.07% that of ^1H .

c.

$$\frac{M_{0\text{H}}}{M_{0\text{17O}}} = \frac{\frac{N\gamma_{1\text{H}}^2\hbar^2B_0I_{1\text{H}}(I_{1\text{H}}+1)}{3k_B T}}{\frac{N\gamma_{17\text{O}}^2\hbar^2B_0I_{17\text{O}}(I_{17\text{O}}+1)}{3k_B T}} = \frac{\gamma_{1\text{H}}^2 \times \frac{1}{2} \left(\frac{1}{2} + 1 \right)}{\gamma_{17\text{O}}^2 \times \frac{5}{2} \left(\frac{5}{2} + 1 \right)} = \frac{(26.7519 \times 10^7 \text{ rad/Ts})^2 \times 0.75}{(-3.6280 \times 10^7 \text{ rad/Ts})^2 \times 8.75} = 4.660$$

So, the bulk magnetization is about 4.7 times as large for ^1H as for ^{17}O , or ^{17}O magnetization is about 21.4% that of ^1H .

- 4).
- How does the sensitivity of the NMR signal compare for ^1H and ^{13}C spins?
 - For equivalent numbers of ^1H and ^{13}C nuclei, how many more scans are necessary to produce ^{13}C spectra with signal-to-noise equivalent to ^1H spectra?

- a. 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:

$$\epsilon \propto dM/dt = \gamma M_0 B$$

Remember, $M_0 = \frac{N\gamma^2 \hbar^2 B_0 I(I+1)}{3k_B T}$ (“ \hbar ” here is “h-bar”, Planck’s constant divided by 2π),

so $\epsilon \propto \gamma M_0 B = \frac{N\gamma^3 \hbar^2 B_0^2 I(I+1)}{3k_B T}$. So, whereas the magnitude of the bulk magnetization was dependent on γ^2 , the sensitivity is dependent on γ^3 .

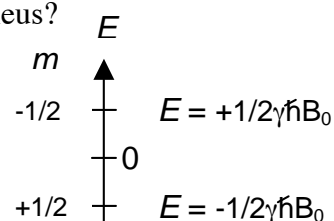
$$\text{Thus, } \frac{\epsilon_{1H}}{\epsilon_{13C}} = \frac{\frac{N\gamma_{1H}^3 \hbar^2 B_0^2 I(I+1)}{3k_B T}}{\frac{N\gamma_{13C}^3 \hbar^2 B_0^2 I(I+1)}{3k_B T}} = \frac{\gamma_{1H}^3}{\gamma_{13C}^3} = \frac{(26.7519 \times 10^7 \text{ rad/Ts})^3}{(6.7283 \times 10^7 \text{ rad/Ts})^3} = 62.856 \quad \text{So, } ^1\text{H}$$

nuclei are about 63 times more sensitive than ^{13}C nuclei, or the sensitivity of a ^{13}C nucleus is about 1.59% that of a ^1H nucleus.

- b. In NMR, signal-to-noise (S/N) improves with the square root of the number of scans ($N^{1/2}$). So, since the ^1H sensitivity – S/N – from “a” above is 62.856 times better than ^{13}C , it will take $(62.856)^2 = 3951$ ^{13}C scans for every ^1H scan to get equivalent S/N for equivalent numbers of ^1H and ^{13}C nuclei.

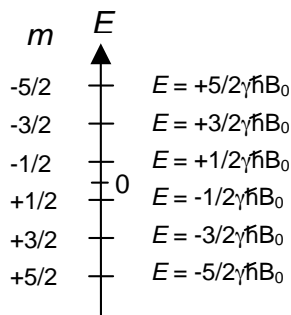
5). A diagram of the Zeeman levels/states for ^1H is shown to the right.

- How do you determine the number of levels/states for a given nucleus?
- How many levels/states are there for ^{17}O ?
- What are the magnetic quantum numbers for the ^{17}O states?
- How do you determine the energy of a given state?
- Draw the Zeeman diagram for ^{17}O .



- The number of Zeeman levels is equal to $2I+1$, where I is the spin quantum number.
- For ^{17}O there are $2(5/2)+1 = 6$ levels
- $m = (-I, -I+1, \dots, I-1, I)$, so, for $I = 5/2$, these are $-5/2, -3/2, -1/2, 1/2, 3/2$, and $5/2$
- $E = \mu_z B_0 = -m\gamma\hbar B_0$

e.



6). The frequency difference ($\Delta\nu$) between two ^1H signals in a ^1H spectrum is 3000 Hz when the spectrum is acquired with a magnetic field strength of 11.74 T (corresponding to a ^1H resonance/observe frequency of 500 MHz).

- What is the chemical shift difference ($\Delta\delta$) between the two signals?
- What would be the frequency difference between the two ^1H signals if the spectrum was acquired with a 14.09 T magnet?
- If the spectrum was acquired with a magnetic field strength of 14.09 T (600 MHz ^1H resonance/observe frequency), what would be the chemical shift difference?

$$\text{a. } \Delta\delta = \frac{\Delta\nu}{\text{observe frequency}} \times 10^6 = \frac{3000 \text{ Hz}}{500 \text{ MHz}} \times 10^6 = \frac{3000 \text{ Hz}}{500 \text{ Hz}} = 6.0 \text{ "ppm"} \text{ ("parts per million")}$$

$$\text{b. } \Delta\nu = \frac{\Delta\delta \times \text{observe frequency}}{10^6} = \frac{6.0 \times 600 \text{ MHz}}{10^6} = 3600 \text{ Hz}$$

c. The chemical shift difference would still be 6.0 ppm. The chemical shift is independent of magnetic field strength.

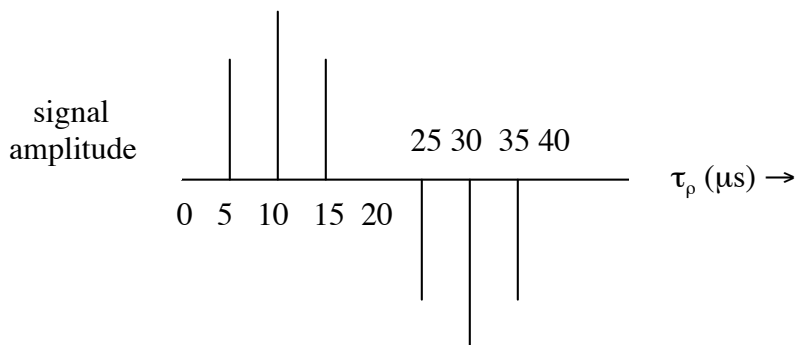
$$\Delta\delta = \frac{\Delta\nu}{\text{observe frequency}} \times 10^6 = \frac{3600 \text{ Hz}}{600 \text{ MHz}} \times 10^6 = \frac{3600 \text{ Hz}}{600 \text{ Hz}} = 6.0 \text{ "ppm"}$$

7). The measured magnitude of $^2J_{\text{H,H}}$ for a particular AX spin system using a 500 MHz (11.74T) magnet is 4.5 Hz. What is the magnitude of this coupling using a 600 MHz (14.09T) magnet?

The measured magnitude for the coupling is the same (4.5 Hz). The magnitudes of scalar couplings are independent of the B_0 field strength.

- You have found that τ_p (pulse width/length) for a 90° ($\pi/2$) pulse for your sample is 10 μs .
 - Sketch a bar graph of signal amplitude versus τ_p for your sample for τ_p values of 0, 5, 10, 15, 20, 25, 30, 35, and 40 μs .
 - Explain, in general, the relationship between the transverse component of the bulk magnetization, M_y , τ_p , the pulse angle α , and the NMR signal amplitude.

a.



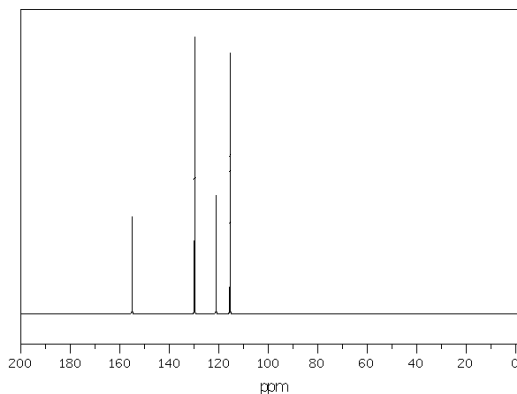
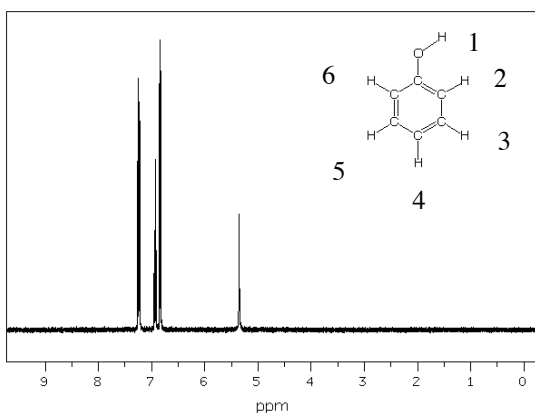
b. The amplitude of the signal induced in the receiver coil of an NMR instrument is proportional to M_y , the transverse component of the bulk magnetization. In turn, both M_y and α are dependent on τ_p . For a given pulse power, α increases from 0° to 90° with incremental increases in τ_p and M_y increases as $M \sin \alpha$.

9. The ^1H and ^{13}C NMR spectra for phenol are shown below. The chemical shifts for the ^1H signals are 5.4, 6.8, 6.9 and 7.25 ppm. The chemical shifts for the ^{13}C signals are 115, 121, 130, and 155 ppm. The ^1H and ^{13}C chemical shifts for benzene are 7.27 and 128 ppm respectively.

a. Match the chemical shifts with the correct proton and carbon atoms:

$^1\text{H}_1 =$	$^{13}\text{C}_1 =$
$^1\text{H}_2 =$	$^{13}\text{C}_2 =$
$^1\text{H}_3 =$	$^{13}\text{C}_3 =$
$^1\text{H}_4 =$	$^{13}\text{C}_4 =$
$^1\text{H}_5 =$	$^{13}\text{C}_5 =$
$^1\text{H}_6 =$	$^{13}\text{C}_6 =$

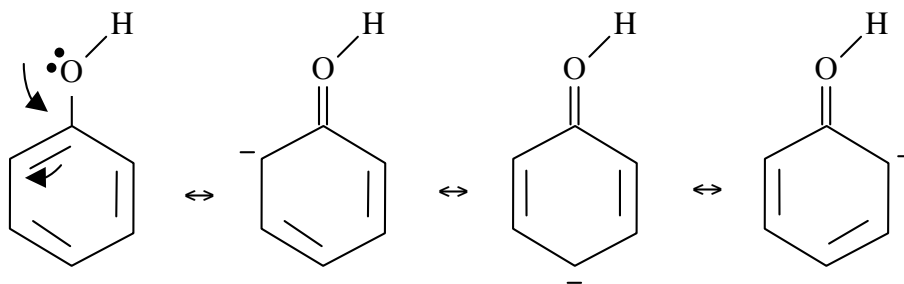
b. Justify your answers to 'a'. Draw resonance structures, state which nuclei are shielded or deshielded relative to one another and to benzene and why.



a.	$^1\text{H}_1 = 5.4$	$^{13}\text{C}_1 = 155$
	$^1\text{H}_2 = 6.8$	$^{13}\text{C}_2 = 115$
	$^1\text{H}_3 = 7.25$	$^{13}\text{C}_3 = 130$
	$^1\text{H}_4 = 6.9$	$^{13}\text{C}_4 = 121$
	$^1\text{H}_5 = 7.25$	$^{13}\text{C}_5 = 130$
	$^1\text{H}_6 = 6.8$	$^{13}\text{C}_6 = 115$

b. In the ^1H spectrum, the signals around 7 ppm are due to the aromatic protons, as in benzene. The hydroxyl signal is the signal at 5.4 ppm, and is deshielded relative to aliphatic protons due to the attached (electronegative) oxygen atom. Likewise, in the ^{13}C spectrum, the signals at 115-130 are due to ^{13}C atoms 2-6, as in benzene, whereas the signal at 155 is due to $^{13}\text{C}_1$, which is deshielded relative to benzene due to attachment to the oxygen atom. Resonance structures can be drawn (below) where the lone pair of electrons on the oxygen is donated to the C-O bond,

thus localizing a negative charge at either the ortho (2 or 6) or para (4) positions. Because the charge density, and thus the shielding, at the ortho and para positions will be greater than at the meta position, the ^1H and ^{13}C chemical shifts at the meta positions will be expected to be larger. Thus, $\delta^1\text{H}_3=\delta^1\text{H}_5=7.25$, and $\delta^{13}\text{C}_3=\delta^{13}\text{C}_5=130$. Finally, one would expect that the charge density at the ortho position would be larger than at the para position because of its proximity to the oxygen and the $\text{C}=\text{O}$ double bond, and thus would be more shielded. So, the ^1H and ^{13}C chemical shifts at the ortho position ($\delta^1\text{H}_2=\delta^1\text{H}_6=6.8$, $\delta^{13}\text{C}_2=\delta^{13}\text{C}_6=115$) are smaller than at the para position ($\delta^1\text{H}_4=6.9$, $\delta^{13}\text{C}_4=121$).



10). If the longitudinal relaxation time for a given nucleus is 10 seconds, how long after a 90° pulse will we have to wait until the magnitude of the z component of the bulk magnetization (M_z) is equal to 95% of the magnitude of the bulk magnetization before the pulse (M_0)?

We assume, as did Bloch, that this relaxation process is first order, and $M_z = M_0(1 - e^{-t/T_1})$.

$$M_z / M_0 = 0.95 = (1 - e^{-t/T_1}) = (1 - e^{-t/10\text{s}}) \quad e^{-t/10\text{s}} = 0.05 \quad -t/10\text{s} = -2.9957 \quad t \approx 30\text{s}$$