

NMR for Physical and Biological Scientists
 Thomas C. Pochapsky and Susan Sondej Pochapsky
Solutions to Chapter 9 Problems

9.1) a)

$$2\hat{\mathbf{I}}_x\hat{\mathbf{S}}_z = \hat{\mathbf{I}}_+\hat{\mathbf{S}}_z + \hat{\mathbf{I}}_-\hat{\mathbf{S}}_z$$

and using Eqs. 9.13,

$$\begin{aligned} 2\hat{\mathbf{I}}_x\hat{\mathbf{S}}_z &= \hat{\mathbf{I}}_+\hat{\mathbf{S}}_z + \hat{\mathbf{I}}_-\hat{\mathbf{S}}_z \\ &= \left[(\hat{\mathbf{I}}_+^{(1,2)} - \hat{\mathbf{I}}_+^{(3,4)}) + (\hat{\mathbf{I}}_-^{(1,2)} - \hat{\mathbf{I}}_-^{(3,4)}) \right] \end{aligned}$$

After evolution during t_1 ,

$$\begin{aligned} 2\hat{\mathbf{I}}_x\hat{\mathbf{S}}_z &= \hat{\mathbf{I}}_+\hat{\mathbf{S}}_z + \hat{\mathbf{I}}_-\hat{\mathbf{S}}_z \\ &= \hat{\mathbf{I}}_+^{(1,2)} \exp[-i\omega_{12}t_1] - \hat{\mathbf{I}}_+^{(3,4)} \exp[-i\omega_{34}t_1] \\ &\quad + \hat{\mathbf{I}}_-^{(1,2)} \exp[i\omega_{12}t_1] - \hat{\mathbf{I}}_-^{(3,4)} \exp[i\omega_{34}t_1] \\ &= \left(\frac{1}{2}\hat{\mathbf{I}}_+ + \hat{\mathbf{I}}_+\hat{\mathbf{S}}_z \right) \exp[-i\omega_{12}t_1] - \left(\frac{1}{2}\hat{\mathbf{I}}_+ - \hat{\mathbf{I}}_+\hat{\mathbf{S}}_z \right) \exp[-i\omega_{34}t_1] \\ &\quad + \left(\frac{1}{2}\hat{\mathbf{I}}_- + \hat{\mathbf{I}}_-\hat{\mathbf{S}}_z \right) \exp[i\omega_{12}t_1] - \left(\frac{1}{2}\hat{\mathbf{I}}_- - \hat{\mathbf{I}}_-\hat{\mathbf{S}}_z \right) \exp[i\omega_{34}t_1] \\ &= \frac{1}{2}\hat{\mathbf{I}}_+ [\exp[-i\omega_{12}t_1] - \exp[-i\omega_{34}t_1]] \\ &\quad + \hat{\mathbf{I}}_+\hat{\mathbf{S}}_z [\exp[-i\omega_{12}t_1] + \exp[-i\omega_{34}t_1]] \\ &\quad + \frac{1}{2}\hat{\mathbf{I}}_- [\exp[i\omega_{12}t_1] - \exp[i\omega_{34}t_1]] \\ &\quad + \hat{\mathbf{I}}_-\hat{\mathbf{S}}_z [\exp[i\omega_{12}t_1] + \exp[i\omega_{34}t_1]] \end{aligned}$$

These terms can be converted back to Cartesian basis using the Euler relationships and recombining terms:

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$$\begin{aligned} & \frac{1}{2} \widehat{\mathbf{I}}_+ [\cos \omega_{12} t_1 - i \sin \omega_{12} t_1 - \cos \omega_{34} t_1 + i \sin \omega_{34} t_1] + \\ & \widehat{\mathbf{I}}_+ \widehat{\mathbf{S}}_z [\cos \omega_{12} t_1 - i \sin \omega_{12} t_1 + \cos \omega_{34} t_1 - i \sin \omega_{34} t_1] + \\ & \frac{1}{2} \widehat{\mathbf{I}}_- [\cos \omega_{12} t_1 + i \sin \omega_{12} t_1 - \cos \omega_{34} t_1 - i \sin \omega_{34} t_1] + \\ & \widehat{\mathbf{I}}_- \widehat{\mathbf{S}}_z [\cos \omega_{12} t_1 + i \sin \omega_{12} t_1 + \cos \omega_{34} t_1 + i \sin \omega_{34} t_1] = \end{aligned}$$

$$\begin{aligned} & \frac{1}{2} (\widehat{\mathbf{I}}_+ + \widehat{\mathbf{I}}_-) \cos \omega_{12} t_1 + (\widehat{\mathbf{I}}_+ \widehat{\mathbf{S}}_z + \widehat{\mathbf{I}}_- \widehat{\mathbf{S}}_z) \cos \omega_{12} t_1 \\ & - \frac{i}{2} (\widehat{\mathbf{I}}_+ - \widehat{\mathbf{I}}_-) \sin \omega_{12} t_1 - i (\widehat{\mathbf{I}}_+ \widehat{\mathbf{S}}_z - \widehat{\mathbf{I}}_- \widehat{\mathbf{S}}_z) \sin \omega_{12} t_1 \\ & - \frac{1}{2} (\widehat{\mathbf{I}}_+ + \widehat{\mathbf{I}}_-) \cos \omega_{34} t_1 + (\widehat{\mathbf{I}}_+ \widehat{\mathbf{S}}_z + \widehat{\mathbf{I}}_- \widehat{\mathbf{S}}_z) \cos \omega_{34} t_1 \\ & + \frac{i}{2} (\widehat{\mathbf{I}}_+ - \widehat{\mathbf{I}}_-) \sin \omega_{34} t_1 - i (\widehat{\mathbf{I}}_+ \widehat{\mathbf{S}}_z - \widehat{\mathbf{I}}_- \widehat{\mathbf{S}}_z) \sin \omega_{34} t_1 \end{aligned}$$

$$\begin{aligned} & = \widehat{\mathbf{I}}_x \cos \omega_{12} t_1 + 2 \widehat{\mathbf{I}}_x \widehat{\mathbf{S}}_z \cos \omega_{12} t_1 \\ & - \widehat{\mathbf{I}}_y \sin \omega_{12} t_1 - 2 \widehat{\mathbf{I}}_y \widehat{\mathbf{S}}_z \sin \omega_{12} t_1 \\ & - \widehat{\mathbf{I}}_x \cos \omega_{34} t_1 + 2 \widehat{\mathbf{I}}_x \widehat{\mathbf{S}}_z \cos \omega_{34} t_1 \\ & + \widehat{\mathbf{I}}_y \sin \omega_{34} t_1 - 2 \widehat{\mathbf{I}}_y \widehat{\mathbf{S}}_z \sin \omega_{34} t_1 \end{aligned}$$

9.2) After the 90 degree pulse on ^1H , but before the 90 degree pulse on ^{15}N , both operators of the coherence of interest are stored along the z -axis in the laboratory frame, and as such are not affected by pulsed field gradients. That is,

$$2 \widehat{\mathbf{S}}_x \widehat{\mathbf{I}}_z \xrightarrow{\pi/2(S)} -2 \widehat{\mathbf{S}}_z \widehat{\mathbf{I}}_x \text{ - crusher gradient - } -2 \widehat{\mathbf{S}}_z \widehat{\mathbf{I}}_z \xrightarrow{\pi/2(I)} 2 \widehat{\mathbf{S}}_z \widehat{\mathbf{I}}_x$$

9.3) At 14 T (600 MHz ^1H), ^{13}C resonates at 150 MHz, so 1 ppm is 150 Hz. The difference between the carbonyl frequency (180 ppm) and the $\text{C}\alpha$ frequency (60 ppm) is 120 ppm, or 18 kHz. Using Eq. 9.9, one obtains a value of 48 μs for the pulse length. Eq. 9.10 indicates that for a pulse of 32 steps, each step will be 1.5 μs in duration, and the phase increment at each step will be 9.72 degrees. Note that the pulse power must still

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be calibrated to generate a π pulse at the carbonyl position. Eqs. 9.9 and 9.10 only specify the phase shift and pulse duration.

9.4) 53.8 μs is the duration, and 10.89 degrees is the phase shift per step. Again, calibration of pulse power is still required.

9.5)

$$\phi_1 = 180 = (\tau/2SW) \times 360$$

$$\tau/2SW = 0.5$$

$$\Delta t_1(0) = 1/20,000 - 4(7.3 \times 10^{-6})/\pi$$

$$= 5 \times 10^{-5} \text{ s} - 9.3 \times 10^{-6} \text{ s} = 40.7 \mu\text{s}$$

In the case of an HSQC experiment, where t_1 is divided by a ^1H π pulse, the appropriate calculation must take the length of that pulse into consideration:

$$\Delta t_1(0) = 1/2,000 - 4(35 \times 10^{-6})/\pi - t_{180}$$

$$= 5 \times 10^{-4} \text{ s} - 4.45 \times 10^{-5} \text{ s} - 14.6 \times 10^{-6} \text{ s}$$

$$= 4.4 \times 10^{-4} \text{ s}$$

9.6)

$$\widehat{\mathbf{S}}_z \xrightarrow{\frac{\pi}{2} \text{ pulse}(\frac{\pi}{2}, S)} \widehat{\mathbf{S}}_x \xrightarrow{\Delta=1/2J_{IS}} 2\widehat{\mathbf{S}}_y \widehat{\mathbf{I}}_z \xrightarrow{\text{pulse}(\phi, I)} 2\widehat{\mathbf{S}}_y \widehat{\mathbf{I}}_z \cos \phi + 2\widehat{\mathbf{S}}_y \widehat{\mathbf{I}}_x \sin \phi \xrightarrow{\Delta=1/2J_{IS}} -\widehat{\mathbf{S}}_x \cos \phi$$

The first pulse in the sequence, a $\pi/2_{(y)}$ pulse on ^1H , creates transverse coherence at the ^1H attached to the heteroatom of interest, e.g., ^{15}N ($\mathbf{S} = ^1\text{H}$, $\mathbf{I} = ^{15}\text{N}$), which then evolves for the $1/2J$ delay time to give the term $2\widehat{\mathbf{S}}_y \widehat{\mathbf{I}}_z$. A (y) pulse on nucleus I of tip angle ϕ results

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in the formation of two terms: $2\widehat{S}_y\widehat{I}_z \cos \phi + 2\widehat{S}_y\widehat{I}_x \sin \phi$. The left-hand term will evolve into observable coherence after $1/2J$, but the right-hand (sine) term is multiple-quantum (MQ) and will not re-evolve into observable coherence. When $\phi = \pi/2$, only the second, MQ term is non-zero, and no signal will be observed from the S spins coupled to I.

9.7) A change in pulse power by a factor of 4 corresponds to a 6 dB change, implying that a factor of 4 change in pulse power is required to double (or halve) the pulse length. (Note that this means that pulse length is not directly proportional to power, but rather to the voltage in the coil, which in turn is proportional to the square of the pulse power). A 50 W to 35 W change corresponds to a factor of 1.4, and taking the square root of this yields the change in the pulse length (by a factor of 1.18, or roughly 1.2). The pulse length should thus increase from 7 to 8.3 μs .

9.8) Part A represents polarization transfer from ^1H to ^{15}N :

$$\widehat{S}_z \rightarrow -2\widehat{S}_z\widehat{N}_y$$

During the constant-time evolution period B, the coherence is modulated by the chemical shift of the ^{15}N , and also evolves with respect to the one-bond N-CO coupling, so at the end of part B, after transfer to the carbonyl ^{13}C , one has:

$$4\widehat{S}_z\widehat{N}_z\widehat{C}'_y (\cos \Omega_N t_1)$$

This term evolves with the Ca-CO coupling to yield:

$$-8\widehat{S}_z\widehat{N}_z\widehat{C}'_x\widehat{C}_z (\cos \Omega_N t_1)$$

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that is transferred by an HMQC (DQ) transfer to the $C\alpha$, so that the C-C coupling does not evolve during t_2 . The refocusing pulse on ^1H and ^{13}CO (indicated as C' in the operators) prevents evolution of the transverse coherence by coupling to $C\alpha$ and ^1H , and refocuses chemical shift evolution due to $C\alpha$ during t_2 , so that at the end of t_2 , prior to transfer back to CO, one has:

$$-8\widehat{S}_z\widehat{N}_z\widehat{C}'_x\widehat{C}'_y(\cos\Omega_N t_1)(\cos\Omega_{C\alpha} t_2)$$

The remaining steps refocus the product operators as follows:

$$\begin{aligned} -8\widehat{S}_z\widehat{N}_z\widehat{C}'_x\widehat{C}'_y(\cos\Omega_N t_1)(\cos\Omega_{C\alpha} t_2) &\rightarrow 4\widehat{S}_z\widehat{N}_z\widehat{C}'_y(\cos\Omega_N t_1)(\cos\Omega_{C\alpha} t_2) \\ &\rightarrow -2\widehat{S}_z\widehat{N}_y(\cos\Omega_N t_1)(\cos\Omega_{C\alpha} t_2) \rightarrow \widehat{S}_x(\cos\Omega_N t_1)(\cos\Omega_{C\alpha} t_2) \end{aligned}$$

The last term represents observable ^1H (NH) coherence that has been modulated at the chemical shifts of the attached ^{15}N during t_1 and the (i-1) $C\alpha$ during t_2 .

9.9) The “soft” WATERGATE sequence involves a series of three pulses and two gradients. Note that in essence, it is a gradient echo experiment (see Ch. 7 and Figure 7...) In the normal course of a gradient echo, coherence that is transverse (all of the ^1H coherences after the 90° pulse that starts the WATERGATE sequence) is dephased by the first gradient, but after the 180° pulse in the center of the gradient echo sequence that changes the sign of the coherences, those coherences will be refocused by the second gradient. In this case, however, the soft 90° pulse on water places the water coherence along the z -axis prior to the 180° pulse. The next soft 90° pulse following the hard 180° pulse amounts to a net reversal of the effect of the 180° pulse on the water coherence, so that the sign of the water coherence is not changed from where it started, and the second

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gradient that refocuses the other ^1H resonances further dephases the water signal, so it is not detected.

9.10)

The primary source of T_2 relaxation for the carbonyl ^{13}C is chemical shift anisotropy (CSA), because there is no attached ^1H , and the carbonyl ^{13}C is sp^2 hybridized, and less spherically symmetric than sp^3 -hybridized ^{13}C , giving rise to greater intrinsic anisotropy. Increasing the magnetic field exaggerates the CSA relaxation. Since magnetization is transferred via the 1-bond couplings to the carbonyl carbon in $\text{HN}(\text{CO})\text{CA}$, but not HNCA , the $\text{HN}(\text{CO})\text{CA}$ experiment is sensitive to changes in the carbonyl carbon CSA.