BCMB/CHEM 8190
ANSWERS TO PROBLEM SET 4

1)

a) The equilibrium density matrix, σ_{eq} is just the sum of the density matrices for the two spins, so it is $\delta\mathbf{I}_{Az}+\delta\mathbf{I}_{Xz}$, or, using the conventions we used in class, $\mathbf{I}_{1z}+\mathbf{I}_{2z}$. So:

$$\sigma_{\mathrm{eq}} = \delta\mathbf{I}_{1z} + \delta\mathbf{I}_{2z} = \frac{1}{2}\delta\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{bmatrix} + \frac{1}{2}\delta\begin{bmatrix}1&0&0&0\\0&-1&0&0\\0&0&1&0\\0&0&0&-1\end{bmatrix} = \delta\begin{bmatrix}2&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-2\end{bmatrix}$$

b) The equilibrium z magnetization is calculated using the standard methods for calculating ensemble observables:

$$\overline{\boldsymbol{Q}}_{\mathrm{macro}} = N\ \mathrm{Tr}\left\{\left[\hat{\boldsymbol{\rho}}\right]\left[\hat{\boldsymbol{Q}}\right]\right\} \qquad M_{z,eq} = M_0 = N\ \mathrm{Tr}\left\{\left[\hat{\boldsymbol{\sigma}}_{eq}\right]\left[\hat{\boldsymbol{\mu}}_z\right]\right\}$$

For the calculation, we'll need the equilibrium density matrix (from part 'a', above). We'll also need the matrix representation of the $\boldsymbol{\mu}_z$ operator:

$$\hat{\boldsymbol{\mu}}_z = \gamma\hbar\hat{\boldsymbol{I}}_{1z} + \gamma\hbar\hat{\boldsymbol{I}}_{2z} = \gamma\hbar\frac{1}{2}\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{bmatrix} + \gamma\hbar\frac{1}{2}\begin{bmatrix}1&0&0&0\\0&-1&0&0\\0&0&1&0\\0&0&0&-1\end{bmatrix} = \gamma\hbar\frac{1}{2}\begin{bmatrix}2&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-2\end{bmatrix} = \gamma\hbar\begin{bmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{bmatrix}$$

We'll need to know the value for δ also:

$$\delta = \frac{\gamma\hbar B_0}{2k_BT}$$

$$M_{z,eq} = M_0 = N\ \mathrm{Tr}\left\{\left[\hat{\boldsymbol{\sigma}}_{eq}\right]\left[\hat{\boldsymbol{\mu}}_z\right]\right\} = N\ \mathrm{Tr}\left\{\delta\begin{bmatrix}2&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-2\end{bmatrix}\gamma\hbar\begin{bmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{bmatrix}\right\} = N\ \mathrm{Tr}\left\{\delta\gamma\hbar\begin{bmatrix}2&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&2\end{bmatrix}\right\}$$

$$= N\ 4\delta\gamma\hbar = N\ 4\frac{\gamma\hbar B_0}{2k_BT}\gamma\hbar = \frac{2N\gamma^2\hbar^2B_0}{k_BT}$$

2)

a) For $\mathbf{I}_x$ and $\mathbf{I}_z$ magnetization, the effects of rotations about the *y*-axis (RF pulse on *y*) are:

$$\mathbf{I}_x \xrightarrow{\alpha \mathbf{I}y} \mathbf{I}_x \cos(\omega_1 t) - \mathbf{I}_z \sin(\omega_1 t) \qquad \mathbf{I}_z \xrightarrow{\alpha \mathbf{I}y} \mathbf{I}_y \cos(\omega_1 t) + \mathbf{I}_x \sin(\omega_1 t)$$

For 90° ($\pi/2$) pulses, $\cos(\pi/2)=0$ and $\sin(\pi/2)=1$, thus:

$$\mathbf{I}_x \xrightarrow{\pi/2\, \mathbf{I}y} -\mathbf{I}_z \qquad \mathbf{I}_z \xrightarrow{\pi/2\, \mathbf{I}y} \mathbf{I}_x$$

So, for the $2\mathbf{I}_{1x}\mathbf{I}_{2z}$ operator:

$$2\mathbf{I}_{1x}\mathbf{I}_{2z} \xrightarrow{\pi/2\, \mathbf{I}_{1y}\ \pi/2\, \mathbf{I}_{2y}} -2\mathbf{I}_{1z}\mathbf{I}_{2x}$$

b) In class we constructed both the matrix representations for both $2\mathbf{I}_{1x}\mathbf{I}_{2z}$ and $2\mathbf{I}_{1z}\mathbf{I}_{2x}$, so:

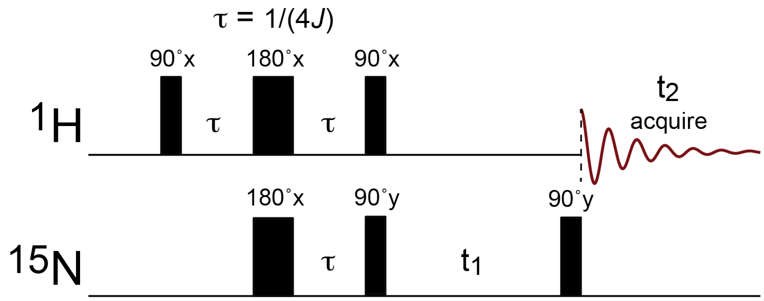
$$2\mathbf{I}_{1x}\mathbf{I}_{2z} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \xrightarrow{\pi/2\, \mathbf{I}_{1y}\ \pi/2\, \mathbf{I}_{2y}} -2\mathbf{I}_{1z}\mathbf{I}_{2x} = -\frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$$\begin{bmatrix} \rho_{\alpha\alpha,\alpha\alpha} & \overline{\overline{\rho_{\alpha\alpha,\alpha\beta}}} & \overrightarrow{\rho_{\alpha\alpha,\beta\alpha}} & \rho_{\alpha\alpha,\beta\beta} \\ \overline{\overline{\rho_{\alpha\beta,\alpha\alpha}}} & \rho_{\alpha\beta,\alpha\beta} & \rho_{\alpha\beta,\beta\alpha} & \overleftarrow{\rho_{\alpha\beta,\beta\beta}} \\ \overrightarrow{\rho_{\beta\alpha,\alpha\alpha}} & \rho_{\beta\alpha,\alpha\beta} & \rho_{\beta\alpha,\beta\alpha} & \overline{\rho_{\beta\alpha,\beta\beta}} \\ \rho_{\beta\beta,\alpha\alpha} & \overleftarrow{\rho_{\beta\beta,\alpha\beta}} & \overline{\rho_{\beta\beta,\beta\alpha}} & \rho_{\beta\beta,\beta\beta} \end{bmatrix}$$

Here, for $2\mathbf{I}_{1z}\mathbf{I}_{2x}$, in the density matrix, the elements representing transitions between α and β for spin 2 with spin 1 in the α state are those with the double bars. Those representing transitions between α and β for spin 2 with spin 1 in the β state are those with the single bars. These elements have opposite signs, so the result is an antiphase doublet.

For spin 1, the elements representing transitions between α and β for spin 1 with spin 2 in the α state are those with the arrows pointing to the right. Those representing transitions between α and β for spin 1 with spin 2 in the β state are those with the arrows pointing to the left. These elements are all zero, so there is no signal for spin 1.

3) The pulse sequence is shown here (assuming $\mathbf{I}_1$ is ^{1}H and $\mathbf{I}_2$ is ^{15}N). First, we'll describe what occurs, using product operators, beginning just before the first pulse, and ending just after the second τ period. We'll explore two routes. The first is the 'long' route, where we consider every pulse and delay, and all chemical shift evolution and coupling:



$$\mathbf{I}_{1z}+\mathbf{I}_{2z}\xrightarrow{\pi/2\,\mathbf{I}1x}-\mathbf{I}_{1y}+\mathbf{I}_{2z}\xrightarrow{\Omega_1\mathbf{I}zt\ \ \Omega_2\mathbf{I}zt}-\mathbf{I}_{1y}\cos(\Omega_1 t)+\mathbf{I}_{1x}\sin(\Omega_1 t)+\mathbf{I}_{2z}$$

$$\xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t}-\mathbf{I}_{1y}\cos(\Omega_1 t)\cos(\pi J_{1,2}\tau)+2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos(\Omega_1 t)\sin(\pi J_{1,2}\tau)$$
$$+\mathbf{I}_{1x}\sin(\Omega_1 t)\cos(\pi J_{1,2}\tau)+2\mathbf{I}_{1y}\mathbf{I}_{2z}\sin(\Omega_1 t)\sin(\pi J_{1,2}\tau)+\mathbf{I}_{2z}$$

$$\xrightarrow{\pi\mathbf{I}1x}\mathbf{I}_{1y}\cos(\Omega_1 t)\cos(\pi J_{1,2}\tau)+2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos(\Omega_1 t)\sin(\pi J_{1,2}\tau)$$
$$+\mathbf{I}_{1x}\sin(\Omega_1 t)\cos(\pi J_{1,2}\tau)-2\mathbf{I}_{1y}\mathbf{I}_{2z}\sin(\Omega_1 t)\sin(\pi J_{1,2}\tau)+\mathbf{I}_{2z}$$

$$\xrightarrow{\pi\mathbf{I}2x}\mathbf{I}_{1y}\cos(\Omega_1 t)\cos(\pi J_{1,2}\tau)-2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos(\Omega_1 t)\sin(\pi J_{1,2}\tau)$$
$$+\mathbf{I}_{1x}\sin(\Omega_1 t)\cos(\pi J_{1,2}\tau)+2\mathbf{I}_{1y}\mathbf{I}_{2z}\sin(\Omega_1 t)\sin(\pi J_{1,2}\tau)-\mathbf{I}_{2z}$$

$$\xrightarrow{\Omega_1\mathbf{I}zt\ \ \Omega_2\mathbf{I}zt}\mathbf{I}_{1y}\cos^2(\Omega_1 t)\cos(\pi J_{1,2}\tau)-\mathbf{I}_{1x}\sin(\Omega_1 t)\cos(\Omega_1 t)\cos(\pi J_{1,2}\tau)$$
$$-2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos^2(\Omega_1 t)\sin(\pi J_{1,2}\tau)-2\mathbf{I}_{1y}\mathbf{I}_{2z}\sin(\Omega_1 t)\cos(\Omega_1 t)\sin(\pi J_{1,2}\tau)$$
$$+\mathbf{I}_{1x}\cos(\Omega_1 t)\sin(\Omega_1 t)\cos(\pi J_{1,2}\tau)+\mathbf{I}_{1y}\sin^2(\Omega_1 t)\cos(\pi J_{1,2}\tau)$$
$$+2\mathbf{I}_{1y}\mathbf{I}_{2z}\cos(\Omega_1 t)\sin(\Omega_1 t)\sin(\pi J_{1,2}\tau)-2\mathbf{I}_{1x}\mathbf{I}_{2z}\sin^2(\Omega_1 t)\sin(\pi J_{1,2}\tau)-\mathbf{I}_{2z}$$

$$\xrightarrow{simplify}\mathbf{I}_{1y}\cos(\pi J_{1,2}\tau)-2\mathbf{I}_{1x}\mathbf{I}_{2z}\sin(\pi J_{1,2}\tau)-\mathbf{I}_{2z}$$

$$\xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t}\mathbf{I}_{1y}\cos^2(\pi J_{1,2}t)-2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos(\pi J_{1,2}\tau)\sin(\pi J_{1,2}t)$$
$$-2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos(\pi J_{1,2}t)\sin(\pi J_{1,2}\tau)-\mathbf{I}_{1y}\sin^2(\pi J_{1,2}t)-\mathbf{I}_{2z}$$

$$\xrightarrow{simplify}\mathbf{I}_{1y}\cos(2\pi J_{1,2}t)-2\mathbf{I}_{1x}\mathbf{I}_{2z}\sin(2\pi J_{1,2}t)-\mathbf{I}_{2z}$$

$$\xrightarrow{t=\tau=1/(4J)}-2\mathbf{I}_{1x}\mathbf{I}_{2z}-\mathbf{I}_{2z}$$

The second route is shorter. We know that there is no net chemical shift evolution during the $\tau - 180° - \tau$ sequence chemical shift evolution is refocused, as long as both spins (1 and 2) experience a 180° pulse. In the homonuclear (^{1}H) case, a single 180° pulse operates on both spins. For the heteronuclear case, a separate 180° pulse is needed on the second (^{15}N) spin. This is the case in this pulse sequence, so we'll ignore chemical shift evolution during the $\tau - 180° - \tau$ period:

$$\mathbf{I}_{1z} + \mathbf{I}_{2z} \xrightarrow{\pi/2\,\mathbf{I}1x} -\mathbf{I}_{1y} + \mathbf{I}_{2z}$$

$$\xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} -\mathbf{I}_{1y}\cos(\pi J_{1,2}t) + \mathbf{2I}_{1x}\mathbf{I}_{2z}\sin(\pi J_{1,2}t) + \mathbf{I}_{2z}$$

$$\xrightarrow{\pi\mathbf{I}1x\pi\mathbf{I}2x} \mathbf{I}_{1y}\cos(\pi J_{1,2}t) - \mathbf{2I}_{1x}\mathbf{I}_{2z}\sin(\pi J_{1,2}t) - \mathbf{I}_{2z}$$

$$\xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} \mathbf{I}_{1y}\cos^2(\pi J_{1,2}t) - \mathbf{2I}_{1x}\mathbf{I}_{2z}\cos(\pi J_{1,2}t)\sin(\pi J_{1,2}t)$$

$$-\mathbf{2I}_{1x}\mathbf{I}_{2z}\cos(\pi J_{1,2}t)\sin(\pi J_{1,2}t) - \mathbf{I}_{1y}\sin^2(\pi J_{1,2}t) - \mathbf{I}_{2z}$$

$$\xrightarrow{simplify} \mathbf{I}_{1y}\cos(2\pi J_{1,2}t) - \mathbf{2I}_{1x}\mathbf{I}_{2z}\sin(2\pi J_{1,2}t) - \mathbf{I}_{2z}$$

$$\xrightarrow{t=\tau=1/(4J)} -\mathbf{2I}_{1x}\mathbf{I}_{2z} - \mathbf{I}_{2z}$$

So, the results are the same for both cases.

The rest of the product operator calculations are on the next page. Following the final 90° pulse, the *first two terms* are the only that have observable $\mathbf{I}_1$ magnetization (antiphase *x*- and *y*-magnetization, $\mathbf{I}_{1x}\mathbf{I}_{2z}$ and $\mathbf{I}_{1y}\mathbf{I}_{2z}$). The next two terms are multiple quantum ($\mathbf{I}_{1x}\mathbf{I}_{2y}$ and $\mathbf{I}_{1y}\mathbf{I}_{2y}$). The remaining terms are all z-magnetization, except for the $\mathbf{I}_{2y}$ term, which is detectable magnetization for spin 2 (not spin 1).

The two observable terms for $\mathbf{I}_1$ magnetization both originated from the $\mathbf{2I}_{1x}\mathbf{I}_{2x}$ term. Thus, this multiple-quantum magnetization was modulated during the t_1 period by the chemical shifts for both spins, and this chemical shift information will be available from the final 2D spectrum.

$$-2\mathbf{I}_{1x}\mathbf{I}_{2z} - \mathbf{I}_{2z} \xrightarrow{\pi/2\,\mathbf{I}1x\ \pi/2\,\mathbf{I}2y} -2\mathbf{I}_{1x}\mathbf{I}_{2x} - \mathbf{I}_{2x}$$ (note the double quantum term)

$$\xrightarrow{\Omega_1\mathbf{I}zt\ \ \Omega_2\mathbf{I}zt} -2(\mathbf{I}_{1x}\cos(\Omega_1 t) + \mathbf{I}_{1y}\sin(\Omega_1 t))(\mathbf{I}_{2x}\cos(\Omega_2 t) + \mathbf{I}_{2y}\sin(\Omega_2 t))$$
$$-\mathbf{I}_{2x}\cos(\Omega_2 t) - \mathbf{I}_{2y}\sin(\Omega_2 t)$$

$$\xrightarrow{expand} -2\mathbf{I}_{1x}\mathbf{I}_{2x}\cos(\Omega_1 t)\cos(\Omega_2 t) - 2\mathbf{I}_{1y}\mathbf{I}_{2x}\sin(\Omega_1 t)\cos(\Omega_2 t)$$
$$-2\mathbf{I}_{1x}\mathbf{I}_{2y}\cos(\Omega_1 t)\sin(\Omega_2 t)\ -2\mathbf{I}_{1y}\mathbf{I}_{2y}\sin(\Omega_1 t)\sin(\Omega_2 t)$$
$$-\mathbf{I}_{2x}\cos(\Omega_2 t) - \mathbf{I}_{2y}\sin(\Omega_2 t)$$

$$\xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} -2\mathbf{I}_{1x}\mathbf{I}_{2x}\cos(\Omega_1 t)\cos(\Omega_2 t) - 2\mathbf{I}_{1y}\mathbf{I}_{2x}\sin(\Omega_1 t)\cos(\Omega_2 t)$$
$$-2\mathbf{I}_{1x}\mathbf{I}_{2y}\cos(\Omega_1 t)\sin(\Omega_2 t)\ -2\mathbf{I}_{1y}\mathbf{I}_{2y}\sin(\Omega_1 t)\sin(\Omega_2 t)$$
$$-\mathbf{I}_{2x}\cos(\Omega_2 t)\cos(\pi J_{1,2}t) - 2\mathbf{I}_{1z}\mathbf{I}_{2x}\cos(\Omega_2 t)\sin(\pi J_{1,2}t)$$
$$-\mathbf{I}_{2y}\sin(\Omega_2 t)\cos(\pi J_{1,2}t) + 2\mathbf{I}_{1z}\mathbf{I}_{2x}\sin(\Omega_2 t)\sin(\pi J_{1,2}t)$$

$$\xrightarrow{\pi/2\,\mathbf{I}2y} +2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos(\Omega_1 t)\cos(\Omega_2 t) + 2\mathbf{I}_{1y}\mathbf{I}_{2z}\sin(\Omega_1 t)\cos(\Omega_2 t)$$
$$-2\mathbf{I}_{1x}\mathbf{I}_{2y}\cos(\Omega_1 t)\sin(\Omega_2 t)\ -2\mathbf{I}_{1y}\mathbf{I}_{2y}\sin(\Omega_1 t)\sin(\Omega_2 t)$$
$$+\mathbf{I}_{2z}\cos(\Omega_2 t)\cos(\pi J_{1,2}t) + 2\mathbf{I}_{1z}\mathbf{I}_{2z}\cos(\Omega_2 t)\sin(\pi J_{1,2}t)$$
$$-\mathbf{I}_{2y}\sin(\Omega_2 t)\cos(\pi J_{1,2}t) - 2\mathbf{I}_{1z}\mathbf{I}_{2z}\sin(\Omega_2 t)\sin(\pi J_{1,2}t)$$