Coherence selection: phase cycling and gradient pulses – problems and exercises

*The more difficult and challenging problems are marked with an asterisk, **

1.

(a) Show, using vector diagrams like those of section 4.1.6, that in a pulse-acquire experiment a phase cycle in which the pulse goes x, y, $-x$, $-y$ and in which the receiver phase is fixed leads to no signal after four transients have been co-added.

(b) In a simple spin echo sequence

$$90° - \tau - 180° - \tau -$$

the EXORCYCLE sequence involves cycling the 180° pulse x, y, $-x$, $-y$ and the receiver x, $-x$, x, $-x$. Suppose that, by accident, the 180° pulse has been omitted. Use vector pictures to show that the four step phase cycle cancels all the signal.

(c) In the simple echo sequence, suppose that there is some z-magnetization present at the end of the first τ delay; also suppose that the 180° pulse is imperfect so that some of the z-magnetization is made transverse. Show that the four steps of EXORCYCLE cancels the signal arising from this magnetization.

*2.

(a) For the INEPT pulse sequence of section 4.1.8, confirm with product operator calculations that: [You should ignore the evolution of offsets as this is refocused by the spin echo; assume that the spin echo delay is $1/(2J_{IS})$].

(i) the sign of the signal transferred from I to S is altered by changing the phase of the second I spin 90° pulse from y to $-y$;

(ii) the signs of both the transferred signal and the signal originating from equilibrium S spin magnetization, S_z, are altered by changing the phase of the first S spin 90° pulse by 180°.

On the basis of your answers to (i) and (ii), suggest a suitable phase cycle, different to that given in the notes, for eliminating the contribution from the equilibrium S spin magnetization.

(b) Imagine that in the INEPT sequence the first I spin 180° pulse is cycled x, y, $-x$, $-y$. Without detailed calculations, deduce the effect of this cycle on the transferred signal and hence determine a suitable phase cycle for the receiver [hint - this 180° pulse is just forming a spin echo]. Does your cycle eliminate the contribution from the equilibrium S spin magnetization?

(c) Suppose now that the first S spin 180° pulse is cycled x, y, $-x$, $-y$; what effect does this have on the signal transferred from I to S?

3.

Determine the coherence order or orders of each of the following operators [you will need to express I_x and I_y in terms of the raising and lowering operators, see section 4.2.1]

$$I_{1+}I_{2-} \quad 4I_{1+}I_{2+}I_{3z} \quad I_{1x} \quad I_{1y} \quad 2I_{1x}I_{2z} \quad \left(2I_{1x}I_{2x}+2I_{1y}I_{2y}\right)$$

In a heteronuclear system a coherence order can be assigned to each spin separately. If *I* and *S* represent different nuclei, assign separate coherence orders for the *I* and *S* spins to the following operators

$$I_x \quad S_y \quad 2I_xS_z \quad 2I_xS_x$$

4.

(a) Consider the phase cycle devised in section 4.3.1 which was designed to select $\Delta p = -3$: the pulse phase goes 0, 90, 180, 270 and the receiver phase goes 0, 270, 180, 90. Complete the following table and use it to show that such a cycle cancels signals arising from a pathway with $\Delta p = 0$.

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

Construct a similar table to show that a pathway with $\Delta p = -1$ is cancelled, but that one with $\Delta p = +5$ is selected by this cycle.

(b) Bodenhausen *et al*. have introduced a notation in which the sequence of possible Δp values is written out in a line; the values of Δp which are selected by the cycle are put into **bold** print, and those that are rejected are put into parenthesis, *viz* (1). Use this notation to describe the pathways selected and rejected by the cycle given above for pathways with Δp between –5 and +5 [the fate of several pathways is given in section 4.3.1, you have worked out two more in part (a) and you may also assume that the pathways with Δp = –5, –4, –2, 3 and 4 are rejected]. Confirm that, as expected for this four-step cycle, the selected values of Δp are separated by 4.

(c) Complete the following table for a *three-step* cycle designed to select $\Delta p = +1$.

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

(d) Without drawing up further tables, use the general rules of section 4.3.2 to show that, in Bodenhausen's notation, the selectivity of the cycle devised in (c) can be written:

–2 (–1) (0) **1** (2)

(e) Use Bodenhausen's notation to describe the selectivity of a 6 step cycle designed to select $\Delta p = +1$; consider Δp values in the range –6 to +6.

5.

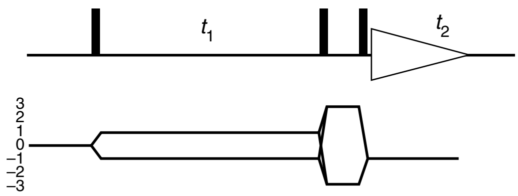
Draw coherence transfer pathways for (a) four-quantum filtered COSY [use the sequence in section 4.3.5.4 as a model]; (b) a 180° pulse used to refocus double-quantum coherence; (c) *N*-type NOESY.

6.

Write down four-step phase cycles to select (a) $\Delta p = -1$ and (b) $\Delta p = +2$. Suppose that the cycles are applied to different pulses. Combine them to give a 16-step cycle as was done in section 4.3.4; give the required receiver phase shifts.

*7.

The CTP and pulse sequence of triple-quantum filtered COSY are



(a) Write down the values of Δp brought about by (i) the first pulse, (iii) the second pulse, (iii) the first and second pulses acting together and considered as a group, (iv) the last pulse.

(b) Imagine the spin system under consideration is able to support multiple quantum coherence up to and including $p = \pm 4$. Consider a phase cycle in which the first two pulses are cycled as a group and, having in mind your answer to (a) (iii), use the notation of Bodenhausen to indicate which pathways need to be selected and which blocked. Hence argue that the required phase cycle must have 6 steps. Draw up such a six-step phase cycle and confirm that the proposed sequence of pulse and receiver phases does indeed discriminate against filtration through double-quantum coherence.

(c) Consider an alternative phase cycle in which just the phase of the last pulse is cycled. As in (b), use Bodenhausen's notation to describe the wanted and unwanted values of Δp. Devise a suitable phase cycle to select the required values of Δp.

(d) Try to devise a cycle which involves shifting just the phase of the second pulse.

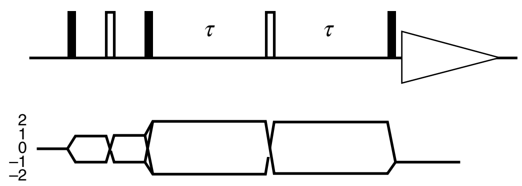
8.

(a) Write down a 16 step cycle which selects the pathways shown in the double quantum spectroscopy pulse sequence of section 4.4.9.1; include in your cycle double-quantum selection and EXORCYCLE phase cycling of the 180° pulse.

(b) Write down an 8 step cycle which selects the pathway for NOESY shown in section 4.3.9.2; include in your cycle explicit axial peak suppression steps.

*9.

The following sequence is one designed to measure the relaxation-induced decay of double-quantum coherence as a function of the time 2τ



The 180° pulse placed in the middle of the double-quantum period is used to refocus evolution due to offsets and inhomogeneous line broadening.

Devise a suitable phase cycle for the second 180° pulse bearing in mind that the 180° pulse may be imperfect. [hint: are four steps sufficient?]

10.

Use the formula given in section 4.5.2 for the overall decay of magnetization during a gradient

$$\frac{2}{\gamma G t r_{max}}$$

to calculate how long a gradient is needed to dephase magnetization to (a) 10% and (b) 1% of its initial value assuming that: G = 0.1 T m^{-1} (10 G cm^{-1}), r_{max} = 0.005 m (0.5 cm) and γ = 2.8 × 10^{8} rad s^{-1}. [Put all the quantities in SI units].

11.

Imagine that two gradients, G_1 and G_2, are placed before and after a radiofrequency pulse. For each of the following ratios between the two gradients, identify *two* coherence transfer pathways which will be refocused:

(a) G_1:G_2 = 1:1 (b) G_1:G_2 = –1:1 (c) G_1:G_2 = 1:–2 (d) G_1:G_2 = 0.5:1

12.

Determine the ratio $G_1{:}G_2$ needed to select the following pathways:

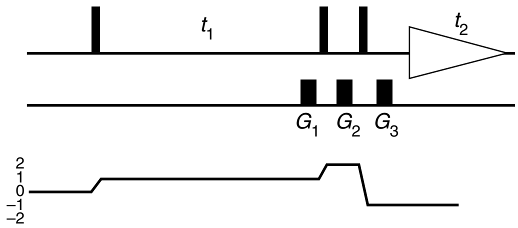
(a) $p = 2 \rightarrow 1$ (b) $p = 3 \rightarrow 1$ (c) $p = -3 \rightarrow 1$

(d) $p = -1 \rightarrow 1$ *and* $p = 1 \rightarrow -1$ (e) $p = 0 \rightarrow 1$

Comment on the way in which case (e) differs from all the others.

13.

Consider a gradient selected *N*-type DQF COSY



We use three gradients; G_1 in t_1 so as to select $p = +1$ during t_1; G_2 to select double quantum during the filter delay and G_3 to refocus prior to acquisition.

(a) Show that the pathway shown, which can de denoted $0 \rightarrow 1 \rightarrow 2 \rightarrow -1$, is selected by gradients in the ratio $G_1{:}G_2{:}G_3 = 1{:}1{:}3$.

(b) Show that this set of gradients also selects the pathway $0 \rightarrow -1 \rightarrow 4 \rightarrow -1$. What kind of spectrum does such a pathway give rise to?

(c) Consider gradients in the ratios $G_1{:}G_2{:}G_3$ (i) $1{:}\frac{1}{2}{:}2$ and (ii) $1{:}\frac{1}{3}{:}\frac{5}{3}$. Show that these combination select the DQ filtered pathway desired. In each case, give another possible pathway which has $p = \pm 1$ during t_1 and $p = -1$ during t_2 that these gradient combinations select.

(d) In the light of (b) and (c), consider the utility of the gradient ratio 1.0 : 0.8 : 2.6

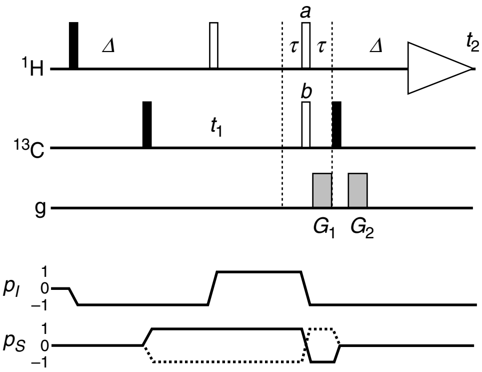
*14.

Devise a gradient selected version of the triple-quantum filtered COSY experiment, whose basic pulse sequence and CTP was given in Qu. 7. Your sequence should include recommendations for the relative size of the gradients used. The resulting spectrum must have pure phase (*i.e.* $p = \pm 1$ must be preserved in t_1) and phase errors due to the evolution of offsets during the gradients must be removed.

How would you expect the sensitivity of your sequence to compare with its phase-cycled counterpart?

*15.

A possible sequence for *P*/*N* selected HMQC is



The intention is to recombine *P*- and *N*-type spectra so as to obtain absorption mode spectra.

(a) Draw CTPs for the *P*-type and *N*-type versions of this experiment [refer to section 4.5.7.3 for some hints].

(b) What is the purpose of the two 180° pulses *a* and *b*, and why are such pulses needed for both proton and carbon-13?

(c) Given that $\gamma_H/\gamma_C = 4$, what ratios of gradients are needed for the *P*-type and the *N*-type spectra?

(d) Compare this sequence with that given in section 4.5.7.3, pointing out any advantages and disadvantages that each has.