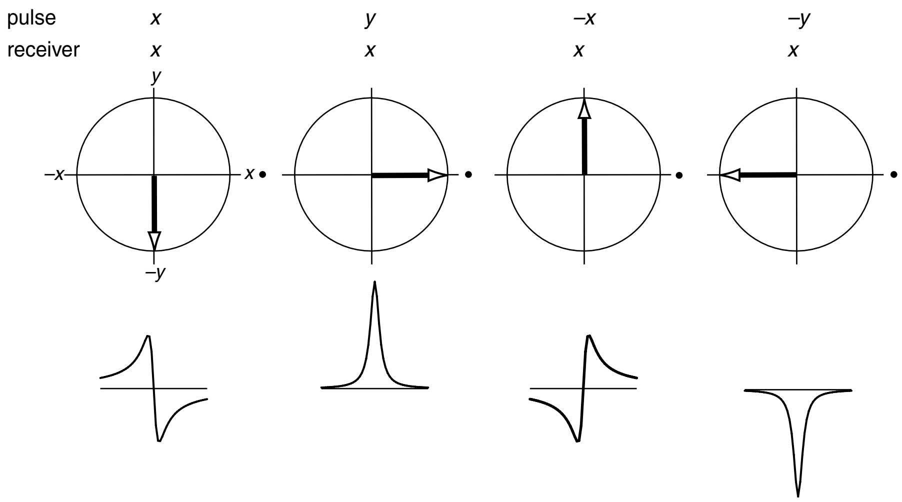
Coherence selection: phase cycling and gradient pulses – solutions to problems and exercises (August 2000)

1.

(a)



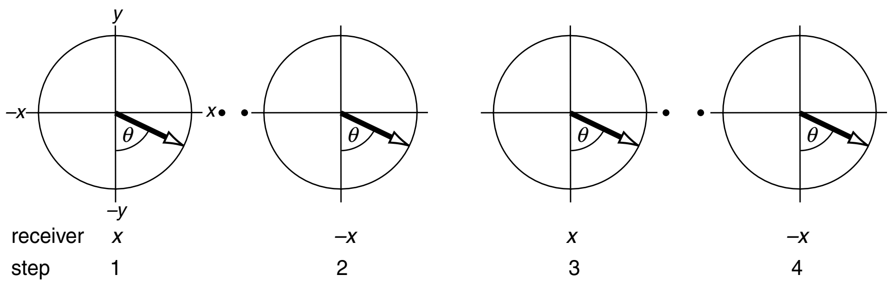
Step 1 cancels with step 3, and step 2 cancels with step 4.

(b)

Without the 180° pulse the sequence becomes

$$90° – 2\tau –$$

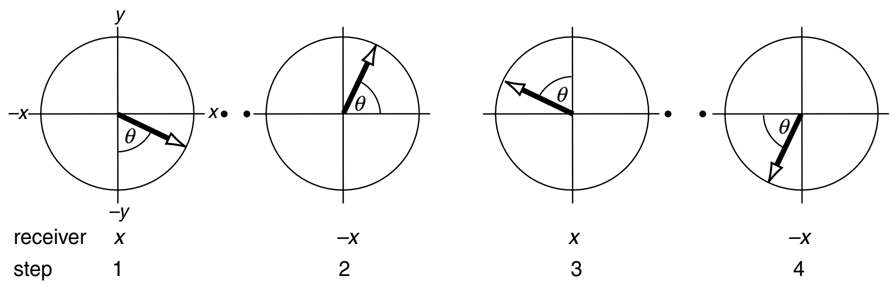
Suppose that the offset is Ω, so that after 2τ the angle through which the vector has precessed in $\Omega(2\tau)$, which we will call θ



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 ± 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° pulse cycles in phase. During the delay τ 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° pulses are ignored]

$$I_z \xrightarrow{(\pi/2)I_x} -I_y \xrightarrow{2\pi J(1/2J)I_zS_z} 2I_xS_z \xrightarrow{\pm(\pi/2)I_y} \mp 2I_zS_z$$
$$\xrightarrow{(\pi/2)S_x} \pm 2I_zS_y \xrightarrow{2\pi J(1/2J)I_zS_z} \mp S_x$$

(ii)

$$I_z \xrightarrow{(\pi/2)I_x} -I_y \xrightarrow{2\pi J(1/2J)I_zS_z} 2I_xS_z \xrightarrow{(\pi/2)I_y} -2I_zS_z$$
$$\xrightarrow{\pm(\pi/2)S_x} \pm 2I_zS_y \xrightarrow{2\pi J(1/2J)I_zS_z} \mp S_x$$

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° pulse to go $\pm x$, the S spin 90° 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° 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° pulse is simply an inversion pulse which achieves the transformation from S_z to $-S_z$ independent of its phase.

3.

$$I_{1+}I_{2-} : p = 0 \quad 4I_{1+}I_{2+}I_{3z} : p = +2$$

$$I_{1x} = \tfrac{1}{2}\left(I_{1+} + I_{1-}\right) : p = \pm 1$$

$$I_{1y} = \tfrac{1}{2i}\left(I_{1+} - I_{1-}\right) : p = \pm 1$$

$$2I_{1x}I_{2z} = 2\tfrac{1}{2}\left(I_{1+} + I_{1-}\right)I_{2z} : p = \pm 1$$

$$\left(2I_{1x}I_{2x} + 2I_{1y}I_{2y}\right) = \tfrac{1}{2}\left(I_{1+}I_{2-} + I_{1-}I_{2+}\right) : p = 0$$

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

$$I_x : p_I = \pm 1, p_S = 0$$

$$S_y : p_I = 0, p_S = \pm 1$$

$$2I_xS_z = 2\tfrac{1}{2}\left(I_{1+} + I_{1-}\right)S_z : p_I = \pm 1, p_S = 0$$

$$2I_xS_x = 2\tfrac{1}{2}\left(I_{1+} + I_{1-}\right)\tfrac{1}{2}\left(S_{1+} + S_{1-}\right) : p_I = \pm 1, p_S = \pm 1$$

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

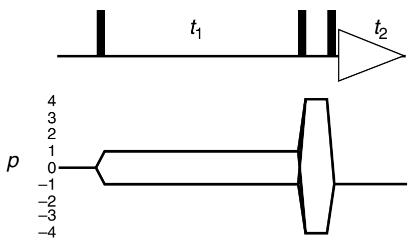
–2 (–1) (0) **1** (2)

(e)

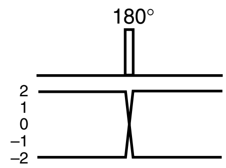
(–6) **–5** (–4) (–3) (–2) (–1) (0) **1** (2) (3) (4) (5) (6)

5.

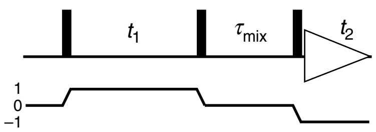
(a)



(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
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
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
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°/6 = 60°

The cycle has the pulses going 0°, 60°, 120°, 180°, 240°, 300° and the receiver going 0°, 180°, 0°, 180°, 0°, 180°.

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° 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° 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° pulse in the double-quantum period as the required pathways are $\Delta p = \pm 4$ *i.e.* Δp values separated by 8. The cycle will go in steps of 45°, therefore.

180° pulse: 0°, 45°, 90°, 135°, 180°, 225°, 270°, 315°

Rx: 0°, 180°, 0°, 180° ,0°, 180°, 0°, 180°

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

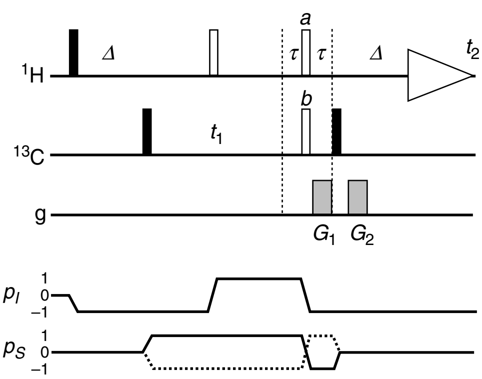
but there are no other pathways of the form $\pm 1 \rightarrow p \rightarrow -1$ which these "irrational" gradients select.

*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° 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 γ 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.

P-type $\gamma_H \times (-1) \times G_1 + \gamma_C \times (1) \times G_1 + \gamma_H \times (-1) \times G_2$
$= 4 \times (-1) \times G_1 + 1 \times (1) \times G_1 + 4 \times (-1) \times G_2$
$= -3\ G_1 - 4\ G_2$
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° pulse to proton, which may cause problems (180° pulses are often the source of imperfections). Compared to the other sequence, though, it has fewer 180° 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.