

1.1.A.

$n = n_\alpha + n_\beta = 2 L = 2 \text{ kg} = (2000/18) = 111.1 \text{ mol} = 6.6913 \cdot 10^{25} \text{ water molecules} = 1.3383 \cdot 10^{26} \text{ proton spins}$. At 3.0 T the proton resonance frequency = 127.66 MHz

Using Eq. [1.24], $(n_\alpha/n_\beta) = 1 + 2.0549 \cdot 10^{-5}$ such that $n_\beta = 6.6912 \cdot 10^{25}$ and the net excess $n_\alpha - n_\beta = 1.3750 \cdot 10^{21}$ spins.

B.

The complete expression for (n_α/n_β) is given by Eq. [1.23] and gives for $n_\alpha - n_\beta = 1.3750 \cdot 10^{21}$ spins at 298.15 K representing an error of 0.001%.

At 4.0 K the full and truncated expressions give $n_\alpha - n_\beta = 1.0249 \cdot 10^{23}$ and $1.0241 \cdot 10^{23}$ spins, respectively, representing an error of 0.077%. Note the increase in net polarization of almost two orders of magnitude at the lower temperature as compared to room temperature.

At 0.01 K the full and truncated expressions give $n_\alpha - n_\beta = 3.9760 \cdot 10^{25}$ and $3.1382 \cdot 10^{25}$ spins, respectively, representing an error of 21%. Note the increase in net polarization of almost more than four orders of magnitude at the lower temperature as compared to room temperature. Further note that the Taylor expansion of Eq. [1.23] remains valid for all temperatures not in the immediate proximity of absolute zero.

1.2.

A cross product can be written as the determinant of a matrix according to:

$$\begin{aligned} \frac{dM}{dt} = \gamma M \times B &= \gamma \begin{vmatrix} [x] & [y] & [z] \\ M_x & M_y & M_z \\ B_x & B_y & B_z \end{vmatrix} \\ &= \gamma \left(\begin{vmatrix} M_y & M_z \\ B_y & B_z \end{vmatrix} [x] - \begin{vmatrix} M_x & M_z \\ B_x & B_z \end{vmatrix} [y] + \begin{vmatrix} M_x & M_y \\ B_x & B_y \end{vmatrix} [z] \right) \end{aligned}$$

$$= \gamma \left([M_y B_z - B_y M_z][x] - [M_x B_z - B_x M_z][y] + [M_x B_y - B_x M_y][z] \right) \quad [s1.1]$$

$$\text{And on the other hand: } \frac{dM}{dt} = \frac{dM_x}{dt}[x] + \frac{dM_y}{dt}[y] + \frac{dM_z}{dt}[z] \quad [s1.2]$$

The combination of Eqs. [s1.1] and [s1.2] gives the Bloch equations in the laboratory frame (Eqs. [1.33]-[1.35]). See standard text books on matrix algebra for more information regarding cross products and determinants.

1.3.

In order to demonstrate that the two expressions are a solution to the Bloch equations, one simply substitutes the expressions into the Bloch equations and show that the expressions are equal:

The left side of Eqs. [1.33] and [1.34] become

$$\frac{dM_x(t)}{dt} = -\omega M_x(0) \sin \omega t + \omega M_y(0) \cos \omega t \quad [s1.3]$$

$$\frac{dM_y(t)}{dt} = -\omega M_y(0) \sin \omega t - \omega M_x(0) \cos \omega t \quad [s1.4]$$

The right side of Eqs. [1.33] and [1.34] become

$$\gamma [M_y(t)B_0 - M_z(t)B_{1y}] = \gamma [M_y(0)B_0 \cos \omega t - M_x(0)B_0 \sin \omega t - M_z(t)B_{1y}] \quad [s1.5]$$

$$\gamma [M_z(t)B_{1x} - M_x(t)B_0] = \gamma [M_z(0)B_{1x} - M_x(0)B_0 \cos \omega t - M_y(0)B_0 \sin \omega t] \quad [s1.6]$$

Using the Larmor relation $\omega = \gamma B_0$ and the fact that the RF field is absent ($B_{1x} = B_{1y} = 0$), the right side of Eqs. [s1.5] and [s1.6] are equal to the right side of Eqs. [s1.3] and [s1.4], respectively, demonstrating that the expressions are solutions to the Bloch equations in the laboratory frame.

1.4A.

The Bloch equations in the rotating frame (Eqs. [1.45]-[1.47]) are related to the Bloch equations in the laboratory frame (Eqs. [1.39]-[1.41]) through a substitution of Eqs. [1.42]-[1.44]. As an example consider Eq. [1.42]. Taking the derivative with respect to time gives

$$\frac{dM'_x(t)}{dt} = \frac{dM_x(t)}{dt} \cos \omega t - \omega M_x(t) \sin \omega t + \frac{dM_y(t)}{dt} \sin \omega t + \omega M_y(t) \cos \omega t$$

[s1.7]

Substituting Eqs. [1.39] and [1.40] for (dM_x/dt) and (dM_y/dt) into Eq. [s1.7] and regrouping terms according to Eqs. [1.42] and [1.43] gives Eq. [1.45] whereby the Larmor relation $\omega_0 = -\gamma B_0$ was used. B_{1x}' and B_{1y}' represent the B_1 fields along the x' and y' axes of the rotating frame of reference, respectively.

B. Direct substitution of Eqs. [1.50] and [1.51] into Eqs. [1.45] and [1.46] confirms the claim.

1.5A.

The peak height of a Lorentzian line is equal to $A(0) = M_0 T_2$ (assuming $T_2 = T_2^*$). To find the frequencies at which the resonance is a half maximum, the following equation must be solved:

$$\frac{A(0)}{2} = \frac{M_0 T_2}{2} = \frac{M_0 T_2}{1 + 4\pi^2 (\nu_0 - \nu)^2 T_2^2}$$

[s1.8]

The solutions are $\nu_0 - \nu = \pm 1/(2\pi T_2)$, such that $\text{FWHM} = 2|\nu_0 - \nu| = 1/(\pi T_2)$.

1.5B.

The expression of a magnitude Lorentzian line is given by Eq. [1.61] which is equal to

$$M(\omega) = \sqrt{A^2(\omega) + D^2(\omega)}$$

[s1.9]

Following arguments outlined under Exercise 1.5A, the FWHM can be obtained by finding the frequencies at half maximum ($M(\omega) = M_0 T_2/2$) and is equal to

$$\text{FWHM} = \frac{\sqrt{3}}{\pi T_2} \quad [\text{s1.10}]$$

Note that the line width of an absolute valued line is circa 1.7 times wider than for a phased absorption line. Therefore, in order to obtain the highest spectral resolution phasing of NMR spectra, where applicable, is highly recommended.

1.5C.

For a symmetric function around $t = 0$, the complex Fourier transformation reduces to a cosine transformation for which the end result is given by

$$A(\omega) = \frac{2M_0 T_2}{1 + 4\pi^2 (\nu_0 - \nu)^2 T_2^2} \quad \text{and} \quad D(\omega) = 0 \quad [\text{s1.11}]$$

1.5D.

Using the indefinite integral relation $\int \frac{1}{a^2 + x^2} dx = \left(\frac{1}{a}\right) \tan^{-1}\left(\frac{x}{a}\right)$ it can be shown that the integrals of Lorentzian lines originating from FID and echo signals are equal to $M_0/2$ and M_0 , respectively.

1.6.A.

For $B_{1y} = 0$ and $(\omega_0 - \omega) = 0$, Eqs. [1.45] – [1.47] reduce (in the absence of relaxation) to:

$$\frac{dM_x(t)}{dt} = 0, \quad \frac{dM_y(t)}{dt} = \gamma B_{1x} M_z(t) \quad \text{and} \quad \frac{dM_z(t)}{dt} = -\gamma B_{1x} M_y(t) \quad [\text{s1.12}]$$

The general solution to the two coupled differential equations is given by:

$$M_y(T) = M_y(0) \cos(\gamma B_{1x} T) - M_z(0) \sin(\gamma B_{1x} T) \quad [\text{s1.13}]$$

$$M_z(T) = M_z(0) \cos(\gamma B_{1x} T) + M_y(0) \sin(\gamma B_{1x} T) \quad [\text{s1.14}]$$

which reduce for $M_y(0) = 0$ and $M_z(0) = M_0$ to:

$$M_y(T) = -M_0 \sin(\gamma B_{1x} T) \text{ and } M_z(T) = M_0 \cos(\gamma B_{1x} T) \quad [s1.15]$$

B.

$\theta = 2\pi\gamma B_1 T$, thus γB_1 (in Hz) = $\theta/(2\pi T) = 250$ Hz, thus B_1 (in μT) = 5.873 μT .

C.

Proton Larmor frequency at 3.0 T = 127.66 MHz = 127.66 million revolutions per second. Thus in 1 ms, the magnetization has precessed over 127,660 cycles.

1.7.A. Solving Eq. [1.38] over the time boundaries [0, t] will lead to:

$$M_z(t) = M_0 - (M_0 - M_z(0))e^{-t/T_1} \quad [s1.16]$$

B. 1. Longitudinal magnetization prior to the excitation pulse $M_1 = M_z$

2. Longitudinal magnetization immediately following the excitation pulse $M_2 = M_z \cos\alpha$

3. Longitudinal magnetization following a recovery delay TR,

$$M_3 = M_0 - (M_0 - M_z \cos\alpha)e^{-TR/T_1}$$

4. When a steady-state situation is achieved, $M_1 = M_3$, i.e.

$M_z = M_0 - (M_0 - M_z \cos\alpha)e^{-TR/T_1}$ which, after re-arranging terms yields Eq. [1.72].

C. Steady-state magnetization = 0.8802 M_0

Longitudinal magnetization prior to excitation pulse 1 = M_0

Longitudinal magnetization prior to excitation pulse 2 = 0.9139 M_0

Longitudinal magnetization prior to excitation pulse 3 = 0.8897 M_0

Longitudinal magnetization prior to excitation pulse 4 = 0.8828 M_0

Longitudinal magnetization prior to excitation pulse 5 = 0.8809 M_0

Longitudinal magnetization prior to excitation pulse 6 = 0.8804 M_0

Longitudinal magnetization prior to excitation pulse 7 = 0.8802 M_0

The longitudinal magnetization is within 1% of the steady-state magnetization after 3 RF pulses.

D.

Average signal during block 1 = $0.5924M_0$

Average signal during block 10 = $0.5658M_0$ (= steady-state transverse magnetization)

The first block has 4.7% more signal than the subsequent blocks. This can be a serious problem during difference experiments, like GABA editing (see Chapter 8).

E.

The Ernst angle is defined as the maximum amount of signal (i.e. M_{xy}) per unit of time under steady-state conditions. Therefore, Eq. [1.72] must be multiplied with $\sin\alpha$ in order to obtain the transverse magnetization. The maximum amount of signal per unit time can be found by differentiating M_{xy} with respect to α , i.e.

$$\frac{dM_{xy}}{d\alpha} = 0 \quad \text{Solving the resulting equation for } \alpha \text{ gives the Ernst angle.}$$

F.

The Ernst angle of the excitation pulse of a spin-echo sequence is generally $180^\circ - \alpha$, where α is the pulse-acquire Ernst angle. This is to compensate for the 180° refocusing pulse inherent to spin-echo methods. For this example, $\alpha_{SE} = 127.34^\circ$

1.8.A.

Resonance frequency at 7.05 T = 300.00 MHz such that 1 ppm corresponds to 300 Hz. Frequency difference between creatine and NAA = 1.02 ppm = 306 Hz making the phase difference $\Delta\phi = 2\pi\Delta\nu t = 55.1^\circ$.

B.

The two points (2.01 ppm, 210°) and (3.22 ppm, 30°) establish the following relationship:

$$\text{phase } \phi \text{ (in degrees)} = -148.76 \times \text{frequency } \nu \text{ (in ppm)} + 509^\circ$$

Therefore a first-order phase correction of +148.76°/ppm is required. The zero-point of first-order phase correction normally occurs on-resonance, such that the zero-order phase correction can be determined from the phase of the water resonance which equals – 190.17°. Note that the calculation given above has an inherent assumption in that the phase of the NAA is exactly 210° and not 210° plus an integer times 360°.

1.9.A.

$$\Delta v_{1/2} = \frac{2\sqrt{\ln 2}}{\pi T_{2G}} \quad [s1.17]$$

B.

The functions $F_L(\omega) = \frac{M_0 T_{2L}}{1 + (\omega_0 - \omega)^2 T_{2L}^2}$ and $F_G(\omega) = \sqrt{\frac{\pi}{4}} M_0 T_{2G} e^{-\frac{(\omega_0 - \omega)^2 T_{2G}^2}{4}}$

are normalized Lorentzian and Gaussian line shapes in that their integral over the interval $-\infty \leq \omega \leq +\infty$ equals $M_0/2$.

For equal line widths the relationship $T_{2G} = 2\sqrt{\ln 2} T_{2L}$ must hold. Since the peak heights of Lorentzian and Gaussian lines are given by $M_0 T_{2L}$ and $\sqrt{(\pi/4)} M_0 T_{2G}$, it follows that a Gaussian line is $\sqrt{\pi \ln 2} \sim 1.476$ higher than a Lorentzian line of equal width.

C.

$$\Delta v_{10\%, \text{Lorentzian}} = \frac{3}{\pi T_{2L}} \quad \Delta v_{10\%, \text{Gaussian}} = \frac{2\sqrt{\ln 10}}{\pi T_{2g}} \quad [s1.18]$$

Using the relation $T_{2G} = 2\sqrt{\ln 2} T_{2L}$, the Lorentzian line is $\frac{3}{\sqrt{\log_2 10}} \sim 1.646$ times

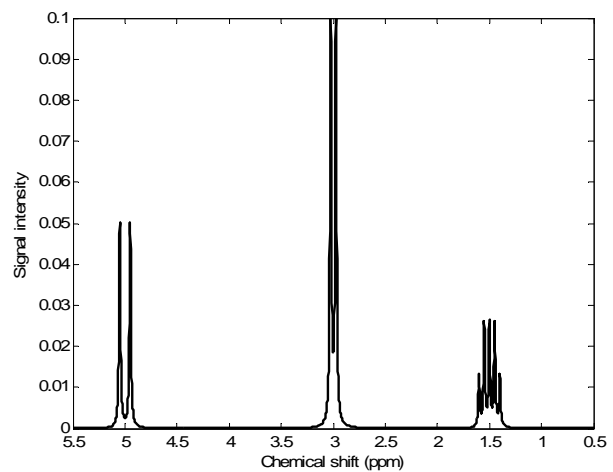
wider than a Gaussian line at 10% height.

1.10.

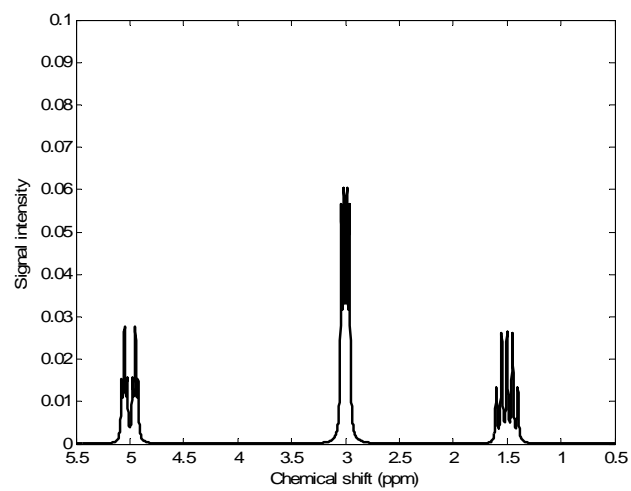
Solution : $O = CH - HC = CH - O - CH_2 - CH_3$

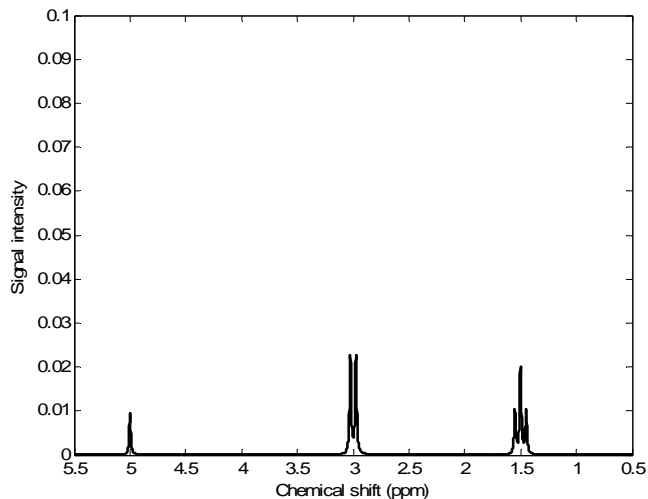
(3-ethoxy-2-propenal, or 3-ethoxy-acrylaldehyde)

1.11.A.



B.





1.12.A.

Dwell-time = $102.4/512 = 0.2$ ms. Spectral width = $1/\text{dwell time} = 5,000$ Hz.

B.

$-1,200$ Hz, because $3,800 \text{ Hz} = F_{\text{Nyquist}} + 1,300 \text{ Hz}$ which will appear at $-F_{\text{Nyquist}} + 1,300 \text{ Hz} = -1,200 \text{ Hz}$ following aliasing.

C.

$-1,000$ Hz, since the signals alias four times from $-16,000$, $-11,000$, $-6,000$ to $-1,000$ Hz.

1.13.A.

Frequency differences are 240 and 455 Hz, respectively. Since DSS is assigned a chemical shift of 0.00 ppm, the other two resonances appear at chemical shifts of 1.41 and 2.67 ppm, respectively.

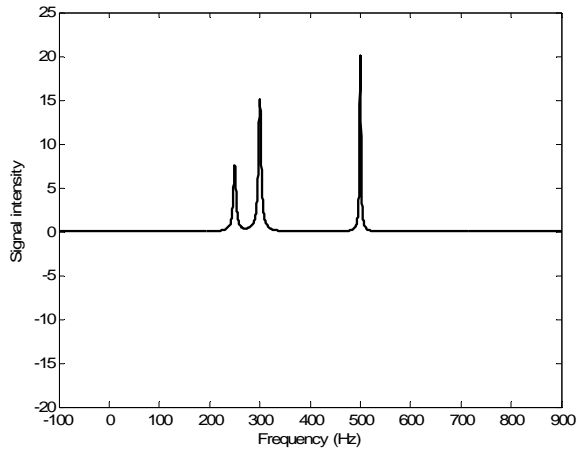
B.

Frequency, resonance 1 = $300.176544 \text{ MHz} + 1.41 \text{ ppm} \times 300 \text{ Hz/ppm} = 300.176967 \text{ MHz}$.

Frequency resonance 2 = $300.176544 \text{ MHz} + 2.67 \text{ ppm} \times 300 \text{ Hz/ppm} = 300.177345 \text{ MHz}$.

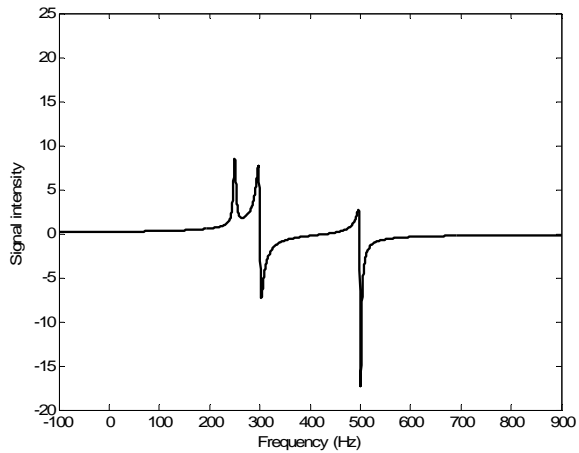
1.14.

A.



Line widths (in Hz) are (6.4, 6.4, 3.2) and peak heights are (7.5, 15, 20).

B.



1.15.

Substituting Eqs. [1.54] and [1.55] into Eqs. [1.58] and [1.59] gives $A(\omega) = A(\omega)$ and $D(\omega) = D(\omega)$ for $\phi = \phi_c$, indicating that the phase correction described by Eqs. [1.58] and [1.59] does yield pure absorption spectra.

1.16.

${}^1J_{\text{CH}}$ is typically a positive number. Using Hund's rule it can be deduced that ${}^2J_{\text{HH}}$ and ${}^3J_{\text{HH}}$ are given by negative and positive numbers, respectively.