Answers to Exercises: Part A

Chapter 1

Exercise 1.1

A radiofrequency pulse is applied to a sample of isolated spin-$\frac{1}{2}$ nuclei in thermal equilibrium with spin state populations n_α (lower level) and n_β (upper level). How will these populations be changed if the pulse flip angle β is: (a) 90°, (b) 180°, and (c) 45°?

Let n_α^{eq} and n_β^{eq} be the equilibrium populations prior to the pulse. M_z (the *z* component of the magnetization) is always proportional to the population difference. The value of M_z after the pulse (flip angle β) is proportional to $\cos\beta$ (Fig. 1.2).

Therefore the population difference after the pulse is:

$$n_\alpha - n_\beta \;=\; n_\alpha^{\text{eq}} - n_\beta^{\text{eq}} \;\cos\beta\,.$$

The total number of spins is, of course, unchanged by the pulse:

$$n_\alpha + n_\beta \;=\; n_\alpha^{\text{eq}} + n_\beta^{\text{eq}}\,.$$

Solving these two equations gives:

$$\begin{aligned} n_\alpha &= \tfrac{1}{2}n_\alpha^{\text{eq}}\;1+\cos\beta \;+\; \tfrac{1}{2}n_\beta^{\text{eq}}\;1-\cos\beta \\ n_\beta &= \tfrac{1}{2}n_\alpha^{\text{eq}}\;1-\cos\beta \;+\; \tfrac{1}{2}n_\beta^{\text{eq}}\;1+\cos\beta\,. \end{aligned}$$

Therefore:

(a) $\beta=90^\circ,\ \cos\beta=0:\ \ n_\alpha=n_\beta=\tfrac{1}{2}\;n_\alpha^{\text{eq}}+n_\beta^{\text{eq}}$ (populations equalized).

(b) $\beta=180^\circ,\ \cos\beta=-1:\ \ n_\alpha=n_\beta^{\text{eq}};\ \ n_\beta=n_\alpha^{\text{eq}}$ (populations exchanged).

(c) $\beta=45^\circ,\ \cos\beta=\tfrac{1}{\sqrt{2}}:\ \ n_\alpha=0.854n_\alpha^{\text{eq}}+0.146n_\beta^{\text{eq}};\ \ n_\beta=0.146n_\alpha^{\text{eq}}+0.854n_\beta^{\text{eq}}$.

Exercise 1.2

The *z* magnetization of a sample of isolated nuclear spins recovers after a 90° pulse according to $M_z=M_0\left[1-\exp\;-t/T_1\;\right]$. How many multiples of T_1 is it necessary to wait for $M_z(t)$ to recover to within 1% of its equilibrium value?

$$M_z/M_0 \;=\; 0.99 \;=\; 1-\exp\;-t/T_1 \quad\Rightarrow\quad \exp\;-t/T_1\; =0.01 \quad\Rightarrow\quad t=T_1\ln 100=4.61T_1\,.$$

Exercise 1.3

Write an equation for the recovery of $M_z(t)$ after a 180° pulse. At what time does $M_z(t)$ change sign from negative to positive?

The required expression is:

$$M_z(t) = M_0\left[1-2\exp\left(-t/T_1\right)\right]$$

where M_0 is the equilibrium magnetization. This clearly has the correct properties: (a) as $t\to\infty$, $M_z\to M_0$; (b) at $t=0$, $M_z=-M_0$; (c) exponential relaxation.

$$M_z(t)=0 \text{ when } \exp\left(-t/T_1\right)=0.5 \quad\Rightarrow\quad t=T_1\ln 2=0.693T_1 .$$

Exercise 1.4

In a $90_x-\tau-180_y-\tau-$ spin echo experiment on a heteronuclear two-spin system (I and S), with pulses applied only to spin I, the magnetization of spin I is refocused along the $-y$ axis. What happens when the phase of the 180° pulse is x instead of y, i.e. $90_x-\tau-180_x-\tau-$?

Suppose that at the end of the first delay the magnetization vector in Fig. 1.6 makes an angle ζ with respect to the $-y$ axis. After a 180° y pulse, this angle becomes $-\zeta$. During the second delay, $\boldsymbol{M}$ accumulates an additional phase angle of ζ so that at 2τ the final phase is 0°, i.e. $\boldsymbol{M}$ lies on the $-y$ axis.

If, instead, the 180° rotation is around the x axis, it changes the phase angle from ζ to $180^\circ-\zeta$. Then, during the second delay, the additional precession (through angle ζ) leaves $\boldsymbol{M}$ with a phase angle of 180°, i.e. on the $+y$ axis.

Exercise 1.5

In a $90_x-\tau-180_y-\tau-$ spin echo experiment on a homonuclear two-spin system with a *J*-coupling of 10 Hz, what delay τ is needed to get a phase difference of π radians between the two components of the I spin (or S spin) doublet at time 2τ ?

The angle between the magnetization vectors at time 2τ is $\left(2\pi J\right)\times\left(2\tau\right)=4\pi J\tau$ (page 8). This equals π when $\tau=1/(4J)=25\,\text{ms}$.

Chapter 2

Exercise 2.1

Verify that Eqns 2.1 and 2.2 are consistent with Eqns 2.3 and 2.4.

Substituting Eqn 2.1 into Eqn 2.2 gives:

$$\begin{aligned}
S(\omega) &= \int_0^\infty \exp(\mathrm{i}\Omega t)\exp(-t/T_2)\exp(-\mathrm{i}\omega t)\,\mathrm{d}t \\
&= \int_0^\infty \exp[-(\mathrm{i}\omega - \mathrm{i}\Omega + 1/T_2)t]\mathrm{d}t \\
&= \left[\frac{-\exp[-(\mathrm{i}\omega - \mathrm{i}\Omega + 1/T_2)t]}{1/T_2 + \mathrm{i}(\omega - \Omega)}\right]_0^\infty \\
&= \frac{1}{1/T_2 + \mathrm{i}(\omega - \Omega)} \\
&= \left(\frac{1}{1/T_2 + \mathrm{i}\Delta\omega}\right)\times\left(\frac{1/T_2 - \mathrm{i}\Delta\omega}{1/T_2 - \mathrm{i}\Delta\omega}\right) \quad \text{where} \quad \Delta\omega = \omega - \Omega \\
&= \frac{1/T_2 - \mathrm{i}\Delta\omega}{(1/T_2)^2 + (\Delta\omega)^2} \\
&= A(\Delta\omega) - \mathrm{i}D(\Delta\omega) \qquad \text{(using Eqn. 2.4).}
\end{aligned}$$

Exercise 2.2

Verify that the full width (in Hz) at half maximum height of the absorption lineshape $A(\Delta\omega)$ in Eqn 2.4 is $1/\pi T_2$.

The absorption lineshape is:

$$A(\Delta\omega) = \frac{1/T_2}{(1/T_2)^2 + (\Delta\omega)^2}.$$

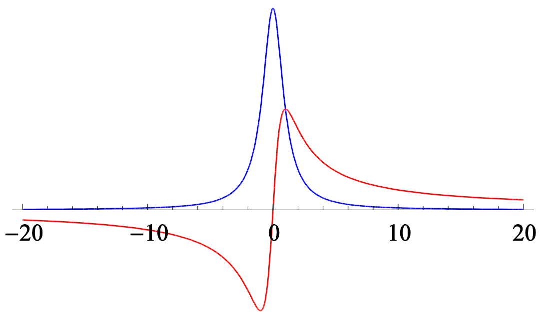
The full height of the line at its centre (where $\Delta\omega = \omega - \Omega = 0$) is $A(0) = T_2$.

The line has half this height when $A(\Delta\omega) = \frac{1}{2}T_2$, i.e. when $\Delta\omega = \pm 1/T_2$.

The full width at half maximum height is therefore $2/T_2$ (in rad s^{-1}) or $1/\pi T_2$ (in Hz).

Exercise 2.3

Plot $A(\Delta\omega)$ and $D(\Delta\omega)$ (Eqn 2.4) to show that $D(\Delta\omega)$ has a lot more intensity in its wings than does $A(\Delta\omega)$. Take T_2 = 1 s and $-20 \le \Delta\omega \le +20$ rad s^{-1}.



$A(\Delta\omega)$: blue. $D(\Delta\omega)$: red.

Exercise 2.4

Determine the appearance of the spectrum corresponding to the model free induction decay:

$[\exp(\mathrm{i}\Omega_\mathrm{A}t) + \mathrm{i}\exp(\mathrm{i}\Omega_\mathrm{B}t)]\exp(-t/T_2)$.

Substituting

$$s(t) = \mathrm{e}^{\mathrm{i}\Omega_\mathrm{A}t}\mathrm{e}^{-t/T_2} + \mathrm{i}\mathrm{e}^{\mathrm{i}\Omega_\mathrm{B}t}\mathrm{e}^{-t/T_2}$$

into Eqn 2.2 gives (by analogy with Eqns 2.1 and 2.3)

$$S(\omega) = [A(\omega-\Omega_\mathrm{A}) - \mathrm{i}D(\omega-\Omega_\mathrm{A})] + \mathrm{i}[A(\omega-\Omega_\mathrm{B}) - \mathrm{i}D(\omega-\Omega_\mathrm{B})].$$

Collecting the real and imaginary parts gives:

$$S(\omega) = [A(\omega-\Omega_\mathrm{A}) + D(\omega-\Omega_\mathrm{B})] + \mathrm{i}[-D(\omega-\Omega_\mathrm{A}) + A(\omega-\Omega_\mathrm{B})].$$

i.e. the real part of $S(\omega)$ comprises an absorption line centred at $\omega = \Omega_\mathrm{A}$ and a dispersion line centred at $\omega = \Omega_\mathrm{B}$.

Exercise 2.5

Determine the appearance of the spectra corresponding to the model free induction decays: (a) $\cos(\pi Jt)\exp(\mathrm{i}\Omega t)\exp(-t/T_2)$ and (b) $\cos^2(\pi Jt)\exp(\mathrm{i}\Omega t)\exp(-t/T_2)$.

(a) Since

$$\cos(\pi Jt) = \tfrac{1}{2}\mathrm{e}^{+\mathrm{i}\pi Jt} + \tfrac{1}{2}\mathrm{e}^{-\mathrm{i}\pi Jt}$$

we can write:

$$s(t) = \cos(\pi J t)\, e^{i\Omega t} e^{-t/T_2} = \tfrac{1}{2} e^{i(\Omega+\pi J)t} e^{-t/T_2} + \tfrac{1}{2} e^{i(\Omega-\pi J)t} e^{-t/T_2}.$$

By analogy with Eqns 2.1 and 2.3:

$$\mathrm{Re}[S(\omega)] = \tfrac{1}{2} A(\omega - (\Omega+\pi J)) + \tfrac{1}{2} A(\omega - (\Omega-\pi J))$$

which corresponds to two lines of intensity $\frac{1}{2}$ centred at frequencies $\Omega \pm \pi J$. That is, a doublet centred at Ω with splitting $2\pi J$.

(b) Similarly,

$$\cos^2(\pi J t) = \tfrac{1}{2} + \tfrac{1}{2}\cos(2\pi J t) = \tfrac{1}{2} + \tfrac{1}{4} e^{+2i\pi J t} + \tfrac{1}{4} e^{-2i\pi J t}$$

so that

$$s(t) = \cos^2(\pi J t)\, e^{i\Omega t} e^{-t/T_2} = \tfrac{1}{4} e^{i(\Omega+2\pi J)t} e^{-t/T_2} + \tfrac{1}{2} e^{i\Omega t} e^{-t/T_2} + \tfrac{1}{4} e^{i(\Omega-2\pi J)t} e^{-t/T_2}.$$

Again by analogy with Eqns 2.1 and 2.3:

$$\mathrm{Re}[S(\omega)] = \tfrac{1}{4} A(\omega - (\Omega+2\pi J)) + \tfrac{1}{2} A(\omega - \Omega) + \tfrac{1}{4} A(\omega - (\Omega-2\pi J))$$

which corresponds to two lines of intensity $\frac{1}{4}$ centred at frequencies $\Omega \pm 2\pi J$ and a line of intensity $\frac{1}{2}$ centred at frequency Ω. That is, a triplet centred at Ω with splitting $2\pi J$.

Exercise 2.6

This Exercise is intended to verify that phase-correction works as depicted in Fig. 2.2. Consider a free induction decay of the general form $s(t) = \exp(i\Omega t)\exp(i\phi)\exp(-t/T_2)$. Show that the spectrum $R\cos\phi + I\sin\phi$ is an absorption lineshape. R and I are the real and imaginary parts of the Fourier transform of $s(t)$.

Using Eqns 2.1 and 2.3, the Fourier transform of

$$s(t) = e^{i\phi} e^{i\Omega t} e^{-t/T_2}$$

is

$$\begin{aligned} S(\omega) &= e^{i\phi}(A - iD) \\ &= (\cos\phi + i\sin\phi)(A - iD) \\ &= (A\cos\phi + D\sin\phi) + i(A\sin\phi - D\cos\phi) \end{aligned}$$

where $A = A(\Delta\omega)$ and $D = D(\Delta\omega)$.

Thus:

$$R = \mathrm{Re}[S(\omega)] = A\cos\phi + D\sin\phi \quad \text{and}$$

$$I = \mathrm{Im}[S(\omega)] = A\sin\phi - D\cos\phi.$$

Therefore:

$$\begin{aligned} R\cos\phi + I\sin\phi &= (A\cos\phi + D\sin\phi)\cos\phi + (A\sin\phi - D\cos\phi)\sin\phi \\ &= A\cos^2\phi + D\sin\phi\cos\phi + A\sin^2\phi - D\sin\phi\cos\phi \\ &= A(\cos^2\phi + \sin^2\phi) \\ &= A \end{aligned}$$

Exercise 2.7

> Show that phase-modulated two-dimensional signals of the general form $s(t_1,t_2) = \exp(\mathrm{i}\Omega t_1)\exp(-t_1/T_2)\exp(\mathrm{i}\Omega t_2)\exp(-t_2/T_2)$ allow quadrature detection in both dimensions but do not give pure absorptive lineshapes.

Using Eqns 2.1 and 2.3, the two-dimensional Fourier transform of

$$s(t_1,t_2) = \mathrm{e}^{\mathrm{i}\Omega_1 t}\,\mathrm{e}^{-t_1/T_2}\mathrm{e}^{\mathrm{i}\Omega_2 t}\,\mathrm{e}^{-t_2/T_2}$$

is

$$S(F_1,F_2) = \left[A_1^+ - \mathrm{i}D_1^+\right]\left[A_2^+ - \mathrm{i}D_2^+\right] = (A_1^+A_2^+ - D_1^+D_2^+) - \mathrm{i}A_1^+D_2^+ - \mathrm{i}D_1^+A_2^+$$

where $A_j^+ = A(F_j - \Omega_j)$ and $D_j^+ = D(F_j - \Omega_j)$, $j = 1, 2$.

The real part of this spectrum

$$\mathrm{Re}\left[S(F_1,F_2)\right] = A_1^+A_2^+ - D_1^+D_2^+$$

is a phase twist lineshape centred at $(F_1,F_2) = (+\Omega_1,+\Omega_2)$. See section 2.4.

Exercise 2.8

> A common error in many real spectrometers is that analogue-to-digital converters are not perfectly balanced. As a consequence, their outputs often contain a constant offset in addition to the free induction signal. What effect will this have on the NMR spectrum obtained by Fourier transformation?

A constant offset can be regarded as a damped oscillation of the form $\mathrm{e}^{\mathrm{i}\Omega t}\mathrm{e}^{-t/T_2}$ with zero frequency ($\Omega = 0$) and infinite decay time ($T_2 \to \infty$, $\mathrm{e}^{-t/T_2} \to 1$). The Fourier transform will therefore be an infinitely narrow 'spike' at $\omega = 0$. In general, there will be a constant offset in both detectors so that the spike can have any phase.

More rigorously, suppose that the free induction decay has the form

$$s(t) = \mathrm{e}^{\mathrm{i}\Omega t}\mathrm{e}^{-t/T_2} + a \quad (t \geq 0),$$

where the offset, a, is a real constant. Fourier transformation, using Eqn 2.2, gives:

$$S(\omega) = A(\omega - \Omega) - \mathrm{i}D(\omega - \Omega) + a\pi\delta(\omega) - \mathrm{i}a/\omega$$

where $\delta(\omega)$ is the Dirac delta function.

Thus the effect of the offset is indeed to give a zero-frequency 'spike' at $\omega = 0$ in the real part of the spectrum.

Exercise 2.9

A second common problem with quadrature detection is that the two detection channels have slightly different sensitivities so that, for example, the same signal would give a slightly bigger output in the real channel than in the imaginary channel. What effect will this have on the NMR spectrum?

Suppose that the free induction decay has the form

$$s(t) = \left[(1+b)\cos\Omega t + \mathrm{i}\sin\Omega t\right]\mathrm{e}^{-t/T_2} \quad (t \geq 0)$$

where b is a real constant.

This rearranges to:

$$\begin{aligned} s(t) &= \mathrm{e}^{\mathrm{i}\Omega t}\mathrm{e}^{-t/T_2} + b\cos\Omega t\,\mathrm{e}^{-t/T_2} \\ &= \mathrm{e}^{\mathrm{i}\Omega t}\mathrm{e}^{-t/T_2} + \left(\frac{b}{2}\right)\left(\mathrm{e}^{\mathrm{i}\Omega t} + \mathrm{e}^{-\mathrm{i}\Omega t}\right)\mathrm{e}^{-t/T_2} \\ &= \left(1+\frac{b}{2}\right)\mathrm{e}^{\mathrm{i}\Omega t}\mathrm{e}^{-t/T_2} + \left(\frac{b}{2}\right)\mathrm{e}^{-\mathrm{i}\Omega t}\mathrm{e}^{-t/T_2}. \end{aligned}$$

Fourier transformation using Eqn 2.2 gives

$$S(\omega) = \left(1+\frac{b}{2}\right)\left[A(\omega-\Omega) - \mathrm{i}D(\omega-\Omega)\right] + \left(\frac{b}{2}\right)\left[A(\omega+\Omega) - \mathrm{i}D(\omega+\Omega)\right],$$

the real part of which is

$$\mathrm{Re}\left[S(\omega)\right] = \left(1+\frac{b}{2}\right)A(\omega-\Omega) + \left(\frac{b}{2}\right)A(\omega+\Omega).$$

Thus the spectrum comprises a line of intensity $(1+b/2)$ at the correct frequency ($\omega = \Omega$) and a 'quadrature image' of intensity $(b/2)$ at the mirror image frequency ($\omega = -\Omega$).

Chapter 3

Exercise 3.1

Show that the pulse sequence $90^\circ_x - \tau - 90^\circ_{-x}$ has the following result: $I_z \longrightarrow I_z \cos\Omega\tau + I_x \sin\Omega\tau$. A sample comprises a dilute solute in an otherwise pure solvent; the solute and solvent each give an NMR singlet. How might this pulse sequence be used to obtain a spectrum of the solute free from the obscuring presence of the solvent line?

$$\begin{aligned} I_z &\xrightarrow{90^\circ I_x} -I_y \\ &\xrightarrow{\Omega\tau I_z} -I_y \cos\Omega\tau + I_x \sin\Omega\tau \, . \\ &\xrightarrow{-90^\circ I_x} I_z \cos\Omega\tau + I_x \sin\Omega\tau \end{aligned}$$

If we choose ω_{rf} such that $\Omega_{\text{solvent}} = 0$ and τ such that $\Omega_{\text{solute}}\tau = \pi/2$, then the result of the pulse sequence will be

solvent: I_z and solute: I_x.

Thus, there will be no observable signal for the solvent. The signal for the solute will be the same as would have been obtained with a single $90^\circ I_y$ pulse. This pulse sequence is known as 'Jump and Return'. See P. Plateau and M. Guéron, *J. Amer. Chem. Soc*. **104** (1982) 7310-7311.

Exercise 3.2

Determine the effect of the "composite pulse" $90^\circ_{-x} - \theta_y - 90^\circ_x$ on the initial states: (a) I_x, (b) I_y and (c) I_z. What geometric operation does this composite pulse perform?

(a)
$$\begin{aligned} I_x &\xrightarrow{-90^\circ I_x} I_x \\ &\xrightarrow{\theta I_y} I_x \cos\theta - I_z \sin\theta \\ &\xrightarrow{90^\circ I_x} I_x \cos\theta + I_y \sin\theta . \end{aligned}$$

(b)
$$\begin{aligned} I_y &\xrightarrow{-90^\circ I_x} -I_z \\ &\xrightarrow{\theta I_y} -I_z \cos\theta - I_x \sin\theta \\ &\xrightarrow{90^\circ I_x} I_y \cos\theta - I_x \sin\theta . \end{aligned}$$

(c)
$$\begin{aligned} I_z &\xrightarrow{-90^\circ I_x} I_y \\ &\xrightarrow{\theta I_y} I_y \\ &\xrightarrow{90^\circ I_x} I_z . \end{aligned}$$

The net effect of this composite "*z*-pulse" is a rotation through an angle θ around the *z* axis. See M. H. Levitt and R. Freeman, *J. Magn. Reson*. **33** (1979) 473-476.

Exercise 3.3

The evolution of the one-spin operators described in Eqns 3.3 and 3.4 and in Figure 3.2 can also be summarised in a 3×3 table. Using the three initial states (I_x, I_y and I_z) to label the rows and the operators corresponding to the three basic transformations (I_x, I_y and I_z) to label the columns, enter into the table the result *towards which each operator evolves*. For example, $I_y \xrightarrow{\beta I_x} I_y\cos\beta + I_z\sin\beta$ (Eqn 3.3) so that the entry in the I_y-row and I_x-column would be I_z. If an operator does not evolve then enter 0 for the corresponding element of the table.

initial state	transformation: I_x	I_y	I_z
I_x	0	$-I_z$	I_y
I_y	I_z	0	$-I_x$
I_z	$-I_y$	I_x	0

Exercise 3.4

Repeat Exercise 3.3 for two-spin operators by forming a table for the 11 initial states (I_q, S_q, $2I_zS_q$, $2I_qS_z$, $q = x,y,z$) evolving under the 7 basic transformations (I_q, S_q, $2I_zS_z$, $q = x,y,z$) considered in this chapter.

initial state	transformation: I_x	I_y	I_z	S_x	S_y	S_z	$2I_zS_z$
I_x	0	$-I_z$	I_y	0	0	0	$2I_yS_z$
I_y	I_z	0	$-I_x$	0	0	0	$-2I_xS_z$
I_z	$-I_y$	I_x	0	0	0	0	0
S_x	0	0	0	0	$-S_z$	S_y	$2I_zS_y$
S_y	0	0	0	S_z	0	$-S_x$	$-2I_zS_x$
S_z	0	0	0	$-S_y$	S_x	0	0
$2I_zS_x$	$-2I_yS_x$	$2I_xS_x$	0	0	$-2I_zS_z$	$2I_zS_y$	S_y
$2I_zS_y$	$-2I_yS_y$	$2I_xS_y$	0	$2I_zS_z$	0	$-2I_zS_x$	$-S_x$
$2I_zS_z$	$-2I_yS_z$	$2I_xS_z$	0	$-2I_zS_y$	$2I_zS_x$	0	0
$2I_xS_z$	0	$-2I_zS_z$	$2I_yS_z$	$-2I_xS_y$	$2I_xS_x$	0	I_y
$2I_yS_z$	$2I_zS_z$	0	$-2I_xS_z$	$-2I_yS_y$	$2I_yS_x$	0	$-I_x$

Exercise 3.5

Consider the coherence transfer operation: $2I_xS_z \xrightarrow{\beta\ I_\phi + S_\phi} -2I_zS_x$. Determine the flip angle β and phase $\phi = +x, +y, -x$ or $-y$ of the pulse.

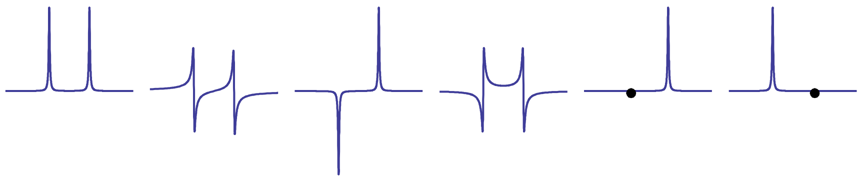
I_x has been rotated to $\pm I_z$ and S_z has been rotated to $\mp S_x$. Therefore the phase of the pulse must be $\phi = \mp y$ and the flip angle must be $\beta = 90^\circ$:

$$2I_xS_z \xrightarrow{\mp 90^\circ I_y} \pm 2I_zS_z \xrightarrow{\mp 90^\circ S_y} -2I_zS_x .$$

Exercise 3.6

Assuming that spectra are phased such that I_y corresponds to absorption-mode lineshapes, sketch the spectra that correspond to the following two-spin product operators: (a) I_y, (b) I_x, (c) $2I_yS_z$, (d) $2I_xS_z$, (e) $\frac{1}{2}\ I_y + 2I_yS_z$, (f) $\frac{1}{2}\ I_y - 2I_yS_z$.

(a) (b) (c) (d) (e) (f)



Exercise 3.7

Section 3.4 analyses the effect of a spin echo pulse sequence on a homonuclear two-spin system. Repeat this analysis using $\pi J_{IS}\tau = \pi/4$ from the outset.

Let $c = \cos\Omega_I\tau;\ \ s = \sin\Omega_I\tau$. Note that $\cos\pi J\tau = \sin\pi J\tau = \frac{1}{\sqrt{2}}$ when $\pi J\tau = \pi/4$.

$$I_z \xrightarrow{90^\circ I_x} -I_y$$

$$\xrightarrow{\Omega_I\tau I_z} -I_yc + I_xs$$

$$\xrightarrow{\pi/4\ 2I_zS_z} -\tfrac{1}{\sqrt{2}}\ I_y - 2I_xS_z\ \ c + \tfrac{1}{\sqrt{2}}\ I_x + 2I_yS_z\ \ s$$

$$\xrightarrow{180^\circ\ I_y + S_y} -\tfrac{1}{\sqrt{2}}\ I_y - 2I_xS_z\ \ c - \tfrac{1}{\sqrt{2}}\ I_x + 2I_yS_z\ \ s$$

$$\begin{aligned}\xrightarrow{\Omega_I\tau I_z}\ & -\tfrac{1}{\sqrt{2}}\ I_yc - I_xs\ \ c + \tfrac{1}{\sqrt{2}}\ 2I_xS_zc + 2I_yS_zs\ \ c - \tfrac{1}{\sqrt{2}}\ I_xc + I_ys\ \ s - \tfrac{1}{\sqrt{2}}\ 2I_yS_zc - 2I_xS_zs\ \ s \\ & = \tfrac{1}{\sqrt{2}}I_y\ \ -c^2 - s^2\ \ + \tfrac{1}{\sqrt{2}}I_x\ \ sc - sc\ \ + \tfrac{1}{\sqrt{2}}2I_xS_z\ \ c^2 + s^2\ \ + \tfrac{1}{\sqrt{2}}2I_yS_z\ \ sc - sc \\ & = -\tfrac{1}{\sqrt{2}}I_y + \tfrac{1}{\sqrt{2}}2I_xS_z\end{aligned}$$

$$\xrightarrow{\pi/4\ 2I_zS_z} -\tfrac{1}{2}\ I_y - 2I_xS_z\ \ + \tfrac{1}{2}\ 2I_xS_z + I_y\ \ = 2I_xS_z$$

Similarly, $S_z \longrightarrow 2I_zS_x$ so that $I_z + S_z \longrightarrow 2I_xS_z + 2I_zS_x$.

Exercise 3.8

Calculate the effect of the spin-echo sequence $\tau - 180^\circ_y - \tau$ on $2I_xS_z$ in a homonuclear two-spin system.

Hence determine the effect of the double spin echo sequence $90^\circ_x - \tau - 180^\circ_y - 2\tau - 180^\circ_y - \tau$ on the initial state I_z. Use previous results to simplify your calculations as much as possible.

We need to determine the effect of $\tau - 180^\circ_y - \tau$ on the two terms in Eqn 3.19: $2I_xS_z$ and $-I_y$.

First, the effect of $\tau - 180^\circ_y - \tau$ on $2I_xS_z$. The offset terms will be refocused by the echo sequence and so can be omitted. Using the abbreviations, $c = \cos\pi J\tau$ and $s = \sin\pi J\tau$:

$$
\begin{aligned}
2I_xS_z &\xrightarrow{\pi J\tau 2I_zS_z} 2I_xS_zc + I_ys \\
&\xrightarrow{180^\circ (I_y+S_y)} 2I_xS_zc + I_ys \\
&\xrightarrow{\pi J\tau 2I_zS_z} (2I_xS_zc + I_ys)c + (I_yc - 2I_xS_zs)s \\
&= 2I_xS_z(c^2 - s^2) + I_y(2sc) \\
&= 2I_xS_z\cos 2\pi J\tau + I_y \sin 2\pi J\tau.
\end{aligned}
$$

The effect of the single echo sequence on I_z is given on page 25:

$$
I_z \xrightarrow{90^\circ I_z} -I_y \xrightarrow{\tau - 180^\circ - \tau} -I_y\cos 2\pi J\tau + 2I_xS_z \sin 2\pi J\tau
$$

the second half of which gives the effect of $\tau - 180^\circ_y - \tau$ on $-I_y$.

So, putting everything together, we get:

$$
\begin{aligned}
-I_y\cos 2\pi J\tau + 2I_xS_z\sin 2\pi J\tau \longrightarrow\ & (-I_y\cos 2\pi J\tau + 2I_xS_z\sin 2\pi J\tau)\cos 2\pi J\tau + (2I_xS_z\cos 2\pi J\tau + I_y\sin 2\pi J\tau)\sin 2\pi J\tau \\
&= -I_y(\cos^2 2\pi J\tau - \sin^2 2\pi J\tau) + 2I_xS_z(2\sin 2\pi J\tau\cos 2\pi J\tau) \\
&= -I_y\cos 4\pi J\tau + 2I_xS_z\sin 4\pi J\tau.
\end{aligned}
$$

Chapter 4

Exercise 4.1

Consider the INEPT pulse sequence in Fig. 4.1 applied to a two-spin system (I and S). Show that insertion of the pulse sequence element $\tau - 180^\circ I_y, 180^\circ S_y - \tau$ immediately before the free induction decay, where τ has the same value as in the first part of the sequence, results in an enhanced *in-phase* spectrum of spin S.

Immediately after the final two pulses, with $\tau = 1/4J_{\mathrm{IS}}$, we have:

$$a2I_zS_y + bS_y \quad \text{(Eqn 4.3).}$$

The $\tau - 180^\circ I_y, 180^\circ S_y - \tau$ sequence does the following:

$$\begin{aligned}
a2I_zS_y + bS_y &\xrightarrow{\pi/4\ 2I_zS_z} \tfrac{1}{\sqrt{2}}\left(a2I_zS_y - aS_x + bS_y - b2I_zS_x\right) \\
&\xrightarrow{180^\circ I_y, 180^\circ S_y} \tfrac{1}{\sqrt{2}}\left(-a2I_zS_y + aS_x + bS_y - b2I_zS_x\right) \\
&\xrightarrow{\pi/4\ 2I_zS_z} aS_x - b2I_zS_x.
\end{aligned}$$

Note that chemical shifts have been omitted because they are refocused. Also, we have used $\pi J_{\mathrm{IS}}\tau = \pi/4$ so that $\cos\pi J_{\mathrm{IS}}\tau = \sin\pi J_{\mathrm{IS}}\tau = 1/\sqrt{2}$.

Thus the enhanced S-spin doublet is indeed in-phase (aS_x).

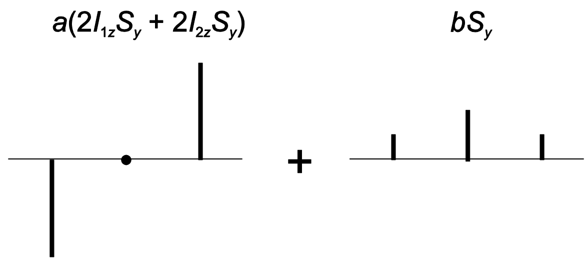
Exercise 4.2

Calculate the product operators arising from an INEPT sequence applied to a CH_2 group and draw the resulting enhanced spectrum. Would phase cycling work in the same way here as it does for a CH group?

$$\begin{aligned}
aI_{1z} + aI_{2z} + bS_y &\xrightarrow{\pi/4\ 2I_{1z}S_z}\xrightarrow{\pi/4\ 2I_{2z}S_z} \tfrac{1}{\sqrt{2}}\left(-aI_{1y} + a2I_{1x}S_z - aI_{2y} + a2I_{2x}S_z + bS_z\right) \\
&\xrightarrow{180^\circ I_y, 180^\circ S_y} \tfrac{1}{\sqrt{2}}\left(-aI_{1y} + a2I_{1x}S_z - aI_{2y} + a2I_{2x}S_z - bS_z\right) \\
&\xrightarrow{\pi/4\ 2I_{1z}S_z}\xrightarrow{\pi/4\ 2I_{2z}S_z} a2I_{1x}S_z + a2I_{2x}S_z - bS_z \\
&\xrightarrow{90^\circ I_{1y}}\xrightarrow{90^\circ I_{2y}} -a2I_{1z}S_z - a2I_{2z}S_z - bS_z \\
&\xrightarrow{90^\circ S_x} +a2I_{1z}S_y + a2I_{2z}S_y + bS_y
\end{aligned}$$

which should be compared with Eqns 4.2 and 4.3.

This is the same as Eqn 4.3 with $a2I_zS_y$ replaced by $a2I_{1z}S_y + a2I_{2z}S_y$. The spectrum comprises an antiphase triplet, amplitude *a*, superimposed on an in-phase triplet, amplitude *b*:



An antiphase triplet can also be seen in Fig. 4.6(b). INEPT on a CH_2 group is substantially simpler than DEPT on a CH_2 group because at no stage during INEPT are S_x or S_y operators produced.

The phase cycling involves replacing the final 90°_y pulse on the I spins by a 90°_{-y} pulse. When this change is made, the last two lines of the above derivation become

$$a2I_{1x}S_z + a2I_{2x}S_z - bS_z \xrightarrow{-90^\circ I_{1y}} \xrightarrow{-90^\circ I_{2y}} a2I_{1z}S_z + a2I_{2z}S_z - bS_z$$
$$\xrightarrow{90^\circ S_x} -a2I_{1z}S_y - a2I_{2z}S_y + bS_y$$

i.e. the enhanced terms change sign and the unenhanced term does not. This is exactly the same result as for a CH group.

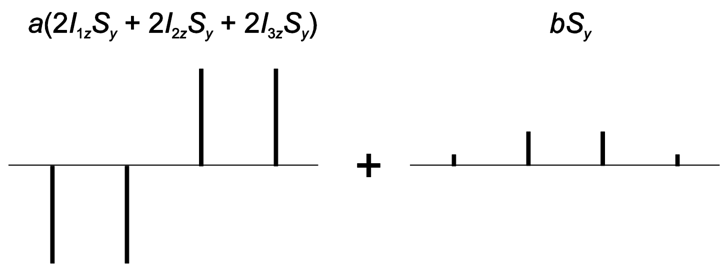
Exercise 4.3

Repeat Exercise 4.2 for a CH_3 group.

Comparing Exercise 4.2 with section 4.2, it should be clear that the end result for a CH_3 group should be:

$$aI_{1z} + aI_{2z} + aI_{3z} + bS_y \longrightarrow +a2I_{1z}S_y + a2I_{2z}S_y + a2I_{3z}S_y + bS_y\,.$$

The spectrum comprises an antiphase quartet, amplitude *a*, superimposed on an in-phase quartet, amplitude *b*:



Exercise 4.4

Would the INEPT pulse sequence in Fig. 4.1 still work if: (a) both 180°_y pulses were replaced by 180°_x pulses? (b) the final $90^\circ S_x$ pulse were replaced by a $90^\circ S_y$ pulse? (c) the final $90^\circ I_y$ pulse were replaced by a $90^\circ I_x$ pulse?

(a) The final stage of the INEPT sequence, as shown in Fig. 4.1, is (Eqn 4.3):

$$a2I_xS_z - bS_z \xrightarrow{90^\circ I_y} -a2I_zS_z - bS_z \xrightarrow{90^\circ S_x} a2I_zS_y + bS_y\ .$$

Shifting the phase of the 180° pulses simply changes the sign of the first term on the left hand side so that the outcome is:

$$-a2I_zS_y + bS_y\ .$$

The sequence still works.

(b) Starting with the left hand side of Eqn 4.3,

$$a2I_xS_z - bS_z\ .$$

It can be seen that changing the final $90^\circ S_x$ pulse to $90^\circ S_y$ just shifts the phase of both terms:

$$a2I_xS_z - bS_z \xrightarrow{90^\circ I_y} -a2I_zS_z - bS_z \xrightarrow{90^\circ S_y} -a2I_zS_x - bS_x\ .$$

The sequence still works.

(c) Again, starting with the left hand side of Eqn 4.3, it can be seen that changing the final $90^\circ I_y$ pulse to $90^\circ I_x$ produces the following result:

$$\begin{aligned} a2I_xS_z - bS_z &\xrightarrow{90^\circ I_x} a2I_xS_z - bS_z \\ &\xrightarrow{90^\circ S_x} -a2I_xS_y + bS_y \\ &\quad = -aDQ_y + aZQ_y + bS_y. \end{aligned}$$

The sequence no longer works. The spectrum contains only the unenhanced S spin doublet.

Exercise 4.5

Prove the results given in Eqn. 4.6.

Using the abbreviations $c_I = \cos\Omega_I t$, $s_I = \sin\Omega_I t$, $c_S = \cos\Omega_S t$, $s_S = \sin\Omega_S t$, Eqn 3.4 gives

$$
\begin{aligned}
I_x &\xrightarrow{\Omega_{\mathrm{I}} t I_z} I_x \cos\Omega_{\mathrm{I}} t + I_y \sin\Omega_{\mathrm{I}} t \;=\; I_x c_{\mathrm{I}} + I_y s_{\mathrm{I}} \\
I_y &\xrightarrow{\Omega_{\mathrm{I}} t I_z} I_y \cos\Omega_{\mathrm{I}} t - I_x \sin\Omega_{\mathrm{I}} t \;=\; I_y c_{\mathrm{I}} - I_x s_{\mathrm{I}} \\
S_x &\xrightarrow{\Omega_{\mathrm{S}} t S_z} S_x \cos\Omega_{\mathrm{S}} t + S_y \sin\Omega_{\mathrm{S}} t \;=\; S_x c_{\mathrm{S}} + S_y s_{\mathrm{S}} \\
S_y &\xrightarrow{\Omega_{\mathrm{S}} t S_z} S_y \cos\Omega_{\mathrm{S}} t - S_x \sin\Omega_{\mathrm{S}} t \;=\; S_y c_{\mathrm{S}} - S_x s_{\mathrm{S}}.
\end{aligned}
$$

Therefore:

$$
\begin{aligned}
2I_x S_x &\xrightarrow{\Omega_{\mathrm{I}} t I_z + \Omega_{\mathrm{S}} t S_z} 2\left(I_x c_{\mathrm{I}} + I_y s_{\mathrm{I}}\right)\left(S_x c_{\mathrm{S}} + S_y s_{\mathrm{S}}\right) \\
&\qquad = 2I_x S_x c_{\mathrm{I}} c_{\mathrm{S}} + 2I_x S_y c_{\mathrm{I}} s_{\mathrm{S}} + 2I_y S_x s_{\mathrm{I}} c_{\mathrm{S}} + 2I_y S_y s_{\mathrm{I}} s_{\mathrm{S}} \\
2I_y S_y &\xrightarrow{\Omega_{\mathrm{I}} t I_z + \Omega_{\mathrm{S}} t S_z} 2\left(I_y c_{\mathrm{I}} - I_x s_{\mathrm{I}}\right)\left(S_y c_{\mathrm{S}} - S_x s_{\mathrm{S}}\right) \\
&\qquad = 2I_y S_y c_{\mathrm{I}} c_{\mathrm{S}} - 2I_y S_x c_{\mathrm{I}} s_{\mathrm{S}} - 2I_x S_y s_{\mathrm{I}} c_{\mathrm{S}} + 2I_x S_x s_{\mathrm{I}} s_{\mathrm{S}}.
\end{aligned}
$$

And so:

$$
\begin{aligned}
DQ_x = \tfrac{1}{2}(2I_x S_x - 2I_y S_y) &\xrightarrow{\Omega_{\mathrm{I}} t I_z + \Omega_{\mathrm{S}} t S_z} \\
&\tfrac{1}{2}2I_x S_x\left(c_{\mathrm{I}} c_{\mathrm{S}} - s_{\mathrm{I}} s_{\mathrm{S}}\right) + \tfrac{1}{2}2I_x S_y\left(c_{\mathrm{I}} s_{\mathrm{S}} + s_{\mathrm{I}} c_{\mathrm{S}}\right) + \tfrac{1}{2}2I_y S_x\left(s_{\mathrm{I}} c_{\mathrm{S}} + c_{\mathrm{I}} s_{\mathrm{S}}\right) + \tfrac{1}{2}2I_y S_y\left(s_{\mathrm{I}} s_{\mathrm{S}} - c_{\mathrm{I}} c_{\mathrm{S}}\right) \\
&= \tfrac{1}{2}\left(2I_x S_x - 2I_y S_y\right)\left(c_{\mathrm{I}} c_{\mathrm{S}} - s_{\mathrm{I}} s_{\mathrm{S}}\right) + \tfrac{1}{2}\left(2I_x S_y + 2I_y S_x\right)\left(c_{\mathrm{I}} s_{\mathrm{S}} + s_{\mathrm{I}} c_{\mathrm{S}}\right) \\
&= DQ_x \cos\left[\left(\Omega_{\mathrm{I}} + \Omega_{\mathrm{S}}\right)t\right] + DQ_y \sin\left[\left(\Omega_{\mathrm{I}} + \Omega_{\mathrm{S}}\right)t\right].
\end{aligned}
$$

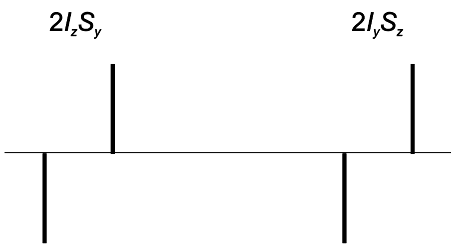
The proof of the ZQ_x bit of Eqn 4.6 proceeds in an exactly similar manner.

Exercise 4.6

What detectable signal results from $2I_z S_z \xrightarrow{\beta(I_x + S_x)}$? Sketch the form of the spectrum. What flip angle gives the maximum detectable signal?

$$
\begin{aligned}
2I_z S_z &\xrightarrow{\beta(I_x + S_x)} 2\left(I_z \cos\beta - I_y \sin\beta\right)\left(S_z \cos\beta - S_y \sin\beta\right) \\
&\qquad = 2I_z S_z \cos^2\beta - 2I_z S_y \cos\beta \sin\beta - 2I_y S_z \sin\beta \cos\beta + 2I_y S_y \sin^2\beta \\
&\qquad = 2I_z S_z \cos^2\beta - \left(2I_z S_y + 2I_y S_z\right)\sin\beta\cos\beta + \left(ZQ_x - DQ_x\right)\sin^2\beta
\end{aligned}
$$

The detectable signal is $-\left(2I_z S_y + 2I_y S_z\right)\sin\beta\cos\beta$, i.e. antiphase doublets for both spins. The maximum signal occurs when $\beta = 45^\circ$. If $\beta = 90^\circ$, there is ZQ and DQ coherence but no detectable signal.



Exercise 4.7.

Four new one-spin product operators can be defined by $I_\pm = I_x \pm \mathrm{i}I_y$ and $S_\pm = S_x \pm \mathrm{i}S_y$. Write $\tfrac{1}{2}(2I_xS_x \pm 2I_yS_y)$ in terms of $I_\pm$ and $S_\pm$ and interpret the results.

Rearrangement of the equations for $I_\pm$ and $S_\pm$ gives:

$$I_x = \frac{I_+ + I_-}{2}, \quad I_y = \frac{I_+ - I_-}{2\mathrm{i}}, \quad S_x = \frac{S_+ + S_-}{2}, \quad S_y = \frac{S_+ - S_-}{2\mathrm{i}},$$

showing that $I_\pm$ and $S_\pm$ are *single quantum* product operators. These expressions can be used to rewrite DQ_x and ZQ_x:

$$\begin{aligned}
DQ_x = \tfrac{1}{2}(2I_xS_x - 2I_yS_y) &= \tfrac{1}{2}\left[2\frac{I_+ + I_-}{2}\frac{S_+ + S_-}{2} - 2\frac{I_+ - I_-}{2\mathrm{i}}\frac{S_+ - S_-}{2\mathrm{i}}\right] \\
&= \tfrac{1}{4}\left[\, I_+S_+ + I_+S_- + I_-S_+ + I_-S_- \; + \; I_+S_+ - I_+S_- - I_-S_+ + I_-S_- \,\right] \\
&= \tfrac{1}{2}\; I_+S_+ + I_-S_- \;; \\
ZQ_x = \tfrac{1}{2}(2I_xS_x + 2I_yS_y) &= \tfrac{1}{2}\left[2\frac{I_+ + I_-}{2}\frac{S_+ + S_-}{2} + 2\frac{I_+ - I_-}{2\mathrm{i}}\frac{S_+ - S_-}{2\mathrm{i}}\right] \\
&= \tfrac{1}{4}\left[\left(I_+S_+ + I_+S_- + I_-S_+ + I_-S_-\right)\left(I_+S_+ - I_+S_- - I_-S_+ + I_-S_-\right)\right] \\
&= \tfrac{1}{2}\left(I_+S_- + I_-S_+\right)
\end{aligned}$$

showing that the *single quantum* operators can be combined to obtain *multiple quantum* product operators.

Exercise 4.8.

Show that the rules for combining DEPT spectra stated after Eqn. 4.20 are correct.

		A	B	C
		$\beta = 45^\circ$	$\beta = 90^\circ$	$\beta = 135^\circ$
CH	$\sin\beta$	$\frac{1}{\sqrt{2}}$	1	$\frac{1}{\sqrt{2}}$
CH_2	$\sin\beta\cos\beta$	$\frac{1}{2}$	0	$-\frac{1}{2}$
CH_3	$\sin\beta\cos^2\beta$	$\frac{1}{2\sqrt{2}}$	0	$\frac{1}{2\sqrt{2}}$

Clearly B has only CH signals.

For the CH_2 signals:

$$A-C=\left(\frac{1}{\sqrt{2}}\times CH+\frac{1}{2}\times CH_2+\frac{1}{2\sqrt{2}}\times CH_3\right)-\left(\frac{1}{\sqrt{2}}\times CH-\frac{1}{2}\times CH_2+\frac{1}{2\sqrt{2}}\times CH_3\right)=CH_2\,.$$

And for the CH_3 signals:

$$\begin{aligned}\sqrt{2}\ A+C\ -2B &= \left(\frac{1}{\sqrt{2}}\times CH+\frac{1}{2}\times CH_2+\frac{1}{2\sqrt{2}}\times CH_3\right)+\left(\frac{1}{\sqrt{2}}\times CH-\frac{1}{2}\times CH_2+\frac{1}{2\sqrt{2}}\times CH_3\right)-2B\\ &= \sqrt{2}\left(\sqrt{2}\times CH+\frac{1}{\sqrt{2}}\times CH_3\right)-2\times CH=CH_3.\end{aligned}$$

Exercise 4.9.

What would happen to a quaternary carbon in a DEPT experiment?

When there are no coupled protons, DEPT simply acts as a $90^\circ_x-\tau-180^\circ_x-\tau$ spin echo sequence.

Chapter 5

Exercise 5.1

Performing the COSY experiment with two 90°_x pulses as in Fig. 5.1 yields diagonal peak signals that are sine modulated as a function of t_1 and cross-peak signals that are cosine modulated (see Eqn 5.2). Show that changing the first pulse to 90°_y results in diagonal peak signals that are cosine modulated as a function of t_1 and cross-peak signals that are sine modulated. (Note that the signals from these two experiments can be used as the inputs to a *hypercomplex Fourier transformation*, as described in Section 2.4.)

We can repeat the calculation in Eqn 5.1 but with an initial 90°_y pulse. Immediately after the second pulse we have:

$$
\begin{aligned}
I_z \xrightarrow{90^\circ\, I_y + S_y} \xrightarrow{\Omega_I t_1 I_z + \Omega_S t_1 S_z} \xrightarrow{\pi J_{IS} t_1 2I_z S_z} \; & +I_x \cos\Omega_I t_1 \cos(\pi J_{IS} t_1) + 2I_y S_z \cos\Omega_I t_1 \sin(\pi J_{IS} t_1) \\
& + I_y \sin\Omega_I t_1 \cos(\pi J_{IS} t_1) - 2I_x S_z \sin\Omega_I t_1 \sin(\pi J_{IS} t_1) \\
\xrightarrow{90^\circ\, I_x + S_x} & + I_x \cos\Omega_I t_1 \cos(\pi J_{IS} t_1) - 2I_z S_y \cos\Omega_I t_1 \sin(\pi J_{IS} t_1) \\
& + I_z \sin\Omega_I t_1 \cos(\pi J_{IS} t_1) - 2I_x S_y \sin\Omega_I t_1 \sin(\pi J_{IS} t_1)
\end{aligned}
$$

Now only the first two terms are observable. If we expand the amplitudes of I_x and $2I_zS_y$ above using trigonometric relations we find:

$$
\begin{aligned}
& I_x \cos\Omega_I t_1 \cos(\pi J_{IS} t_1) - 2I_z S_y \cos\Omega_I t_1 \sin(\pi J_{IS} t_1) \\
& \quad = I_x \tfrac{1}{2}\left[\cos((\Omega_I + \pi J_{IS}) t_1) + \cos((\Omega_I - \pi J_{IS}) t_1)\right] \\
& \quad - 2I_z S_y \tfrac{1}{2}\left[\sin((\Omega_I + \pi J_{IS}) t_1) - \sin((\Omega_I - \pi J_{IS}) t_1)\right].
\end{aligned}
$$

The term corresponding to the diagonal peak (I_x) is cosine modulated as a function of t_1, whereas the cross-peak term ($2I_zS_y$) is sine modulated as a function of t_1.

Exercise 5.2

Eqn 5.3 shows 8 product operators present at the start of the t_2 (acquisition) period of a COSY experiment performed on a three-spin ISR system. Write down the 16 product operators you would expect to find at the start of the t_2 period of a COSY experiment performed on a four-spin ISQR system. (There is no need to give the signs, associated modulations, or to perform the complete product operator calculation.)

With the COSY experiment shown in Fig. 5.1, the 16 product operators would be: I_z, $2I_xS_y$, I_x, $2I_zS_y$, $2I_xR_y$, $4I_zS_yR_y$, $2I_zR_y$, $4I_xS_yR_y$, $2I_xQ_y$, $2I_zQ_y$, $4I_zS_yQ_y$, $4I_xS_yQ_y$, $4I_zR_yQ_y$, $4I_xR_yQ_y$, $8I_xS_yR_yQ_y$, $8I_zS_yR_yQ_y$.

Note that the first 8 of these 16 are the same as those found on the right-hand side of Eqn 5.3.

Exercise 5.3

A cosine modulated signal is obtained as a function of t_1 for the HMQC pulse sequence in Fig. 5.10 (see Eqn 5.21). How might the pulse sequence be modified to obtain a sine modulated signal?

A sine modulated signal as a function of t_1 can be obtained by replacing the first 90°_x pulse on spin S in Fig. 5.10 with a 90°_y pulse. In this case, Eqn 5.18 becomes:

$$\begin{aligned}&= 2I_xS_z\cos\Omega_I\tau + 2I_yS_z\sin\Omega_I\tau\\ &\xrightarrow{90^\circ S_y} 2I_xS_x\cos\Omega_I\tau + 2I_yS_x\sin\Omega_I\tau.\end{aligned}$$

And then we can continue with the rest of the product operator analysis of the sequence:

$$\begin{aligned}&\xrightarrow{180^\circ I_x} 2I_xS_x\cos\Omega_I\tau - 2I_yS_x\sin\Omega_I\tau\\ &\xrightarrow{\Omega_S t_1 S_z} 2I_xS_x\cos\Omega_I\tau\cos\Omega_S t_1 + 2I_xS_y\cos\Omega_I\tau\sin\Omega_S t_1\\ &\qquad - 2I_yS_x\sin\Omega_I\tau\cos\Omega_S t_1 - 2I_yS_y\sin\Omega_I\tau\sin\Omega_S t_1\\ &\xrightarrow{90^\circ S_x} 2I_xS_z\cos\Omega_I\tau\sin\Omega_S t_1 - 2I_yS_z\sin\Omega_I\tau\sin\Omega_S t_1\end{aligned}$$

Note that we have only retained observable terms in the final line above and that these are now sine modulated signal as a function of t_1.

$$\begin{aligned}&\xrightarrow{\Omega_I\tau I_z} 2I_xS_z\cos^2\Omega_I\tau\ \sin\Omega_S t_1 + 2I_yS_z\cos\Omega_I\tau\sin\Omega_I\tau\ \sin\Omega_S t_1\\ &\qquad - 2I_yS_z\cos\Omega_I\tau\sin\Omega_I\tau\sin\Omega_S t_1 + 2I_xS_z\sin^2\Omega_I\tau\ \sin\Omega_S t_1\\ &\quad = 2I_xS_z\sin\Omega_S t_1\\ &\xrightarrow{\pi J_{IS}\tau\, 2I_zS_z} I_y\sin\Omega_S t_1.\end{aligned}$$

As with the COSY experiment in Exercise 5.1, the signals from the cosine and sine modulated HMQC experiments can be used as the inputs to a hypercomplex Fourier transformation, as described in Section 2.4.

Exercise 5.4

The HMQC experiment is normally performed to correlate I and S spins through their one-bond *J*-couplings, ${}^1J_{IS}$. The Heteronuclear Multiple-Bond Correlation (HMBC) experiment is a version of HMQC that allows correlation through multiple-bond J-couplings: ${}^2J_{IS}$, ${}^3J_{IS}$, ${}^4J_{IS}$, etc. Suggest the most simple modification of HMQC that allows such correlations to be observed.

Multiple-bond J_{IS} couplings are invariably much smaller than one-bond J_{IS} couplings, with 10 Hz a typical rough estimate for ${}^2J_{IS}$, ${}^3J_{IS}$, ${}^4J_{IS}$, etc., with I = ^{1}H and S = ^{13}C or ^{15}N. Therefore, the simplest modification of the HMQC sequence to allow correlations through multiple-bond heteronuclear couplings (HMBC) is to lengthen the first τ delay in Fig. 5.10 to $1/(2\times{}^nJ_{IS})$, with ${}^nJ_{IS}$ = 10 Hz.

What about the second τ delay? It is tempting to lengthen this to $1/(2\times{}^nJ_{IS})$ too. However, we need to remember that homonuclear *J*-couplings, J_{II}, will be present between the I = ^{1}H spins and that these could be safely ignored in Eqns 5.17 – 5.21 (and in Exercise 5.3) because ${}^nJ_{II} << {}^1J_{IS}$. But ${}^nJ_{II} \approx {}^nJ_{IS}$, the homonuclear *J*-couplings will evolve to a significant extent during the extended τ delays, and there is no mechanism in the pulse sequence in Fig. 5.10 for refocusing of these couplings. As a result, it would be impossible to phase the resulting spectrum in the F_2 (I = ^{1}H) dimension. The pragmatic (but somewhat crude) solution to this problem normally adopted is to omit the second τ delay completely and hence, because the spin I signals are then antiphase with respect to the S spins at the start of the acquisition period, to also omit any decoupling of the S spins; no attempt is made to phase the spectrum and it is presented in magnitude mode.

Exercise 5.5

In the early years of two-dimensional NMR, heteronuclear correlation experiments were usually carried out by having ^{1}H magnetization evolve during the t_1 period and detecting the ^{13}C or ^{15}N signal directly in the t_2 period. However, this approach is much less sensitive than that used in the so-called inverse experiments HMQC and HSQC and has fallen out of favour. Despite this overwhelming sensitivity disadvantage, suggest some *advantages* of the direct detection approach.

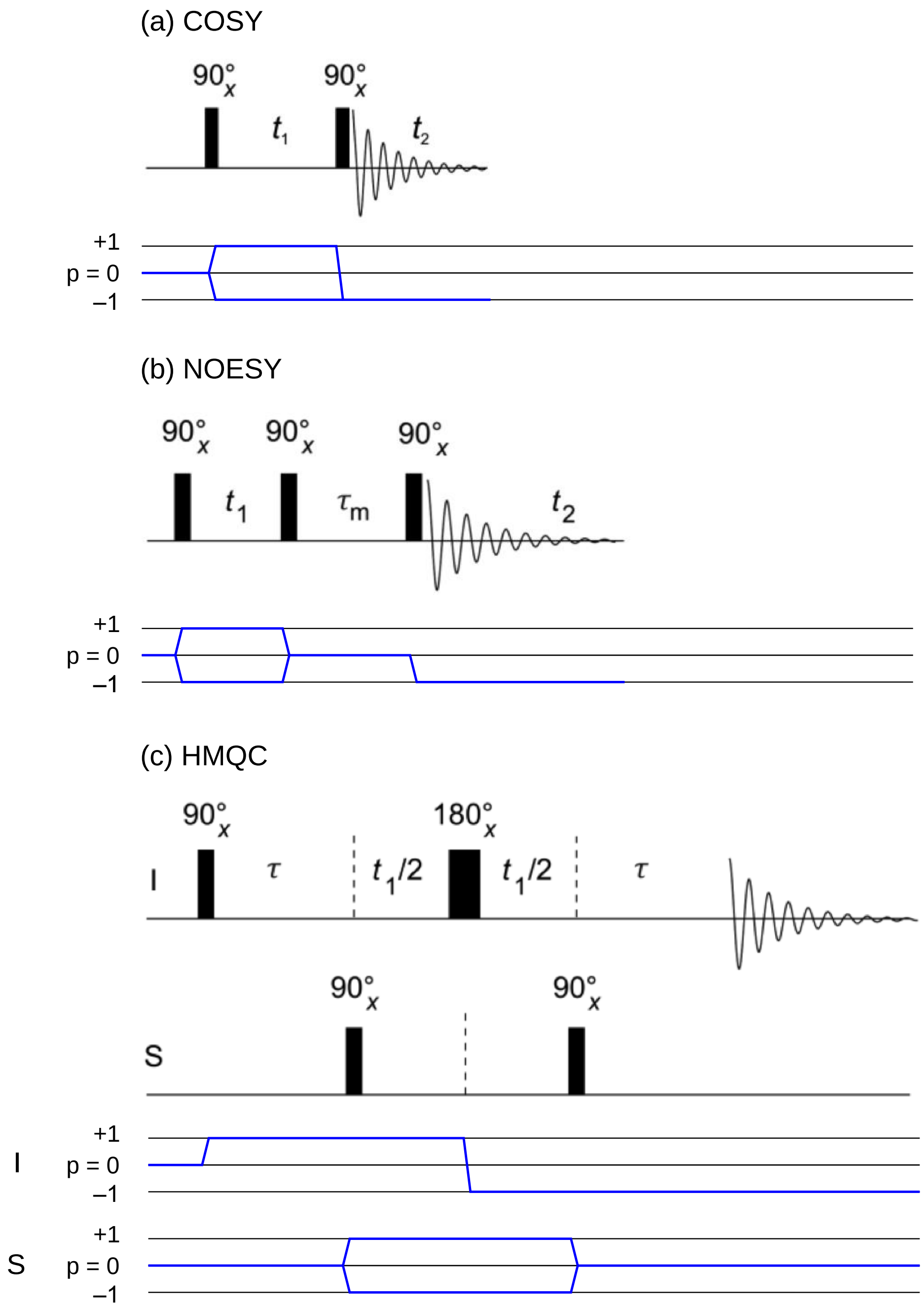
^{13}C or ^{15}N NMR signals cover a much wider range of chemical shifts than ^{1}H signals and yet can have much narrower line widths in absolute terms. Therefore, in a heteronuclear correlation experiment, it is possible that there will be a need to record the spin S (e.g. ^{13}C or ^{15}N) dimension with *much* higher resolution than the spin I (^{1}H) dimension. In purely practical terms, this very high resolution might be easier to obtain in the F_2 dimension (simply by having a long acquisition time t_2) than in the F_1 dimension, where a large number of small (because of the wide chemical shift range) t_1 increments will be needed to achieve a large enough value of t_1 to resolve closely spaced spin S signals.

A second possible advantage of direct detection of the (lower γ, usually less abundant) spin S nucleus is that the direct detection of the I = ^{1}H nucleus can be complicated by the presence of very strong signals that are not involved with the desired I–S correlation, e.g., those arising from a solvent, such as water, that cannot always be replaced by its deuterated form for chemical reasons.

Chapter 6

Exercise 6.1

Draw coherence transfer pathway diagrams for (a) the COSY experiment (Fig. 5.1), the NOESY experiment (Fig. 5.7), and the HMQC experiment (Fig. 5.10). (For the heteronuclear HMQC experiment, remember that you will need to draw separate coherence transfer pathway diagrams for the I and S spins.)



Exercise 6.2

Remembering that, in experimental practice, the flip angles of the pulses may deviate slightly from 90°, design a two-step phase cycle for the COSY experiment (Fig. 5.1).

If the first pulse in the COSY pulse sequence in Fig. 5.1 deviates from 90° then we will have $p = 0$ magnetization present during the t_1 period and this must be eliminated. (Spin-lattice relaxation will also give rise to $p = 0$ magnetization even if the pulses are perfect.) Thus, we need to cycle the phase of the first 90° pulse (ϕ_1) to select $\Delta p = +1$ *and* $\Delta p = -1$ simultaneously, rejecting the unwanted $\Delta p = 0$. Note that this is identical to the axial peak suppression we used in the DQF-COSY experiment in Section 6.3. These two steps are

$$\phi_1 = 0^\circ, 180^\circ$$

and the First Rule gives the corresponding receiver phase cycle as

$$\phi_{\text{Rx}} = 0^\circ, 180^\circ.$$

Alternatively, we can cycle the phase of the second 90° pulse (ϕ_2) to select $\Delta p = 0$ *and* $\Delta p = -2$ simultaneously, rejecting the unwanted $\Delta p = -1$. These two steps are

$$\phi_2 = 0^\circ, 180^\circ$$

and the First Rule gives the corresponding receiver phase cycle as

$$\phi_{\text{Rx}} = 0^\circ, 0^\circ.$$

Exercise 6.3

The NOESY experiment (Fig. 5.7) requires a two-step phase cycle to suppress axial peaks and a four-step phase cycle to select $p = 0$ during τ_{m}. Write down these two phase cycles separately and then nest them to give the final eight-step NOESY phase cycle.

The two-step phase cycle of the first pulse in the NOESY sequence in Fig. 5.7 that suppresses axial peaks is, as we have seen for COSY and DQF-COSY:

$$\phi_1 = 0^\circ, 180^\circ$$

$$\phi_{\text{Rx}} = 0^\circ, 180^\circ.$$

For selection of $p = 0$ during the τ_{m} period it is usual to cycle the third 90° pulse through four steps and to select $\Delta p = -1$:

$$\phi_3 = 0°, 90°, 180°, 270°$$

$$\phi_{Rx} = 0°, 90°, 180°, 270°.$$

Nesting these two phase cycles together gives

$$\begin{array}{rcccccccc}
\phi_1 = & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 180^\circ & 180^\circ & 180^\circ & 180^\circ \\
\phi_2 = & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ \\
\phi_3 = & 0^\circ & 90^\circ & 180^\circ & 270^\circ & 0^\circ & 90^\circ & 180^\circ & 270^\circ \\
\phi_{Rx} = & 0^\circ & 90^\circ & 180^\circ & 270^\circ & 180^\circ & 270^\circ & 0^\circ & 90^\circ
\end{array}$$

Exercise 6.4

Confirm that cycling the phases ϕ_2 and ϕ_3 in the DQF-COSY experiment (Fig. 6.1) yields the same eight-step phase cycle (but performed in a different order) as that obtained by cycling phases ϕ_1 and ϕ_3 (Eqn 6.8), as described in Section 6.3.

Phase cycling the second 90° pulse (ϕ_2) in Fig. 6.1, we need to select $\Delta p = +3$, $\Delta p = +1$, $\Delta p = -1$ *and* $\Delta p = -3$, rejecting the unwanted $\Delta p = 0$ and $\Delta p = \pm 2$. This can be achieved by the two-step phase cycle:

$$\phi_2 = 0°, 180°$$

$$\phi_{Rx} = 0°, 180°.$$

The phase cycle for the third 90° pulse (ϕ_3) has already been given in Eqns 6.2 and 6.4:

$$\phi_3 = 0°, 90°, 180°, 270°$$

$$\phi_{Rx} = 0°, 270°, 180°, 90°$$

Nesting these two phase cycles together gives

$$\begin{array}{rcccccccc}
\phi_1 = & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ \\
\phi_2 = & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 180^\circ & 180^\circ & 180^\circ & 180^\circ \\
\phi_3 = & 0^\circ & 90^\circ & 180^\circ & 270^\circ & 0^\circ & 90^\circ & 180^\circ & 270^\circ \\
\phi_{Rx} = & 0^\circ & 270^\circ & 180^\circ & 90^\circ & 180^\circ & 90^\circ & 0^\circ & 270^\circ
\end{array}$$

Now this does not appear to be quite the same phase cycle as in Eqn 6.8; the first four steps are the same but the second four are different. However, without altering the performance of the phase cycle, we can arbitrarily add 180° to all four phases in steps five to eight to obtain

$$\begin{array}{lrrrrrrrr}
\phi_1 = & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 180^\circ & 180^\circ & 180^\circ & 180^\circ \\
\phi_2 = & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ & 0^\circ \\
\phi_3 = & 0^\circ & 90^\circ & 180^\circ & 270^\circ & 180^\circ & 270^\circ & 0^\circ & 90^\circ \\
\phi_{\mathrm{Rx}} = & 0^\circ & 270^\circ & 180^\circ & 90^\circ & 0^\circ & 270^\circ & 180^\circ & 90^\circ
\end{array}$$

This is now identical to the phase cycle given in Eqn 6.8 except that the order in which steps five to eight are performed has been changed.

Exercise 6.5

Confirm that cycling the phases ϕ_1 and ϕ_2 in the DQF-COSY experiment (Fig. 6.1) alone cannot suppress $p=0$ during the Δ delay, as described in Section 6.3.

Phase cycling the first 90° pulse (ϕ_1) in Fig. 6.1, we can select $p=+1$ and -1 coherences during t_1. But then, as we have seen in Exercise 6.4, the second pulse (ϕ_2) must select $\Delta p=+3$, $\Delta p=+1$, $\Delta p=-1$ *and* $\Delta p=-3$. Unfortunately, it easily seen that the change $\Delta p=-1$ applied to $p=+1$ and the change $\Delta p=+1$ applied to $p=-1$ both yield $p=0$ magnetization during the Δ delay. One solution to this is to phase cycle the second pulse to select only $\Delta p=+3$ and $\Delta p=-3$ but this will lead to a loss of signal as two of the four pathways leading to double-quantum coherences are blocked. A much better solution is, as described in Section 6.3 and Exercise 6.4, to phase cycle either ϕ_1 and ϕ_3 or, alternatively, ϕ_2 and ϕ_3 with retention of the full signal intensity.

Exercise 6.6

A strong pulsed field gradient is often applied before the very first radiofrequency pulse is applied in a pulse sequence. Suggest why this is beneficial.

When time averaging an NMR experiment, it is sometimes necessary to use a shorter than optimal relaxation delay between acquisitions in order to optimise the signal-to-noise ratio in a finite total experiment time. With a short relaxation delay, it is possible that some transverse magnetization or multiple-quantum coherences may survive from the previous acquisition and give rise to observable signal in the current acquisition. In order words, we may have coherences other than $p=0$ present at the start of the pulse sequence, which could defeat the design and purpose of our phase cycle. Therefore, one obvious solution to this potential problem is to apply a strong pulsed magnetic field gradient before the first pulse in the pulse sequence and so to dephase completely any coherences left over from the previous acquisition.

Answers to Exercises: Part B

Chapter 7

Exercise 7.1

Consider the kets $|\psi_a\rangle = |1\rangle + |2\rangle$, $|\psi_b\rangle = |1\rangle + \mathrm{i}|2\rangle$, and $|\psi_c\rangle = |1\rangle + \sqrt{3}\mathrm{i}|2\rangle$. Find the corresponding normalised kets $|\psi_a'\rangle$, and so on, and the corresponding normalised bras.

We can normalise a ket by dividing it by its length: in general

$$|\psi'\rangle = \frac{|\psi\rangle}{\sqrt{\langle\psi|\psi\rangle}}.$$

Start by finding the un-normalised bras

$$\langle\psi_a| = \langle 1| + \langle 2| \qquad \langle\psi_b| = \langle 1| - \mathrm{i}\langle 2| \qquad \langle\psi_c| = \langle 1| - \sqrt{3}\mathrm{i}\langle 2|$$

remembering to take the complex conjugates of the coefficients. The inner products can be evaluated using

$$\begin{aligned}
\langle\psi_a|\psi_a\rangle &= \langle 1| + \langle 2| \quad |1\rangle + |2\rangle \\
&= \langle 1|1\rangle + \langle 1|2\rangle + \langle 2|1\rangle + \langle 2|2\rangle \\
&= 1 + 0 + 0 + 1 \\
&= 2
\end{aligned}$$

and similarly

$$\begin{aligned}
\langle\psi_b|\psi_b\rangle &= \langle 1| - \mathrm{i}\langle 2| \quad |1\rangle + \mathrm{i}|2\rangle \\
&= \langle 1|1\rangle + \mathrm{i}\langle 1|2\rangle - \mathrm{i}\langle 2|1\rangle - \mathrm{i}(+\mathrm{i})\langle 2|2\rangle \\
&= 1 + 0 + 0 + 1 \\
&= 2
\end{aligned}$$

and

$$\begin{aligned}
\langle\psi_c|\psi_c\rangle &= \langle 1| - \sqrt{3}\mathrm{i}\langle 2| \quad |1\rangle + \sqrt{3}\mathrm{i}|2\rangle \\
&= \langle 1|1\rangle + \sqrt{3}\mathrm{i}\langle 1|2\rangle - \sqrt{3}\mathrm{i}\langle 2|1\rangle - \sqrt{3}\mathrm{i}(+\sqrt{3}\mathrm{i})\langle 2|2\rangle \\
&= 1 + 0 + 0 + 3\times 1 \\
&= 4
\end{aligned}$$

Note that these inner products, which are the squares of the lengths of the vectors, are all positive real numbers as required. We could have done these calculations using matrix forms, e.g.

$$
\begin{aligned}
\langle \psi_b | \psi_b \rangle &= \boldsymbol{\psi}_b^{\dagger} \boldsymbol{\psi}_b \\
&= \begin{matrix} 1 & -\mathrm{i} \end{matrix} \begin{pmatrix} 1 \\ \mathrm{i} \end{pmatrix} \\
&= 1 - \mathrm{i}^2 \\
&= 2
\end{aligned}
$$

giving precisely the same answers. Alternatively note that since $|1\rangle$ and $|2\rangle$ are orthogonal and normalised the square of the length is just the sum of the squares of the absolute values of the coefficients. Either way, the lengths are $\sqrt{2}$ for $|\psi_a\rangle$ and $|\psi_b\rangle$ and 2 for $|\psi_c\rangle$.

Putting all this together gives

$$
\begin{matrix}
|\psi_a'\rangle = \tfrac{1}{\sqrt{2}}|1\rangle + \tfrac{1}{\sqrt{2}}|2\rangle & |\psi_b'\rangle = \tfrac{1}{\sqrt{2}}|1\rangle + \tfrac{\mathrm{i}}{\sqrt{2}}|2\rangle & |\psi_c'\rangle = \tfrac{1}{2}|1\rangle + \tfrac{\sqrt{3}\mathrm{i}}{2}|2\rangle \\
\langle\psi_a'| = \tfrac{1}{\sqrt{2}}\langle 1| + \tfrac{1}{\sqrt{2}}\langle 2| & \langle\psi_b'| = \tfrac{1}{\sqrt{2}}\langle 1| - \tfrac{\mathrm{i}}{\sqrt{2}}\langle 2| & \langle\psi_c'| = \tfrac{1}{2}\langle 1| - \tfrac{\sqrt{3}\mathrm{i}}{2}\langle 2|
\end{matrix}.
$$

Exercise 7.2

Calculate the inner products $\langle \psi_a | \psi_b \rangle$ and $\langle \psi_a' | \psi_b' \rangle$ and comment on your answers.

$$
\begin{aligned}
\langle \psi_a | \psi_b \rangle &= \langle 1| + \langle 2| \;\; |1\rangle + \mathrm{i}|2\rangle \\
&= \langle 1|1\rangle + \mathrm{i}\langle 1|2\rangle + \langle 2|1\rangle + \mathrm{i}\langle 2|2\rangle \\
&= 1 + 0 + 0 + \mathrm{i} \\
&= 1 + \mathrm{i}
\end{aligned}
$$

$$
\begin{aligned}
\langle \psi_a' | \psi_b' \rangle &= \tfrac{1}{\sqrt{2}}\langle 1| + \tfrac{1}{\sqrt{2}}\langle 2| \;\; \tfrac{1}{\sqrt{2}}|1\rangle + \tfrac{1}{\sqrt{2}}\mathrm{i}|2\rangle \\
&= \tfrac{1}{2}\langle 1|1\rangle + \tfrac{\mathrm{i}}{2}\langle 1|2\rangle + \tfrac{1}{2}\langle 2|1\rangle + \tfrac{\mathrm{i}}{2}\langle 2|2\rangle \\
&= \tfrac{1}{2} + 0 + 0 + \tfrac{\mathrm{i}}{2} \\
&= \tfrac{1}{2} + \tfrac{\mathrm{i}}{2} \\
&= \tfrac{1}{2}\; 1 + \mathrm{i}
\end{aligned}
$$

Note that $\langle \psi_a' | \psi_b' \rangle$ could have been obtained directly from $\langle \psi_a | \psi_b \rangle$ by dividing it by the product of the lengths of $|\psi_a\rangle$ and $|\psi_b\rangle$.

Exercise 7.3

Calculate the inner products $\langle \psi_a' | \psi_c' \rangle$ and $\langle \psi_c' | \psi_a' \rangle$ and comment on your answers.

The method is the same as before, but we can now miss out unnecessary steps.

$$\begin{aligned}\langle\psi_a'|\psi_c'\rangle &= \tfrac{1}{\sqrt{2}}\langle 1| + \tfrac{1}{\sqrt{2}}\langle 2| \quad \tfrac{1}{2}|1\rangle + \tfrac{\sqrt{3}\mathrm{i}}{2}|2\rangle \\ &= \tfrac{1}{2\sqrt{2}} + \tfrac{\sqrt{3}\mathrm{i}}{2\sqrt{2}} \\ &= \tfrac{1}{2\sqrt{2}}\; 1+\sqrt{3}\,\mathrm{i}\end{aligned}$$

$$\begin{aligned}\langle\psi_c'|\psi_a'\rangle &= \tfrac{1}{2}\langle 1| - \tfrac{\sqrt{3}\mathrm{i}}{2}\langle 2| \quad \tfrac{1}{\sqrt{2}}|1\rangle + \tfrac{1}{\sqrt{2}}|2\rangle \\ &= \tfrac{1}{2\sqrt{2}} - \tfrac{\sqrt{3}\mathrm{i}}{2\sqrt{2}} \\ &= \tfrac{1}{2\sqrt{2}}\; 1-\sqrt{3}\,\mathrm{i}\end{aligned}$$

Note that these two results are complex conjugates: $\langle\psi_c'|\psi_a'\rangle = \langle\psi_a'|\psi_c'\rangle^*$. This makes sense because from the properties of the adjoint $\langle\psi_c'|\psi_a'\rangle = \langle\psi_a'|\psi_c'\rangle^\dagger$, and the adjoint of a number is its complex conjugate.

Exercise 7.4

Write down the matrix forms of $\boldsymbol{\psi}_\alpha$ and $\boldsymbol{\psi}_\beta$ corresponding to the basis kets $|\alpha\rangle$ and $|\beta\rangle$. Hence show that the matrices $\boldsymbol{I}_x$, $\boldsymbol{I}_y$ and $\boldsymbol{I}_z$ (Eqns 7.23 and 7.26) act as described in Eqns 7.21 and 7.25.

We have

$$\boldsymbol{\psi}_\alpha = \begin{pmatrix}1\\0\end{pmatrix} \qquad \boldsymbol{\psi}_\beta = \begin{pmatrix}0\\1\end{pmatrix}$$

and so

$$\boldsymbol{I}_x\boldsymbol{\psi}_\alpha = \begin{pmatrix}0 & \frac{1}{2}\\ \frac{1}{2} & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\times 1+\frac{1}{2}\times 0\\ \frac{1}{2}\times 1+0\times 0\end{pmatrix} = \begin{pmatrix}0\\ \frac{1}{2}\end{pmatrix} = \tfrac{1}{2}\boldsymbol{\psi}_\beta$$

$$\boldsymbol{I}_y\boldsymbol{\psi}_\alpha = \begin{pmatrix}0 & -\frac{1}{2}\mathrm{i}\\ \frac{1}{2}\mathrm{i} & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\times 1-\frac{1}{2}\mathrm{i}\times 0\\ \frac{1}{2}\mathrm{i}\times 1+0\times 0\end{pmatrix} = \begin{pmatrix}0\\ \frac{1}{2}\mathrm{i}\end{pmatrix} = \tfrac{1}{2}\mathrm{i}\boldsymbol{\psi}_\beta$$

$$\boldsymbol{I}_z\boldsymbol{\psi}_\alpha = \begin{pmatrix}\frac{1}{2} & 0\\ 0 & -\frac{1}{2}\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}\frac{1}{2}\times 1+0\times 0\\ 0\times 1-\frac{1}{2}\times 0\end{pmatrix} = \begin{pmatrix}\frac{1}{2}\\ 0\end{pmatrix} = \tfrac{1}{2}\boldsymbol{\psi}_\alpha$$

and similarly

$$\boldsymbol{I}_x\boldsymbol{\psi}_\beta = \begin{pmatrix}0 & \frac{1}{2}\\ \frac{1}{2} & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}\frac{1}{2}\\ 0\end{pmatrix} = \tfrac{1}{2}\boldsymbol{\psi}_\alpha$$

$$\boldsymbol{I}_y\boldsymbol{\psi}_\beta = \begin{pmatrix}0 & -\frac{1}{2}\mathrm{i}\\ \frac{1}{2}\mathrm{i} & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}-\frac{1}{2}\mathrm{i}\\ 0\end{pmatrix} = -\tfrac{1}{2}\mathrm{i}\boldsymbol{\psi}_\alpha$$

$$I_z \psi_\beta = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} == \begin{pmatrix} 0 \\ -\frac{1}{2} \end{pmatrix} = -\tfrac{1}{2} \psi_\beta \,.$$

Exercise 7.5

Show that $B,A = - A,B$ and that $A,B+C = A,B + A,C$

These are easily shown by direct expansion

$$\begin{aligned} B,A &= BA - AB \\ &= - \; AB - BA \\ &= - \; A,B \end{aligned}$$

$$\begin{aligned} A,B+C &= A \;\; B+C \;\; - \;\; B+C \;\; A \\ &= AB + AC - BA - CA \\ &= \;\; AB - BA \;\; + \;\; AC - CA \\ &= \;\; A,B \; + \; A,C \end{aligned}$$

Exercise 7.6

Determine the nine possible binary products of the matrices I_x, I_y and I_z, and hence show that these matrices have the correct commutation relations to represent angular momentum.

By direct multiplication

$$I_x I_y = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 & -\frac{1}{2}\mathrm{i} \\ \frac{1}{2}\mathrm{i} & 0 \end{pmatrix} = \begin{pmatrix} 0+\frac{1}{4}\mathrm{i} & 0 \\ 0+0 & -\frac{1}{4}\mathrm{i}+0 \end{pmatrix} = \tfrac{1}{2}\mathrm{i} \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

The complete set of nine binary products is

$$I_x I_x = \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix} = \tfrac{1}{4}\mathbf{1} \qquad I_x I_y = \begin{pmatrix} \frac{1}{4}\mathrm{i} & 0 \\ 0 & -\frac{1}{4}\mathrm{i} \end{pmatrix} = \tfrac{1}{2}\mathrm{i} I_z \qquad I_x I_z = \begin{pmatrix} 0 & -\frac{1}{4} \\ \frac{1}{4} & 0 \end{pmatrix} = -\tfrac{1}{2}\mathrm{i} I_y$$

$$I_y I_x = \begin{pmatrix} -\frac{1}{4}\mathrm{i} & 0 \\ 0 & \frac{1}{4}\mathrm{i} \end{pmatrix} = -\tfrac{1}{2}\mathrm{i} I_z \qquad I_y I_y = \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix} = \tfrac{1}{4}\mathbf{1} \qquad I_y I_z = \begin{pmatrix} 0 & \frac{1}{4}\mathrm{i} \\ \frac{1}{4}\mathrm{i} & 0 \end{pmatrix} = \tfrac{1}{2}\mathrm{i} I_x$$

$$I_z I_x = \begin{pmatrix} 0 & \frac{1}{4} \\ -\frac{1}{4} & 0 \end{pmatrix} = \tfrac{1}{2}\mathrm{i} I_y \qquad I_z I_y = \begin{pmatrix} 0 & -\frac{1}{4}\mathrm{i} \\ -\frac{1}{4}\mathrm{i} & 0 \end{pmatrix} = -\tfrac{1}{2}\mathrm{i} I_x \qquad I_z I_z = \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix} = \tfrac{1}{4}\mathbf{1}$$

confirming equations 7.28 and 7.29. Then

$$\left[I_x, I_y\right] = I_x I_y - I_y I_x = \tfrac{1}{2}\mathrm{i} I_z - \;\; -\tfrac{1}{2}\mathrm{i} I_z \;\; = \mathrm{i} I_z$$

and so on.

Exercise 7.7

Use the methods in Appendix D and E to confirm equations 7.52 and 7.53. Find the corresponding result for $\boldsymbol{I}_y$.

Equation 7.52 is easy: as $\boldsymbol{I}_z$ is diagonal matrix exponentials of terms proportional to it can be calculated directly:

$$\mathrm{e}^{-\mathrm{i}\omega_0 t \boldsymbol{I}_z} = \exp\begin{pmatrix} -\frac{1}{2}\mathrm{i}\omega_0 t & 0 \\ 0 & \frac{1}{2}\mathrm{i}\omega_0 t \end{pmatrix} = \begin{pmatrix} \mathrm{e}^{-\frac{1}{2}\mathrm{i}\omega_0 t} & 0 \\ 0 & \mathrm{e}^{\frac{1}{2}\mathrm{i}\omega_0 t} \end{pmatrix}.$$

The complete calculation of equation 7.53 is given in appendix E; the result can be found in equation E4 choosing the minus sign. The corresponding result for $\boldsymbol{I}_y$ can be done in a very similar way to that for $\boldsymbol{I}_x$. First we find the eigenvalues of $k\boldsymbol{I}_y$,

$$\left|k\boldsymbol{I}_y - \lambda\boldsymbol{1}\right| = \begin{vmatrix} -\lambda & -\frac{1}{2}k\mathrm{i} \\ \frac{1}{2}k\mathrm{i} & -\lambda \end{vmatrix} = \lambda^2 + \ \tfrac{1}{2}k\mathrm{i}\ ^2 = \lambda^2 - \tfrac{1}{4}k^2 = 0\,,$$

and so

$$\lambda = \pm k/2\,,$$

the same as for $\boldsymbol{I}_x$. The eigenvectors are, however, different. For $\lambda = k/2$

$$\begin{pmatrix} -\frac{1}{2}k & -\frac{1}{2}k\mathrm{i} \\ \frac{1}{2}k\mathrm{i} & -\frac{1}{2}k \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},$$

has the solution $x_2 = \mathrm{i}x_1$, while $\lambda = k/2$ has the solution $x_2 = -\mathrm{i}x_1$. The eigenvectors can be normalised by choosing $x_1 = 1/\sqrt{2}$ as before, and so matrices the $\boldsymbol{\Lambda}$ and **S** are now given by

$$\boldsymbol{\Lambda} = \begin{pmatrix} \frac{1}{2}k & 0 \\ 0 & -\frac{1}{2}k \end{pmatrix}, \qquad \boldsymbol{S} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ \mathrm{i} & -\mathrm{i} \end{pmatrix}.$$

As a check we can evaluate

$$\begin{aligned} \boldsymbol{S\Lambda S}^{\dagger} &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ \mathrm{i} & -\mathrm{i} \end{pmatrix}\begin{pmatrix} \frac{1}{2}k & 0 \\ 0 & -\frac{1}{2}k \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -\mathrm{i} \\ 1 & \mathrm{i} \end{pmatrix} \\ &= \frac{1}{2}\begin{pmatrix} 1 & 1 \\ \mathrm{i} & -\mathrm{i} \end{pmatrix}\begin{pmatrix} \frac{1}{2}k & -\frac{1}{2}k\mathrm{i} \\ -\frac{1}{2}k & -\frac{1}{2}k\mathrm{i} \end{pmatrix} \\ &= \frac{1}{2}\begin{pmatrix} 0 & -k\mathrm{i} \\ k\mathrm{i} & 0 \end{pmatrix} \\ &= k\boldsymbol{I}_y \end{aligned} \quad .$$

as required. Finally we have

$$\begin{aligned}
e^{kI_y} &= \boldsymbol{S}e^{\Lambda}\boldsymbol{S}^{-1} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}\begin{pmatrix} e^{k/2} & 0 \\ 0 & e^{-k/2} \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} e^{k/2}+e^{-k/2} & -i\left[e^{k/2}-e^{-k/2}\right] \\ i\left[e^{k/2}-e^{-k/2}\right] & e^{k/2}+e^{-k/2} \end{pmatrix}.
\end{aligned}$$

Choosing $k = -i\omega_1 t$ gives

$$\begin{aligned}
e^{k/2}+e^{-k/2} &= e^{-i\omega_1 t/2}+e^{i\omega_1 t/2} \\
&= \left[\cos(-\omega_1 t/2)+i\sin(-\omega_1 t/2)\right]+\left[\cos(\omega_1 t/2)+i\sin(\omega_1 t/2)\right] \\
&= \cos(\omega_1 t/2) - i\sin(-\omega_1 t/2)+\cos(\omega_1 t/2)+i\sin(\omega_1 t/2) \\
&= 2\cos(\omega_1 t/2)
\end{aligned}$$

and

$$\begin{aligned}
e^{k/2}-e^{-k/2} &= e^{-i\omega_1 t/2}-e^{i\omega_1 t/2} \\
&= \left[\cos(-\omega_1 t/2)+i\sin(-\omega_1 t/2)\right]-\left[\cos(\omega_1 t/2)+i\sin(\omega_1 t/2)\right] \\
&= \cos(\omega_1 t/2) - i\sin(-\omega_1 t/2)-\cos(\omega_1 t/2)-i\sin(\omega_1 t/2) \\
&= -2i\sin(\omega_1 t/2)
\end{aligned}$$

Putting all this together gives

$$\begin{aligned}
e^{kI_y} &= \boldsymbol{S}e^{\Lambda}\boldsymbol{S}^{-1} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}\begin{pmatrix} e^{k/2} & 0 \\ 0 & e^{-k/2} \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} 2\cos(\omega_1 t/2) & -i\left[-2i\sin(\omega_1 t/2)\right] \\ i\left[-2i\sin(\omega_1 t/2)\right] & 2\cos(\omega_1 t/2) \end{pmatrix} \\
&= \begin{pmatrix} \cos(\omega_1 t/2) & -\sin(\omega_1 t/2) \\ \sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{pmatrix}.
\end{aligned}$$

Exercise 7.8

Repeat the calculations in Section 7.5 using matrix exponentials. Repeat the calculations in Section 7.6 for a *y*-pulse.

The general solution is

$$\boldsymbol{\psi}(t) = e^{-i\boldsymbol{H}t}\,\boldsymbol{\psi}(0)\,.$$

In section 7.5

$$\boldsymbol{H} = \omega_0 \boldsymbol{I}_z$$

and

$$\boldsymbol{\psi}(0)=\begin{pmatrix}\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{pmatrix}.$$

Thus

$$\boldsymbol{\psi}(t)=\begin{pmatrix}\mathrm{e}^{-\frac{1}{2}\mathrm{i}\omega_0 t} & 0\\ 0 & \mathrm{e}^{\frac{1}{2}\mathrm{i}\omega_0 t}\end{pmatrix}\begin{pmatrix}\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{pmatrix}=\begin{pmatrix}\frac{1}{\sqrt{2}}\mathrm{e}^{-\frac{1}{2}\mathrm{i}\omega_0 t}\\ \frac{1}{\sqrt{2}}\mathrm{e}^{\frac{1}{2}\mathrm{i}\omega_0 t}\end{pmatrix}.$$

in agreement with Eqn 7.39, and the rest of the calculation is unchanged. In section 7.6

$$\boldsymbol{H}=\omega_1\boldsymbol{I_y}$$

and

$$\boldsymbol{\psi}(0)=\begin{pmatrix}1\\ 0\end{pmatrix}$$

so

$$\boldsymbol{\psi}(t)=\begin{pmatrix}\cos\ \omega_1 t/2 & -\sin\ \omega_1 t/2\\ \sin\ \omega_1 t/2 & \cos\ \omega_1 t/2\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix}=\begin{pmatrix}\cos\ \omega_1 t/2\\ \sin\ \omega_1 t/2\end{pmatrix}.$$

In this case

$$\begin{aligned}\left\langle \hat{I}_x\right\rangle &=\mathrm{Re}\left[\cos\ \tfrac{1}{2}\omega_1 t\ \ \sin\ \tfrac{1}{2}\omega_1 t\ \right]=\tfrac{1}{2}\sin\ \omega_1 t\\ \left\langle \hat{I}_y\right\rangle &=-\mathrm{Im}\left[\cos\ \tfrac{1}{2}\omega_1 t\ \ \sin\ \tfrac{1}{2}\omega_1 t\ \right]=0 \qquad .\\ \left\langle \hat{I}_z\right\rangle &=\tfrac{1}{2}\left[\cos^2\ \tfrac{1}{2}\omega_1 t\ -\sin^2\ \tfrac{1}{2}\omega_1 t\ \right]=\tfrac{1}{2}\cos\ \omega_1 t\ .\end{aligned}$$

Chapter 8

Exercise 8.1

Consider the ket $|\psi_a\rangle = \cos\,\theta/2\,|\alpha\rangle + \sin\,\theta/2\,\mathrm{e}^{\mathrm{i}\phi}|\beta\rangle$. Show that $|\psi_a\rangle$ is normalised and find the corresponding density matrix $\boldsymbol{\rho}_a$.

It is easiest to do this using matrix representations. First

$$\begin{aligned}
\langle\psi_a|\psi_a\rangle &= \boldsymbol{\psi}_a^\dagger\boldsymbol{\psi}_a \\
&= \begin{pmatrix}\cos\,\theta/2 & \sin\,\theta/2\,\mathrm{e}^{-\mathrm{i}\phi}\end{pmatrix}\begin{pmatrix}\cos\,\theta/2 \\ \sin\,\theta/2\,\mathrm{e}^{\mathrm{i}\phi}\end{pmatrix} \\
&= \cos^2\,\theta/2 + \sin^2\,\theta/2 \\
&= 1
\end{aligned}$$

and so $|\psi_a\rangle$ is normalised. Then

$$\begin{aligned}
\boldsymbol{\rho}_a &= \boldsymbol{\psi}_a\boldsymbol{\psi}_a^\dagger \\
&= \begin{pmatrix}\cos\,\theta/2 \\ \sin\,\theta/2\,\mathrm{e}^{\mathrm{i}\phi}\end{pmatrix}\begin{pmatrix}\cos\,\theta/2 & \sin\,\theta/2\,\mathrm{e}^{-\mathrm{i}\phi}\end{pmatrix} \\
&= \begin{pmatrix}\cos^2\,\theta/2 & \cos\,\theta/2\,\sin\,\theta/2\,\mathrm{e}^{-\mathrm{i}\phi} \\ \cos\,\theta/2\,\sin\,\theta/2\,\mathrm{e}^{\mathrm{i}\phi} & \sin^2\,\theta/2\end{pmatrix}.
\end{aligned}$$

The matrix $\boldsymbol{\rho}_a$ can be written in a different form using trigonometric identities

$$\boldsymbol{\rho}_a = \frac{1}{2}\begin{pmatrix}1+\cos\theta & \sin\theta\,\mathrm{e}^{-\mathrm{i}\phi} \\ \sin\theta\,\mathrm{e}^{\mathrm{i}\phi} & 1-\cos\theta\end{pmatrix}.$$

explaining the use of $\theta/2$ in the original description of $|\psi_a\rangle$. This form can then be easily related to the *Bloch sphere* description of spin states.

Exercise 8.2

Show that $\boldsymbol{\rho}_a$ is Hermitian and has trace 1.

A matrix $\boldsymbol{M}$ is Hermitian if it is equal to its adjoint, $\boldsymbol{M}^\dagger = \left(\boldsymbol{M}^{\mathrm{T}}\right)^*$. In this case

$$\boldsymbol{\rho}_a^{\mathrm{T}} = \begin{pmatrix}\cos^2\,\theta/2 & \cos\,\theta/2\,\sin\,\theta/2\,\mathrm{e}^{\mathrm{i}\phi} \\ \cos\,\theta/2\,\sin\,\theta/2\,\mathrm{e}^{-\mathrm{i}\phi} & \sin^2\,\theta/2\end{pmatrix}$$

and taking the complex conjugate gives $\boldsymbol{\rho}_a$. (Note that we assume her that θ and ϕ are real.) The trace of $\boldsymbol{\rho}_a$ is the sum of the diagonal elements:

$$\mathrm{Tr}\ \boldsymbol{\rho}_a = \cos^2\theta/2 + \sin^2\theta/2 = 1$$

as required.

Exercise 8.3

Consider the ket $|\psi_b\rangle = \mathrm{e}^{\mathrm{i}\gamma}|\psi_a\rangle$. Find $\boldsymbol{\rho}_b$ and comment on your answer.

This can be done by direct calculation using matrix forms:

$$\begin{aligned}\boldsymbol{\rho}_b &= \boldsymbol{\psi}_b\boldsymbol{\psi}_b^\dagger \\ &= \begin{pmatrix}\mathrm{e}^{\mathrm{i}\gamma}\cos\theta/2 \\ \mathrm{e}^{\mathrm{i}\gamma}\sin\theta/2\ \mathrm{e}^{\mathrm{i}\phi}\end{pmatrix}\begin{pmatrix}\mathrm{e}^{-\mathrm{i}\gamma}\cos\theta/2 & \mathrm{e}^{-\mathrm{i}\gamma}\sin\theta/2\ \mathrm{e}^{-\mathrm{i}\phi}\end{pmatrix} \\ &= \begin{pmatrix}\cos^2\theta/2 & \cos\theta/2\sin\theta/2\ \mathrm{e}^{-\mathrm{i}\phi} \\ \cos\theta/2\sin\theta/2\ \mathrm{e}^{\mathrm{i}\phi} & \sin^2\theta/2\end{pmatrix} \\ &= \boldsymbol{\rho}_a\end{aligned}$$

where we have assumed that γ is real. More directly

$$|\psi_b\rangle\langle\psi_b| = \mathrm{e}^{\mathrm{i}\gamma}|\psi_a\rangle\langle\psi_a|\mathrm{e}^{-\mathrm{i}\gamma} = \mathrm{e}^{\mathrm{i}\gamma}\mathrm{e}^{-\mathrm{i}\gamma}|\psi_a\rangle\langle\psi_a| = |\psi_a\rangle\langle\psi_a|$$

where we have used the fact that $\mathrm{e}^{-\mathrm{i}\gamma}$ is just a number an d so commutes with everything. Terms like $\mathrm{e}^{\mathrm{i}\gamma}$ are called global phases; as they have no effect on the density matrix they cannot affect any observable quantities.

Exercise 8.4

Show that mixed state density matrices are Hermitian and have trace 1. (Hint: consider Eqn 8.25.)

From Eqn 8.25, any mixed state density matrix is a linear combination of pure state density matrices, which are themselves Hermitian with trace 1 (see Exercise 8.2). The weighted sum of two Hermitian matrices is itself Hermitian as long as the weights are real numbers; this is obvious by considering individual elements, or can be deduced from the fact that the transpose and conjugate operations are both linear. For a mixed state the weights are probabilities, which are always positive real numbers. Similarly the trace operation is linear and so, using matrix representations,

$$\mathrm{Tr}\ \boldsymbol{\rho} = \mathrm{Tr}\ \sum_i p_i\boldsymbol{\rho}_i = \sum_i p_i\,\mathrm{Tr}\ \boldsymbol{\rho}_i = \sum_i p_i = 1$$

where we use the fact that the probabilities must sum to 1.

Exercise 8.5

Does the matrix $\boldsymbol{I}_z$ represent a mixed state? If not, does it matter?

As shown in Exercise 8.4 above, every mixed state density matrix has trace 1, but the trace of the matrix $\boldsymbol{I}_z$ is 0, so $\boldsymbol{I}_z$ cannot be a proper mixed state! By comparing $\boldsymbol{I}_z$ with Eqn 8.30 the cause of the problem because obvious: in the case of $\boldsymbol{I}_z$ one of the "probabilities" in the linear combination is negative.

Fortunately this doesn't matter at all. Although $\boldsymbol{I}_z$ is not a proper density matrix it can be used in all calculations as if it were one. The easiest way to see this is to follow the approach discussed beneath Eqn 8.32: we can replace $\boldsymbol{I}_z$ (which is not a proper density matrix) by $\tfrac{1}{2}\boldsymbol{1}+\boldsymbol{I}_z$ (which is), but since the $\tfrac{1}{2}\boldsymbol{1}$ part has no effect on any observable terms it can be dropped with complete safety.

Exercise 8.6

Confirm the results of Eqns 8.37 and 8.38.

This is just an exercise in matrix multiplication. We have

$$
\begin{aligned}
\boldsymbol{\rho}(t) &= \mathrm{e}^{-\mathrm{i}\omega_1 t \boldsymbol{I}_x}\boldsymbol{I}_z\mathrm{e}^{+\mathrm{i}\omega_1 t \boldsymbol{I}_x} \\
&= \begin{pmatrix} \cos(\tfrac{1}{2}\omega_1 t) & -\mathrm{i}\sin(\tfrac{1}{2}\omega_1 t) \\ -\mathrm{i}\sin(\tfrac{1}{2}\omega_1 t) & \cos(\tfrac{1}{2}\omega_1 t) \end{pmatrix}\begin{pmatrix} \tfrac{1}{2} & 0 \\ 0 & -\tfrac{1}{2} \end{pmatrix}\begin{pmatrix} \cos(\tfrac{1}{2}\omega_1 t) & +\mathrm{i}\sin(\tfrac{1}{2}\omega_1 t) \\ +\mathrm{i}\sin(\tfrac{1}{2}\omega_1 t) & \cos(\tfrac{1}{2}\omega_1 t) \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} \cos(\tfrac{1}{2}\omega_1 t) & -\mathrm{i}\sin(\tfrac{1}{2}\omega_1 t) \\ -\mathrm{i}\sin(\tfrac{1}{2}\omega_1 t) & \cos(\tfrac{1}{2}\omega_1 t) \end{pmatrix}\begin{pmatrix} \cos(\tfrac{1}{2}\omega_1 t) & +\mathrm{i}\sin(\tfrac{1}{2}\omega_1 t) \\ -\mathrm{i}\sin(\tfrac{1}{2}\omega_1 t) & -\cos(\tfrac{1}{2}\omega_1 t) \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} \cos^2(\tfrac{1}{2}\omega_1 t)-\sin^2(\tfrac{1}{2}\omega_1 t) & 2\mathrm{i}\cos(\tfrac{1}{2}\omega_1 t)\sin(\tfrac{1}{2}\omega_1 t) \\ -2\mathrm{i}\cos(\tfrac{1}{2}\omega_1 t)\sin(\tfrac{1}{2}\omega_1 t) & \sin^2(\tfrac{1}{2}\omega_1 t)-\cos^2(\tfrac{1}{2}\omega_1 t) \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} \cos(\omega_1 t) & \mathrm{i}\sin(\omega_1 t) \\ -\mathrm{i}\sin(\omega_1 t) & -\cos(\omega_1 t) \end{pmatrix}
\end{aligned}
$$

as required. Then

$$
\begin{aligned}
\langle \hat{I}_x \rangle &= \mathrm{Tr}\ \boldsymbol{\rho}\boldsymbol{I}_x \\
&= \tfrac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} \cos\omega_1 t & \mathrm{i}\sin\omega_1 t \\ -\mathrm{i}\sin\omega_1 t & -\cos\omega_1 t \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right] \\
&= \tfrac{1}{4}\mathrm{Tr}\begin{pmatrix} \mathrm{i}\sin\omega_1 t & \cos\omega_1 t \\ -\cos\omega_1 t & -\mathrm{i}\sin\omega_1 t \end{pmatrix} \\
&= 0
\end{aligned}
$$

where for simplicity we have moved all the factors of $\tfrac{1}{2}$ to the front. Similarly

$$
\begin{aligned}
\langle \hat{I}_y \rangle &= \mathrm{Tr}\ \boldsymbol{\rho I_y} \\
&= \tfrac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} \cos\omega_1 t & \mathrm{i}\sin\omega_1 t \\ -\mathrm{i}\sin\omega_1 t & -\cos\omega_1 t \end{pmatrix}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}\right] \\
&= \tfrac{1}{4}\mathrm{Tr}\begin{pmatrix} -\sin\omega_1 t & -\mathrm{i}\cos\omega_1 t \\ -\mathrm{i}\cos\omega_1 t & -\sin\omega_1 t \end{pmatrix} \\
&= \tfrac{1}{4}\ -2\sin\omega_1 t \\
&= -\tfrac{1}{2}\sin\omega_1 t
\end{aligned}
$$

and

$$
\begin{aligned}
\langle \hat{I}_z \rangle &= \mathrm{Tr}\ \boldsymbol{\rho I_z} \\
&= \tfrac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} \cos\omega_1 t & \mathrm{i}\sin\omega_1 t \\ -\mathrm{i}\sin\omega_1 t & -\cos\omega_1 t \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right] \\
&= \tfrac{1}{4}\mathrm{Tr}\begin{pmatrix} \cos\omega_1 t & -\mathrm{i}\sin\omega_1 t \\ -\mathrm{i}\sin\omega_1 t & \cos\omega_1 t \end{pmatrix} \\
&= \tfrac{1}{2}\cos\omega_1 t.
\end{aligned}
$$

Exercise 8.7

Repeat these calculations to find the evolution of $\boldsymbol{I_z}$ under $\boldsymbol{H} = \omega_1 \boldsymbol{I_y}$.

The calculation is very similar to the previous one, and the critical matrix, describing evolution under $\omega_1 \boldsymbol{I_y}$, was worked out in Exercise 7.7. The adjoint is easy to calculate, and then it is a simple matter of multiplying matrices. First we find the density matrix

$$
\begin{aligned}
\boldsymbol{\rho}(t) &= \mathrm{e}^{-\mathrm{i}\omega_1 t \boldsymbol{I_y}} \boldsymbol{I_z} \mathrm{e}^{+\mathrm{i}\omega_1 t \boldsymbol{I_y}} \\
&= \begin{pmatrix} \cos(\tfrac{1}{2}\omega_1 t) & -\sin(\tfrac{1}{2}\omega_1 t) \\ \sin(\tfrac{1}{2}\omega_1 t) & \cos(\tfrac{1}{2}\omega_1 t) \end{pmatrix}\begin{pmatrix} \tfrac{1}{2} & 0 \\ 0 & -\tfrac{1}{2} \end{pmatrix}\begin{pmatrix} \cos(\tfrac{1}{2}\omega_1 t) & \sin(\tfrac{1}{2}\omega_1 t) \\ -\sin(\tfrac{1}{2}\omega_1 t) & \cos(\tfrac{1}{2}\omega_1 t) \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} \cos(\tfrac{1}{2}\omega_1 t) & -\sin(\tfrac{1}{2}\omega_1 t) \\ \sin(\tfrac{1}{2}\omega_1 t) & \cos(\tfrac{1}{2}\omega_1 t) \end{pmatrix}\begin{pmatrix} \cos(\tfrac{1}{2}\omega_1 t) & \sin(\tfrac{1}{2}\omega_1 t) \\ \sin(\tfrac{1}{2}\omega_1 t) & -\cos(\tfrac{1}{2}\omega_1 t) \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} \cos^2(\tfrac{1}{2}\omega_1 t) - \sin^2(\tfrac{1}{2}\omega_1 t) & 2\cos(\tfrac{1}{2}\omega_1 t)\sin(\tfrac{1}{2}\omega_1 t) \\ 2\cos(\tfrac{1}{2}\omega_1 t)\sin(\tfrac{1}{2}\omega_1 t) & \sin^2(\tfrac{1}{2}\omega_1 t) - \cos^2(\tfrac{1}{2}\omega_1 t) \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} \cos(\omega_1 t) & \sin(\omega_1 t) \\ \sin(\omega_1 t) & -\cos(\omega_1 t) \end{pmatrix}
\end{aligned}
$$

and then we calculate expectation values

$$\begin{aligned}
\langle \hat{I}_x \rangle &= \mathrm{Tr}\ \boldsymbol{\rho I}_x \\
&= \tfrac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} \cos\omega_1 t & \sin\omega_1 t \\ \sin\omega_1 t & -\cos\omega_1 t \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right] \\
&= \tfrac{1}{4}\mathrm{Tr}\begin{pmatrix} \sin\omega_1 t & \cos\omega_1 t \\ -\cos\omega_1 t & \sin\omega_1 t \end{pmatrix} \\
&= \tfrac{1}{2}\sin\omega_1 t
\end{aligned}$$

$$\begin{aligned}
\langle \hat{I}_y \rangle &= \mathrm{Tr}\ \boldsymbol{\rho I}_y \\
&= \tfrac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} \cos\omega_1 t & \sin\omega_1 t \\ \sin\omega_1 t & -\cos\omega_1 t \end{pmatrix}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}\right] \\
&= \tfrac{1}{4}\mathrm{Tr}\begin{pmatrix} \mathrm{i}\sin\omega_1 t & -\mathrm{i}\cos\omega_1 t \\ -\mathrm{i}\cos\omega_1 t & -\mathrm{i}\sin\omega_1 t \end{pmatrix} \\
&= 0
\end{aligned}$$

$$\begin{aligned}
\langle \hat{I}_z \rangle &= \mathrm{Tr}\ \boldsymbol{\rho I}_z \\
&= \tfrac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} \cos\omega_1 t & \sin\omega_1 t \\ \sin\omega_1 t & -\cos\omega_1 t \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right] \\
&= \tfrac{1}{4}\mathrm{Tr}\begin{pmatrix} \cos\omega_1 t & -\sin\omega_1 t \\ \sin\omega_1 t & \cos\omega_1 t \end{pmatrix} \\
&= \tfrac{1}{2}\cos\omega_1 t.
\end{aligned}$$

Exercise 8.8

Use similar calculations to calculate the result of the spin echo shown in Fig. 1.6 applied to an isolated nucleus with offset frequency Ω. Determine the density matrix at each point in the spin echo sequence and interpret it as a linear combination of $\boldsymbol{I}_x$, $\boldsymbol{I}_y$ and $\boldsymbol{I}_z$.

This is just an extension of the same sort of calculation as above, but by now the number of matrices involved is becoming so large that it is sensible to pause at each step in the process and consider the result.

The first stage is a 90°_x pulse applied to the initial state $\boldsymbol{I}_z$. The evolution under an *x*-pulse was calculated in Exercise 8.6, and all we need to do is set $\omega_1 t = \pi/2$. Thus

$$\begin{aligned}
\boldsymbol{\rho}_1 &= \frac{1}{2}\begin{pmatrix} \cos\pi/2 & \mathrm{i}\sin\pi/2 \\ -\mathrm{i}\sin\pi/2 & \cos\pi/2 \end{pmatrix} \quad \tau \\
&= \frac{1}{2}\begin{pmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{pmatrix}
\end{aligned}$$

Here it fairly easy to recognise $-\boldsymbol{I}_y$ by inspection, but this could instead be determined by evaluating the expectation values

$$\langle \hat{I}_x \rangle = 0 \qquad \langle \hat{I}_y \rangle = -\tfrac{1}{2} \qquad \langle \hat{I}_z \rangle = 0$$

and then doubling them to get

$$\boldsymbol{\rho}_1 = -\boldsymbol{I}_y \,.$$

Now we evolve the state under $\boldsymbol{H} = \Omega \boldsymbol{I}_z$ (we are working in a rotating frame, and so ω_0 must be replaced by Ω). After evolution for a time τ the density matrix is

$$\begin{aligned}
\boldsymbol{\rho}_2 &= \mathrm{e}^{-\mathrm{i}\Omega\tau \boldsymbol{I}_z} \boldsymbol{\rho}_1 \mathrm{e}^{+\mathrm{i}\Omega\tau \boldsymbol{I}_z} \\
&= \frac{1}{2}\begin{pmatrix} \mathrm{e}^{-\mathrm{i}\Omega\tau/2} & 0 \\ 0 & \mathrm{e}^{\mathrm{i}\Omega\tau/2} \end{pmatrix} \begin{pmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{pmatrix} \begin{pmatrix} \mathrm{e}^{\mathrm{i}\Omega\tau/2} & 0 \\ 0 & \mathrm{e}^{-\mathrm{i}\Omega\tau/2} \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} \mathrm{e}^{-\mathrm{i}\Omega\tau/2} & 0 \\ 0 & \mathrm{e}^{\mathrm{i}\Omega\tau/2} \end{pmatrix} \begin{pmatrix} 0 & \mathrm{i}\mathrm{e}^{-\mathrm{i}\Omega\tau/2} \\ -\mathrm{i}\mathrm{e}^{\mathrm{i}\Omega\tau/2} & 0 \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} 0 & \mathrm{i}\mathrm{e}^{-\mathrm{i}\Omega\tau} \\ -\mathrm{i}\mathrm{e}^{\mathrm{i}\Omega\tau} & 0 \end{pmatrix}
\end{aligned}$$

Now calculate expectation values:

$$\begin{aligned}
\langle \hat{I}_x \rangle &= \mathrm{Tr}\ \boldsymbol{\rho}_2 \boldsymbol{I}_x \\
&= \tfrac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} 0 & \mathrm{i}\mathrm{e}^{-\mathrm{i}\Omega\tau} \\ -\mathrm{i}\mathrm{e}^{\mathrm{i}\Omega\tau} & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right] \\
&= \tfrac{1}{4}\mathrm{Tr}\begin{pmatrix} \mathrm{i}\mathrm{e}^{-\mathrm{i}\Omega\tau} & 0 \\ 0 & -\mathrm{i}\mathrm{e}^{\mathrm{i}\Omega\tau} \end{pmatrix} \\
&= \tfrac{1}{2}\sin\Omega\tau
\end{aligned}$$

$$\begin{aligned}
\langle \hat{I}_y \rangle &= \mathrm{Tr}\ \boldsymbol{\rho}_2 \boldsymbol{I}_y \\
&= \tfrac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} 0 & \mathrm{i}\mathrm{e}^{-\mathrm{i}\Omega\tau} \\ -\mathrm{i}\mathrm{e}^{\mathrm{i}\Omega\tau} & 0 \end{pmatrix} \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}\right] \\
&= \tfrac{1}{4}\mathrm{Tr}\begin{pmatrix} -\mathrm{e}^{-\mathrm{i}\Omega\tau} & 0 \\ 0 & -\mathrm{e}^{\mathrm{i}\Omega\tau} \end{pmatrix} \\
&= -\tfrac{1}{2}\cos\Omega\tau
\end{aligned}$$

$$\begin{aligned}
\langle \hat{I}_z \rangle &= \mathrm{Tr}\ \boldsymbol{\rho}_2 \boldsymbol{I}_z \\
&= \tfrac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} 0 & \mathrm{i}e^{-\mathrm{i}\Omega\tau} \\ -\mathrm{i}e^{\mathrm{i}\Omega\tau} & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right] \\
&= \tfrac{1}{4}\mathrm{Tr}\begin{pmatrix} 0 & -\mathrm{i}e^{-\mathrm{i}\Omega\tau} \\ -\mathrm{i}e^{\mathrm{i}\Omega\tau} & 0 \end{pmatrix} \\
&= 0.
\end{aligned}$$

Doubling these coefficients we see that

$$\boldsymbol{\rho}_2 = \sin\,\Omega\tau\ \boldsymbol{I}_x - \cos\,\Omega\tau\ \boldsymbol{I}_y .$$

Next we have the 180°_y pulse. The effect of evolution under $\omega_1 \boldsymbol{I}_y$ was calculated in Exercise 7.7, and setting $\omega_1 t = \pi$ gives

$$e^{-\mathrm{i}\pi \boldsymbol{I}_y} = \begin{pmatrix} \cos\,\pi/2 & -\sin\,\pi/2 \\ \sin\,\pi/2 & \cos\,\pi/2 \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}.$$

So

$$\begin{aligned}
\boldsymbol{\rho}_3 &= e^{-\mathrm{i}\pi \boldsymbol{I}_y}\boldsymbol{\rho}_2 e^{+\mathrm{i}\pi \boldsymbol{I}_y} \\
&= \frac{1}{2}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & \mathrm{i}e^{-\mathrm{i}\Omega\tau} \\ -\mathrm{i}e^{\mathrm{i}\Omega\tau} & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} -\mathrm{i}e^{-\mathrm{i}\Omega\tau} & 0 \\ 0 & -\mathrm{i}e^{\mathrm{i}\Omega\tau} \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} 0 & \mathrm{i}e^{\mathrm{i}\Omega\tau} \\ -\mathrm{i}e^{-\mathrm{i}\Omega\tau} & 0 \end{pmatrix}
\end{aligned}$$

The expectation values are now

$$\langle \hat{I}_x \rangle = -\tfrac{1}{2}\sin\,\Omega\tau \qquad \langle \hat{I}_y \rangle = -\tfrac{1}{2}\cos\,\Omega\tau \qquad \langle \hat{I}_z \rangle = 0$$

so

$$\boldsymbol{\rho}_3 = -\sin\,\Omega\tau\ \boldsymbol{I}_x - \cos\,\Omega\tau\ \boldsymbol{I}_y .$$

Finally we have the second period of free precession, leading to the final density matrix

$$
\begin{aligned}
\boldsymbol{\rho}_4 &= \mathrm{e}^{-\mathrm{i}\Omega\tau \boldsymbol{I}_z}\boldsymbol{\rho}_3\mathrm{e}^{+\mathrm{i}\Omega\tau \boldsymbol{I}_z} \\
&= \frac{1}{2}\begin{pmatrix} \mathrm{e}^{-\mathrm{i}\Omega\tau/2} & 0 \\ 0 & \mathrm{e}^{\mathrm{i}\Omega\tau/2} \end{pmatrix}\begin{pmatrix} 0 & \mathrm{i}\mathrm{e}^{\mathrm{i}\Omega\tau} \\ -\mathrm{i}\mathrm{e}^{-\mathrm{i}\Omega\tau} & 0 \end{pmatrix}\begin{pmatrix} \mathrm{e}^{\mathrm{i}\Omega\tau/2} & 0 \\ 0 & \mathrm{e}^{-\mathrm{i}\Omega\tau/2} \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} \mathrm{e}^{-\mathrm{i}\Omega\tau/2} & 0 \\ 0 & \mathrm{e}^{\mathrm{i}\Omega\tau/2} \end{pmatrix}\begin{pmatrix} 0 & \mathrm{i}\mathrm{e}^{\mathrm{i}\Omega\tau/2} \\ -\mathrm{i}\mathrm{e}^{-\mathrm{i}\Omega\tau/2} & 0 \end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{pmatrix}
\end{aligned}
$$

or

$$\boldsymbol{\rho}_4 = -\boldsymbol{I}_y \,.$$

Doing all these calculations "by hand" is a lot of work, and it is easy to make a mistake. Computer assistance can be extremely helpful in checking calculations like these.

Exercise 8.9

Repeat this calculation using the methods in Section 8.6.

To repeat the calculation using the methods in Section 8.6 it is necessary to consider the commutators between the initial state and the Hamiltonian at each stage.

We start from $\boldsymbol{\rho}_0 = \boldsymbol{I}_z$ and apply the Hamiltonian $\boldsymbol{H}_1 = \omega_1 \boldsymbol{I}_x$. The first commutators is

$$\boldsymbol{A}_1, \boldsymbol{B}_1 = \boldsymbol{I}_z, \boldsymbol{I}_x = \mathrm{i}\boldsymbol{I}_y = \mathrm{i}\boldsymbol{C}_1 \,.$$

(here $b_1 = \omega_1$), and so we must check

$$\boldsymbol{B}_1, \boldsymbol{C}_1 = \left[\boldsymbol{I}_x, \boldsymbol{I}_y\right] = \mathrm{i}\boldsymbol{I}_z = \mathrm{i}\boldsymbol{A}_1 \,.$$

Since the commutation relations fit the pattern in Eqn 8.46 we can apply the solution in Eqn 8.47 to get

$$\boldsymbol{\rho}_1(t) = \boldsymbol{A}_1 \cos b_1 t - \boldsymbol{C}_1 \sin b_1 t = \boldsymbol{I}_z \cos\omega_1 t - \boldsymbol{I}_y \sin\omega_1 t \,.$$

and setting $\omega_1 t = \pi/2$ gives

$$\boldsymbol{\rho}_1 = -\boldsymbol{I}_y \,.$$

During the second time period $\boldsymbol{H}_2 = \Omega \boldsymbol{I}_z$ and the commutators are now

$$\boldsymbol{A}_2, \boldsymbol{B}_2 = \left[-\boldsymbol{I}_y, \boldsymbol{I}_z\right] = -\left[\boldsymbol{I}_y, \boldsymbol{I}_z\right] = -\mathrm{i}\boldsymbol{I}_x = \mathrm{i}\boldsymbol{C}_2 \,,$$

$$\boldsymbol{B}_2, \boldsymbol{C}_2 = \boldsymbol{I}_z, -\boldsymbol{I}_x = -\boldsymbol{I}_z, \boldsymbol{I}_x = -\mathrm{i}\boldsymbol{I}_y = \mathrm{i}\boldsymbol{A}_2 \,.$$

Once again these fit the pattern so

$$\boldsymbol{\rho}_2(\tau) = \boldsymbol{A}_2 \cos b_2 t - \boldsymbol{C}_2 \sin b_2 t = -\boldsymbol{I}_y \cos \Omega t + \boldsymbol{I}_x \sin \Omega t \;.$$

During the 180° pulse $\boldsymbol{H}_3 = \omega_1 \boldsymbol{I}_y$ so $\boldsymbol{B}_3 = \boldsymbol{I}_y$ and $b_3 = \omega_1$. The calculation is apparently made complicated by the form of the initial state

$$\boldsymbol{A}_3 = \boldsymbol{\rho}_2 = -\boldsymbol{I}_y \cos \Omega t + \boldsymbol{I}_x \sin \Omega t \,,$$

as the commutators rules are no longer obeyed. Performing the naïve calculation gives

$$\begin{aligned} \boldsymbol{A}_3, \boldsymbol{B}_3 &= \left[-\boldsymbol{I}_y \cos \Omega t + \boldsymbol{I}_x \sin \Omega t, \boldsymbol{I}_y\right] \\ &= -\left[\boldsymbol{I}_y, \boldsymbol{I}_y\right] \cos \Omega t + \left[\boldsymbol{I}_x, \boldsymbol{I}_y\right] \sin \Omega t \\ &= \mathrm{i}\boldsymbol{I}_z \sin \Omega t \\ &= \mathrm{i}\boldsymbol{C}_3 \end{aligned} \,,$$

and then

$$\begin{aligned} \boldsymbol{B}_3, \boldsymbol{C}_3 &= \left[\boldsymbol{I}_y, \boldsymbol{I}_z\right] \sin \Omega t \\ &= \mathrm{i}\boldsymbol{I}_x \sin \Omega t \\ &\neq \mathrm{i}\boldsymbol{A}_3 \end{aligned}$$

which does not fit the pattern of Eqn 8.46. However, closer inspection indicates that the second commutators has produced the second of the two parts making up the initial state, while removing the first part.

The right approach here is to note that because the Liouville–von Neumann equation is linear we can consider the two parts of $\boldsymbol{A}_3$ separately. The first part, which is proportional to $\boldsymbol{I}_y$, commutes with the Hamiltonian, and so does not evolve. The second part does not commute with the Hamiltonian, but its commutators *do* fit the pattern of Eqn 8.46, and so it evolves in the usual way:

$$\boldsymbol{I}_x \xrightarrow{\omega_1 \boldsymbol{I}_y} \boldsymbol{I}_x \cos \omega_1 t - \boldsymbol{I}_z \sin \omega_1 t \;.$$

Reassembling the two parts with the appropriate weights gives

$$\boldsymbol{\rho}_3(t) = -\boldsymbol{I}_y \cos\Omega t + \boldsymbol{I}_x \sin\Omega t \cos\omega_1 t - \boldsymbol{I}_z \sin\Omega t \sin\omega_1 t$$

and choosing $\omega_1 t = \pi$ leads to the simple result

$$\boldsymbol{\rho}_3 = -\boldsymbol{I}_y \cos\Omega t - \boldsymbol{I}_x \sin\Omega t$$

For the last stage it is again convenient to divide up the initial state into two parts, each of which obeys the appropriate commutation relations, and so:

$$\begin{aligned} &\boldsymbol{I}_y \xrightarrow{\Omega \boldsymbol{I}_z} \boldsymbol{I}_y \cos\Omega\tau - \boldsymbol{I}_x \sin\Omega\tau \\ &\boldsymbol{I}_x \xrightarrow{\Omega \boldsymbol{I}_z} \boldsymbol{I}_x \cos\Omega\tau + \boldsymbol{I}_y \sin\Omega\tau \end{aligned}$$

Thus reassembling everything gives

$$\begin{aligned} \boldsymbol{\rho}_4 &= - \ \boldsymbol{I}_y \cos\Omega\tau - \boldsymbol{I}_x \sin\Omega\tau \ \cos\Omega t - \ \boldsymbol{I}_x \cos\Omega\tau + \boldsymbol{I}_y \sin\Omega\tau \ \sin\Omega t \\ &= -\boldsymbol{I}_y \cos^2\Omega\tau + \boldsymbol{I}_x \sin\Omega\tau \cos\Omega t - \boldsymbol{I}_x \cos\Omega t \sin\Omega\tau - \boldsymbol{I}_y \sin^2\Omega\tau \\ &= -\boldsymbol{I}_y \ \cos^2\Omega\tau + \sin^2\Omega\tau \\ &= -\boldsymbol{I}_y \end{aligned}$$

This exercise conveys clearly the irresistible attraction of the product operator formalism, which enables complex calculations to be performed by applying a few simple rules. Commutators can be easily found and checked by examining Table L1, although in practice it is rarely necessarily to do so. Diagrams such as Figures 3.2 and 3.7 indicate important triples of product operators which have the right commutation relationships and so will evolve in a simple way.

Chapter 9

Exercise 9.1

Use direct products to calculate the two-spin operator matrix $\boldsymbol{S}_x$ and show that it acts on the four basis states ($\boldsymbol{\psi}_{\alpha\alpha}$ and so on) as expected.

$$\boldsymbol{S}_x = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} = \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix}.$$

Then

$$\boldsymbol{S}_x \boldsymbol{\psi}_{\alpha\alpha} = \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{1}{2} \\ 0 \\ 0 \end{pmatrix} = \tfrac{1}{2} \boldsymbol{\psi}_{\alpha\beta}$$

$$\boldsymbol{S}_x \boldsymbol{\psi}_{\alpha\beta} = \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \\ 0 \\ 0 \\ 0 \end{pmatrix} = \tfrac{1}{2} \boldsymbol{\psi}_{\alpha\alpha}$$

$$\boldsymbol{S}_x \boldsymbol{\psi}_{\beta\alpha} = \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{2} \end{pmatrix} = \tfrac{1}{2} \boldsymbol{\psi}_{\beta\beta}$$

$$\boldsymbol{S}_x \boldsymbol{\psi}_{\beta\beta} = \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \frac{1}{2} \\ 0 \end{pmatrix} = \tfrac{1}{2} \boldsymbol{\psi}_{\beta\alpha}$$

Exercise 9.2

Confirm that the relationships in Eqns 7.28–7.30 hold for spin S in a two-spin system

We have calculated $\boldsymbol{S}_x$ above, $\boldsymbol{S}_x$ is given in Eqn 9.5, and using direct products

$$\boldsymbol{S}_z = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}.$$

Multiplying matrices gives

$$\boldsymbol{S}_x^2 = \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & \frac{1}{4} & 0 & 0 \\ 0 & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \end{pmatrix} = \tfrac{1}{4}\boldsymbol{1},$$

$$\boldsymbol{S}_x\boldsymbol{S}_y = \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 & -\frac{1}{2}\mathrm{i} & 0 & 0 \\ \frac{1}{2}\mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2}\mathrm{i} \\ 0 & 0 & \frac{1}{2}\mathrm{i} & 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{4}\mathrm{i} & 0 & 0 & 0 \\ 0 & -\frac{1}{4}\mathrm{i} & 0 & 0 \\ 0 & 0 & \frac{1}{4}\mathrm{i} & 0 \\ 0 & 0 & 0 & -\frac{1}{4}\mathrm{i} \end{pmatrix} = \tfrac{1}{2}\mathrm{i}\boldsymbol{S}_z,$$

$$\boldsymbol{S}_y\boldsymbol{S}_x = \begin{pmatrix} 0 & -\frac{1}{2}\mathrm{i} & 0 & 0 \\ \frac{1}{2}\mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2}\mathrm{i} \\ 0 & 0 & \frac{1}{2}\mathrm{i} & 0 \end{pmatrix} \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix} = \begin{pmatrix} -\frac{1}{4}\mathrm{i} & 0 & 0 & 0 \\ 0 & \frac{1}{4}\mathrm{i} & 0 & 0 \\ 0 & 0 & -\frac{1}{4}\mathrm{i} & 0 \\ 0 & 0 & 0 & \frac{1}{4}\mathrm{i} \end{pmatrix} = -\tfrac{1}{2}\mathrm{i}\boldsymbol{S}_z,$$

as required. Finally

$$\left[\boldsymbol{S}_x, \boldsymbol{S}_y\right] = \boldsymbol{S}_x\boldsymbol{S}_y - \boldsymbol{S}_y\boldsymbol{S}_x = \tfrac{1}{2}\mathrm{i}\boldsymbol{S}_z - \ -\tfrac{1}{2}\mathrm{i}\boldsymbol{S}_z \ = \mathrm{i}\boldsymbol{S}_z.$$

Exercise 9.3

Use a computer package such as *Mathematica* to calculate the matrix representations of the three-spin operators in Section 4.4.

The simplest approach is to use the inbuilt function `KroneckerProduct` which can multiply any number of matrices together, and the multiply the result by 4.

In[1]:=
```
Ax = {{0, 1 / 2}, {1 / 2, 0}};
Ay = {{0, -1 / 2 I}, {1 / 2 I, 0}}; Az = {{1 / 2, 0}, {0, -1 / 2}};
```

In[3]:=
```
MatrixForm[4 * KroneckerProduct[Ax, Az, Az]]
```

Out[3]//MatrixForm=

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 \end{pmatrix}$$

In[4]:=
```
MatrixForm[4 * KroneckerProduct[Ax, Ax, Az]]
```

Out[4]//MatrixForm=

$$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} \\ 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

In[5]:=
```
MatrixForm[4 * KroneckerProduct[Ax, Ax, Ax]]
```

Out[5]//MatrixForm=

$$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

In[6]:=
```
MatrixForm[4 * KroneckerProduct[Az, Az, Az]]
```

Out[6]//MatrixForm=

$$\begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}$$

Exercise 9.4

Repeat the calculations in Eqn 9.16–9.20 for a 90°_y pulse.

The propagator for a single spin 90°_y pulse can be obtained from the results of Exercise 7.7 by setting $\omega_1 t = \pi/2$ to get. Then following Eqn 9.18 gives

$$\mathrm{e}^{-\mathrm{i}(\pi/2)\boldsymbol{F}_y} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \otimes \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & 1 & 1 \end{pmatrix}$$

and the adjoint is easily found. Then the density matrix after the pulse is given by

$$\begin{aligned} \mathrm{e}^{-\mathrm{i}(\pi/2)\boldsymbol{F}_y}\boldsymbol{F}_z\mathrm{e}^{\mathrm{i}(\pi/2)\boldsymbol{F}_y} &= \frac{1}{2}\begin{pmatrix} 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & 1 & 1 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}\frac{1}{2}\begin{pmatrix} 1 & 1 & 1 & 1 \\ -1 & 1 & -1 & 1 \\ -1 & -1 & 1 & 1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \\ &= \frac{1}{4}\begin{pmatrix} 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & 1 & 1 \end{pmatrix}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 1 & 1 & -1 \end{pmatrix} \\ &= \frac{1}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} \\ &= \boldsymbol{F}_x \end{aligned}$$

where $\boldsymbol{F}_x = \boldsymbol{I}_x + \boldsymbol{S}_x$,and so on, and matrix forms have been taken from Appendix I.

Exercise 9.5

Use a computer package such as *Mathematica* to repeat the double spin echo calculations in Section 9.6. What happens if the 180° pulses are applied with phases of $+x$ and $-x$? How about $+y$ and $-y$?

These calculations are fairly straightforward:

```
Ax = {{0, 1 / 2}, {1 / 2, 0}};
Ay = {{0, -1 / 2 I}, {1 / 2 I, 0}};
Az = {{1 / 2, 0}, {0, -1 / 2}};
ONE = {{1, 0}, {0, 1}};
Ix = KroneckerProduct[Ax, ONE];
Iy = KroneckerProduct[Ay, ONE];
Iz = KroneckerProduct[Az, ONE];
Sx = KroneckerProduct[ONE, Ax];
Sy = KroneckerProduct[ONE, Ay];
Sz = KroneckerProduct[ONE, Az];
Fx = Ix + Sx;
Fy = Iy + Sy;
Fz = Iz + Sz;
In[13]:= H = ΩI * Iz + ΩS * Sz + π * J * 2 * Iz.Sz;
U = MatrixExp[-I * H * τ];
In[15]:= Upx = MatrixExp[-I * π * Fx];
Umx = MatrixExp[-I * π * -Fx];
Upy = MatrixExp[-I * π * Fy];
Umy = MatrixExp[-I * π * -Fy];
In[19]:= MatrixExp[-I * π * J * 2 * Iz.Sz * 4 τ]
Out[19]= {{e^(-2 i J π τ), 0, 0, 0}, {0, e^(2 i J π τ), 0, 0}, {0, 0, e^(2 i J π τ), 0}, {0, 0, 0, e^(-2 i J π τ)}}
In[20]:= U1 = Simplify[U.Upx.U.U.Upx.U]
Out[20]= {{e^(-2 i J π τ), 0, 0, 0}, {0, e^(2 i J π τ), 0, 0}, {0, 0, e^(2 i J π τ), 0}, {0, 0, 0, e^(-2 i J π τ)}}
In[21]:= U2 = Simplify[U.Umx.U.U.Upx.U]
Out[21]= {{e^(-2 i J π τ), 0, 0, 0}, {0, e^(2 i J π τ), 0, 0}, {0, 0, e^(2 i J π τ), 0}, {0, 0, 0, e^(-2 i J π τ)}}
In[22]:= U3 = Simplify[U.Umy.U.U.Upy.U]
Out[22]= {{e^(-2 i J π τ), 0, 0, 0}, {0, e^(2 i J π τ), 0, 0}, {0, 0, e^(2 i J π τ), 0}, {0, 0, 0, e^(-2 i J π τ)}}
```

Note that the propagator is the same in all cases: it does not matter what phases are used for the two 180° pulses as long as the phases are either identical or differ by 180°. If, however, 180°_x and 180°_y pulses are used then the evolution will not be quite the same.

Exercise 9.6

Use the methods in Section 9.6 to calculate the effects of a spin echo in a heteronuclear spin system. Devise pulse sequences to produce the three different average Hamiltonians $\Omega_I \boldsymbol{I}_z$, $\Omega_S \boldsymbol{S}_z$ and $\pi J 2\boldsymbol{I}_z\boldsymbol{S}_z$.

Start with a simple spin echo where the 180° pulse is only applied to spin I. The combined propagator is

$$\boldsymbol{U} = \mathrm{e}^{-\mathrm{i}\tau\,\Omega_I \boldsymbol{I}_z + \Omega_S \boldsymbol{S}_z + \pi J 2\boldsymbol{I}_z\boldsymbol{S}_z}\ \mathrm{e}^{-\mathrm{i}\pi \boldsymbol{I}_x}\ \mathrm{e}^{-\mathrm{i}\tau\,\Omega_I \boldsymbol{I}_z + \Omega_S \boldsymbol{S}_z + \pi J 2\boldsymbol{I}_z\boldsymbol{S}_z}$$

and since the three parts of the free precession Hamiltonian all commute with each other and the S-spin terms commutes with the I-spin pulse this can be reordered to give

$$\boldsymbol{U} = \mathrm{e}^{-\mathrm{i}\tau\pi J 2\boldsymbol{I}_z\boldsymbol{S}_z}\,\mathrm{e}^{-\mathrm{i}\tau\Omega_I\boldsymbol{I}_z}\,\mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}\tau\Omega_I\boldsymbol{I}_z}\,\mathrm{e}^{-\mathrm{i}\tau\pi J 2\boldsymbol{I}_z\boldsymbol{S}_z}\,\mathrm{e}^{-\mathrm{i}\tau\Omega_S\boldsymbol{S}_z}\,\mathrm{e}^{-\mathrm{i}\tau\Omega_S\boldsymbol{S}_z}\,.$$

Using Eqn 9.33 we know that

$$\mathrm{e}^{-\mathrm{i}\tau\Omega_I\boldsymbol{I}_z}\,\mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}\tau\Omega_I\boldsymbol{I}_z} = \mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}$$

and the last two terms can be combined to get

$$\boldsymbol{U} = \mathrm{e}^{-\mathrm{i}\tau\pi J 2\boldsymbol{I}_z\boldsymbol{S}_z}\,\mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}\tau\pi J 2\boldsymbol{I}_z\boldsymbol{S}_z}\,\mathrm{e}^{-\mathrm{i}2\tau\Omega_S\boldsymbol{S}_z}\,.$$

The last stage of the simplification requires two-spin matrices

$$\mathrm{e}^{-\mathrm{i}\tau\pi J 2\boldsymbol{I}_z\boldsymbol{S}_z}\,\mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}\tau\pi J 2\boldsymbol{I}_z\boldsymbol{S}_z} = \begin{pmatrix} \mathrm{e}^{-\mathrm{i}\varphi} & 0 & 0 & 0 \\ 0 & \mathrm{e}^{\mathrm{i}\varphi} & 0 & 0 \\ 0 & 0 & \mathrm{e}^{\mathrm{i}\varphi} & 0 \\ 0 & 0 & 0 & \mathrm{e}^{-\mathrm{i}\varphi} \end{pmatrix} \begin{pmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ -\mathrm{i} & 0 & 0 & 0 \\ 0 & -\mathrm{i} & 0 & 0 \end{pmatrix} \begin{pmatrix} \mathrm{e}^{-\mathrm{i}\varphi} & 0 & 0 & 0 \\ 0 & \mathrm{e}^{\mathrm{i}\varphi} & 0 & 0 \\ 0 & 0 & \mathrm{e}^{\mathrm{i}\varphi} & 0 \\ 0 & 0 & 0 & \mathrm{e}^{-\mathrm{i}\varphi} \end{pmatrix}$$

where

$$\varphi = \mathrm{i}\tau\pi J/2$$

is introduced as a convenient shorthand. Multiplying everything out gives

$$\mathrm{e}^{-\mathrm{i}\tau\pi J 2\boldsymbol{I}_z\boldsymbol{S}_z}\,\mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}\tau\pi J 2\boldsymbol{I}_z\boldsymbol{S}_z} = \begin{pmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ -\mathrm{i} & 0 & 0 & 0 \\ 0 & -\mathrm{i} & 0 & 0 \end{pmatrix} = \mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}$$

so the overall propagator for the single echo is

$$\boldsymbol{U} = \mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}2\tau\Omega_S\boldsymbol{S}_z}\,.$$

Finally, the propagator for the double spin echo is easily obtained

$$\begin{aligned} \boldsymbol{U} &= \mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}2\tau\Omega_S\boldsymbol{S}_z}\,\mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}2\tau\Omega_S\boldsymbol{S}_z} \\ &= \mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}2\tau\Omega_S\boldsymbol{S}_z}\,\mathrm{e}^{-\mathrm{i}2\tau\Omega_S\boldsymbol{S}_z} \\ &= \mathrm{e}^{-\mathrm{i}2\pi\boldsymbol{I}_x}\,\mathrm{e}^{-\mathrm{i}4\tau\Omega_S\boldsymbol{S}_z} \\ &= -\mathrm{e}^{-\mathrm{i}4\tau\Omega_S\boldsymbol{S}_z} \end{aligned}\,.$$

In this case a minus sign is seen from the spinor behaviour of the 360°_x rotation, but this minus sign can be safely ignored because it will cancel with a corresponding minus sign in $\boldsymbol{U}^\dagger$ (see Exercise 8.3). Thus, up to an irrelevant minus sign the double spin echo is equivalent to evolution under the average Hamiltonian

$\boldsymbol{H}_{av} = \Omega_S \boldsymbol{S}_z$. As before it is nescessary to use a double spin echo to remove the direct effects of the 180° pulse, although in many NMR experiments these effects are not critical and a single spin echo is sufficient.

The average Hamiltonian $\boldsymbol{H}_{av} = \Omega_I \boldsymbol{I}_z$ can be created in very much the same way by applying the 180° pulses to spin S instead of spin I. Finally the pure coupling Hamiltonian can be achieved by applying the 180° pulses to both spins, imitating the homonuclear case.

Exercise 9.7

Repeat the calculations in Eqn 9.40 for the other three product operators involved in two-spin multiple quantum coherences.

The four two-spin product operators involved in multiple quantum coherence are given in section 4.3 as $2I_xS_x$, $2I_xS_y$, $2I_yS_x$, and $2I_yS_y$, and we need to find the commutators of each of these terms with $2I_zS_z$. The calculation for the second term is shown in Eqn 9.40, and the other three are done in exactly the same way:

$$\begin{aligned}
\boldsymbol{I}_x\boldsymbol{S}_x,\boldsymbol{I}_z\boldsymbol{S}_z &= \boldsymbol{I}_x\boldsymbol{S}_x\boldsymbol{I}_z\boldsymbol{S}_z - \boldsymbol{I}_z\boldsymbol{S}_z\boldsymbol{I}_x\boldsymbol{S}_x \\
&= \boldsymbol{I}_x\boldsymbol{I}_z\boldsymbol{S}_x\boldsymbol{S}_z - \boldsymbol{I}_z\boldsymbol{I}_x\boldsymbol{S}_z\boldsymbol{S}_x \\
&= \;-\tfrac{1}{2}\mathrm{i}\boldsymbol{I}_y \quad -\tfrac{1}{2}\mathrm{i}\boldsymbol{S}_y \;-\; \tfrac{1}{2}\mathrm{i}\boldsymbol{I}_y \quad \tfrac{1}{2}\mathrm{i}\boldsymbol{S}_y \\
&= -\tfrac{1}{4}\boldsymbol{I}_y\boldsymbol{S}_y + \tfrac{1}{4}\boldsymbol{I}_y\boldsymbol{S}_y \\
&= 0
\end{aligned}$$

$$\begin{aligned}
\left[\boldsymbol{I}_y\boldsymbol{S}_x,\boldsymbol{I}_z\boldsymbol{S}_z\right] &= \boldsymbol{I}_y\boldsymbol{S}_x\boldsymbol{I}_z\boldsymbol{S}_z - \boldsymbol{I}_z\boldsymbol{S}_z\boldsymbol{I}_y\boldsymbol{S}_x \\
&= \boldsymbol{I}_y\boldsymbol{I}_z\boldsymbol{S}_x\boldsymbol{S}_z - \boldsymbol{I}_z\boldsymbol{I}_y\boldsymbol{S}_z\boldsymbol{S}_x \\
&= \;\tfrac{1}{2}\mathrm{i}\boldsymbol{I}_x \quad -\tfrac{1}{2}\mathrm{i}\boldsymbol{S}_y \;-\; -\tfrac{1}{2}\mathrm{i}\boldsymbol{I}_x \quad \tfrac{1}{2}\mathrm{i}\boldsymbol{S}_y \\
&= \tfrac{1}{4}\boldsymbol{I}_x\boldsymbol{S}_y - \tfrac{1}{4}\boldsymbol{I}_x\boldsymbol{S}_y \\
&= 0
\end{aligned}$$

$$\begin{aligned}
\left[\boldsymbol{I}_y\boldsymbol{S}_y,\boldsymbol{I}_z\boldsymbol{S}_z\right] &= \boldsymbol{I}_y\boldsymbol{S}_y\boldsymbol{I}_z\boldsymbol{S}_z - \boldsymbol{I}_z\boldsymbol{S}_z\boldsymbol{I}_y\boldsymbol{S}_y \\
&= \boldsymbol{I}_y\boldsymbol{I}_z\boldsymbol{S}_y\boldsymbol{S}_z - \boldsymbol{I}_z\boldsymbol{I}_y\boldsymbol{S}_z\boldsymbol{S}_y \\
&= \;\tfrac{1}{2}\mathrm{i}\boldsymbol{I}_x \quad \tfrac{1}{2}\mathrm{i}\boldsymbol{S}_x \;-\; -\tfrac{1}{2}\mathrm{i}\boldsymbol{I}_x \quad -\tfrac{1}{2}\mathrm{i}\boldsymbol{S}_x \\
&= -\tfrac{1}{4}\boldsymbol{I}_x\boldsymbol{S}_x + \tfrac{1}{4}\boldsymbol{I}_x\boldsymbol{S}_x \\
&= 0
\end{aligned}$$

Chapter 10

Exercise 10.1

Explain why the eigenvectors of $\boldsymbol{H}_{\mathrm{IS}}$ must have the general form shown in Eqn 10.2, for some value of θ. (Two eigenvectors can be spotted immediately, and then use the fact that the remaining eigenvectors of $\boldsymbol{H}_{\mathrm{IS}}$ will be orthogonal unit vectors.)

The matrix $\boldsymbol{H}_{\mathrm{IS}}$ has the *block diagonal* structure

$$\begin{pmatrix} \boxed{\bullet} & \cdot & \cdot & \cdot \\ \cdot & \bullet & \bullet & \cdot \\ \cdot & \bullet & \bullet & \cdot \\ \cdot & \cdot & \cdot & \boxed{\bullet} \end{pmatrix}$$

where large circles in boxes indicate non-zero elements, and small circles indicate zeroes. Note that the matrix can be partitioned into three boxes, with each box being completely disconnected from the other two, that is all the elements which could connect the boxes are zero. From this it can be immediately deduced that the eigenvectors have the corresponding structures

$$\begin{pmatrix} \boxed{\bullet} \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} \quad \begin{pmatrix} \cdot \\ \bullet \\ \bullet \\ \cdot \end{pmatrix} \quad \begin{pmatrix} \cdot \\ \bullet \\ \bullet \\ \cdot \end{pmatrix} \quad \begin{pmatrix} \cdot \\ \cdot \\ \cdot \\ \boxed{\bullet} \end{pmatrix}$$

The first and last eigenvectors are obvious: they can only contain a single non-zero element and so must be

$$\boldsymbol{\psi}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \boldsymbol{\psi}_4 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

while $\boldsymbol{\psi}_2$ and $\boldsymbol{\psi}_3$ must be linear combinations of $\boldsymbol{\psi}_{\alpha\beta}$ and $\boldsymbol{\psi}_{\beta\alpha}$, and these two vectors must be normalised and orthogonal to each other. Choosing

$$\boldsymbol{\psi}_2 = \begin{pmatrix} 0 \\ \cos\theta \\ \sin\theta \\ 0 \end{pmatrix}$$

(where the value of θ is still to be determined) guarantees that it will be normalised, and this forces the choice

$$\boldsymbol{\psi}_3 = \begin{pmatrix} 0 \\ -\sin\theta \\ \cos\theta \\ 0 \end{pmatrix}$$

to ensure that $\boldsymbol{\psi}_2$ and $\boldsymbol{\psi}_3$ are orthogonal to each other.

But is this choice for $\boldsymbol{\psi}_2$ the only possible form? If we assume that the coefficients must be real, then this is indeed the most general form possible: any set of coefficient for a normalised vector will take this form for some value of θ. But why can we assume that the coefficients must be real? In general they could be complex numbers.

Here we must distinguish between two possibilities. The two coefficients could both be complex *in the same way*, so that we can write the state as

$$\boldsymbol{\psi}_2 = \begin{pmatrix} 0 \\ e^{i\gamma}\cos\theta \\ e^{i\gamma}\sin\theta \\ 0 \end{pmatrix} = e^{i\gamma}\begin{pmatrix} 0 \\ \cos\theta \\ \sin\theta \\ 0 \end{pmatrix}.$$

As shown in Exercise 8.3 such *global phases* have no effect and can be ignored. More importantly the two coefficients could differ by a *relative phase*

$$\boldsymbol{\psi}_2 = \begin{pmatrix} 0 \\ \cos\theta \\ e^{i\phi}\sin\theta \\ 0 \end{pmatrix}$$

and the assumption of real coefficients is equivalent to the assumption that the relative phase ϕ must be either 0 or π.

How might such a restriction arise? The simplest way to see this is to note that $\boldsymbol{H}_{\mathrm{IS}}$ is almost symmetric between the two spins I and S, and so the eigenstates must also be almost symmetric, leading to this restriction.

Exercise 10.2

Verify the eigenvalues listed in Eqn 10.1.

The eigenvalues for the two trivial eigenvectors, λ_1 and λ_4, can just be read off from the corresponding diagonal elements of the matrix $\boldsymbol{H}_{\mathrm{IS}}$. For the other two we have to set up the eigenvalue equation

$$D = \begin{vmatrix} 2\pi\nu + \pi J/2 - \lambda & 0 & 0 & 0 \\ 0 & \pi\delta - \pi J/2 - \lambda & \pi J & 0 \\ 0 & \pi J & -\pi\delta - \pi J/2 - \lambda & 0 \\ 0 & 0 & 0 & -2\pi\nu + \pi J/2 - \lambda \end{vmatrix} = 0$$

and solve it. The determinant D can be partly expanded to give

$$\begin{aligned} D &= \ 2\pi\nu + \pi J/2 - \lambda \begin{vmatrix} \pi\delta - \pi J/2 - \lambda & \pi J & 0 \\ \pi J & -\pi\delta - \pi J/2 - \lambda & 0 \\ 0 & 0 & -2\pi\nu + \pi J/2 - \lambda \end{vmatrix} \\ &= \ 2\pi\nu + \pi J/2 - \lambda \ \ -2\pi\nu + \pi J/2 - \lambda \begin{vmatrix} \pi\delta - \pi J/2 - \lambda & \pi J \\ \pi J & -\pi\delta - \pi J/2 - \lambda \end{vmatrix} \end{aligned}$$

where we have used the block diagonal structure to expand the determinant in an intelligent fashion. The eigenvalues are the four roots of this quartic equation (the four values of λ for which $D = 0$), and two of these values are immediately obvious

$$\lambda_1 = 2\pi\nu + \pi J/2 \qquad \lambda_4 = -2\pi\nu + \pi J/2$$

and the last two are obtained by solving the remaining quadratic equation in λ

$$\begin{aligned} \begin{vmatrix} \pi\delta - \pi J/2 - \lambda & \pi J \\ \pi J & -\pi\delta - \pi J/2 - \lambda \end{vmatrix} &= 0 \\ \pi\delta - \pi J/2 - \lambda \ \ -\pi\delta - \pi J/2 - \lambda \ - \ \pi J^{\ 2} &= 0 \\ \lambda^2 + \lambda\pi J + \pi^2 \ -\delta^2 - 3J^2/4 \ &= 0 \end{aligned}$$

Using the quadratic formula gives

$$\begin{aligned} \lambda &= \frac{-\pi J \pm \pi\sqrt{J^2 - 4 \ -\delta^2 - 3J^2/4}}{2} \\ &= -\tfrac{1}{2}\pi J \pm \tfrac{1}{2}\pi\sqrt{J^2 + 4\delta^2 + 3J^2} \\ &= -\tfrac{1}{2}\pi J \pm \pi\sqrt{J^2 + \delta^2} \\ &= -\tfrac{1}{2}\pi J \pm \pi\varepsilon \end{aligned}$$

as required for λ_2 and λ_3.

Exercise 10.3

Use λ_2 and $|\psi_2\rangle$ to find an expression for $\tan\theta$ and then use double angle formulae to verify the expression for $\tan 2\theta$.

Concentrating on the central block of the matrix gives

$$\begin{pmatrix} \pi\delta - \pi J/2 - \lambda_2 & \pi J \\ \pi J & -\pi\delta - \pi J/2 - \lambda_2 \end{pmatrix}\begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

And multiplying out gives the two equations

$$\begin{aligned} (\pi\delta - \pi J/2 - \lambda_2)\cos\theta + \pi J \sin\theta &= 0 \\ \pi J\cos\theta + (-\pi\delta - \pi J/2 - \lambda_2)\sin\theta &= 0 \end{aligned}$$

These equations are equivalent, so we can concentrate on the top one, which rearranges to

$$\sin\theta = \frac{\lambda_2 + \pi J/2 - \pi\delta}{\pi J}\cos\theta$$

or

$$\tan\theta = \frac{-\pi J/2 + \pi\varepsilon + \pi J/2 - \pi\delta}{\pi J} = \frac{\varepsilon - \delta}{J}.$$

Now the double angle formula for tangents gives

$$\begin{aligned} \tan 2\theta &= \frac{2\tan\theta}{1 - \tan^2\theta} \\ &= \frac{2(\varepsilon - \delta)/J}{1 - (\varepsilon - \delta)^2/J^2} \\ &= \frac{2J(\varepsilon - \delta)}{J^2 - (\varepsilon - \delta)^2} \\ &= \frac{2J(\varepsilon - \delta)}{J^2 - \varepsilon^2 - \delta^2 + 2\varepsilon\delta} \\ &= \frac{2J(\varepsilon - \delta)}{J^2 - J^2 - \delta^2 - \delta^2 + 2\varepsilon\delta} \\ &= \frac{2J(\varepsilon - \delta)}{2\delta(\varepsilon - \delta)} \\ &= J/\delta. \end{aligned}$$

Exercise 10.4

Use a computer package such as *Mathematica* to verify Eqns 10.14 and 10.15 directly.

A possible solution is shown below.

```
In[1]:= Ax = {{0, 1 / 2}, {1 / 2, 0}};
        Ay = {{0, -1 / 2 I}, {1 / 2 I, 0}};
        Az = {{1 / 2, 0}, {0, -1 / 2}};
        ONE = {{1, 0}, {0, 1}};
        Ix = KroneckerProduct[Ax, ONE];
        Iy = KroneckerProduct[Ay, ONE];
        Iz = KroneckerProduct[Az, ONE];
        Sx = KroneckerProduct[ONE, Ax];
        Sy = KroneckerProduct[ONE, Ay];
        Sz = KroneckerProduct[ONE, Az];
        Fx = Ix + Sx;
        Fy = Iy + Sy;
        Fz = Iz + Sz;

In[14]:= H = ΩI * Iz + ΩS * Sz + 2 * π * J * (Ix.Sx + Iy.Sy + Iz.Sz);

In[15]:= ρ = MatrixExp[-I * H * t].MatrixExp[-I * π / 2 * Fx].
            Fz.MatrixExp[I * π / 2 * Fx].MatrixExp[I * H * t];

In[16]:= FID = Simplify[-Tr[Fy.ρ] + I * Tr[Fx.ρ]];
         FID = Simplify[FID /. {ΩI → 2 π * (ν + δ / 2), ΩS → 2 π * (ν - δ / 2)}];
         FID = ExpandAll[PowerExpand[FID /. {-J^2 - δ^2 → -ϵ^2}]]
```

Out[18]=
$$\frac{1}{2}e^{-iJ\pi t-i\pi t\epsilon+2i\pi t\nu}+\frac{1}{2}e^{iJ\pi t-i\pi t\epsilon+2i\pi t\nu}+\frac{1}{2}e^{-iJ\pi t+i\pi t\epsilon+2i\pi t\nu}+\frac{1}{2}e^{iJ\pi t+i\pi t\epsilon+2i\pi t\nu}-\frac{e^{-iJ\pi t-i\pi t\epsilon+2i\pi t\nu}J}{2\epsilon}+\frac{e^{iJ\pi t-i\pi t\epsilon+2i\pi t\nu}J}{2\epsilon}+\frac{e^{-iJ\pi t+i\pi t\epsilon+2i\pi t\nu}J}{2\epsilon}-\frac{e^{iJ\pi t+i\pi t\epsilon+2i\pi t\nu}J}{2\epsilon}$$

```
In[19]:= FID == ExpandAll[(1 / 2) * (Exp[I * ω13 * t] (1 - Sin[2 θ]) + Exp[I * ω24 * t] (1 + Sin[2 θ]) +
              Exp[I * ω12 * t] (1 + Sin[2 θ]) + Exp[I * ω34 * t] (1 - Sin[2 θ])) /.
           {ω13 → 2 π * ν + π * ϵ + π * J, ω24 → 2 π * ν + π * ϵ - π * J, ω12 → 2 π * ν - π * ϵ + π * J,
            ω34 → 2 π * ν - π * ϵ - π * J, Sin[2 θ] → J / ϵ}]

Out[19]= True
```

Getting a "nice" result out of a *Mathematica* calculation typically requires a judicious use of commands such as `Simplify`, `ExpandAll` and `PowerExpand`, as well as using substitution commands to change notation, as indicated by the arrows in the code above. It is usually necessary to experiment to find the most effective route, and example calculations such as that above sometimes benefit greatly from hindsight.

Exercise 10.5

Use your program to explore the spectrum for a range of values of the ratio J/δ and convince yourself that weak coupling and equivalent spin behaviour emerges in the appropriate limits.

This could be done by simply plotting spectra, for example using the program in Fig 10.2. Alternatively it is possible to extend the program in Exercise 10.4 by taking appropriate limits to get the analytic form of the two extreme spectra.

```
In[20]:= (FID /. {J / ϵ → 0}) /. {ϵ → δ}
```

Out[20]= $\frac{1}{2} e^{-i J \pi t - i \pi t \delta + 2 i \pi t \nu} + \frac{1}{2} e^{i J \pi t - i \pi t \delta + 2 i \pi t \nu} + \frac{1}{2} e^{-i J \pi t + i \pi t \delta + 2 i \pi t \nu} + \frac{1}{2} e^{i J \pi t + i \pi t \delta + 2 i \pi t \nu}$

```
In[21]:= FID /. {ϵ → J}
```

Out[21]= $2 e^{2 i \pi t \nu}$

Exercise 10.6

Expand your program to verify Eqns 10.18 and 10.19.

This is a fairly simple extension of the previous code; as before the main difficulty is in finding a good route to "tidy up" the result.

```
In[1]:= Ax = {{0, 1 / 2}, {1 / 2, 0}};
        Ay = {{0, -1 / 2 I}, {1 / 2 I, 0}};
        Az = {{1 / 2, 0}, {0, -1 / 2}};
        ONE = {{1, 0}, {0, 1}};
        Ix = KroneckerProduct[Ax, ONE];
        Iy = KroneckerProduct[Ay, ONE];
        Iz = KroneckerProduct[Az, ONE];
        Sx = KroneckerProduct[ONE, Ax];
        Sy = KroneckerProduct[ONE, Ay];
        Sz = KroneckerProduct[ONE, Az];
        Fx = Ix + Sx;
        Fy = Iy + Sy;
        Fz = Iz + Sz;

In[14]:= H = ΩI * Iz + ΩS * Sz + 2 * π * J * (Ix.Sx + Iy.Sy + Iz.Sz);
         U = MatrixExp[-I * H * τ];
         Uadj = MatrixExp[I * H * τ];

In[17]:= ρ = U.MatrixExp[-I * π * Fx].U.MatrixExp[-I * π / 2 * Fx].
            Fz.MatrixExp[I * π / 2 * Fx].Uadj.MatrixExp[I * π * Fx].Uadj;

In[18]:= fx = Simplify[Tr[Fx.ρ]]

Out[18]= 0

In[19]:= fy = FullSimplify[PowerExpand[
              Simplify[Simplify[Tr[Fy.ρ]] /. {ΩI → 2 π * (ν + δ / 2), ΩS → 2 π * (ν - δ / 2)}] /.
               {-J^2 - δ^2 → -ϵ^2}]] /. {J^2 + δ^2 → ϵ^2}
```

Out[19]=
$$\frac{2\,\delta^2\,\mathrm{Cos}[2\,J\,\pi\,\tau] + J\,(J+\epsilon)\,\mathrm{Cos}[2\,\pi\,(J-\epsilon)\,\tau] + J\,(J-\epsilon)\,\mathrm{Cos}[2\,\pi\,(J+\epsilon)\,\tau]}{\epsilon^2}$$

```
In[20]:= Simplify[fy == Simplify[
            (2 * (Cos[2 θ])^2 * Cos[2 π * J * τ] - Sin[2 θ] (1 - Sin[2 θ]) * Cos[2 π * (J + ϵ) * τ] +
               Sin[2 θ] (1 + Sin[2 θ]) * Cos[2 π * (J - ϵ) * τ]) /. {Sin[2 θ] → J / ϵ, Cos[2 θ] → δ / ϵ}]]

Out[20]= True
```

Exercise 10.7

Use matrix representations to prove Eqn 10.31.

Taking the matrix representations from Appendix I

$$2I_yS_z - 2I_zS_y = \frac{1}{2}\begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{pmatrix} - \frac{1}{2}\begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & \end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix} 0 & i & -i & 0 \\ -i & 0 & 0 & i \\ i & 0 & 0 & -i \\ 0 & -i & i & 0 \end{pmatrix}$$

$$\boldsymbol{I}_x + \boldsymbol{S}_x = \frac{1}{2}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} - \frac{1}{2}\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$
$$= \frac{1}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}$$

and so the commutator is

$$\frac{1}{4}\begin{pmatrix} 0 & \mathrm{i} & -\mathrm{i} & 0 \\ -\mathrm{i} & 0 & 0 & \mathrm{i} \\ \mathrm{i} & 0 & 0 & -\mathrm{i} \\ 0 & -\mathrm{i} & \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} - \frac{1}{4}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & \mathrm{i} & -\mathrm{i} & 0 \\ -\mathrm{i} & 0 & 0 & \mathrm{i} \\ \mathrm{i} & 0 & 0 & -\mathrm{i} \\ 0 & -\mathrm{i} & \mathrm{i} & 0 \end{pmatrix}$$
$$= \frac{1}{4}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} - \frac{1}{4}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$
$$= 0$$

Exercise 10.8

Use operator commutators to prove Eqn 10.31, and hence evaluate the commutators between the sum term $2\boldsymbol{I}_y\boldsymbol{S}_z + 2\boldsymbol{I}_z\boldsymbol{S}_y$ and $\boldsymbol{F}_x$.

We can expand the final commutators as the sum of four individual commutators and then look up the elementary commutators in Table L1 to get

$$\begin{aligned}\left[2\boldsymbol{I}_y\boldsymbol{S}_z - 2\boldsymbol{I}_z\boldsymbol{S}_y, \boldsymbol{I}_x + \boldsymbol{S}_x\right] &= \left[2\boldsymbol{I}_y\boldsymbol{S}_z, \boldsymbol{I}_x\right] - \left[2\boldsymbol{I}_z\boldsymbol{S}_y, \boldsymbol{I}_x\right] + \left[2\boldsymbol{I}_y\boldsymbol{S}_z, \boldsymbol{S}_x\right] - \left[2\boldsymbol{I}_z\boldsymbol{S}_y, \boldsymbol{S}_x\right] \\ &= -\mathrm{i}2\boldsymbol{I}_z\boldsymbol{S}_z - \mathrm{i}2\boldsymbol{I}_y\boldsymbol{S}_y + \mathrm{i}2\boldsymbol{I}_y\boldsymbol{S}_y + \mathrm{i}2\boldsymbol{I}_z\boldsymbol{S}_z \\ &= 0.\end{aligned}$$

For the sum term, the minus signs before the second and fourth terms on the first line become plus signs, and so the commutators add together rather than cancelling out:

$$\begin{aligned}\left[2\boldsymbol{I}_y\boldsymbol{S}_z + 2\boldsymbol{I}_z\boldsymbol{S}_y, \boldsymbol{I}_x + \boldsymbol{S}_x\right] &= \left[2\boldsymbol{I}_y\boldsymbol{S}_z, \boldsymbol{I}_x\right] + \left[2\boldsymbol{I}_z\boldsymbol{S}_y, \boldsymbol{I}_x\right] + \left[2\boldsymbol{I}_y\boldsymbol{S}_z, \boldsymbol{S}_x\right] + \left[2\boldsymbol{I}_z\boldsymbol{S}_y, \boldsymbol{S}_x\right] \\ &= -\mathrm{i}2\boldsymbol{I}_z\boldsymbol{S}_z + \mathrm{i}2\boldsymbol{I}_y\boldsymbol{S}_y + \mathrm{i}2\boldsymbol{I}_y\boldsymbol{S}_y - \mathrm{i}2\boldsymbol{I}_z\boldsymbol{S}_z \\ &= 2\ \ -\mathrm{i}2\boldsymbol{I}_z\boldsymbol{S}_z + \mathrm{i}2\boldsymbol{I}_y\boldsymbol{S}_y\ \ .\end{aligned}$$