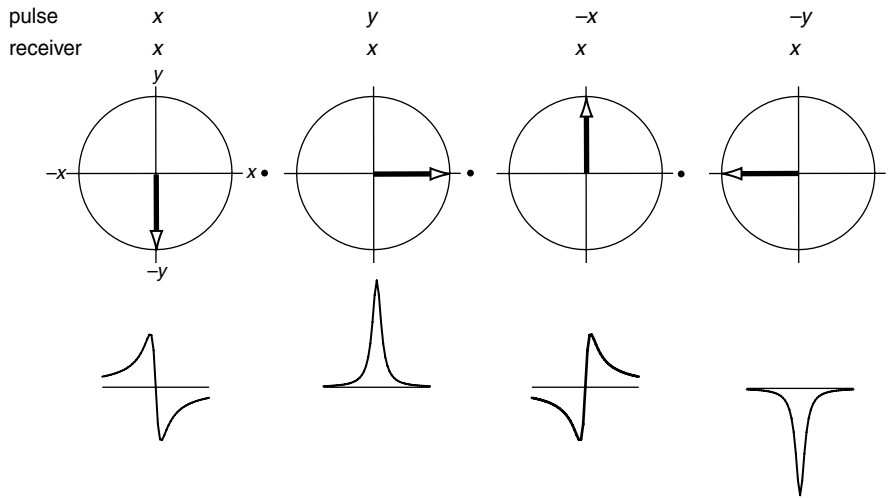


**Coherence selection: phase cycling and gradient pulses – solutions to problems and exercises (August 2000)**

1.

(a)



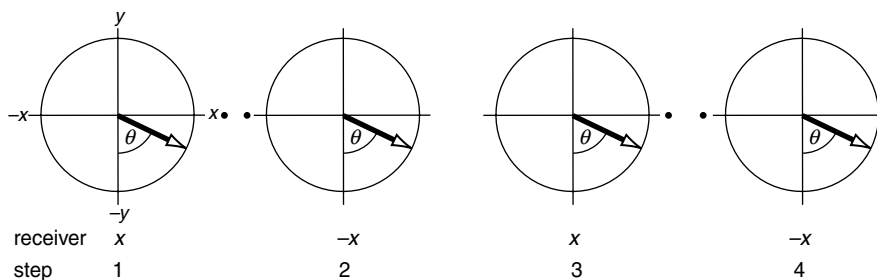
Step 1 cancels with step 3, and step 2 cancels with step 4.

(b)

Without the  $180^\circ$  pulse the sequence becomes

$$90^\circ - 2\tau -$$

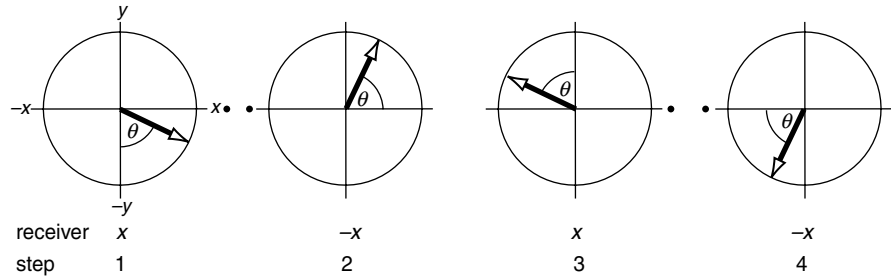
Suppose that the offset is  $\Omega$ , so that after  $2\tau$  the angle through which the vector has precessed is  $\Omega(2\tau)$ , which we will call  $\theta$



Clearly, the  $x$ -components of the magnetization vector are equal and opposite in steps 1 and 2; the same is true of the  $y$ -components. So, the signals from steps 1 and 2 cancel. Likewise, those from steps 3 and 4 cancel. This is simply difference spectroscopy, in which the receiver is going  $\pm$  and the magnetization is fixed; the result is complete cancellation.

(c)

The transverse component of the magnetization will appear along the  $-y$ ,  $x$ ,  $-x$  and  $y$  axes as the imperfect  $180^\circ$  pulse cycles in phase. During the delay  $\tau$  the magnetization precesses through an angle  $\theta = \Omega\tau$



The  $x$ -component from step 1 cancels with that from step 3; likewise that from step 2 cancels with that from step 4. The same is true of the  $y$ -components.

\*2.

(a) (i)

[For simplicity, the  $180^\circ$  pulses are ignored]

$$I_z \xrightarrow{(\pi/2)I_x} -I_y \xrightarrow{2\pi J(1/2J)I_z S_z} 2I_x S_z \xrightarrow{\pm(\pi/2)I_y} \mp 2I_z S_z$$

$$\xrightarrow{(\pi/2)S_x} \pm 2I_z S_y \xrightarrow{2\pi J(1/2J)I_z S_z} \mp S_x$$

(ii)

$$I_z \xrightarrow{(\pi/2)I_x} -I_y \xrightarrow{2\pi J(1/2J)I_z S_z} 2I_x S_z \xrightarrow{(\pi/2)I_y} -2I_z S_z$$

$$\xrightarrow{\pm(\pi/2)S_x} \pm 2I_z S_y \xrightarrow{2\pi J(1/2J)I_z S_z} \mp S_x$$

and starting with  $S_z$

$$S_z \xrightarrow{\pm(\pi/2)S_x} \mp S_y$$

so both the transferred and  $S$ -spin derived signal change sign.

A suitable phase cycle is therefore for the second  $I$  spin  $90^\circ$  pulse to go  $\pm x$ , the  $S$  spin  $90^\circ$  pulse to go  $\pm x$  and the receiver to remain fixed. The wanted signal experiences both phase shifts and so adds, the unwanted signal experiences only the second phase shift and so cancels.

(b)

The  $I$  spin  $180^\circ$  is forming a spin echo so it can be cycled according to the EXORCYCLE procedure: pulse  $x, y, -x, -y$ ; receiver  $x, -x, x, -x$ . This cycle suppresses the contribution from the equilibrium  $S$  spin magnetization as this does not experience the pulse.

(c)

This has no effect as the first  $S$  spin  $180^\circ$  pulse is simply an inversion pulse which achieves the transformation from  $S_z$  to  $-S_z$  independent of its phase.

3.

$$\begin{aligned}
 I_{1+}I_{2-} : p = 0 \quad 4I_{1+}I_{2+}I_{3z} : p = +2 \\
 I_{1x} = \frac{1}{2}(I_{1+} + I_{1-}) : p = \pm 1 \\
 I_{1y} = \frac{1}{2i}(I_{1+} - I_{1-}) : p = \pm 1 \\
 2I_{1x}I_{2z} = 2\frac{1}{2}(I_{1+} + I_{1-})I_{2z} : p = \pm 1 \\
 (2I_{1x}I_{2x} + 2I_{1y}I_{2y}) = \frac{1}{2}(I_{1+}I_{2-} + I_{1-}I_{2+}) : p = 0
 \end{aligned}$$

[In the last example, several terms cancel; care needed with signs]

$$\begin{aligned}
 I_x : p_I = \pm 1, p_S = 0 \\
 S_y : p_I = 0, p_S = \pm 1 \\
 2I_xS_z = 2\frac{1}{2}(I_{1+} + I_{1-})S_z : p_I = \pm 1, p_S = 0 \\
 2I_xS_x = 2\frac{1}{2}(I_{1+} + I_{1-})\frac{1}{2}(S_{1+} + S_{1-}) : p_I = \pm 1, p_S = \pm 1
 \end{aligned}$$

4.

(a)

step	pulse phase	phase shift experienced by pathway with $\Delta p = 0$	equivalent phase	rx. phase for $\Delta p = -3$	difference
1	0	0	0	0	0
2	90	0	0	270	270
3	180	0	0	180	180
4	270	0	0	90	90

It is clear that the pathway with  $\Delta p = 0$  will cancel as the difference phases go "round the clock".

step	pulse phase	phase shift experienced by pathway with $\Delta p = -1$	equivalent phase	rx. phase for $\Delta p = -3$	difference
1	0	0	0	0	0
2	90	90	90	270	180
3	180	180	180	180	0
4	270	270	270	90	-180

It is clear that the pathway with  $\Delta p = -1$  will cancel as step 1 cancels with step 2, and 3 with 4.

step	pulse phase	phase shift experienced by pathway with $\Delta p = 5$	equivalent phase	rx. phase for $\Delta p = -3$	difference
1	0	0	0	0	0
2	90	-450	270	270	0
3	180	-900	180	180	0
4	270	-1350	90	90	0

It is clear that the pathway with  $\Delta p = 5$  is selected.

(b)

(-5) (-4) **-3** (-2) (-1) (0) **1** (2) (3) (4) **5**

The selected pathways differ by 4, as expected.

(c)

step	pulse phase	phase shift experienced by pathway with $\Delta p = +1$	equivalent phase	rx. phase
1	0	0	0	0
2	120	-120	240	240
4	240	-240	120	120

(d)

The three-step cycle must select pathways which differ by 3, so if +1 is selected so is +1 -3 = -2; the pathways in between are cancelled

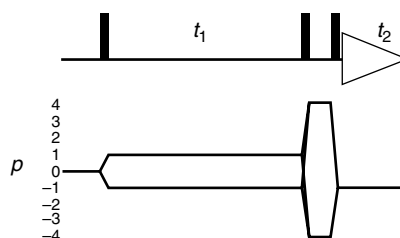
**-2** (-1) (0) **1** (2)

(e)

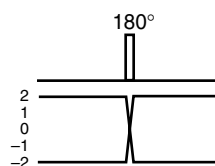
(-6) **-5** (-4) (-3) (-2) (-1) (0) **1** (2) (3) (4) (5) (6)

5.

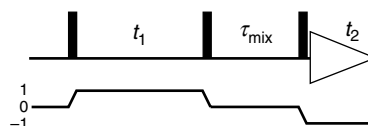
(a)



(b)



(c)



N-type means that the coherence order in  $t_1$  is of opposite sign to that in  $t_2$ .

6.

(a)  $\Delta p = -1$ : pulse  $x, y, -x, -y$ ; receiver  $x, y, -x, -y$ .

(b)  $\Delta p = +2$ : pulse  $x, y, -x, -y$ ; receiver  $x, -x, x, -x$  (like EXORCYLCE)

Step	phase of 1st pulse	phase for $\Delta p = -1$	phase of 2nd pulse	phase for $\Delta p = +2$	total phase	equivalent phase = rx. phase
1	0	0	0	0	0	0
2	90	90	0	0	90	90
3	180	180	0	0	180	180
4	270	270	0	0	270	270
<hr/>						
5	0	0	90	-180	-180	180
6	90	90	90	-180	-90	270
7	180	180	90	-180	0	0
8	270	270	90	-180	90	90
<hr/>						
9	0	0	180	-360	-360	0
10	90	90	180	-360	-270	90
11	180	180	180	-360	-180	180
12	270	270	180	-360	-90	270
<hr/>						
13	0	0	270	-540	-540	180
14	90	90	270	-540	-450	270
15	180	180	270	-540	-360	0
16	270	270	270	-540	-270	90

\*7.

(a) (i)  $\Delta p = \pm 1$ ; (ii)  $\Delta p = \pm 2, \pm 4$ ; (iii)  $\Delta p = \pm 3$ ; (iv)  $\Delta p = -4$  and  $+2$ .

(b)

(-4) -3 (-2) (-1) (0) (1) (2) **3** (4)

The pathways which we need to select are separated by 6, so we need a 6 step cycle. This would be in increments of  $360^\circ/6 = 60^\circ$

The cycle has the pulses going  $0^\circ, 60^\circ, 120^\circ, 180^\circ, 240^\circ, 300^\circ$  and the receiver going  $0^\circ, 180^\circ, 0^\circ, 180^\circ, 0^\circ, 180^\circ$ .

Double-quantum suppression: consider  $\Delta p = -2$ :

Step	Phase of 1st and 2nd pulse	phase for $\Delta p = -3$	equivalent phase = rx. phase	phase for $\Delta p = -2$	difference
1	0	0	0	0	0
2	60	180	180	120	-60 = 300
3	120	360	0	240	240
4	180	540	180	360	180
5	240	720	0	480	480 = 120
6	300	900	180	600	420 = 60

The difference column shows that the phases are distributed equally round the clock, so the pathway with  $\Delta p = -2$  is cancelled.

(c)

**-4** (-3) (-2) (-1) (0) (1) **2** (3) (4)

As the required pathways are separated by 6, a 6 step cycle is required.

Step	Phase of last pulse	phase for $\Delta p = +2$	equivalent phase = rx. phase
1	0	0	0
2	60	-120	240
3	120	-240	120
4	180	-360	0
5	240	-480	240
6	300	-600	120

The same cycle is easily shown to select  $\Delta p = -4$ .

(d) "Try to devise a cycle which involves shifting just the phase of the second pulse" – it is not possible to find a cycle which selects all of the required pathways at once.

8.

(a)

Choose to cycle the first 3 pulses to select  $\Delta p = \pm 2$ , and then to cycle the  $180^\circ$  pulse to select  $\Delta p = \pm 2$  independently

1st and 3rd pulse: 0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3

$180^\circ$  pulse: 0 1 2 3 1 2 3 0 2 3 0 1 3 0 1 2

4th pulse: 0 throughout

Rx: 0 2 0 2 2 0 2 0 0 2 0 2 2 0 2 0

(b)

Choose to select  $\Delta p = -1$  on the last pulse and (separately) axial peak suppression using the first pulse

1st pulse: 0 0 0 0 2 2 2 2

last pulse: 0 1 2 3 0 1 2 3

Rx: 0 1 2 3 2 3 0 1

\*9.

We need an 8 step cycle for the  $180^\circ$  pulse in the double-quantum period as the required pathways are  $\Delta p = \pm 4$  *i.e.*  $\Delta p$  values separated by 8. The cycle will go in steps of  $45^\circ$ , therefore.

$180^\circ$  pulse:  $0^\circ, 45^\circ, 90^\circ, 135^\circ, 180^\circ, 225^\circ, 270^\circ, 315^\circ$

Rx:  $0^\circ, 180^\circ, 0^\circ, 180^\circ, 0^\circ, 180^\circ, 0^\circ, 180^\circ$

10.

(a) 0.14 ms; (b) 1.4 ms.

11.

(a)  $\pm p \rightarrow \mp p$  for any  $p$

(b)  $p \rightarrow p$  for any  $p$

(c)  $2p \rightarrow p$  for any  $p$

(d)  $\pm 2p \rightarrow \mp p$  for any  $p$

12.

(a)  $G_1 : G_2 = 1 : -2$

(b)  $G_1 : G_2 = 1 : -3$

(c)  $G_1 : G_2 = 1 : 3$

(d)  $G_1 : G_2 = 1 : 1$

(e) can use a purge gradient to select  $p = 0$ , but really cannot select this pathway in the way that you can (a) – (d).

13.

(a)

A nice way of writing this is to multiply the coherence order (for clarity written in a bracket) by relative gradient length/strength and then sum these over all the gradients. For a selected pathway, this sum will be zero.

So for  $1 \rightarrow 2 \rightarrow -1$  with gradients 1:1:3 the result is

$$(1) \times 1 + (2) \times 1 + (-1) \times 3 = 1 + 2 - 3 = 0$$

The pathway is therefore selected

(b)

$(-1) \times 1 + (4) \times 1 + (-1) \times 3 = -1 + 4 - 3 = 0$ ; selected. This would give a  $P$ -type four-quantum filtered COSY.

(c)

(i)  $(1) \times 1 + (2) \times \frac{1}{2} + (-1) \times 2 = 1 + 1 - 2 = 0$ ; selected

Alternative has to have

$$(\pm 1) \times 1 + (p) \times \frac{1}{2} + (-1) \times 2 = 0$$

which has solutions  $-1 + \frac{1}{2}p = 0$  *i.e.*  $p = 2$  the pathway  $1 \rightarrow 2 \rightarrow -1$

or  $-3 + \frac{1}{2}p = 0$  *i.e.*  $p = 6$  the pathway  $-1 \rightarrow 6 \rightarrow -1$

(ii)  $(1) \times 1 + (2) \times \frac{1}{3} + (-1) \times \frac{5}{3} = 1 + \frac{2}{3} - \frac{5}{3} = 0$ ; selected

Alternative has to have

$(\pm 1) \times 1 + (p) \times \frac{1}{3} + (-1) \times \frac{5}{3} = 0$

which has solutions  $-\frac{2}{3} + \frac{1}{3}p = 0$  i.e.  $p = 2$  the pathway  $1 \rightarrow 2 \rightarrow -1$

or  $-\frac{8}{3} + \frac{1}{3}p = 0$  i.e.  $p = 8$  the pathway  $-1 \rightarrow 8 \rightarrow -1$

(d)

The problem is that the gradient ratios considered in (c) select pathways other than the one we want. The proposed ratios in (d) also select the required pathway

(ii)  $(1) \times 1.0 + (2) \times 0.8 + (-1) \times 2.6 = 1.0 + 1.6 - 2.6 = 0$ ; selected

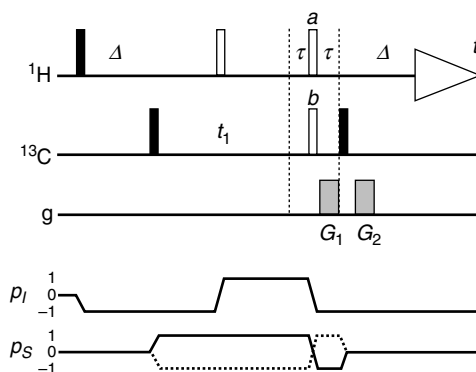
but there are no other pathways of the form  $\pm 1 \rightarrow p \rightarrow -1$  which these "irrational" gradients select.

\*14.

This should be identical to the DQF COSY sequence shown on p. 4-39 except that the gradients should be in the ratio 1:3 or -1:3. The sensitivity will be half that of an equivalent phase-cycled experiment.

\*15.

(a)



*P*-type shown dashed and *N*-type shown solid.

(b)

The two  $180^\circ$  pulses *a* and *b* are needed to refocus the evolution of the offsets of the proton and carbon-13 during the gradient  $G_1$ . Two pulses are needed as at this point in the sequence heteronuclear MQ is present, which evolves under the offset of both carbon-13 and proton.

(c)

This time we need to include the values of  $\gamma$  in order to work out the gradients. It is sufficient to assume that  $\gamma_H = 4$  and  $\gamma_C = 1$

*N*-type  $\gamma_H \times (-1) \times G_1 + \gamma_C \times (-1) \times G_1 + \gamma_H \times (-1) \times G_2$

$= 4 \times (-1) \times G_1 + 1 \times (-1) \times G_1 + 4 \times (-1) \times G_2$

$= -5 G_1 - 4 G_2$



To refocus this sum needs to be zero so  $G_2:G_1$  must be  $-5:4$  Note that  $G_1$  dephases both carbon-13 and proton.

$$\begin{aligned} P\text{-type } & \gamma_H \times (-1) \times G_1 + \gamma_C \times (1) \times G_1 + \gamma_H \times (-1) \times G_2 \\ & = 4 \times (-1) \times G_1 + 1 \times (1) \times G_1 + 4 \times (-1) \times G_2 \\ & = -3 G_1 - 4 G_2 \end{aligned}$$

To refocus this sum needs to be zero so  $G_2:G_1$  must be  $-3:4$

(d)

This sequence is superior in respect of diffusion effects – the gradients are closer together. However, it has an extra  $180^\circ$  pulse to proton, which may cause problems ( $180^\circ$  pulses are often the source of imperfections). Compared to the other sequence, though, it has fewer  $180^\circ$  carbon-13 pulses, which may be an advantage. Finally, with this sequence, switching from  $P$ - to  $N$ -type selection requires changing the length/strength of a gradient, whereas in the other sequence we only needed to alter the sign; this may be an advantage.

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