The INADEQUATE Analysis PhL 1.25.08

Part I. Effect of page 405 lower pulse sequence on two spins

1. First pulse. We start with I_z and get quickly to $+I_y = I_{1y}+I_{2y}$ with the first $(\pi/2)_{-x}$ pulse.

2. The free run. If we use the lower picture on page 405, the free run uses $U = \exp(-i\pi J 2I_{1z}I_{2z}t)$ because this is what is meant by "only J-couplings". We go at once to sandwich rules (6) which says:

$$\exp(-i\phi[2j_zJ_z])\ J_y \exp(+i\phi[2j_zJ_z]) = J_y\cos\phi - [2j_zJ_x]\sin(\phi) \qquad j,k,\ell \text{ anti-cyclic}$$

and set $\phi = \pi J\tau$. So let's apply this like so:

$$\exp(-i\phi[2I_{1z}I_{2z}])\ I_{1y} \exp(+i\phi[2I_{1z}I_{2z}]) = I_{1y}\cos\phi - [2I_{1x}I_{2z}]\sin(\phi)$$

However, we are supposed to assume that we have the "official" SES value $2J\tau = 1$, meaning that $\phi = \pi J\tau = \pi/2$ so only the second term survives. We then end up with

$$\rho = -\ 2I_{1x}I_{2z} - (1\leftrightarrow 2)$$

3. The second pulse. Our usual rules are R_x pulse are and we want $\pi/2$ so

$$\exp(-i\theta J_x)\ J_y \exp(+i\theta J_x) = J_y\cos\theta + J_z\sin\theta = +J_z$$
$$\exp(-i\theta J_x)\ J_z \exp(+i\theta J_x) = J_z\cos\theta - J_y\sin\theta = -J_y$$

so we have

$$\rho = -\ 2I_{1x}I_{2z} + (1\leftrightarrow 2)$$
$$\rightarrow +\ 2I_{1x}I_{2y} + (1\leftrightarrow 2)$$

and we comment that this includes orders 2 and 0.

4. The third pulse. I already verified these so I won't do them again. The main conclusion is this: you end up with, averaged over the cycle,

$$a_{-\alpha} = +1 \qquad \Omega_{-\alpha} = \Omega^0_1 + \pi J$$
$$a_{-\beta} = -1 \qquad \Omega_{-\alpha} = \Omega^0_1 - \pi J$$

and the same for the two which have the - first, but they are at Ω^0_1. Thus, we get in the single spectrum two pairs of anti-phase lines, and we have blocked the string peaks from the single-C^{13} molecules.

Part II. Verify the coherence flow diagram shown on page 410.

1. First pulse. We start with I_z and get quickly to $+I_y = -I_{1y} - I_{2y}$ with the first $(\pi/2)_x$ pulse. Since these terms contain both I^+ and I^-, we draw the diagram going to both the -1 and +1 levels. That is, we can change order in either direction. We have both $\rho_{-\alpha}$ and $\rho_{+\beta}$ non-vanishing matrix elements of ρ.

2. The first free-run. We know that each coherence just picks up phase, so the lines don't change. So ignoring these phases, but in general we end up with messy stuff as we saw in COSY when you run this full free propagator. After this free run, I no longer know the matrices without actually doing them.

But, imagine that you DID know the matrices, and that you wrote them out in full detail. You could have terms of the following kind (all of which have order 1 or you might say ± 1).

$$\rho = aI_1^+ + bI_1^- + cI_2^+ + dI_2^-$$

3. The $(\pi)_x$ pulse out in the middle. Our usual rules are R_x pulse are and we want $\theta = \pi$ so

$$\exp(-i\theta J_x)\ J_\pm \exp(+i\theta J_x) = \exp(-i\theta J_x)\,[J_x \pm iJ_y]\exp(+i\theta J_x)$$

$$= J_x \pm i\ \exp(-i\theta J_x)\,J_y\,\exp(+i\theta J_x) = J_x \pm i\,[J_y\cos\theta + J_z\sin\theta] = J_x \mp i\,J_y = J_\mp$$

$$\rho = a[I_1^+] + b[I_1^-] + c[I_2^+] + d[I_2^-]$$

$$\rightarrow\ a[I_1^-] + b[I_1^+] + c[I_2^-] + d[I_2^+]$$

This says that we have a complete $+ \leftrightarrow -$ interchange through this pulse, and now for the very first time I understand why he draws what he does on 410, the coherence flows swap!

4. The second free run. Coherences just phase, so diagram shows nothing. At the end of this time period we still have something of the form $\rho = aI_1^+ + bI_1^- + cI_2^+ + dI_2^-$ but these are not the same as before because more phases were picked up. To do this right, need to add the projectors, but I don't need to do that here.

5. The third pulse which is again $(\pi/2)_x$. Let's now run our coherence stream into the next $(\pi/2)_x$ pulse, starting again with this -- but let's add some extra stuff

$$\rho = aI_1^+ + bI_1^- + cI_2^+ + dI_2^- + eI_z +$$

This time we have $\theta = \pi/2$ so get

$$\exp(-i\theta J_x)\ J_\pm \exp(+i\theta J_x) = J_x \pm i\,[J_y\cos\theta + J_z\sin\theta] = J_x \pm iJ_z = (J_+ + J_-)/2 \pm iJ_z$$

How does this give only order ± 2 Well, the terms I show above seem to "leak through", giving ±1 on the RHS. So I think one has to back up and look more carefully at the first free run.

6. First free run revisited.

We come into this thing with $\rho = -I_{1y} - I_{2y}$. I know from my COSY notes that the free run is going to result in this where $\phi = \pi J\tau$ and $\theta 1 = \Omega^0_1 \tau$:

$$\rho = -I_{1y}C\phi C\theta_1 + 2I_{1x}I_{2z}\,S\phi C\theta_1 + I_{1x}\,C\phi\,S\theta_1 + 2I_{1y}I_{2z}\,S\phi\,S\theta_1 + (1\leftrightarrow 2)$$

Not sure whether to use $\phi = \pi J\tau = \pi/2$. If we do, then we get this since $C_\phi = 0$ $S_\phi = 1$

$$\rho = + 2I_{1x}I_{2z}\,C\theta_1 + 2I_{1y}I_{2z}\,S\theta_1 + (1\leftrightarrow 2)$$

7. The π pulse revisited. Do this now with $\theta = \pi$, so

$$\exp(-i\theta J_x)\; J_y \exp(+i\theta J_x) = J_y\cos\theta + J_z\,\sin\theta = -J_y$$
$$\exp(-i\theta J_x)\; J_z \exp(+i\theta J_x) = J_z\cos\theta - J_y\,\sin\theta = -J_z$$

and we get

$$\rho = -I_{1y}C\phi C\theta_1 + 2I_{1x}I_{2z}\,S\phi C\theta_1 + I_{1x}\,C\phi\,S\theta_1 + 2I_{1y}I_{2z}\,S\phi\,S\theta_1 + (1\leftrightarrow 2)$$
$$\rightarrow + I_{1y}C\phi C\theta_1 - 2I_{1x}I_{2z}\,S\phi C\theta_1 + I_{1x}\,C\phi\,S\theta_1 + 2I_{1y}I_{2z}\,S\phi\,S\theta_1 + (1\leftrightarrow 2)$$

and in our special τ case we get

$$-2I_{1x}I_{2z}\,C\theta_1 + 2I_{1y}I_{2z}\,S\theta_1 + (1\leftrightarrow 2)$$

Part III. Start over and use the SES rules.

1. First $(\pi/2)_x$ pulse. After the first pulse we know we have

$$\rho = -I_{1y} - I_{2y}$$

2. The SES. The next two free runs and π pulse form a SES. But top page 382 says we can replace this as shown where the free run has only J. The table middle of page 383 gives the total effect of the "tuned" SES, and it is easy to apply it to the above. We get

$$\rho = -I_{1y} - I_{2y}$$
$$\rightarrow -2I_{1x}I_{2z} - 2I_{1z}I_{2x}$$

So this then is what enters the last π/2 pulse shown on page 410. Our rules are (with $\theta = \pi/2$)

$$\exp(-i\theta J_x)\; J_y \exp(+i\theta J_x) = J_y\cos\theta + J_z\,\sin\theta = +J_z$$
$$\exp(-i\theta J_x)\; J_z \exp(+i\theta J_x) = J_z\cos\theta - J_y\,\sin\theta = -J_y$$

So we get

$\rho = \; - \; 2I_{1x}I_{2z} \; - \; 2I_{1z}I_{2x}$

$\rightarrow \; + \; 2I_{1x}I_{2y} \; + \; 2I_{1y}I_{2x}$

This agrees with page 411 where I have circled ? mark. Am I missing something? Let's write this guys out:

$= \; + \; 2I_{1x}I_{2y} \; + \; 2I_{1y}I_{2x}$

$= \; + 2\,(I_{1+} \; + I_{1-})/2(I_{2+} \; - I_{2-})/(2i) \; + (1 \leftrightarrow 2)$

$= (1/2i)\; \{\; I_{1+}I_{2+} + I_{1-}I_{2+} - I_{1+}I_{2-} - \; I_{1-}I_{2-} \quad + \; I_{1+}I_{2+} + I_{2-}I_{1+} - I_{2+}I_{1-} - \; I_{1-}I_{2-} \;\}$

$= (1/i)\; \{\; I_{1+}I_{2+} - I_{1-}I_{2-} \;\}$

so mystery resolved! Well, there it is now as 13.6, I missed it! So NOW I see that what emerges from the SES is only order = ±2, just as he says.

3. The final π/2 pulse. This is the one that gets cycled. Start with $I_{1+}I_{2+} - I_{1-}I_{2-}$ without the -i.

$(\pi/2)_x$: Start with these rules:

$$\exp(-\,i\,\theta\,J_x)\;\; J_{\pm}\; \exp(+\,i\,\theta\,J_x) \;=\; J_x \;\pm i\,[\,J_y \cos\theta \;+ J_z \sin\theta] \;=\; J_x \;\pm iJ_z$$

$$I_{1+}I_{2+} - I_{1-}I_{2-} \;\rightarrow\; (\,J_{1x} \;+\; iJ_{1z})(\,J_{2x} \;+\; iJ_{2z}) \;-\; (\,J_{1x} \;-\; iJ_{1z})(\,J_{2x} \;-\; iJ_{2z})$$

$$= (x+y)(a+b) - (x-y)(a-b) \;= (\,xa + ya + xb + yb) - (\,xa - ya - xb + yb)$$

$$= xa + ya + xb + yb - xa + ya + xb - yb$$
$$= \quad + ya + xb + \qquad + ya + xb \qquad = 2(ya + xb)$$

$$I_{1+}I_{2+} - I_{1-}I_{2-} \;\rightarrow 2(\,iJ_{1z}\,J_{2x} \;+\; J_{1x}\,iJ_{2z}) \;= 2i\,(J_{1z}\,J_{2x} \;+\; J_{1x}\,J_{2z}\;) \;= \text{order} \pm 1$$

I think this was the hard way. Use instead

$\rho = + \; 2I_{1x}I_{2y} \; + \; 2I_{1y}I_{2x}$

Then apply $(\pi/2)_x$ just in your head to get

$\rho = 2I_{1x}I_{2y} \; + \; 2I_{1y}I_{2x}$

$\rightarrow \; 2I_{1x}I_{2z} \; + \; 2I_{1z}I_{2x}$

Then apply $(\pi)_x$ just in your head to get

$\rho = 2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

$\rightarrow \quad -2I_{1x}I_{2y} - 2I_{1y}I_{2x}$

Then apply $(-\pi/2)_x$ just in your head to get

$\rho = 2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

$\rightarrow -2I_{1x}I_{2z} - 2I_{1z}I_{2x}$

Then apply $(0)_x$ to get

$\rho = 2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

$\rightarrow \quad 2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

Now what happens if I just add all these second lines?

$2I_{1x}I_{2z} + 2I_{1z}I_{2x} - 2I_{1x}I_{2y} - 2I_{1y}I_{2x} - 2I_{1x}I_{2z} - 2I_{1z}I_{2x} + 2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

All terms cancel and the result is 0.

BUT I did this all wrong. Start over

$\rho = +2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

Apply $(\pi/2)_y$

$\rho = 2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

$\rightarrow -2I_{1z}I_{2y} - 2I_{1y}I_{2z}$

Then apply $(\pi/2)_{-x}$

$\rho = 2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

$\rightarrow -2I_{1x}I_{2z} - 2I_{1z}I_{2x}$

Then apply $(\pi/2)_{-y}$

$\rho = 2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

$\rightarrow 2I_{1z}I_{2y} + 2I_{1y}I_{2z}$

Then apply $(\pi/2)_x$

$\rho = 2I_{1x}I_{2y} + 2I_{1y}I_{2x}$

$\rightarrow 2I_{1x}I_{2z} + 2I_{1z}I_{2x}$

Now add up all the results:

$$-\ 2I_{1z}I_{2y}\ -\ 2I_{1y}I_{2z}\ \ -2I_{1x}I_{2z}\ -\ 2I_{1z}I_{2x} + 2I_{1z}I_{2y}\ +\ 2I_{1y}I_{2z} + 2I_{1x}I_{2z}\ +\ 2I_{1z}I_{2x}$$

And try to cancel terms. Again, they all cancel.

So, it seems that phase cycling the last $\pi/2$ pulse in this way blocks the specific combination coming in which was

$$+\ 2I_{1x}I_{2y}\ +\ \ 2I_{1y}I_{2x}\ \ =\ (1/i)\ \{\ \ I_{1+}I_{2+} - I_{1-}I_{2-}\ \}$$

So in this cycling experiment with an AX system, nothing gets through!

BUT I forgot the effect of the digital phase cycling at the same time. So then we really get this:

$$(-\ 2I_{1z}I_{2y}\ -\ 2I_{1y}I_{2z})1\ \ +(\ \ -2I_{1x}I_{2z}\ -\ 2I_{1z}I_{2x}\ )\ (+i)$$
$$+\ (2I_{1z}I_{2y}\ +\ \ 2I_{1y}I_{2z}\ )(-1)\ \ +(2I_{1x}I_{2z}\ +\ \ 2I_{1z}I_{2x})(-i)$$

$$=\ -\ \ 4I_{1z}I_{2y} - 4I_{1y}I_{2z} - i\ 4I_{1x}I_{2z}\ \ - i\ 4\ I_{1z}I_{2x}$$

$$=\ 4\ (\ -\ I_{1z}I_{2y} -\ \ i\ I_{1z}I_{2x}\ -\ I_{1y}I_{2z} - i\ I_{1x}I_{2z})$$

$$=\ 4\ \ \ \{\ I_{1z}\ (-I_{2y}\ \ - i\ I_{2x}) + I_{2z}\ (-iI_{1x} - I_{1y})\ \}$$
$$=\ (4i)\ \{\ I_{1z}\ (-iI_{2y}\ \ + I_{2x}) + I_{2z}\ (I_{1x} - i\ I_{1y})\ \}$$

$$=\ 2i\ \{\ 2\ I_{1z}\ I_{2-}\ \ +\ \ 2\ I_{2z}\ I_{1-}\}$$

And now divide by 4 because we are averaging each cycle position,

$$=\ (i/2)\ \{2\ I_{1z}\ I_{2-}\ \ +\ \ 2I_{2z}\ I_{1-}\}$$

So I would say this was the "effective" density matrix at the output with full cycling. This finally is what I want to be seeing. This means all the "energy" has been funneled into the - coherences. Now we can go to the actual coherences themselves:

$$2I_{1z}\ I_{2-} =\ 2\ I_2^-\ \ I_{1z}\ (I_1^{\alpha} + I_1^{\beta})\ \ =\ \ I_2^-\ \ (I_1^{\alpha} - I_1^{\beta})\ \ =\ \ I_2^-\ \ I_1^{\alpha}\ -\ \ I_2^-\ \ I_1^{\beta}\ \ \ = I_1^{\alpha}\ I_2^-\ -\ \ I_1^{\beta}\ \ I_2^-$$

So our complete answer is this (before final FID)

$$\rho = (i/2)\ \{\ I_1^{\alpha}\ I_2^-\ \ -\ \ I_1^{\beta}\ \ I_2^-\ \ \ +(1\leftrightarrow 2)\ \ \ \}$$

This is still in matrix form, but we can quickly get the matrix elements as follows (at FID start)

$$\rho_{\alpha-}\ \ = i/2 \qquad\qquad a = 2i\rho\ \ = -1$$

$\rho_{\beta-}$ = -i/2 a = -1 when phase considered, etc etc

$\rho_{-\alpha}$ = i/2

$\rho_{-\beta}$= -i/2

No recall that the first and third are very close and separated by $2\pi J$ so we get four peaks and they are in doublets and the picture shown is pretty good on page 410.

Now look at the flow picture on page 410. Anything that comes in on the +2 or -2 lines is going to get funneled by the cycling into the -1 line! Finally that drawing is making sense.