Exercises for "Homonuclear Dipolar Recoupling in Solid State NMR: Analysis with Average Hamiltonian Theory", prepared by R. Tycko, 1/17/08.

I. Relevant quantum mechanical principles

1. Consider a sample that contains many molecules, each with two spin-1/2 nuclei. At time t = 0, the two nuclei in each molecule are in state |a> or state |b>, with equal probability. If $\left|a\right\rangle = \frac{1}{\sqrt{2}}\{\left|++\right\rangle + \left|--\right\rangle\}$ and $\left|b\right\rangle = \frac{1}{2}\{\left|++\right\rangle + \left|+-\right\rangle + \left|-+\right\rangle + i\left|--\right\rangle\}$ at t = 0, what is the 4 X 4 density matrix for the entire system at t = 0? Use the direct-product basis |++>, |+->, |-+>, |--> to evaluate the density matrix.

Hint: Use Eq. (I.6). In this problem, $\rho(0) = \frac{1}{2}\{|a><a| + |b><b|\}$.

2. What is the NMR signal at t = 0 for the system in question 1? Use $S(t) = \mathrm{Tr}\{I_+\rho(t)\}$, with $I_+ = I_x + iI_y$. Hints: $I_x = I_{x1} + I_{x2}$,

$$I_{x1} = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix}, \text{ and}$$

$$I_{x2} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \end{pmatrix}.$$

3. If a spin system is initially in the state $\rho(0) = I_x$ at t = 0, and $H = \hbar\omega_0 I_z$, show that $S(t) \propto e^{i\omega_0 t}$. Hint: $e^{-iI_z\theta} I_x e^{iI_z\theta} = I_x \cos\theta + I_y \sin\theta$

II. Useful Mathematical Identities and Tricks

1. Prove that Eq. (II.3) is correct.
Hint: Expand e^B in a Taylor series, i.e., $e^B = 1 + B + B^2/2 + B^6/6 + \ldots$ Then insert $AA^{-1} = 1$ between successive factors of B, and resum the series.

2. Prove that Eq. (II.6b) is correct.

3. Prove that Eq. (II.9) is correct to first order in A and B.

4. Show that $e^{-iI_x\pi/2} e^{iI_z\varepsilon} e^{iI_x\pi/2} e^{iI_y\pi} e^{iI_x\pi/2} e^{iI_z\varepsilon} e^{-iI_x\pi/2} e^{-iI_y\pi} = 1$.

5. Without using any matrices, show that $\mathrm{Tr}\{I_x e^{-iI_y\theta} I_z^2 e^{iI_y\theta}\} = 0$ for all values of θ.
Hint: Use Eq. (II.2) with a clever choice of A, and the general rule that x must be zero if x = -x.

6. Show that $e^{-iI_y\pi} e^{-iI_x\pi} = e^{iI_z\pi}$.
Hint: Use $e^{-iI_y\pi} = e^{-iI_y\pi/2} e^{-iI_y\pi/2}$.

III. Nuclear spin interactions under MAS

1. Rewrite Eq. (III.2) in a form where the time dependence from MAS appears as factors $e^{\pm i(\omega_R t+\gamma)}$ and $e^{\pm i(2\omega_R t+2\gamma)}$.
Hint: AX + BY = [(A-iB)(X+iY) + (A+iB)(X-iY)]/2

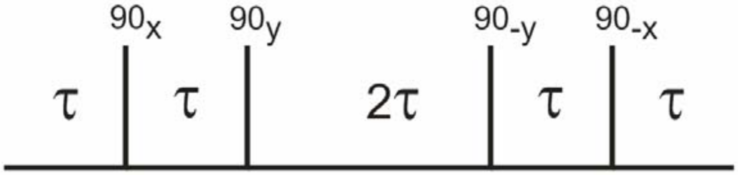
2. Prove that Eqs. (III.4) are correct.

3. For a system with only dipole-dipole couplings (*i.e.*, H_D is the entire Hamiltonian), show that the NMR signal after a hard 90_y pulse is entirely in the "x" channel (*i.e.*, the "y" channel signal is zero). Why is this not true if there are non-zero chemical shifts in addition to the dipole-dipole couplings?

4. Since you and your NMR spectrometer live in the laboratory frame, rather than living in the rotating frame, NMR signals are actually measured in the laboratory frame. Yet, we analyze NMR experiments in the rotating frame. Why is this O.K.?
Hints: In the laboratory frame, the Hamiltonian in Eq. (III.1) contains an additional term equal to ωI_z, where ω is the rf carrier frequency, and $H_{RF}(t) = 2\omega_1(t) I_x \cos(\omega t+\phi(t))$. Signals in the laboratory frame are $S(t) = \mathrm{Tr}\{I_x \rho(t)\}$ as they come out of your NMR probe, but your spectrometer sends these signals to two separate channels. In one channel, the signals are multiplied by $\cos\omega t$ and then filtered (i.e., high frequencies are discarded). In the other channel, the signals are multiplied by $\sin\omega t$ and then filtered.

IV. Average Hamiltonian Theory in simple terms

1. Eqs. (IV.6) show that the interaction representation Hamiltonian terms are obtained from the corresponding rotating frame terms by rotating them by $U_{RF}(t)^{-1}$, not by $U_{RF}(t)$. Assuming a static sample (i.e., $\omega_R = 0$) and only dipole-dipole couplings, show that the following pulse sequence produces $\tilde{H}_{D,\mathrm{ave}} = 0$ if $\tilde{H}_D = U_{RF}(t)^{-1} H_D U_{RF}(t)$, but not if $\tilde{H}_D(t) = U_{RF}(t) H_D U_{RF}(t)^{-1}$. In other words, it is important to calculate the interaction representation Hamiltonian correctly. This is the famous WAHUHA sequence for homonuclear decoupling in solids.



2. Prove that Eq. (I.4) implies $i\frac{d}{dt}[U(t)^{-1}] = -U(t)^{-1}H(t)$, as required for Eq. (IV.4) to be correct.

V. Homonuclear dipolar recoupling mechanisms

1. Show that the 2Q-HORROR recoupling sequence, which produces the average dipole-dipole Hamiltonian in Eq. (V.12), is "gamma-encoded". In other words, show that the magnitude of the average Hamiltonian is independent of the Euler angle γ.
Hint: The square of the magnitude of a Hamiltonian can be defined as $\| H \|^2 = \mathrm{Tr}\{H^2\}$.

2. Show that the average dipole-dipole Hamiltonian for the DRAMA recoupling sequence, given in (Eq. V.4), has the same orientation dependence as a static dipole-dipole Hamiltonian in the limit $(\tau_2 - \tau_1)/\tau_R << 1$, so that the powder pattern lineshape becomes a Pake doublet.

3. Show that the average chemical shift Hamiltonians are zero for the 2Q-HORROR sequence when $\omega_1 = \omega_R/2$. What happens to the average dipole-dipole and chemical shift Hamiltonians when $\omega_1 = \omega_R$? Are there any other values of ω_1 where the average dipole-dipole Hamiltonian is non-zero but the average chemical shift Hamiltonians are zero?

4. Show that the average chemical shift Hamiltonians are zero for the fpRFDR sequence with XY-4 phases.

5. What happens to the average Hamiltonians for the fpRFDR sequence if the π pulses are 180_x-180_x-180_{-x}-180_{-x}, instead of 180_x-180_y-180_x-180_y?

6. Verify that Eqs. (V.19) and (V.20) are correct.

7. Consider the effect of including $H_{CSA}(t)$ in the analysis of rotational resonance. How does this change Eqs. (V.17-21)? Does including CSA lead to additional rotational resonance conditions, beyond $n = 1$ and $n = 2$?

VI. Symmetry principles for recoupling sequences

1. Why are Eqs. (VI.3) and (VI.4) true?

2. Verify that Eq. (VI.6) is correct for $N = 5$.

3. Verify Eqs. (VI.9-VI.12).