Exercises for Chapters 6, 7, 8 & 9

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

Chapter 6: Product operators

E6-1 Using the standard rotations from section 6.1.4, express the following rotations in terms of sines and cosines:

$$\exp(-i\theta I_x) I_y \exp(i\theta I_x) \quad \exp(-i\theta I_z)(-I_y)\exp(i\theta I_z) \quad -\exp(-i\theta I_y) I_z \exp(i\theta I_y)$$

$$\exp(-i\tfrac{1}{2}\theta I_y) I_x \exp(i\tfrac{1}{2}\theta I_y) \quad \exp(-i\theta I_x) I_x \exp(i\theta I_x) \quad \exp(i\theta I_x)(-I_z)\exp(-i\theta I_x)$$

Express all of the above transformations in the shorthand notation of section 6.1.5.

E6-2. Repeat the calculation in section 6.1.6 for a spin echo with the 180° pulse about the *y*-axis. You should find that the magnetization refocuses onto the –*y* axis.

E6-3. Assuming that magnetization *along the y-axis* gives rise to an absorption mode lineshape, draw sketches of the spectra which arise from the following operators

$$I_{1y} \qquad I_{2x} \qquad 2I_{1y}I_{2z} \qquad 2I_{1z}I_{2x}$$

E6-4. Describe the following terms in words:

$$I_{1y} \qquad I_{2z} \qquad 2I_{1y}I_{2z} \qquad 2I_{1x}I_{2x}$$

E6-5. Give the outcome of the following rotations

$$I_{1x} \xrightarrow{\omega_1 t_p I_{1y}}$$

$$2I_{1x}I_{2z} \xrightarrow{(\pi/2)(I_{1y}+I_{2y})}$$

$$2I_{1x}I_{2z} \xrightarrow{-\pi I_{2y}}$$

$$I_{1x} \xrightarrow{\Omega_1 t I_{1z}} \xrightarrow{\Omega_2 t I_{2z}}$$

$$-I_{1x} \xrightarrow{2\pi J_{12} t I_{1z} I_{2z}}$$

$$-2I_{1z}I_{2y} \xrightarrow{2\pi J_{12} t I_{1z} I_{2z}}$$

Describe the outcome in words in each case.

E6-6. Consider the spin echo sequence

$$-\ \tau - 180°(x, \text{ to spin 1 and spin 2}) - \tau -$$

applied to a two-spin system. Starting with magnetization along *y*, represented by I_{1y}, show that overall effect of the sequence is

$$I_{1y} \xrightarrow{\text{spin echo}} -\cos(2\pi J_{12}\tau) I_{1y} + \sin(2\pi J_{12}\tau) 2I_{1x}I_{2z}$$

You should ignore the effect of offsets, which are refocused, are just consider evolution due to coupling.

Is your result consistent with the idea that this echo sequence is equivalent to

$$-\,2\tau - 180°(x, \text{ to spin 1 and spin 2})$$

[This calculation is rather more complex than that in section 6.4.1. You will need the identities

$$\cos 2\theta = \cos^2\theta - \sin^2\theta \quad \text{and} \quad \sin 2\theta = 2\cos\theta\sin\theta \;]$$

E6-7. For a two-spin system, what delay, τ, in a spin echo sequence would you use to achieve the following overall transformations (do not worry about signs)? [cos π/4 = sin π/4 = 1/√2]

$$I_{2y} \longrightarrow 2I_{1z}I_{2x}$$

$$2I_{1z}I_{2x} \longrightarrow I_{2x}$$

$$I_{1x} \longrightarrow \left(\tfrac{1}{\sqrt{2}}\right)I_{1x} + \left(\tfrac{1}{\sqrt{2}}\right)2I_{1y}I_{2z}$$

$$I_{1x} \longrightarrow -I_{1x}$$

E6-8. Confirm by a calculation that spin echo sequence *c* shown on page **6**–11 does not refocus the evolution of the offset of spin 1. [Start with a state I_{1x} or I_{1y}; you may ignore the evolution due to coupling].

***E6-9.** Express $2I_{1x}I_{2y}$ in terms of raising and lowering operators: see section 6.5.2. Take the *zero-quantum part* of your expression and then re-write this in terms of Cartesian operators using the procedure shown in section 6.5.2.

E6-10. Consider three coupled spins in which $J_{23} > J_{12}$. Following section 6.6, draw a sketch of the doublet and doublets expected for the multiplet on spin 2 and label each line with the spin states of the coupled spins, 1 and 3. Lable the splittings, too.

Assuming that magnetization along *x* gives an absorption mode lineshape, sketch the spectra from the following operators:

$$I_{2x} \quad 2I_{1z}I_{2x} \quad 2I_{2y}I_{3z} \quad 4I_{1z}I_{2x}I_{3z}$$

E6-11. Complete the following rotations.

$$I_{2x} \xrightarrow{\Omega_1 t I_{1z}} \xrightarrow{\Omega_2 t I_{2z}} \xrightarrow{\Omega_3 t I_{3z}}$$

$$2I_{1y}I_{2z} \xrightarrow{(\pi/2)\left(I_{1y}+I_{2y}+I_{3y}\right)}$$

$$4I_{1x}I_{2z}I_{3z} \xrightarrow{(\pi/2)\left(I_{1y}+I_{2y}+I_{3y}\right)}$$

$$2I_{1z}I_{2x} \xrightarrow{2\pi J_{12} t I_{1z} I_{2z}}$$

$$2I_{1z}I_{2x} \xrightarrow{2\pi J_{23} t I_{2z} I_{3z}}$$

$$4I_{1z}I_{2y}I_{3z} \xrightarrow{2\pi J_{23} t I_{2z} I_{3z}}$$

$$I_{1x} \xrightarrow{2\pi J_{12} t I_{1z} I_{2z}} \xrightarrow{2\pi J_{13} t I_{1z} I_{3z}}$$

Chapter 7: Two-dimensional NMR

E7-1. Sketch the COSY spectra you would expect from the following arrangements of spins. In the diagrams, a line represents a coupling. Assume that the spins have well separated shifts; do not concern yourself with the details of the multiplet structures of the cross- and diagonal-peaks.

A——B——C A——B——C

A——B C

E7-2. Sketch labelled two-dimensional spectra which have peaks arising from the following transfer processes

	frequencies in F_1 / Hz		frequencies in F_2 / Hz
a	30	Transferred to	30
b	30 and 60	transferred to	30
c	60	transferred to	30 and 60
d	30	transferred to	20, 30 and 60
e	30 and 60	transferred to	30 and 60

E7-3. What would the diagonal-peak multiplet of a COSY spectrum of two spins look like if we assigned the absorption mode lineshape in F_2 to magnetization along x and the absorption mode lineshape in F_1 to sine modulated data in t_1?

What would the cross-peak multiplet look like with these assignments?

E7-4. The smallest coupling that will gives rise to a discernible cross-peak in a COSY spectra depends on both the linewidth and the signal-to-noise ratio of the spectrum. Explain this observation.

***E7-5.** Complete the analysis of the DQF COSY spectrum by showing in detail that both the cross and diagonal-peak multiplets have the same lineshape and are in anti-phase in both dimensions. Start from the expression in the middle of page 7–10, section 7.4.21. [You will need the identity $\cos A \sin B = \tfrac{1}{2}[\sin(B+A) + \sin(B-A)]$].

***E7-6.** Consider the COSY spectrum for a three-spin system. Start with magnetization just on spin 1. The effect of the first pulse is

$$I_{1z} \xrightarrow{(\pi/2)(I_{1x}+I_{2x}+I_{3x})} -I_{1y}$$

Then, only the offset of spin 1 has an effect

$$-I_{1y} \xrightarrow{\Omega_1 t_1 I_{1z}} -\cos \Omega_1 t_1 I_{1y} + \sin \Omega_1 t_1 I_{1x}$$

Only the term in I_{1x} leads to cross- and diagonal peaks, so consider this term only from now on.

First allow it to evolve under the coupling to spin 2 and then the coupling to spin 3

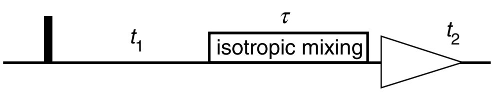
$$\sin \Omega_1 t_1 I_{1x} \xrightarrow{2\pi J_{12} t_1 I_{1z} I_{2z}} \xrightarrow{2\pi J_{13} t_1 I_{1z} I_{3z}}$$

Then, consider the effect of a 90°(x) pulse applied to all three spins. After this pulse, you should find one term which represents a diagonal-peak multiplet, one which represents a cross-peak multiplet between spin 1 and spin 2, and one which represents a cross-peak multiplet between spin 1 and spin 3. What does the fourth term represent?

[More difficult] Determine the form of the cross-peak multiplets, using the approach adopted in section 6.4.1. Sketch the multiplets for the case $J_{12} \approx J_{23} > J_{13}$. [You will need the identity

$$\sin A \sin B = \tfrac{1}{2}[\cos(A+B) - \cos(A-B)] \quad]$$

***E7-7.** The pulse sequence for two-dimensional TOCSY (total correlation spectroscopy) is shown below



The mixing time, of length τ, is a period of *isotropic mixing*. This is a multiple-pulse sequence which results in the transfer of *in-phase* magnetization from one spin to another. In a two spin system the mixing goes as follows:

$$I_{1x} \xrightarrow{\text{isotropic mixing for time } \tau} \cos^2 \pi J_{12} \tau \, I_{1x} + \sin^2 \pi J_{12} \tau \, I_{2x}$$

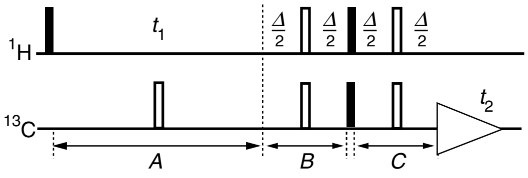
We can assume that all terms other than I_{1x} do not survive the isotropic mixing sequence, and so can be ignored.

Predict the form of the two-dimensional TOCSY spectrum for a two-spin system. What is the value of τ which gives the strongest cross peaks? For this optimum value of τ, what happens to the diagonal peaks? Can you think of any advantages that TOCSY might have over COSY?

E7-8. Repeat the analysis for the HMQC experiment , section 7.4.3.1, with the phase of the first spin-2 (carbon-13) pulse set to $-x$ rather than $+x$. Confirm that the observable signals present at the end of the sequence do indeed change sign.

E7-9. Why must the phase of the second spin-1 (proton) 90° pulse in the HSQC sequence, section 7.4.3.2, be y rather than x?

E7-10. Below is shown the pulse sequence for the HETCOR (heteronuclear correlation) experiment



This sequence is closely related to HSQC, but differs in that the signal is observed on carbon-13, rather than being transferred back to proton for observation. Like HSQC and HMQC the resulting spectrum shows cross peaks whose co-ordinates are the shifts of directly attached carbon-13 proton pairs. However, in contrast to these sequences, in HETCOR the proton shift is in F_1 and the carbon-13 shift is in F_2. In the early days of two-dimensional NMR this was a popular sequence for shift correlation as it is less demanding of the spectrometer; there are no strong signals from protons not coupled to carbon-13 to suppress.

We shall assume that spin 1 is proton, and spin 2 is carbon-13. During period A, t_1, the offset of spin 1 evolves but the coupling between spins 1 and 2 is refocused by the centrally placed 180° pulse. During period B the coupling evolves, but the offset is refocused. The optimum value for the time Δ is $1/(2J_{12})$, as this leads to complete conversion into anti-phase. The two 90° pulses transfer the anti-phase magnetization to spin 2.

During period C the anti-phase magnetization rephases (the offset is refocused) and if Δ is $1/(2J_{12})$ the signal is purely in-phase at the start of t_2.

Make an informal analysis of this sequence, along the lines of that given in section 7.4.3.2, and hence predict the form of the spectrum. In the first instance assume that Δ is set to its optimum value. Then, make the analysis slightly more complex and show that for an arbitrary value of Δ the signal intensity goes as $\sin^2 \pi J_{12} \Delta$.

Does altering the phase of the second spin-1 (proton) 90° pulse from x to y make any difference to the spectrum?

[Harder] What happens to carbon-13 magnetization, I_{2z}, present at the beginning of the sequence? How could the contribution from this be removed?

Chapter 8: Relaxation

E8-1. In an inversion-recovery experiment the following peak heights (*S*, arbitrary units) were measured as a function of the delay, *t*, in the sequence:

t / s	0.1	0.5	0.9	1.3	1.7	2.1	2.5	2.9
S	–98.8	–3.4	52.2	82.5	102.7	115.2	120.7	125.1

The peak height after a single 90° pulse was measured as 130.0 Use a graphical method to analyse these data and hence determine a value for the longitudinal relaxation rate constant and the corresponding value of the relaxation time, T_1.

E8-2. In an experiment to estimate T_1 using the sequence [180° – τ – 90°] acquire three peaks in the spectrum were observed to go through a null at 0.5, 0.6 and 0.8 s respectively. Estimate T_1 for each of these resonances.

A solvent resonance was still inverted after a delay of 1.5 s; what does this tell you about the relaxation time of the solvent?

***E8-3.** Using the diagram at the top of page 8–5, write down expressions for dn_1/dt, dn_2/dt *etc.* in terms of the rate constants *W* and the populations n_i. [Do this without looking at the expressions given on page 8–6 and then check carefully to see that you have the correct expressions].

***E8-4.** Imagine a modified experiment, designed to record a transient NOE enhancement, in which rather than spin S being inverted at the beginning of the experiment, it is *saturated*. The initial conditions are thus

$$I_z(0) = I_z^0 \qquad S_z(0) = 0$$

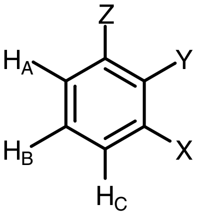
Using these starting conditions rather than those of Eq. [16] on page 8-10, show that in the initial rate limit the NOE enhancement builds up at a rate proportional to σ_{IS} rather than $2\sigma_{IS}$. You should use the method given in Section 8.4.1 for your analysis.

Without detailed calculation, sketch a graph, analogous to that given on page 8-12, for the behaviour of I_z and S_z for these new initial conditions as a function of mixing time.

E8-5. Why is it that in a two spin system the size of transient NOE enhancements depends on R_I, R_S and σ_{IS}, whereas in a steady state experiment the enhancement only depends on R_I and σ_{IS}? [Spin S is the target].

In a particular two-spin system, S relaxes quickly and I relaxes slowly. Which experiment would you choose in order to measure the NOE enhancement between these two spins? Include in your answer an explanation of which spin you would irradiate.

E8-6. For the molecule shown on the right, a transient NOE experiment in which H_B is inverted gave equal initial NOE build-up rates on H_A and H_C. If H_A was inverted the initial build-up rate on H_B was the same as in the first experiment; no enhancement is seen of H_C. In steady state experiments, irradiation of H_B gave equal enhancements on H_A and H_B. However, irradiation of H_A gave a much smaller enhancement on H_B than for the case where H_B was the irradiated spin and the enhancement was observed on H_A. Explain.



E8-7. What do you understand by the terms *correlation time* and *spectral density*? Why are these quantities important in determining NMR relaxation rate constants?

E8-8. The simplest form of the spectral density, $J(\omega)$, is the Lorentzian:

$$J(\omega) = \frac{2\tau_c}{1+\omega^2\tau_c^2}$$

Describe how this spectral density varies with both ω and τ_c. For a given frequency, ω_0, at what correlation time is the spectral density a maximum? Show how this form of the spectral density leads to the expectation that, for a given Larmor frequency, T_1 will have a minimum value at a certain value of the correlation time, τ_c.

E8-9. Suppose that he Larmor frequency (for proton) is 800 MHz. What correlation time will give the minimum value for T_1? What kind of molecule might have such a correlation time?

E8-10. Explain why the NOE enhancements observed in small molecules are positive whereas those observed for large molecules are negative.

E8-11. Explain how it is possible for the sign of an NOE enhancement to change when the magnetic field strength used by the spectrometer is changed.

E8-12. What is transverse relaxation and how it is different from longitudinal relaxation? Explain why it is that the rate constant for transverse relaxation increases with increasing correlation times, whereas that for longitudinal relaxation goes through a maximum.

Chapter 9: Coherence selection: phase cycling and gradient pulses

E9-1. (a) Show, using vector diagrams like those of section 9.1.6, 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.

***E9-2.** (a) For the INEPT pulse sequence of section 9.1.8, 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*?

E9-3. 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 9.3.1]

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

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

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

E9-4. (a) Consider the phase cycle devised in section 9.5.1 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 9.5.1, 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 9.5.2 to show that, in Bodenhausen's notation, the selectivity of the cycle devised in (c) can be written:

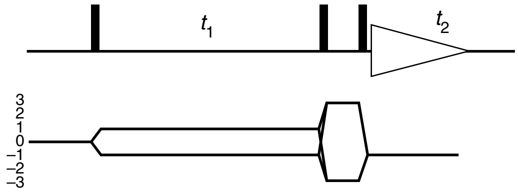
–2 (–1) (0) **1** (2)

(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.

E9-5. Draw coherence transfer pathways for (a) four-quantum filtered COSY [use the sequence in section 9.5.5.4 as a model]; (b) a 180° pulse used to refocus double-quantum coherence; (c) *N*-type NOESY.

E9-6. 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 9.5.4; give the required receiver phase shifts.

***E9-7.** 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.

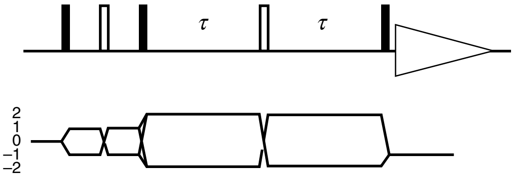
(c) Consider an alternative phase cycle in which just the phase of the last pulse is cycled. As in (b), use Bodenhausen's notation to describe the wanted and unwanted values of Δp. Devise a suitable phase cycle to select the required values of Δp.

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

E9-8. (a) Write down a 16 step cycle which selects the pathways shown in the double quantum spectroscopy pulse sequence of section 9.5.9.1; 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 9.5.9.2; include in your cycle explicit axial peak suppression steps.

***E9-9.** 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?]

E9-10. Use the formula given in section 9.6.2 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 $\gamma = 2.8 \times 10^8$ rad s^{-1}. [Put all the quantities in SI units].

E9-11. 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

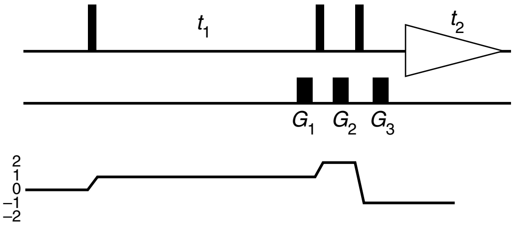
E9-12. Determine the ratio G_1:G_2 needed to select the following pathways:

(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.

E9-13. 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→1→2→–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→–1→4→–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.

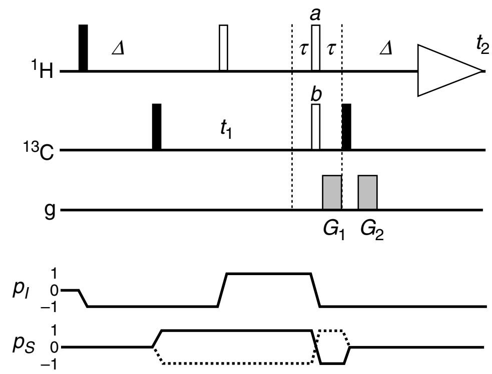
(d) In the light of (b) and (c), consider the utility of the gradient ratio 1.0 : 0.8 : 2.6

***E9-14.**

Devise a gradient selected version of the triple-quantum filtered COSY experiment, whose basic pulse sequence and CTP was given in **E9-7**. 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?

***E9-1.** 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 9.6.7.3 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 9.6.7.3, pointing out any advantages and disadvantages that each has.