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° – 2τ –

Suppose that the offset is Ω, so that after 2τ the angle through which the vector has precessed in Ω(2τ), 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 θ = Ωτ
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]

$$
I_z \xrightarrow{(\pi/2)I_z} -I_y \xrightarrow{2\pi(1/2)I_yS_y} 2I_yS_y \xrightarrow{\pi(\pi/2)I_y} \mp 2I_yS_y
$$

(ii)

$$
I_z \xrightarrow{(\pi/2)I_z} -I_y \xrightarrow{2\pi(1/2)I_yS_y} 2I_yS_y \xrightarrow{\pi(\pi/2)I_y} -2I_yS_y
$$

and starting with $S_z$

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

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.

\[ I_{1s}I_{2s} : p = 0 \quad 4I_{1s}I_{2s}I_{3s} : p = +2 \]
\[ I_{1s} = \frac{1}{2}(I_{1s} + I_{1s}) : p = \pm 1 \]
\[ I_{1s} = \frac{1}{2}(I_{1s} - I_{1s}) : p = \pm 1 \]
\[ 2I_{1s}I_{2s} = 2\frac{1}{2}(I_{1s} + I_{1s})I_{2s} : p = \pm 1 \]
\[ (2I_{1s}I_{2s} + 2I_{1s}I_{2s}) = \frac{1}{2}(I_{1s}I_{2s} + I_{1s}I_{2s}) : p = 0 \]

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

\[ I_1 : p_1 = \pm 1, p_2 = 0 \]
\[ S_2 : p_1 = 0, p_2 = \pm 1 \]
\[ 2I_1S_2 = 2\frac{1}{2}(I_{1s} + I_{1s})S_2 : p_1 = \pm 1, p_2 = 0 \]
\[ 2I_1S_2 = 2\frac{1}{2}(I_{1s} + I_{1s})\frac{1}{2}(S_{1s} + S_{1s}) : p_1 = \pm 1, p_2 = \pm 1 \]

4.

(a)

<table>
<thead>
<tr>
<th>step</th>
<th>pulse phase</th>
<th>phase shift experienced by path with ( \Delta p = 0 )</th>
<th>equivalent phase</th>
<th>rx. phase for ( \Delta p = -3 )</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
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<td>180</td>
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<tr>
<td>4</td>
<td>270</td>
<td>0</td>
<td>0</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>step</th>
<th>pulse phase</th>
<th>phase shift experienced by path with ( \Delta p = -1 )</th>
<th>equivalent phase</th>
<th>rx. phase for ( \Delta p = -3 )</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
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<td>0</td>
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<tr>
<td>2</td>
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<tr>
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<td>180</td>
<td>180</td>
<td>0</td>
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<tr>
<td>4</td>
<td>270</td>
<td>270</td>
<td>270</td>
<td>90</td>
<td>-180</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>step</th>
<th>pulse phase</th>
<th>phase shift experienced by path with ( \Delta p = 5 )</th>
<th>equivalent phase</th>
<th>rx. phase for ( \Delta p = -3 )</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>-450</td>
<td>270</td>
<td>270</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>-900</td>
<td>180</td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>270</td>
<td>-1350</td>
<td>90</td>
<td>90</td>
<td>0</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>step</th>
<th>pulse phase</th>
<th>phase shift experienced by pathway with $\Delta p = +1$</th>
<th>equivalent phase</th>
<th>rx. phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>-120</td>
<td>240</td>
<td>240</td>
</tr>
<tr>
<td>4</td>
<td>240</td>
<td>-240</td>
<td>120</td>
<td>120</td>
</tr>
</tbody>
</table>

(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 $t_2$. 

Solutions-4
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)

<table>
<thead>
<tr>
<th>Step</th>
<th>Phase of 1st pulse for $\Delta p = -1$</th>
<th>Phase of 2nd pulse for $\Delta p = +2$</th>
<th>Total phase for $\Delta p = +2$</th>
<th>Equivalent phase = rx. phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>90</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>180</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>4</td>
<td>270</td>
<td>270</td>
<td>0</td>
<td>270</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>90</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>270</td>
</tr>
<tr>
<td>7</td>
<td>180</td>
<td>180</td>
<td>90</td>
<td>0</td>
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<td>270</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td>0</td>
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<td>360</td>
<td>90</td>
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<td>180</td>
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<td>180</td>
<td>360</td>
<td>90</td>
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<td>180</td>
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<td>270</td>
<td>540</td>
<td>270</td>
</tr>
<tr>
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<tr>
<td>16</td>
<td>270</td>
<td>270</td>
<td>540</td>
<td>90</td>
</tr>
</tbody>
</table>

*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 $\Delta p = -2$:

<table>
<thead>
<tr>
<th>Step</th>
<th>Phase of 1st and 2nd pulse for $\Delta p = -3$</th>
<th>Equivalent phase = rx. phase</th>
<th>Phase for $\Delta p = -2$</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>180</td>
<td>120</td>
<td>-60 = 300</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>360</td>
<td>240</td>
<td>240</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
<td>540</td>
<td>360</td>
<td>180</td>
</tr>
<tr>
<td>5</td>
<td>240</td>
<td>720</td>
<td>480</td>
<td>480 = 120</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>900</td>
<td>600</td>
<td>420 = 60</td>
</tr>
</tbody>
</table>

The difference column shows that the phases are distributed equally round the clock, so the pathway with $\Delta p = -2$ is cancelled.
As the required pathways are separated by 6, a 6 step cycle is required.

<table>
<thead>
<tr>
<th>Step</th>
<th>Phase of last pulse</th>
<th>phase for $\Delta p = +2$</th>
<th>equivalent phase = rx. phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>-120</td>
<td>240</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>-240</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
<td>-360</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>240</td>
<td>-480</td>
<td>240</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>-600</td>
<td>120</td>
</tr>
</tbody>
</table>

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. $\Delta p$ 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) 

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

(c) 

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

Alternative has to have

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

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

or $-3 + \frac{1}{2} p = 0 \text{ i.e. } p = 6$ 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)**

\[P\text{-type shown dashed and } N\text{-type shown solid.}\]

**(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 \(\gamma\) in order to work out the gradients. It is sufficient to assume that \(\gamma_H = 4\) and \(\gamma_C = 1\)

\[N\text{-type } \gamma_H \times (-1) \times G_1 + \gamma_C \times (-1) \times G_1 + \gamma_H \times (-1) \times G_2 = 4 \times (-1) \times G_1 + 1 \times (-1) \times G_1 + 4 \times (-1) \times G_2 = -5 G_1 - 4 G_2\]

Solutions–8
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.

$$P\text{-type } \gamma_H \times (-1) \times G_1 + \gamma_C \times (1) \times G_1 + \gamma_H \times (-1) \times G_2$$

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

$$= -3 \ G_1 - 4 \ G_2$$

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.

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