Appendix 17.10. Phase Cycling. PhL 1.26.08

I think this very long appendix section should be done next, since referenced in the above on page 411. But I think also I will sign off now Dec 18 7:30PM and go on my Cape Cod trip. Then I will continue in chapter 13. // Continuing here at 10 AM on Jan 5, 2008, with the tail end of a cold.

17.10.1 Coherence transfer pathways (601). The diagram is called a CTP diagram, example shown. In this example, the +1 path dumps into the -1 path due to the way the quadrature receiver works, see page 587 for example.

Page 602 gives another example of a pathway. The dark lines show the paths that are allowed, and the implication is that all other paths are blocked. You start off with coherence order 0 because that is what obtains in thermal equilibrium.

Comment 1: Having now done the COSY in detail for the pulse sequence shown on page 601, I know that in fact the final $(\pi/2)_{\mathbf{x}}$ pulse generates 0, ±1 and ±2 order results in ρ. This picture picks out only 1 of these 5 outputs (the -1) and draws it. One must conclude that the dark lines show the "desired pathway" connecting the desired input to the desired output. Perhaps when there are multiple outputs like this, energy is lost in the receiver.

Comment 2: In this same picture, he says States would fail if one of the internal paths were blocked. In the COS sequence, the States term is $2I_{1z}I_{2y}\,(C_{\theta 1-\phi} - C_{\theta 1+\phi})/2 + 2I_{2z}I_{1y}\,(C_{\theta 2-\phi} - C_{\theta 2+\phi})/2$. If you think of $I_{2y} = (1/2i)[\, I_2^{+} - I_2^{-}]$, then "blocking one of the pathways" would get rid of one of these + or - terms, and then the States term would not have a_ℓ = real, so I guess that explains his claim.

17.10.2. Coherence Transfer Amplitudes (602). Now Malcolm attempts a formal analysis of this pathway subject, but I have several problems with his approach. The picture top page 603 needs some words to go with it.

(1) We have somehow a system here that allows M_z spin values in the range shown, from +2 to -2. In our INADEQUATE example on p 410, we see the +2 and -2 levels being involved. Question: how do these levels arise when our system has two spin-1/2 nuclei? Well, these are spin *transition values*, not total spin values. If one spin changes +1 and the other also changes +1, you get the +2, and so on. We are talking about non-zero off-diagonal matrix elements of the ρ operator. The most we can have in this case is going from -1/2 -1/2 to +1/2 + 1/2 which is +1+1 = +2 change in M_z total.

(2) The figure here makes us examine a very specific process: if we arrive at pulse start with some ρ_{rs} coherence like the one shown, how much of this "gets into" the ρ_{uv} coherence at the end of the pulse"? We have seen in earlier examples how a given ρ_{rs} gets exploded into lots of output coherences. A good example is page 392 where a single input ρ_{rs} element (my red square) results in equal amplitudes in all the output coherences, and this was represented as a tree diagram page 393. This idea that a particular output side coherence (ie, after pulse) is "fed" by a particular input coherence (ie, before pulse) is what is meant by the term "coherence transfer amplitude". The quantity written as Z(ϕ) is in fact precisely the quantum mechanical "amplitude" for this transfer. The first factor is the amplitude for state r to propagate into state u, while the second is the amplitude for state s to propagate into state v. Unfortunately,

Malcolm's presentation is hazy. He should have written equations involving ρ itself. Here is I think a much better presentation: [think of A = U = the rotation operator of the pulse. Sometimes he just refers to A = U as "the pulse"]

$\rho_2 = A\rho_1 A^+$ where t1 = before pulse and t2 = after pulse

$$\langle u|\rho_2|v\rangle = \langle u|A\rho_1 A^+|v\rangle = \Sigma_{r,s}\langle u|A|r\rangle\langle r|\rho_1|s\rangle\langle s|A^+|v\rangle = \Sigma_{r,s}(\rho_1)_{rs}\langle u|A|r\rangle\langle s|A^+|v\rangle$$
$$= \Sigma_{r,s}(\rho_1)_{rs}\langle u|A|r\rangle\langle s|A^+|v\rangle = \Sigma_{r,s}(\rho_1)_{rs} Z_{rs;uv} = (\rho_2)_{uv}$$

This shows clearly that the output coherence $(\rho_2)_{uv}$ is "fed" by exactly the terms shown, and we are examining just one particular r,s input situation. It shows that things are additive, and so on. Nothing new would have been required for Malcolm to do this presentation. He backslid into vague notation when he did not have to. I think the above equation will be very useful!

17.10.3 Coherence orders and phase shifts (603). On page 604 we write the general possible U in its "Euler angle form" from page 264. Here ϕ is what we called ϕ_p earlier. Consider this definition:

$$Z_{rs;uv}(\phi) = \langle u|A_\phi|r\rangle\langle s|A_\phi^+|v\rangle$$

If we do the outer z rotations, we quickly find that

$$Z_{rs;uv}(\phi) = Z_{rs;uv}(0)\ \exp(-i\phi[\,p_{\mu\upsilon} - p_{rs}\,]) = Z_{rs;uv}(0)\ \exp(-i\phi\Delta p) \qquad (17.48)$$

where those things in the exponent ARE the orders of coherence, like $p_{\mu\upsilon} = M_\mu - M_\upsilon$= final - initial. So finally we have these things sitting in an equation somewhere. Define $\Delta p = p_{\mu\upsilon} - p_{rs}$ = final minus initial order.

17.10.4. The pathway phase (605). Our result (17.48) applies to a single pulse exactly as shown top of page 603. A pulse is only part of a "path". What would the conclusion be for going through two abutting pulses which we might call $A_{\phi A}$ and $B_{\phi B}$? Or through some general pulse sequence?

When we say a "path", we mean a specific heavy black line as shown for example on page 605.

Consider the first pulse A. How would we apply the drawing top of page 603 to this initial pulse? On the left we have only populations, no coherences, but our general equation given above would still apply:

$$(\rho_2)_{uv} = \Sigma_{r,s}(\rho_1)_{rs}\langle u|A|r\rangle\langle s|A^+|v\rangle = \Sigma_{r,s}(\rho_1)_{rs} Z_{rs;uv}(\phi_A)$$

BUT, for such an initial pulse, we have $(\rho_1)_{rs} = \delta_{r,s}(\rho_1)_{rr}$, meaning the TE starting density matrix is diagonal. In this case we would get

$$(\rho_2)_{uv} = \Sigma_{r,s}(\rho_1)_{rs} Z_{rs;uv} = \Sigma_r(\rho_1)_{rr} Z_{rr;uv}(\phi_A)$$

so there is only a single sum. We could apply (17.48) here with $\Delta p = p_{uv} - p_{rr} = p_{uv}$. In other words, we can think of the coherence order at the start as 0, just as the dark line shows. In this example, $\Delta p_A = 1\text{-}0 = 1$.

But how do we think about the different values of r? From page 366, we see that ρ_1 is very close to the identity matrix times 1/4. If we ignore the small Boltzman B value, we can think of all four diagonal elements being the same, so then we can say

$(\rho_2)_{uv} = \Sigma_r (\rho_1)_{rr} Z_{rr;uv}(\phi_A) \approx Z_{rr;uv}(\phi_A)$ where r is any of the four values.

So this tells us then that

$(\rho_2)_{uv} \approx Z_{rr;uv}(\phi_A) = Z_{rr;uv}(0) \exp(-i\, p_{uv}\, \phi_A)$

So this gets us through the first pulse shown on page 605, where we have $\Delta p_A = p_{uv} = 1$ in our example.

During the free propagation between pulse A and B, we know that nothing happens at all if we are exactly on resonance, and if we are a little off, we get phasing results like (10.30) on page 293. Malcolm just ignores this phase. Perhaps τ is short enough, or we are very close to resonance so we can ignore this phase. More generally, you might say that all coherences experience exactly the same phase (10.30),

When we get to the second pulse, we handle that using the method already presented page 603 top, and we expose thereby another phase factor of the form $\exp(-i\Delta p_B \phi)$. For our particular example on page 605, we have $\Delta p_B = -1 - 1 = -2$.

Now what is this thing s appearing on page 605? The claim is that the NMR signal is a sum of signals through various coherence pathways!

Comment: The interested reader might at this point consult document "phil theory of coherence flow.doc" where we develop the "matrix theory of coherence flow" using Z and P matrices which act directly on coherence vectors formed from the matrix elements of the density matrix. In Section 4 of that document, we write out explicitly the path sum formulas Levitt refers to in this appendix.

17.10.5 A sum theorem (606). This is a famous result I have seen in many worlds of application. If you add up the phasors shown, you get exactly 0 unless the ratio p/n is an integer, in which case all the terms in the sum are unity. A fine proof is given here.

17.10.6 Pathway Selection I (607). We are going to consider various cases, and this is Case I. In this case, we set all phases to 0 but we cycle phase ϕ_A as shown. We are cycling through a pattern of 4 phases. So this introduces a new level of "summation" not yet mentioned. We are going to look at a specific path (we are not yet going to sum over paths), and we are going to sum over our cycle phases! If we sum just over 4 pulses, we get the sum shown above (17.56) page 608. But from our theorem, this sum over phasors will be exactly 0 unless $\Delta p_A/4$ = an integer. In this example, Δp_A is the change in coherence order going through the first pulse, so this is why only the dark lines shown in figure 17.14 are "allowed" in this case. Any path other than one of these will have zero contribution. So, by simply cycling your first pulse in this simple manner, you can create a "filter" as shown. Very good, so much for Case I.

Review added: Suppose we do our path cycle by varying the phase of pulse 3 in our formalism alluded to above, then we have this, where Σ_K represents our phase cycle sum (we don't bother to average). Here, the object $s_{ikmn}(\phi_K,\phi_2,\phi_1)$ is one of many coherence paths through our pulse sequence when ends up causing the NMR signal s.

$$s(\text{result of a cycle of pulses}) = \Sigma_K\, s_{ikmn}(\phi_K,\phi_2,\phi_1) = s_{ikmn}(0,0,0)\,\Sigma_K \exp(-i\ \Phi_{ikmn})$$

$$= s_{ikmn}(0,0,0)\,\Sigma_K \exp(-i\ [\,\phi_3(K)\,\Delta p^{ik} + \phi_2\,\Delta p^{km} + \phi_1\,\Delta p^{mn}\,])$$

$$= s_{ikmn}(0,0,0) \exp(-i\ [\,\phi_2\,\Delta p^{km} + \phi_1\,\Delta p^{mn}\,])\,\Sigma_K \exp(-i\ [\,\phi_3(K)\,\Delta p^{ik}])$$

$$= F_{ikmn}\ \Sigma_K \exp(-i\ [\,\phi_3(K)\,\Delta p^{ik}])$$

This shows that, *regardless* of what all the other pulses are doing and propagations and what have you, (as long as they are the same on each phase of our cycle), you will have a "blocking filter" if you can arrange for $\Sigma_K \exp(-i\ [\,\phi_3(K)\,\Delta p^{ik} + \phi_{dig}(K)]) = 0$, where now I have added this digital phase which I omitted before. It is something you can change on each cycled shot if you want. In our first example it is kept at 0. So we are looking at

$$\text{sum} = S = \Sigma_K \exp(-i\ [\,\phi_3(K)\,\Delta p^{ik}])$$

suppose we *try out* $\phi_3(K) = K(\pi/2)$ for K = 0,1,2,3 as shown in the table page 607. Then we get

$$S = \Sigma_K \exp(-i\ [\ K(\pi/2)\Delta p^{ik}]) = \Sigma_K \exp(-i\ [\ 4K(\pi/2)\Delta p^{ik}]/4\ ) = \Sigma_K \exp(-i\ [2\pi(\Delta p^{ik})/4])^K$$

so the term we are summing in the theorem on page 606 is $x = \exp(-i\ [2\pi(\Delta p^{ik})/4])$ and we can then identify $p = \Delta p^{ik}$ and n = 4. The sum vanishes if $\Delta p^{ik}/4 \neq$ integer, and so we get the filter as shown in the picture on page 608.

Review: if you cycle a particular pulse in this way, in our case pulse 3, then you block any path through the pulse which has $\Delta p^{ik} \neq 4$. The indices i and k refer to the two sides of the pulse, in fact as we ordered things, k is the input side and i is the output side. (matrix order). So we can apply this discovery two ways in the pictures on page 608. If we start with order 0 and cycle pulse A, then the gray paths are blocked and only the black ones are allowed. If we are interested in what gets to order 0 at the output of pulse B and we cycle B instead, then the grey paths cannot get to the output and the black ones can.

Comment: As we gradually take the limit $\beta \to 0$ in our pulse, the ability to filter must gradually go away somehow. Recall that, in my example of the referenced document,

$$s(0,0,0) = \Sigma_{ikmn}\ M_{-1,i}(Z_3(0))_{ik}(Z_2(0))_{km}(Z_1(0))_{mn}\,(\rho_{in})_n \exp\{+i\,[\,\Omega_b\,\tau_b + \Omega_a\,\tau_a]\}$$

In our filtration sum, we have the object Δp^{ik} for our pulse 3. And we see in our s(0,0,0) that we have the factor $(Z_3(\phi=0,\,\beta))_{ik}$. If we go to the limit $\beta \to 0$, this matrix becomes more and more diagonal, so paths that don't have i=k contribute less and less to the output NMR signal amplitude s(0,0,0). Eventually we

have to have i=k to have any signal at all. But then $\Delta p^{ik} = 0$ and our use of the "sum rule" becomes impossible. This sum theorem is only applicable (and you can only get a filter) if coherences i and k are different, so that $\Delta p_{ik} \neq 0$.

Comment: Notice that these filters act to filter "order of coherence", they can't filter actual specific coherences. That is to say, all coherences of the same order are grouped together for filtration.

17.10.7 Pathway Selection II (609). Having seen the previous case, we can now state the formalism more fully. The sum over cycles which appears on page 608 is really this:

$$\text{cycle sum} = \Sigma_{m=0}^{N-1} \exp(-i \Phi_{path}(m))$$

where

$$\Phi_{path}(m) = \Delta p_A \, \phi_A(m) + \Delta p_B \, \phi_B(m) + \phi_{rec}(m) + \phi_{dig}(m)$$

The items Δp_A and Δp_B are determined by the "keep path" that you choose in the coherence transfer diagram. Then for that path, you select phases so that all N cycles have the *same* phase for your selected path, and those add together. You will then find that on each side of your keep path, you get suppression until you move N paths offset from your keep path.

So in this example, our goal is to select as our keeper path the path $0 \rightarrow +1 \rightarrow -1$ as shown Fig 17.16. This means $\Delta p_A = +1$ and $\Delta p_B = -2$. Then we have

$$\Phi_{pathkeep}(m) = \phi_A(m) - 2 \, \phi_B(m) + \phi_{rec}(m) + \phi_{dig}(m)$$

Since we have full control over both $\phi_{rec}(m)$ and $\phi_{dig}(m)$, let's ignore $\phi_{rec}(m)$ and go with this most general form:

$$\Phi_{pathkeep}(m) = \phi_A(m) - 2 \, \phi_B(m) + \phi_{dig}(m)$$

where we are free to set N and the value of each phase for each cycle step as we wish. If we set all phases to 0, then we get no filtering because we would then have, for an arbitrary path,

$$\Phi_{path}(m) = \Delta p_A \, \phi_A(m) + \Delta p_B \, \phi_B(m) + \phi_{dig}(m) = \Delta p_A 0 + \Delta p_B 0 + 0 = 0 \text{ // any path}$$

To get a path selection, we have to make phases change in either the $\phi_A(m)$ or $\phi_B(m)$ column, otherwise all paths get the same phase in each cycle step m. The book *suggests* setting N = 4 and then $\phi_A(m) = 2\pi(m/4)$ and then matching that with $\phi_{dig}(m) = -\phi_A(m)$. Let's see what this suggestion does:

$$\Phi_{path}(m) = \Delta p_A \, 2\pi(m/4) + \Delta p_B \, 0 - 2\pi(m/4) = 2\pi(m/4) [\Delta p_A - 1]$$

Now let's restate the "sum theorem" as follows:

$$\Sigma_{m=0}^{N-1} \exp[-i2\pi m(p/N)] = (p/N = \text{integer}) \; ? \; N : 0 \qquad (17.52) \qquad \textbf{sum theorem}$$

In our example, then, we have N = 4 and $p = -[\ \Delta p_A\ - 1\ ]$. Thus, we get a sum = 4 only when $[\ \Delta p_A\ - 1\ ]/4$ = integer = M, so $\Delta p_A\ - 1 = 4M$ or $\Delta p_A\ = 1 + 4M$ = 1,5,9... and -3,-7,-11 ... . So the "suggestion" results in a "filter" as desired.

Now, suppose we set $\phi_{dig}(m) = -\ J\ \phi_A(m)$ where J is an integer. Then we would get

$$\Phi_{path}(m) = \Delta p_A\ 2\pi(m/4) + \Delta p_B\ 0 - J\ 2\pi(m/4) \ = \ 2\pi(m/4)\ [\ \Delta p_A\ - J\ ]$$

and we would then have pass-paths have $\Delta p_A\ = J + 4M$. So by adjusting J, we can adjust which path we select.

Let's repeat this with a general value of N and see what we get:

$\phi_A(m) = 2\pi(m/N)$ and then matching that with $\phi_{dig}(m) = -\ J\phi_A(m)$.

$$\Phi_{path}(m) = \Delta p_A\ 2\pi(m/N) + \Delta p_B\ 0 - 2\pi J\ (m/N) \ = \ 2\pi(m/N)\ [\ \Delta p_A\ - J\ ]$$

Then we have pass-path has $\Delta p_A\ = J + N*M$ = J, J±N, J±2N, etc. We have selected path J, and rejected N-1 paths on each side.

Now, in following the book's suggestion, we set $\phi_B(m) = 0$, so this means there is no selection at all on path portions going through pulse B. The phase contribution from pulse B is the same for all paths, so really it is the A pulse that is doing all the filtering work here.

The final three instructions on page 611 are exactly in accord with the above discussion.

17.10.8 Pathway Selection III (611). Now what happens if we set $\phi_A(m) = 0$ and try to cycle $\phi_B(m)$ instead? Recall that we start with

$$\Phi_{pathkeep}(m) = \phi_A(m)\ - 2\ \phi_B(m) + \phi_{dig}(m)$$

Suppose we just try $\phi_A(m) = 0$ and $\phi_B(m) = 2\pi(m/N)$, swapping the two from the previous case, and we try this time $\phi_{dig}(m) = +2\ J\phi_B(m)$. This gives

$$\Phi_{path}(m) = \Delta p_A\ \phi_A(m)\ + \Delta p_B\ \phi_B(m) + \phi_{dig}(m) \ = \ \Delta p_B\ \phi_B(m) + 2\ J\ \phi_B(m) \ = \ [\ \Delta p_B\ + 2J]\ \phi_B(m)$$
$$= [\ \Delta p_B\ + 2J]\ *\ 2\pi\ (\ m/N)$$

Our sum theorem says

$$\Sigma_{m=0}^{N-1}\ \exp[\ -i2\pi m(p/N)\ ] \ = \ (\ p/N = \text{integer})\ ?\ N : 0 \qquad (17.52) \qquad \textbf{sum theorem}$$
$$= \Sigma_{m=0}^{N-1}\ \exp(\ -i\ \Phi_{path}(m)\ )$$

So we identify in this case that $\Phi_{path}(m) \ = \ [\ \Delta p_B\ + 2J]\ *\ 2\pi\ (\ m/N) = 2\pi m(p/N)$ or $[\ \Delta p_B\ + 2J] = p$. In this case, we get

pass-path occurs when $[\ \Delta p_B\ + 2J]/N = M \qquad [\ \Delta p_B\ + 2J] = N*M$

$\Delta p_B = -2J + N*M$

If J=1, we get $\Delta p_B = -2,\ -2 \pm N, -2 \pm 2N$, etc. So this program selects the +1 to -1 path through the second B pulse, and rejects paths up to N on each side. So this gives a very similar result to the previous case, in fact the same result, but the filtering is now being done by the B pulse, and the A pulse is allowing everything to pass through. This is a digital filter.

So far, then, we have a method of selecting a single path, but we have to accept paths ±N*M on either side, so we are not really selecting just a single path.

17.10.9 Selection of a single pathway I (612). Nothing new here for me. He just says if you select N = 8 instead of N = 4, you get twice the rejection sideband on each side. Just for fun, he has chosen a different keeper path in this case, the one that goes $0 \rightarrow -3 \rightarrow -1$. In general, more rejection requires a longer cycle. In this example, he chooses to cycle the ϕ_B phase as in case III above.

17.10.10. Selection of a single pathway II (613) Here we do another N=8 example where we cycle ϕ_A instead of ϕ_B. The steps are always the same. First, choose N to get desired amount of rejection. Second, decide whether you will cycle A or B (we pick A here). Third, set $\phi_A = 2\pi m/N$. Fourth, for your keeper path, require that $\phi_{path} = 0$ which means need $\Delta p_A\ 2\pi m/N + \phi_{dig} = 0$, so then this determines the ϕ_{dig} column of your cycling chart.

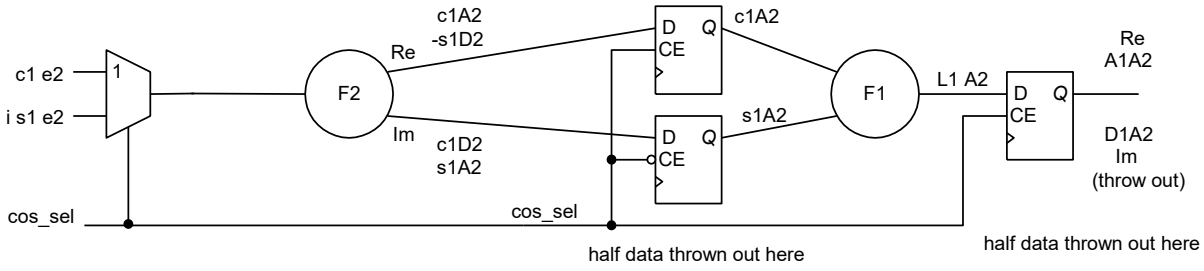
We then have an unusual hardware comment. The table on page 614 cannot be implemented with existing hardware because such hardware does not allow $\pi/4$ multiple digital phase shifts! This was a 2001 restriction. We are now in 2007. But even with this restriction, the solution is to use the table on page 612 instead.

17.10.11 Dual pathway selection (614). If you want the two paths shown, your only choice is to make a cycle with N = 2 as shown top of page 615. You get lousy rejection as illustrated on page 615 bottom figures.

Now, Malcolm claims that the two paths shown on page 614 are exactly those we want to maintain in the COSY scheme. Remember how the States procedure worked! We set the pulse sequence as on the top of page 390 and collected lots of "COS" data. Then we adjusted to the second pulse sequence as shown below on page 390 and we collected more "SIN" data. Then we "added" the collected data in the funny manner shown on page 119 and also page 117 equation (5.29).

There are many things to consider in this COSY comment. It would take me perhaps a week of reading and work to clarify this, but I don't want to be a COSY expert right now. [But I became one.]

<u>Comment on COSY:</u> I think Malcolm has misled the reader here. You *could* set up a little N=2 cycle as the "front end" of a COSY process, but not in the normal manner. The normal manner means you *add* the output of all the phases of the cycle, and only then do you get the "filter" action. So, if you were to do this addition using an N=2 cycle which alternates the two COSY pulse sequences, you would indeed have a filter which would remove the order ±2 and 0 components from the stream between the pulses. But when we start with TE, there are no such components there in the first place during either cycle phase coming out of pulse A. This little N=2 cycle would act as a filter, but I claim it has nothing at all to do with the COSY/States process. It just *looks* like it does! Here is the States COSY hardware (see COSY.doc)



get one output sample for every two input samples

From the cos input sample we register the cos1*A2 data, and then from the subsequent i sin1*e2 input sample we register the sin1*A2 data in the lower register. So these two complex input samples are never added at any point in the processing path. Thus, this is not an example of a filter of the form Fig 17.20 on page 614.

17.10.12 Internal Phases I (616). On page 614 we had two pulses called A and B and we wrote a cycle chart in (17.62) as an example of an N=2 filter. In this example we selected 0 $\rightarrow$-1$\rightarrow$-1 as our keeper pathway and designed the filter and obtained the table and picture shown.

Now, suppose *inside* the blocks A and B we have "more logic". This situation is shown on page 616. We could apply the same table just mentioned to this pulse sequence. The author's point is simply this: you apply a phase like ϕ_A to the entire A block as a rigid object. What this means is that all pulses inside the block A are having ϕ_A added to their phases. It was Malcolm's neglect to say what ϕ_1 meant that confused me at first.

Now look back at our earlier notion of path summation:

$$s_{ikmn}(\phi_3,\phi_2,\phi_1) = s_{ikmn}(0,0,0)\exp(-i\ [\ \phi_3\,\Delta p^{ik} + \phi_2\,\Delta p^{km} + \phi_1\,\Delta p^{mn}\ ])$$

$$s(\phi_3,\phi_2,\phi_1) = \Sigma_{ikmn}\, s_{ikmn}(\phi_3,\phi_2,\phi_1)$$

Suppose pulses 1 and 2 are inside box A as shown and that we do a phase cycle on the entire box. What happens in our equation if we "phase cycle" the entire box A? We can rewire the phase as

$$[\ \phi_3\,\Delta p^{ik} + \phi_2\,\Delta p^{km} + \phi_1\,\Delta p^{mn}\ ] = [\ \phi_3\,\Delta p^{ik} + (\phi_A + \pi/2)\Delta p^{km} + \phi_A\,\Delta p^{mn}\ ]$$

$$= [\ \phi_3\,\Delta p^{ik} + (\pi/2)\Delta p^{km} + \phi_A\,(\,\Delta p^{km} + \Delta p^{mn})\ ]$$

Note that index m refers to a specific "line" between the two pulses inside block A. But recall

$$\Delta p^{ij} = [p_i - p_j\ ] \qquad \text{so } \Delta p^{km} + \Delta p^{mn} = [p_k - p_m\ ] + [p_m - p_n\ ] = [p_k - p_n\ ] = \Delta p^{kn}$$

and this is true for any internal path m. Our phase is now

$$= [\ \phi_3\,\Delta p^{ik} + (\pi/2)\Delta p^{km} + \phi_A\ \Delta p^{kn}\ ]$$

where now k and n refer to the two outside edges of box A ! If we apply a phase cycle sum Σ_K as we did earlier, on the right of our summed NMR signal we will have this

$$\text{sum} = S = \Sigma_K \exp(-i [\phi_A(K) \Delta p^{kn}])$$

This says that if we "phase cycle the entire block A" we get the same filter we got before, and this justifies Malcolm's drawing of the flow lines on page 616.

Here should be the main point of this section: If you phase cycle a rigid block like block A, the filter results are the same as if you cycled a single pulse, and what is inside the box does not matter whatsoever! In the earlier sections, we never cared what kind of pulse we had (we did not need to know β), and here we generalize that don't care notion. The phase cycling creates a filter. If β=0, we have no pulse and then amplitudes are straight through

17.10.13 Internal Phases II (617) We are now going to do another example of the confused section above. We have a tiny advantage here in that we know what the coherence "flow" looks like inside the first block, because this is shown on page 410. However, I don't know how to derive the flow shown on page 410 in any good way, just brute force mess. [But now I do, see notes for that section.]

So fine, we are drawing the INADEQUATE pulse sequence as if it were two blocks. The phases ϕ_A and ϕ_B are "block phases" for these blocks which move all pulses inside in lockstep.

So why on earth do we want to view INADEQUATE in this manner?

Well, on page 618 we are playing only with ϕ_B so we are only using the single pulse B as our "filter". We want to design an N=4 phase cycle such that the inputs +2 and -2 are mapped to -1. We know that we can adjust ϕ_{dig} to make this work.

So let's just take this as an "exercise" and do it. The first step is that we want either of these paths with N=4, and either will imply both. So consider the path taking -2 to -1 (pencil oval p 617). It has Δp_B = -1 - - 2 = +1. We have

$$\Phi_{path}(m) = \Delta p_B \, \phi_B(m) + \phi_{dig}(m)$$

and we choose the usual form $\phi_B(m)= 2\pi(m/N)$. We have

$$\Sigma_{m=0}^{N-1} \exp[-i2\pi m(p/N)] = (p/N = \text{integer}) \; ? \; N : 0 \qquad (17.52) \qquad \textbf{sum theorem}$$
$$= \Sigma_{m=0}^{N-1} \exp(-i \Phi_{path}(m))$$

We know that we want N = 4, and we suspect that we want $\phi_{dig}(m) = - \phi_B(m) = - 2\pi(m/4)$, so we have

$$\Phi_{path}(m) = \Delta p_B \, 2\pi(m/4) - 2\pi(m/4) = [\Delta p_B - 1] \, 2\pi(m/4)$$

and we identify that p = [Δp_B - 1] so we get passage if [Δp_B - 1] = 4*M. In our sample path above, we said that Δp_B = +1, so this pathway gets "conduction" and that is what we want. Therefore, we have just shown that the first table on page 618 gives the result we want for filtering properties of the second pulse. Since the B pulse has a $\pi/2$ offset since it is a y-pulse, when we write the table out showing the ϕ_1 type phases, we get 17.66.

Now what about his last paragraph? If we select the last pulse as $(\pi/2)_{\mathbf{y}}$, we are in effect setting $\phi_{\mathbf{4}} = \pi/2$ for our first cycle phase. But this is really arbitrary. This was done in the table on page 404 because it led to certain useful results in the analysis of that section. This relates to the nature of the resonance peaks, recall has phase shifts which always mess them around.

17.10.14 Nested Phase Cycles I (618). The picture shows the special "double-quantum filtered" COSY that was mentioned in the text but was not analyzed there. The pulse sequence is shown and we define three blocks. We are not really going to do anything with block B so its phase is always 0.

What we want to do is make block A (one pulse) act as a filter which passes the two lines shown, so it needs an N=2 sequence. At the same time, we want block C (one pulse) to be an N=4 filter which passes the flows shown. To get both these filters running at once, you do "nesting". The table shown has the A sequence inside the C sequence, and he has a little error in his text in this regard. Because we are doing this nesting, that makes the "floor" function convenient relative to our counter which runs m=0..7 to take in both cycles. Then as usual, we tune the $\phi_{\mathbf{dig}}$ so make the second filter select exactly the two 4-separated paths we want, the ones that are shown on page 618. There is nothing I don't understand in this example.

So, this was an example of a "double filter" where you get flow filtration at each of two pulses in your pulse sequence. The two filters had different values of N so "nesting" was used to make this work.

Double-quantum-filtered COSY: Is it supposed to be clear how this double phase-cycle solves the COSY problem with those off diagonal peaks? We recognize the A + B blocks as being our page 390 "COS" pulse sequence. Recall what the output was leaving block B:

$$\rho^{\mathbf{cos}} = -I_{\mathbf{1z}}C_{\phi}C_{\boldsymbol{\theta}\mathbf{1}} - 2I_{\mathbf{1x}}I_{\mathbf{2y}}S_{\phi}C_{\boldsymbol{\theta}\mathbf{1}} + I_{\mathbf{1x}}C_{\phi}S_{\boldsymbol{\theta}\mathbf{1}} - 2I_{\mathbf{1z}}I_{\mathbf{2y}}S_{\phi}S_{\boldsymbol{\theta}\mathbf{1}} + (1\leftrightarrow 2)$$

Now, what happens due to our phase-cycling of the first block A? It will cause things to start off after the first pulse half the time with $+I_{\mathbf{y}}$ instead of $-I_{\mathbf{y}}$. But this is compensated by $\phi_{\mathbf{dig}}$ as shown in the page 620 table for each pair of cycle steps. So we really do have a "filter" with our pulse A, and only orders ± 1 emerge. So really this phase cycling has not affected things in terms of what leaves. Of course without doing this phase cycling, we got $-I_{\mathbf{y}}$ and it only had ± 1, so this part of the cycle is not affecting the front end, it is not killing off our signal, for example. [so why do they do it??]

Now, this means that half the time, what arrives after pulse B is the negative of the above $\rho^{\mathbf{cos}}$, and we are comping this with the $\phi_{\mathbf{dig}}$ as just stated. Now I think at the same time we are making C do a separate phase cycle, and we are just combining these into one 8 step cycle. So no doubt the second part acts as the filter they say. It seems to me then that only the ±2 order part of $\rho^{\mathbf{cos}}$ gets through the second filter and influences the FID signal. Specifically, $I_{\mathbf{1x}} = (1/2)\,[\,I_{\mathbf{1+}} + I_{\mathbf{1-}}]$ and $I_{\mathbf{2y}} = (1/2i)\,[\,I_{\mathbf{2+}} - I_{\mathbf{2-}}]$, so

$$\rho^{\mathbf{cos}} = -2I_{\mathbf{1x}}I_{\mathbf{2y}}S_{\phi}C_{\boldsymbol{\theta}\mathbf{1}} + (1 \leftrightarrow 2)$$

$$= -2(1/2)(1/2i)(I_{\mathbf{1+}}I_{\mathbf{2+}} - I_{\mathbf{1-}}I_{\mathbf{2-}})S_{\phi}C_{\boldsymbol{\theta}\mathbf{1}} + (1 \leftrightarrow 2) \qquad \text{// keeping only } \pm 2$$

$$= -(1/2i)(I_{\mathbf{1+}}I_{\mathbf{2+}} - I_{\mathbf{1-}}I_{\mathbf{2-}})(S_{\phi}C_{\boldsymbol{\theta}\mathbf{1}} + S_{\phi}C_{\boldsymbol{\theta}\mathbf{2}})$$

$$= +(1/4i)(I_{\mathbf{1+}}I_{\mathbf{2+}} - I_{\mathbf{1-}}I_{\mathbf{2-}})\,[\,(S_{\boldsymbol{\theta}\mathbf{1}-\phi} - S_{\boldsymbol{\theta}\mathbf{1}+\phi}) + (S_{\boldsymbol{\theta}\mathbf{2}-\phi} - S_{\boldsymbol{\theta}\mathbf{2}+\phi})\,]$$

since $S_\phi\, C_{\theta 1} = -(S_{\theta 1-\phi} - S_{\theta 1+\phi})/2$. In a sense, our peak information (the sines) is being "carried" on the ± 2 coherence terms at this point.

If we look at the ρ^{SIN} starting point in COSY it is this:

$$\rho^{SIN} = -I_{1z}\, C_\phi\, S_{\theta 1} - 2I_{1x}I_{2y}\, S_\phi\, S_{\theta 1} - I_{1x}C_\phi C_{\theta 1} + 2I_{1z}I_{2y}\, S_\phi C_{\theta 1} + (1\leftrightarrow 2)$$

Recall the rule for going from COS to SIN

$$C_{\theta 1} \rightarrow S_{\theta 1}$$
$$S_{\theta 1} \rightarrow -C_{\theta 1}$$

So we could apply this directly to our end result above to get

$$\rho^{SIN} = -(1/2i)\,(I_{1+}I_{2+} - I_{1-}I_{2-})\,(S_\phi S_{\theta 1} + S_\phi S_{\theta 2})$$

$$= +(1/4i)\,(I_{1+}I_{2+} - I_{1-}I_{2-})\,[\,(C_{\theta 1-\phi} - C_{\theta 1+\phi}) + (C_{\theta 2-\phi} - C_{\theta 2+\phi})\,]$$

since $2S_\phi\, S_{\theta 1} = C_{\theta 1-\phi} - C_{\theta 1+\phi}$. So this is very promising. The effective ρ in the gap between pulse B and C is going to be

$$\rho^{COS} = +(1/4i)\,(I_{1+}I_{2+} - I_{1-}I_{2-})\,[\,(S_{\theta 1-\phi} - S_{\theta 1+\phi}) + (S_{\theta 2-\phi} - S_{\theta 2+\phi})\,]$$
$$\rho^{SIN} = +(1/4i)\,(I_{1+}I_{2+} - I_{1-}I_{2-})\,[\,(C_{\theta 1-\phi} - C_{\theta 1+\phi}) + (C_{\theta 2-\phi} - C_{\theta 2+\phi})\,]$$

We can then just run this through the final as-is $(\pi/2)_x$ pulse to get:

$$R_{1x}(\pi/2)\; I_{1\pm}\; R_{1x}(-\pi/2) = I_{1x} \pm i\, I_{1z} \qquad \text{// sandwich rules doc}$$

So we get

$$I_{1\pm}I_{2\pm} \rightarrow (I_{1x} \pm i\, I_{1z})(I_{2x} \pm i\, I_{2z}) = I_{1x}I_{2x} \pm i\, I_{1z}I_{2x} \pm iI_{1x}I_{2z} - I_{1z}I_{2z}$$

and we need keep only the order = –1 piece of this which is

$$I_{1\pm}I_{2\pm} \rightarrow \pm i\, I_{1z}I_{2x} \pm iI_{1x}I_{2z}$$

so that $I_{1+}I_{2+} - I_{1-}I_{2-} = (+i\, I_{1z}I_{2x} + iI_{1x}I_{2z}) - (-i\, I_{1z}I_{2x} - iI_{1x}I_{2z}) = 2i\,(I_{1z}I_{2x} + I_{1x}I_{2z})$

So then we get

$$\rho^{COS} \rightarrow +(1/2)(I_{1z}I_{2x} + I_{1x}I_{2z})\,[\,(S_{\theta 1-\phi} - S_{\theta 1+\phi}) + (S_{\theta 2-\phi} - S_{\theta 2+\phi})\,]$$
$$\rho^{SIN} \rightarrow +(1/2)(I_{1z}I_{2x} + I_{1x}I_{2z})\,[\,(C_{\theta 1-\phi} - C_{\theta 1+\phi}) + (C_{\theta 2-\phi} - C_{\theta 2+\phi})\,]$$

at the start of the FID! Now we see that our two expressions are reversed in name, but who cares. We rename them like this:

$$\rho^{sin} \rightarrow +(1/2)(I_{1z}\, I_{2x} + I_{1x}\, I_{2z})\ [\ (S_{\theta 1-\phi} - S_{\theta 1+\phi})\ +\ (S_{\theta 2-\phi} - S_{\theta 2+\phi})\ ]$$
$$\rho^{cos} \rightarrow +(1/2)(I_{1z}\, I_{2x} + I_{1x}\, I_{2z})\ [\ (C_{\theta 1-\phi} - C_{\theta 1+\phi})\ +(C_{\theta 2-\phi} - C_{\theta 2+\phi})\ ] \qquad \text{//DQF}$$

The location of the peaks is exactly as it was in COSY.doc (Section E) but now ALL the peaks meet the STATES criteria, so this does exactly what he says. Of course you still have to use the correct registered FT hardware that I drew up elsewhere. Compare this to the regular COSY results:

$$\rho^{COS} = +\ I_{1x}(S_{\theta 1-\phi} + S_{\theta 1+\phi})/2 \ -\ 2I_{1z}I_{2y}\,(C_{\theta 1-\phi} - C_{\theta 1+\phi})/2 \quad +\ (1\leftrightarrow 2) \qquad \text{// REGULAR}$$
$$\rho^{SIN} = -\ I_{1x}\,(C_{\theta 1-\phi} + C_{\theta 1+\phi})/2 - \ 2I_{1z}I_{2y}\,(S_{\theta 1-\phi} - S_{\theta 1+\phi})/2 \quad +(1\leftrightarrow 2)$$

We get the full anti-phase quartet now for both the cross-peaks and the diagonal peaks.

So, this little phase cycle is easy to run for the two experiments that make up COSY, no reason not to do it this way!

Comment on the above: I just read through Problem 13.2 and it is exactly what I just did above! He does not bother doing a phase cycle on the first pulse, so I guess that was just a little extra to perhaps reduce hardware errors, or perhaps he just did it to illustrate a double nested loop. The page 433 Problem does not bother with this first phase cycle. Also, it sets ϕ_1 to -π/2 which means we have a $(\pi/2)_{-y}$ as the first pulse and he is now calling this the "cos" sequence, swapping the naming just as I did above. I have answered all the parts of the problem, but I am not sure what the disadvantage of doing this is. Maybe the constants above are showing that we only get half the final amplitudes compared to the "regular" so it would take twice the time to get the same noise figure?

In any event, I am very happy to get this **DQF-COSY under my belt**.

17.10.15 Nested Phase Cycles II (620) . The pulse sequence shown on page 621 is the same as that shown on page 405. The new feature in this section is that the final pulse is changed to a filter. In the previous section we had an n=2 filter on the A pulse and n=4 filter on the last pulse which here is called D. Here we also run another n=2 filter on the middle π_x pulse. This gives a triply nested cycle of 2*2*4 = 16 phases and the table is shown page 621. As usual, the ϕ_{dig} column is computed last be selecting one of the pass signals. Once again, the floor function is useful. The algorithm can be concisely stated and leads to a table with no man-made errors!

We do not learn why this central filter adds anything useful, but surely it does. Perhaps all the pulse sequences leak a little bit and this reduces the overall leakage.

17.10.16. Suppressing receiver artifacts I (622). This section says that if you add one more outer loop where you cycle through different values of ϕ_{rec} , you can suppress certain hardware artifacts, such as pulses not being exactly π/2 long, and imbalanced channels. Malcolm does not say how this all works, he is just giving examples of multiple nested cycle algorithms in this appendix 17.10. Here he takes the 4-phase cycle and amps it up to a 16 phase cycle shown on page 624. Fine.

17.10.17. Suppressing receiver artifacts II (625). If your "commercial spectrometer" does not allow programming of $\phi_{\mathtt{rec}}$, this section discusses a "clumsy workaround". Don't care right now, and don't really follow what he is saying. I think a "transient" is a single pulse sequence.

17.10.18. (625) He comments here that people don't yet really know how to optimally design these phase cycles, it is an "open problem", at least it was in 2001. A slightly different approach is to program phase changes between the blocks, rather than deal with the absolute phases of each block, sort of a differential modulation idea. I wonder if there is some mapping from this world into that of modulation in comm?

17.10.19 Pulsed Field Gradients (625) . We saw field gradients used in imaging. The idea is that you can use gradients to cancel signals you don't want to see, a whole different idea really. Probably requires well defined sample dimensions. Advantage is that you need less sample pulsing time to get a result. In practice, the cycling and gradient method are often combined together.

And we so conclude this bunbuster 26 page "appendix" on phase cycling. I get the general idea: you use phase cycling to create "filters" that select out coherence flow paths you want to have be active.