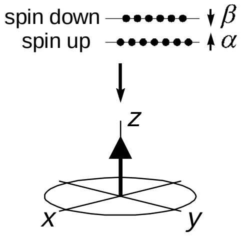
2 Product Operators

The product operator formalism is a complete and rigorous quantum mechanical description of NMR experiments; the formalism is a version of density matrix theory and is well suited to calculating the outcome of modern multiple-pulse experiments.

One particularly appealing feature is the fact that the operators have a clear physical meaning and that the effects of pulses and delays can be thought of as geometrical rotations. To emphasise this connection the discussion will start with a brief summary of the vector model.

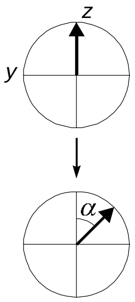


Unequal populations of the two energy levels give rise to a net magnetization, represented as a vector along the *z*-axis.

2.1 Vector model of NMR

The vector model is a complete description of the behaviour of an ensemble (a macroscopic sample) of non-interacting spin-half nuclei. Each spin has two energy levels and at equilibrium the lower of these is more populated. The result is a net magnetization of the sample along the direction of the applied magnetic field (taken to be the *z*-direction). The vector model focuses entirely on the behaviour of this magnetization, which can be represented as a vector.

Radiofrequency pulses are represented as rotations about the *x*- or *y*-axes; if the radiofrequency field strength is ω_1 (rad s^{-1}) then a pulse applied for a time t causes a rotation through an angle α, where $\alpha = \omega_1 t$. For example a 90° pulse about the *x*-axis has $\omega_1 t = \pi/2$ and rotates magnetization from the *z*-axis onto the –*y*-axis.



A pulse about the *x*-axis rotates the magnetization through an angle α in the *yz*-plane. The picture shows the view down the *x*-axis.

Free precession is represented as a rotation about the *z*-axis at frequency Ω (rad s^{-1}), where Ω is the offset (that is the difference between the Larmor frequency and the transmitter frequency). Free precession for a time t causes a rotation through an angle α, where $\alpha = \Omega t$.

Only *x*- and *y*-magnetization are directly observable in an NMR experiment; it is the precession of the magnetization in the *xy*-plane which gives rise to the free induction signal.

2.1.1 Example – the conventional pulse-acquire experiment

Assume that the system starts at equilibrium; a pulse of flip angle α is applied and then the free induction signal is recorded. Let the equilibrium magnetization (aligned along the *z*-axis) have size M_0. After the pulse the *z*- and *y*-magnetization (M_z and M_y, respectively) are

$$M_z = \cos\alpha\, M_0 \qquad M_y = -\sin\alpha\, M_0$$

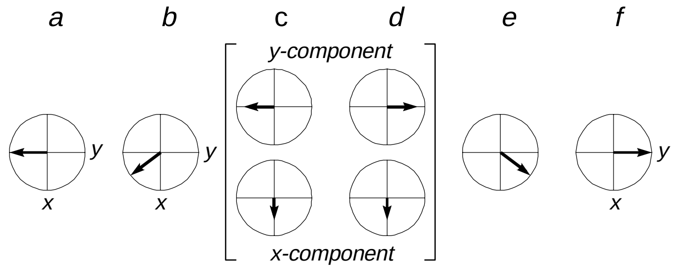
Free precession, which is a rotation about the *z*-axis, has no effect on the *z*-component. The *y*-component rotates in the *xy*-plane giving the following transverse components after time t

$$M_y(t) = -\sin\alpha\cos\Omega t\, M_0 \qquad M_x(t) = \sin\alpha\sin\Omega t\, M_0$$

It is these transverse (that is, x and y) components of the magnetization that are detected in NMR experiments. It is seen that these are oscillating at frequency Ω, and that their overall size depends on the sine of the flip angle *i.e.* they are a maximum for a 90° pulse.

2.1.2 Example – the spin echo

$$90^\circ(x)\overset{a}{\rule[0.5ex]{2em}{0.4pt}}\text{delay }\tau\overset{b}{\rule[0.5ex]{2em}{0.4pt}}180^\circ(x)\overset{e}{\rule[0.5ex]{2em}{0.4pt}}\text{delay }\tau\overset{f}{\rule[0.5ex]{2em}{0.4pt}}\text{acquire}$$



After the delay, point b, the vector can be resolved into y- and x-components as shown in c. The 180° pulse about the x-axis has no effect on the x-component of the magnetization; in contrast the y-component is rotated by 180° in the yz-plane, ending up along the opposite axis. The individual components after the 180° pulse are shown in d, and corresponding vector is shown in e. The effect of the 180° pulse about the x-axis is to reflect the vector in the xz-plane. During the second time τ the vector precesses in the same direction as it did during the first time τ and through the same angle, ending up along the y-axis.

At the end of the sequence the vector always ends up along the y-axis, regardless of the time τ and the offset; the sequence is said to "refocus the offset (or shift)".

2.2 Operators for one spin

2.2.1 Operators

Operators are mathematical functions which arise in quantum mechanics (see lecture 1); as their name suggest, they operate on functions. In quantum mechanics operators represent observable quantities, such as energy, angular momentum and magnetization.

For a single spin-half, the x- y- and z-components of the magnetization are represented by the spin angular momentum operators I_x, I_y and I_z respectively. Thus at any time the state of the spin system, in quantum mechanics the density operator, σ, can be represented as a sum of different amounts of these three operators

$$\sigma(t) = a(t) I_x + b(t) I_y + c(t) I_z$$

The amounts of the three operators will vary with time during pulses and delays. This expression of the density operator as a combination of the spin angular momentum operators is exactly analogous to specifying the three components of a magnetization vector.

At equilibrium the density operator is proportional to I_z (there is only z-magnetization present). The constant of proportionality is usually unimportant, so it is usual to write $\sigma_{\mathrm{eq}} = I_z$.

2.2.2 Hamiltonians for pulses and delays

In order to work out how the density operator varies with time we need to know the Hamiltonian (which is also an operator) which is acting during that time.

The free precession Hamiltonian (*i.e.* that for a delay), H_{free}, is

$$H_{\mathrm{free}} = \Omega I_z$$

In the vector model free precession involves a rotation at frequency Ω about the z-axis; in the quantum mechanical picture the Hamiltonian involves the z-angular momentum operator, I_z – there is a direct correspondence.

The Hamiltonian for a pulse about the x-axis, H_{pulse}, is

$$H_{\mathrm{pulse,x}} = \omega_1 I_x$$

and for a pulse about the y-axis it is

$$H_{\mathrm{pulse,y}} = \omega_1 I_y$$

Again there is a clear connection to the vector model where pulses result in rotations about the x- or y-axes.

2.2.3 Equation of motion

The density operator at time t, $\sigma(t)$, is computed from that at time 0, $\sigma(0)$, using the following relationship

$$\sigma(t) = \exp(-iHt)\ \sigma(0)\ \exp(iHt)$$

where H is the relevant hamiltonian. If H and σ are expressed in terms of the angular momentum operators if turns out that this equation can be solved easily with the aid of a few rules.

Suppose that an x-pulse, of duration t_p, is applied to equilibrium magnetization. In this situation $H = \omega_1 I_x$ and $\sigma(0) = I_z$; the equation to be solved is

$$\sigma\left(t_\mathrm{p}\right) = \exp\left(-i\omega_1 t_\mathrm{p} I_x\right)\ I_z \exp\left(i\omega_1 t_\mathrm{p}\ I_x\right)$$

Such equations involving angular momentum operators are common in quantum mechanics and the solution to them are already all know. The identity required here to solve this equation is

$$\exp\left(-i\theta I_x\right)\ I_z \exp\left(i\theta I_x\right) \equiv \cos\theta\ I_z - \sin\theta\ I_y \qquad [2.1]$$

This is interpreted as a *rotation* of I_z by an angle θ about the x-axis. By putting $\theta = \omega_1 t_\mathrm{p}$ this identity can be used to solve Eqn. [2.1]

$$\sigma\left(t_\mathrm{p}\right) = \cos\omega_1 t_\mathrm{p}\ \ I_z - \sin\omega_1 t_\mathrm{p}\ \ I_y$$

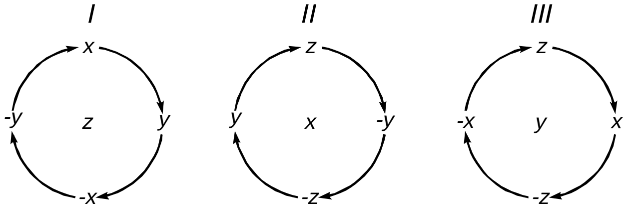
The result is exactly as expected from the vector model: a pulse about the x-axis rotates z-magnetization towards the $-y$-axis, with a sinusoidal dependence on the flip angle, θ.

2.2.4 Standard rotations

Given that there are only three operators, there are a limited number of identities of the type of Eqn. [2.1]. They all have the same form

$$\begin{aligned}&\exp\left(-i\theta I_a\right)\ \{\text{old operator}\} \exp\left(i\theta I_a\right)\\ &\equiv \cos\theta\ \ \{\text{old operator}\} + \sin\theta\ \{\text{new operator}\}\end{aligned}$$

where {old operator}, {new operator} and I_a are determined from the three possible angular momentum operators according to the following diagrams; the label in the centre indicates which axis the rotation is about



Angle of rotation = Ωt for offsets and $\omega_1 t_\mathrm{p}$ for pulses

First example: find the result of rotating the operator I_y by θ about the x-axis, that is

$$\exp\left(-i\theta I_x\right)\, I_y \,\exp\left(i\theta I_x\right)$$

For rotations about x the middle diagram *II* is required. The diagram shows that I_y (the "old operator") is rotated to I_z (the "new operator"). The required identity is therefore

$$\exp(-i\theta I_x)\, I_y \exp(i\theta I_x) \equiv \cos\theta\, I_y + \sin\theta\, I_z$$

Second example: find the result of

$$\exp(-i\theta I_y)\,\{-I_z\}\,\exp(i\theta I_y)$$

This is a rotation about y, so diagram *III* is required. The diagram shows that $-I_z$ (the "old operator") is rotated to $-I_x$ (the "new operator"). The required identity is therefore

$$\begin{aligned}\exp\left(-i\theta I_y\right)\left\{-I_z\right\}\exp\left(i\theta I_y\right) &\equiv \cos\theta\left\{-I_z\right\}+\sin\theta\left\{-I_x\right\}\\ &\equiv -\cos\theta\; I_z - \sin\theta\; I_x\end{aligned}$$

Finally, note that a rotation of an operator about its own axis has no effect *e.g.* a rotation of I_x about x leaves I_x unaltered.

2.2.5 Shorthand notation

To save writing, the arrow notation is often used. In this, the term *Ht* is written over an arrow which connects the old and new density operators. So, for example, the following

$$\sigma\left(t_\mathrm{p}\right) = \exp\left(-i\omega_1 t_\mathrm{p} I_x\right)\,\sigma(0)\exp\left(i\omega_1 t_\mathrm{p} I_x\right)$$

is written

$$\sigma(0) \xrightarrow{\omega_1 t_{\mathrm{p}} I_x} \sigma\left(t_{\mathrm{p}}\right)$$

For the case where $\sigma(0) = I_z$

$$I_z \xrightarrow{\omega_1 t_{\mathrm{p}} I_x} \cos\omega_1 t_{\mathrm{p}}\, I_z - \sin\omega_1 t_{\mathrm{p}}\, I_y$$

2.2.6 Example calculation: spin echo

$$90°(x) \overset{a}{\text{———}} \text{delay}\ \tau \overset{b}{\text{———}} 180°(x) \overset{e}{\text{———}} \text{delay}\ \tau \overset{f}{\text{———}} \text{acquire}$$

At *a* the density operator is $-I_{\mathrm{y}}$. The transformation from *a* to *b* is free precession, for which the Hamiltonian is ΩI_{z}; the delay τ therefore corresponds to a rotation about the *z*-axis at frequency Ω. In the short-hand notation this is

$$-I_y \xrightarrow{\Omega\tau I_x} \sigma(b)$$

To solve this diagram *I* above is needed with the angle = $\Omega\tau$; the "new operator" is I_x

$$-I_y \xrightarrow{\Omega\tau I_z} -\cos\Omega\tau\, I_y + \sin\Omega\tau\, I_x$$

In words this says that the magnetization precesses from $-y$ towards $+x$.

The pulse about *x* has the Hamiltonian $\omega_1 I_x$; the pulse therefore corresponds to a rotation about *x* for a time t_{p} such that the angle, $\omega_1 t_{\mathrm{p}}$, is π radians. In the shorthand notation

$$-\cos\Omega\tau\, I_y + \sin\Omega\tau\, I_x \xrightarrow{\omega_1 t_{\mathrm{p}} I_x} \sigma(e) \qquad [2.2]$$

Each term on the left is dealt with separately. The first term is a rotation of *y* about *x*; the relevant diagram is thus *II*

$$-\cos\Omega\tau\, I_y \xrightarrow{\omega_1 t_{\mathrm{p}} I_x} -\cos\Omega\tau\cos\omega_1 t_{\mathrm{p}}\, I_y - \cos\Omega\tau\sin\omega_1 t_{\mathrm{p}}\, I_z$$

However, the flip angle of the pulse, $\omega_1 t_p$, is π so the second term on the right is zero and the first term just changes sign ($\cos\pi = -1$); overall the result is

$$-\cos\Omega\tau\, I_y \xrightarrow{\pi I_x} \cos\Omega\tau\, I_y$$

The second term on the left of Eqn. [2.2] is easy to handle as it is unaffected by a rotation about x. Overall, the effect of the 180° pulse is then

$$-\cos\Omega\tau\, I_y + \sin\Omega\tau\, I_x \xrightarrow{\pi I_x} \cos\Omega\tau\, I_y + \sin\Omega\tau\, I_x \qquad [2.3]$$

As was shown using the vector model, the y-component just changes sign. The next stage is the evolution of the offset for time τ. Again, each term on the right of Eqn. [2.3] is considered separately

$$\cos\Omega\tau\, I_y \xrightarrow{\Omega\tau I_z} \cos\Omega\tau\cos\Omega\tau\, I_y - \sin\Omega\tau\cos\Omega\tau\, I_x$$
$$\sin\Omega\tau\, I_x \xrightarrow{\Omega\tau I_z} \cos\Omega\tau\sin\Omega\tau\, I_x + \sin\Omega\tau\sin\Omega\tau\, I_y$$

Collecting together the terms in I_x and I_y the final result is

$$\left(\cos\Omega\tau\cos\Omega\tau + \sin\Omega\tau\sin\Omega\tau\right) I_y + \left(\cos\Omega\tau\sin\Omega\tau - \sin\Omega\tau\cos\Omega\tau\right) I_x$$

The bracket multiplying I_x is zero and the bracket multiplying I_y is =1 because of the identity $\cos^2\theta + \sin^2\theta = 1$. Thus the overall result of the spin echo sequence can be summarised

$$I_z \xrightarrow{90°(x)-\tau-180°(x)-\tau-} I_y$$

In words, the outcome is independent of the offset, Ω, and the delay τ, even though there is evolution during the delays. The offset is said to be *refocused* by the spin echo.

In general the sequence

$$-\ \tau - 180°(x) - \tau - \qquad [2.4]$$

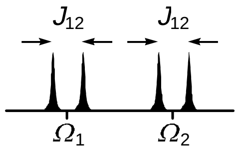
refocuses any evolution due to offsets; this is a very useful feature which is much used in multiple-pulse NMR experiments.

One further point is that as far as the offset is concerned the spin echo sequence of Eqn. [2.4] is just equivalent to 180°(x).

2.3 Operators for two spins

2.3.1 Product operators for two spins

The product operator approach comes into its own when coupled spin systems are considered; such systems cannot be treated by the vector model. However, product operators provide a clean and simple description of the important phenomena of coherence transfer and multiple quantum coherence.



The spectrum from two coupled spins, with offsets Ω_1 and Ω_2 (rad s^{-1}) and mutual coupling J_{12} (Hz).

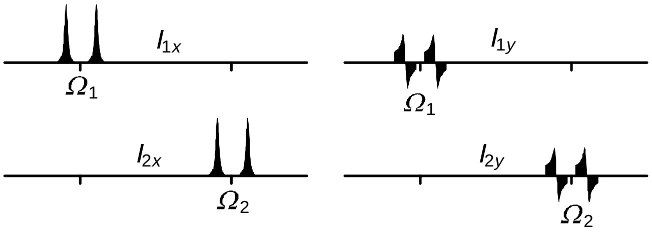
2.3.2 Product operators for two spins

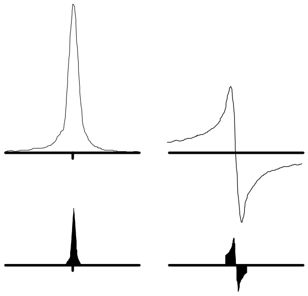
For a single spin the three operators needed for a complete description are I_x, I_y and I_z. For two spins, three such operators are needed for each spin; an additional subscript, 1 or 2, indicates which spin they refer to.

$$\text{spin 1: } I_{1x} \quad I_{1y} \quad I_{1z} \qquad \text{spin 2: } I_{2x} \quad I_{2y} \quad I_{2z}$$

I_{1z} represents z-magnetization of spin 1, and I_{2z} likewise for spin 2. I_{1x} represents x-magnetization on spin 1. As spin 1 and 2 are coupled, the spectrum consists of two doublets and the operator I_{1x} can be further identified with the two lines of the spin-1 doublet. In the language of product operators I_{1x} is said to represent *in-phase* magnetization of spin 1; the description in-phase means that the two lines of the spin 1 doublet have the same sign and lineshape.

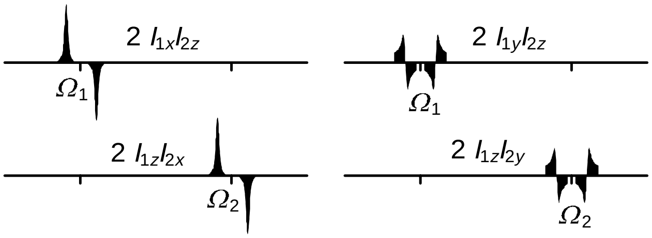
Following on in the same way I_{2x} represents in-phase magnetization on spin 2. I_{1y} and I_{2y} also represent in-phase magnetization on spins 1 and 2, respectively, but this magnetization is aligned along y and so will give rise to a different lineshape. Arbitrarily, an absorption mode lineshape will be assigned to magnetization aligned along x and a dispersion mode lineshape to magnetization along y.



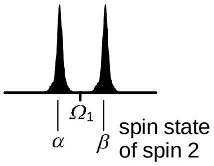


The absorption and dispersion lineshapes. The absorption lineshape is a maximum on resonance, whereas the dispersion goes through zero at this point. The "cartoon" forms of the lineshapes are shown in the lower part of the diagram.

There are four additional operators which represent *anti-phase* magnetization: $2I_{1x}I_{2z}$, $2I_{1y}I_{2z}$, $2I_{1z}I_{2x}$, $2I_{1z}I_{2y}$ (the factors of 2 are needed for normalization purposes). The operator $2I_{1x}I_{2z}$ is described as magnetization on spin 1 which is anti-phase with respect to the coupling to spin 2.



Note that the two lines of the spin-1 multiplet are associated with different spin states of spin-2, and that in an anti-phase multiplet these two lines have different signs. Anti-phase terms are thus sensitive to the spin states of the coupled spins.



The two lines of the spin-1 doublet can be associated with different spin states of spin 2.

There are four remaining product operators which contain two transverse (*i.e.* x- or y-operators) terms and correspond to multiple-quantum coherences; they are not observable

$$\text{multiple quantum: } 2I_{1x}I_{2y} \quad 2I_{1y}I_{2x} \quad 2I_{1x}I_{2x} \quad 2I_{1y}I_{2y}$$

Finally there is the term $2I_{1z}I_{2z}$ which is also not observable and corresponds to a particular kind of non-equilibrium population distribution.

2.3.3 Evolution under offsets and pulses

The operators for two spins evolve under offsets and pulses in the same way as do those for a single spin. The rotations have to be applied separately to each spin and it must be remembered that rotations of spin 1 do not affect spin 2, and *vice versa.*

For example, consider I_{1x} evolving under the offset of spin 1 and spin 2. The relevant Hamiltonian is

$$H_{\text{free}} = \Omega_1 I_{1z} + \Omega_2 I_{2z}$$

where Ω_1 and Ω_2 are the offsets of spin 1 and spin 2 respectively. Evolution under this Hamiltonian can be considered by applying the two terms sequentially (the order is immaterial)

$$I_{1x} \xrightarrow{H_{\text{free}}t}$$
$$I_{1x} \xrightarrow{\Omega_1 t I_{1z} + \Omega_2 t I_{2z}}$$
$$I_{1x} \xrightarrow{\Omega_1 t I_{1z}} \xrightarrow{\Omega_2 t I_{2z}}$$

The first "arrow" is a rotation about z

$$I_{1x} \xrightarrow{\Omega_1 t I_{1z}} \cos\Omega_1 t\, I_{1x} + \sin\Omega_1 t\, I_{1y} \xrightarrow{\Omega_2 t I_{2z}}$$

The second arrow leaves the intermediate state unaltered as spin-2 operators have not effect on spin-1 operators. Overall, therefore

$$I_{1x} \xrightarrow{\Omega_1 t I_{1z} + \Omega_2 t I_{2z}} \cos\Omega_1 t\, I_{1x} + \sin\Omega_1 t\, I_{1y}$$

A second example is the term $2I_{1x}I_{2z}$ evolving under a 90° pulse about the y-axis applied to both spins. The relevant Hamiltonian is

$$H = \omega_1 I_{1y} + \omega_1 I_{2y}$$

The evolution can be separated into two successive rotations

$$2I_{1x}I_{2z} \xrightarrow{\omega_1 t I_{1y}} \xrightarrow{\omega_1 t I_{2y}}$$

The first arrow affects only the spin-1 operators; a 90° rotation of I_{1x} about y gives – I_{1z} (remembering that $\omega_1 t = \pi/2$ for a 90° pulse)

$$2I_{1x}I_{2z} \xrightarrow{\omega_1 t I_{1y}} \cos\omega_1 t\, 2I_{1x}I_{2z} - \sin\omega_1 t\, 2I_{1z}I_{2z} \xrightarrow{\omega_1 t I_{2y}}$$

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

The second arrow only affects the spin 2 operators; a 90° rotation of z about y takes it to x

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

The overall result is that anti-phase magnetization of spin 1 has been transferred into anti-phase magnetization of spin 2. Such a process is called *coherence transfer* and is exceptionally important in multiple-pulse NMR.

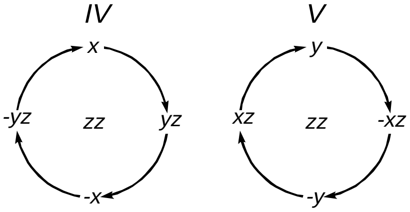
2.3.4 Evolution under coupling

The new feature which arises when considering two spins is the effect of coupling between them. The Hamiltonian representing this coupling is itself a product of two operators:

$$H_{\mathrm{J}} = 2\pi J_{12}\, I_{1z} I_{2z}$$

where J_{12} is the coupling in Hz.

Evolution under coupling causes the interconversion of in-phase and anti-phase magnetization according to the following diagrams



angle = πJt

For example, in-phase magnetization along x becomes anti-phase along y according to the diagram *d*

$$I_{1x} \xrightarrow{2\pi J_{12} t\, I_{1z} I_{2z}} \cos \pi J_{12} t\, I_{1x} + \sin \pi J_{12} t\, 2 I_{1y} I_{2z}$$

note that the angle is $\pi J_{12} t$ *i.e.* half the angle for the other rotations, *I–III*.

Anti-phase magnetization along x becomes in-phase magnetization along y; using diagram *V*:

$$2 I_{1x} I_{2z} \xrightarrow{2\pi J_{12} t\, I_{1z} I_{2z}} \cos \pi J_{12} t\, 2 I_{1x} I_{2z} + \sin \pi J_{12} t\, I_{1y}$$

The diagrams apply equally well to spin-2; for example

$$-2 I_{1z} I_{2y} \xrightarrow{2\pi J_{12} t\, I_{1z} I_{2z}} -\cos \pi J_{12} t\, 2 I_{1z} I_{2y} + \sin \pi J_{12} t\, I_{2x}$$

Complete interconversion of in-phase and anti-phase magnetization requires a delay such that $\pi J_{12} t = \pi/2$ *i.e.* a delay of $1/(2J_{12})$. A delay of $1/J_{12}$ causes in-phase magnetization to change its sign:

$$I_{1x} \xrightarrow{2\pi J_{12} t\, I_{1z} I_{2z} \quad t=1/2 J_{12}} 2 I_{1y} I_{2z} \qquad I_{2y} \xrightarrow{2\pi J_{12} t\, I_{1z} I_{2z} \quad t=1/J_{12}} -I_{2y}$$

2.4 Spin echoes

It was shown in section 2.2.6 that the offset is refocused in a spin echo. In this section it will be shown that the evolution of the scalar coupling is not necessarily refocused.

2.4.1 Spin echoes in homonuclear spin system

In this kind of spin echo the 180° pulse affects both spins *i.e.* it is a non-selective pulse:

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

At the start of the sequence it will be assumed that only in-phase *x*-magnetization on spin 1 is present: I_{1x}. In fact the starting state is not important to the overall effect of the spin echo, so this choice is arbitrary.

It was shown in section 2.2.6 that the spin echo applied to one spin refocuses the offset; this conclusion is not altered by the presence of a coupling so the offset will be ignored in the present calculation. This greatly simplifies things.

For the first delay τ only the effect of evolution under coupling need be considered therefore:

$$I_{1x} \xrightarrow{2\pi J_{12}\tau I_{1z}I_{2z}} \cos\pi J_{12}\tau\; I_{1x} + \sin\pi J_{12}\tau\; 2I_{1y}I_{2z}$$

The 180° pulse affects both spins, and this can be calculated by applying the 180° rotation to each in succession

$$\cos\pi J_{12}\tau\; I_{1x} + \sin\pi J_{12}\tau\; 2I_{1y}I_{2z} \xrightarrow{\pi I_{1x}} \xrightarrow{\pi I_{2x}}$$

where it has already been written in that $\omega_1 t_p = \pi$, for a 180° pulse. The 180° rotation about *x* for spin 1 has no effect on the operator I_{1x} and I_{2z}, and it simply reverses the sign of the operator I_{1y}

$$\cos\pi J_{12}\tau I_{1x} + \sin\pi J_{12}\tau 2I_{1y}I_{2z} \xrightarrow{\pi I_{1x}} \cos\pi J_{12}\tau I_{1x} - \sin\pi J_{12}\tau 2I_{1y}I_{2z} \xrightarrow{\pi I_{2x}}$$

The 180° rotation about *x* for spin 2 has no effect on the operators I_{1x} and I_{1y}, but simply reverses the sign of the operator I_{2z}. The final result is thus

$$\begin{aligned}&\cos\pi J_{12}\tau I_{1x} + \sin\pi J_{12}\tau 2I_{1y}I_{2z} \xrightarrow{\pi I_{1x}} \cos\pi J_{12}\tau I_{1x} - \sin\pi J_{12}\tau 2I_{1y}I_{2z}\\ &\xrightarrow{\pi I_{2x}} \cos\pi J_{12}\tau I_{1x} + \sin\pi J_{12}\tau 2I_{1y}I_{2z}\end{aligned}$$

Nothing has happened; the 180° pulse has left the operators unaffected! So, for the purposes of the calculation it is permissible to ignore the 180° pulse and simply allow the coupling to evolve for 2τ. The final result can therefore just be written down:

$$I_{1x} \xrightarrow{\tau-180°(x)-\tau} \cos 2\pi J_{12}\tau\ I_{1x} + \sin 2\pi J_{12}\tau\ 2I_{1y}I_{2z}$$

From this it is easy to see that complete conversion to anti-phase magnetization requires $2\pi J_{12}\tau = \pi/2$ *i.e.* $\tau = 1/(4\ J_{12})$.

The calculation is not quite as simple if the initial state is chosen as I_{1y} (see exercises), but the final result is just the same – the coupling evolves for 2τ:

$$I_{1y} \xrightarrow{\tau-180°(x)-\tau} -\cos 2\pi J_{12}\tau\, I_{1y} + \sin 2\pi J_{12}\tau\ 2I_{1x}I_{2z}$$

In fact, the general result is that the sequence

– τ – 180°(*x*, to spin 1 and spin 2) – τ –

is equivalent to the sequence

– 2τ – 180°(*x*, to spin 1 and spin 2)

in which the offset is ignored and coupling is allowed to act for time 2τ.

2.4.2 Interconverting in-phase and anti-phase states

So far, spin echoes have been demonstrated as being useful for generating anti-phase terms, independent of offsets. For example, the sequence

90°(*x*) – 1/(4J_{12}) – 180°(*x*) – 1/(4J_{12}) –

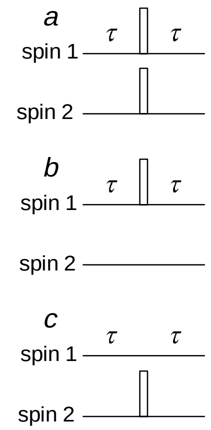
generates pure anti-phase magnetization.

Equally useful is the sequence

– 1/(4J_{12}) – 180°(*x*) – 1/(4J_{12}) –

which will convert pure anti-phase magnetization, such as $2I_{1x}I_{2z}$ into in-phase magnetization, I_{1y}.

2.4.3 Spin echoes in heteronuclear spin systems



Three different spin echo sequences that can be applied to heteronuclear spin systems. The open rectangles represent 180° pulses.

If spin 1 and spin 2 are different nuclear species, such as ^{13}C and ^{1}H, it is possible to choose to apply the 180° pulse to either or both spins; the outcome of the sequence depends on the pattern of 180° pulses.

Sequence *a* has already been analysed: the result is that the offset is refocused but that the coupling evolves for time 2τ. Sequence *b* still refocuses the offset of spin 1, but it turns out that the coupling is also refocused. Sequence *c* refocuses the coupling but leaves the evolution of the offset unaffected.

2.4.3.1 *Sequence b*

It will be assumed that the offset is refocused, and attention will therefore be restricted to the effect of the coupling

$$I_{1x} \xrightarrow{2\pi J_{12}\tau I_{1z}I_{2z}} \cos\pi J_{12}\tau\ I_{1x} + \sin\pi J_{12}\tau\ 2I_{1y}I_{2z}$$

The 180°(x) pulse is only applied to spin 1

$$\cos\pi J_{12}\tau\ I_{1x} + \sin\pi J_{12}\tau\ 2I_{1y}I_{2z} \xrightarrow{\pi I_{1x}} \cos\pi J_{12}\tau\ I_{1x} - \sin\pi J_{12}\tau\ 2I_{1y}I_{2z} \quad [2.5]$$

The two terms on the right each evolve under the coupling during the second delay:

$$\begin{aligned}
&\cos\pi J_{12}\tau\ I_{1x} \xrightarrow{2\pi J_{12}\tau I_{1z}I_{2z}} \\
&\qquad \cos\pi J_{12}\tau\cos\pi J_{12}\tau\ I_{1x} + \sin\pi J_{12}\tau\cos\pi J_{12}\tau\ 2I_{1y}I_{2z} \\
&-\sin\pi J_{12}\tau\ 2I_{1y}I_{2z} \xrightarrow{2\pi J_{12}\tau I_{1z}I_{2z}} \\
&\qquad -\cos\pi J_{12}\tau\sin\pi J_{12}\tau\ 2I_{1y}I_{2z} + \sin\pi J_{12}\tau\ \sin\pi J_{12}\tau\ I_{1x}
\end{aligned}$$

Collecting the terms together and noting that $\cos^2\theta + \sin^2\theta = 1$ the final result is just I_{1x}. In words, the effect of the coupling has been refocused.

2.4.3.2 *Sequence c*

As there is no 180° pulse applied to spin 1, the offset of spin 1 is not refocused, but continues to evolve for time 2τ. The evolution of the coupling is easy to calculate:

$$I_{1x} \xrightarrow{2\pi J_{12}\tau I_{1z}I_{2z}} \cos\pi J_{12}\tau\ I_{1x} + \sin\pi J_{12}\tau\ 2I_{1y}I_{2z}$$

This time the 180°(*x*) pulse is applied to spin 2

$$\cos\pi J_{12}\tau\ I_{1x} + \sin\pi J_{12}\tau\ 2I_{1y}I_{2z} \xrightarrow{\pi I_{2x}} \cos\pi J_{12}\tau\ I_{1x} - \sin\pi J_{12}\tau\ 2I_{1y}I_{2z}$$

The results is exactly as for sequence *b* (Eqn. [2.5]), so the final result is the same *i.e.* the coupling is refocused.

2.4.3.3 Summary

In heteronuclear systems it is possible to choose whether or not to allow the offset and the coupling to evolve; this gives great freedom in generating and manipulating anti-phase states which play a key role in multiple pulse NMR experiments.

2.5 Multiple quantum terms

2.5.1 Coherence order

In NMR the directly observable quantity is the transverse magnetization, which in product operators is represented by terms such as I_{1x} and $2I_{1z}I_{2y}$. Such terms are examples of single quantum coherences, or more generally coherences with order, *p*, = ±1. Other product operators can also be classified according to coherence order *e.g.* $2I_{1z}I_{2z}$ has $p = 0$ and $2I_{1x}I_{2y}$ has both $p = 0$ (zero-quantum coherence) and ±2 (double quantum coherence). Only single quantum coherences are observable.

In heteronuclear systems it is sometimes useful to classify operators according to their coherence orders with respect to each spin. So, for example, $2I_{1z}I_{2y}$ has $p = 0$ for spin 1 and $p = \pm 1$ for spin 2.

2.5.2 Raising and lowering operators

The classification of operators according to coherence order is best carried out be re-expressing the Cartesian operators I_x and I_y in terms of the raising and lowering operators, I_+ and I_-, respectively. These are defined as follows

$$I_+ = I_x + iI_y \qquad I_- = I_x - iI_y \qquad [2.6]$$

where *i* is the square root of –1 (further details of why these operators are called the raising and lowering operators will be given in lecture 1). I_+ has coherence order +1 and I_- has coherence order –1; coherence order is a *signed* quantity.

Using the definitions of Eqn. [2.6] I_x and I_y can be expressed in terms of the raising and lowering operators

$$I_x = \tfrac{1}{2}\left(I_+ + I_-\right) \qquad I_y = \tfrac{1}{2i}\left(I_+ - I_-\right) \qquad [2.7]$$

from which it is seen that I_x and I_y are both mixtures of coherences with $p = +1$ and -1.

The operator product $2I_{1x}I_{2x}$ can be expressed in terms of the raising and lowering operators in the following way (note that separate operators are used for each spin: $I_{1\pm}$ and $I_{2\pm}$)

$$\begin{aligned} 2I_{1x}I_{2x} &= 2 \times \tfrac{1}{2}\left(I_{1+} + I_{1-}\right) \times \tfrac{1}{2}\left(I_{2+} + I_{2-}\right) \\ &= \tfrac{1}{2}\left(I_{1+}I_{2+} + I_{1-}I_{2-}\right) + \tfrac{1}{2}\left(I_{1+}I_{2-} + I_{1-}I_{2+}\right) \end{aligned} \qquad [2.8]$$

The first term on the right of Eqn. [2.8] has $p = (+1+1) = 2$ and the second term has $p = (-1-1) = -2$; both are double quantum coherences. The third and fourth terms both have $p = (+1-1) = 0$ and are zero quantum coherences. The value of p can be found simply by noting the number of raising and lowering operators in the product.

The pure double quantum part of $2I_{1x}I_{2x}$ is, from Eqn. [2.8],

$$\text{double quantum part}\left[2I_{1x}I_{2x}\right] = \tfrac{1}{2}\left(I_{1+}I_{2+} + I_{1-}I_{2-}\right) \qquad [2.9]$$

The raising and lowering operators on the right of Eqn. [2.9] can be re-expressed in terms of the Cartesian operators:

$$\begin{aligned} \tfrac{1}{2}\left(I_{1+}I_{2+} + I_{1-}I_{2-}\right) &= \tfrac{1}{2}\left[\left(I_{1x} + iI_{1y}\right)\left(I_{2x} + iI_{2y}\right) + \left(I_{1x} - iI_{1y}\right)\left(I_{2x} - iI_{2y}\right)\right] \\ &= \tfrac{1}{2}\left[2I_{1x}I_{2x} + 2I_{1y}I_{2y}\right] \end{aligned}$$

So, the pure double quantum part of $2I_{1x}I_{2x}$ is $\tfrac{1}{2}\left(2I_{1x}I_{2x} + 2I_{1y}I_{2y}\right)$; by a similar method the pure zero quantum part can be shown to be $\tfrac{1}{2}\left(2I_{1x}I_{2x} - 2I_{1y}I_{2y}\right)$. Some further useful relationships are given in section 2.9

2.5.3 Definition of coherence order

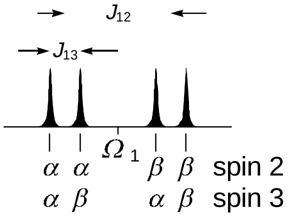
The formal definition of coherence order depends on the response of a particular operator to a rotation about the z-axis. A coherence or operator of order p acquires a phase $p\phi$ when rotated about the z-axis through an angle ϕ:

$$\sigma^{(p)} \xrightarrow{\text{rotate by } \phi \text{ about } z} \sigma^{(p)} \exp(-ip\phi)$$

This property will be used extensively as part of the description of coherence selection by phase cycling or gradient pulses, lecture 4.

2.6 Three spins

The product operator formalism can be extended to three or more spins. No really new features arise, but some of the key ideas will be highlighted in this section. The description will assume that spin 1 is coupled to spins 2 and 3 with coupling constants J_{12} and J_{13}; in the diagrams it will be assumed that $J_{12} > J_{13}$.

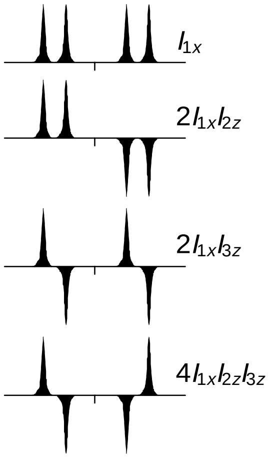


The doublet of doublets from spin 1 coupled to two other spins. The spin states of the coupled spins are also indicated.

2.6.1 Types of operators

I_{1x} represents in-phase magnetization on spin 1; $2I_{1x}I_{2z}$ represents magnetization anti-phase with respect to the coupling to spin 2 and $2I_{1x}I_{3z}$ represents magnetization anti-phase with respect to the coupling to spin 3. $4I_{1x}I_{2z}I_{3z}$ represents magnetization which is doubly anti-phase with respect to the couplings to both spins 2 and 3.

As in the case of two spins, the presence of more than one transverse operator in the product represents multiple quantum coherence. For example, $2I_{1x}I_{2x}$ is a mixture of double- and zero-quantum coherence between spins 1 and 2. The product $4I_{1x}I_{2x}I_{3z}$ is the same mixture, but anti-phase with respect to the coupling to spin 3. Products such as $4I_{1x}I_{2x}I_{3x}$ contain, amongst other things, triple-quantum coherences.



Representations of different types of operators.

2.6.2 Evolution

Evolution under offsets and pulses is simply a matter of applying sequentially the relevant rotations for each spin, remembering that rotations of spin 1 do not affect operators of spins 2 and 3. For example, the term $2I_{1x}I_{2z}$ evolves under the offset in the following way:

$$2I_{1x}I_{2z} \xrightarrow{\Omega_1 t I_{1z}} \xrightarrow{\Omega_2 t I_{2z}} \xrightarrow{\Omega_3 t I_{3z}} \cos\Omega_1 t \; 2I_{1x}I_{2z} + \sin\Omega_1 t \; 2I_{1y}I_{2z}$$

The first arrow, representing evolution under the offset of spin 1, affects only the spin 1 operator I_{1x}. The second arrow has no effect as the spin 2 operator I_{2z} and this is unaffected by a z-rotation. The third arrow also has no effect as there are no spin 3 operators present.

The evolution under coupling follows the same rules as for a two-spin system. For example, evolution of I_{1x} under the influence of the coupling to spin 3 generates $2I_{1y}I_{3z}$

$$I_{1x} \xrightarrow{2\pi J_{13} t I_{1z} I_{3z}} \cos \pi J_{13} t \; I_{1x} + \sin \pi J_{13} t \; 2 I_{1y} I_{3z}$$

Further evolution of the term $2I_{1y}\,I_{3z}$ under the influence of the coupling to spin 2 generates a double anti-phase term

$$2 I_{1y} I_{3z} \xrightarrow{2\pi J_{12} t I_{1z} I_{2z}} \cos \pi J_{12} t \; 2 I_{1y} I_{3z} - \sin \pi J_{13} t \; 4 I_{1x} I_{2z} I_{3z}$$

In this evolution the spin 3 operator if unaffected as the coupling does not involve this spin. The connection with the evolution of I_{1y} under a coupling can be made more explicit by writing $2I_{3z}$ as a "constant" γ

$$\gamma I_{1y} \xrightarrow{2\pi J_{12} t I_{1z} I_{2z}} \cos \pi J_{12} t \; \gamma I_{1y} - \sin \pi J_{13} t \; 2 \gamma I_{1x} I_{2z}$$

which compares directly to

$$I_{1y} \xrightarrow{2\pi J_{12} t I_{1z} I_{2z}} \cos \pi J_{12} t \; I_{1y} - \sin \pi J_{13} t \; 2 I_{1x} I_{2z}$$

2.7 Alternative notation

In this chapter different spins have been designated with a subscript 1, 2, 3 ... Another common notation is to distinguish the spins by using a different letter to represent their operators; commonly *I* and *S* are used for two of the symbols

$$2 I_{1x} I_{2z} \;\equiv\; 2 I_x S_z$$

Note that the order in which the operators are written is not important, although it is often convenient (and tidy) always to write them in the same sequence.

In heteronuclear experiments a notation is sometimes used where the letter represents the nucleus. So, for example, operators referring to protons are given the letter *H*, carbon-13 atoms the letter *C* and nitrogen-15 atoms the letter *N*; carbonyl carbons are sometimes denoted *C'*. For example, $4C_xH_zN_z$ denotes magnetization on carbon-13 which is anti-phase with respect to coupling to both proton and nitrogen-15.

2.8 Conclusion

The product operator method as described here only applies to spin-half nuclei. It can be extended to higher spins, but significant extra complexity is introduced; details can be found in the article by Sørensen *et al.* (*Prog. NMR*

Spectrosc. **16**, 163 (1983)).

The main difficulty with the product operator method is that the more pulses and delays that are introduced the greater becomes the number of operators and the more complex the trigonometrical expressions multiplying them. If pulses are either 90° or 180° then there is some simplification as such pulses do not increase the number of terms. As will be seen in lecture 3, it is important to try to simplify the calculation as much as possible, for example by recognizing when offsets or couplings are refocused by spin echoes.

A number of computer programs are available for machine computation using product operators within programs such as *Mathematica* or *Maple*. These can be very labour saving.

2.9 Multiple -quantum coherence

2.9.1 Multiple-quantum terms

In the product operator representation of multiple quantum coherences it is usual to distinguish between *active* and *passive* spins. Active spins contribute transverse operators, such as I_x, I_y and I_+, to the product; passive spins contribute only z-operators, I_z. In a sense the spins contributing transverse operators are "involved" in the coherence, while those contributing z-operators are simply spectators.

For double- and zero-quantum coherence in which spins i and j are active it is convenient to define the following set of operators which represent pure multiple quantum states of given order. The operators can be expressed in terms of the Cartesian or raising and lowering operators.

$$\begin{aligned}
&\text{double quantum, } p = \pm 2\\
&\mathrm{DQ}_x^{(ij)} \equiv \tfrac{1}{2}\left(2I_{ix}I_{jx} - 2I_{iy}I_{jy}\right) \equiv \tfrac{1}{2}\left(I_{i+}I_{j+} + I_{i-}I_{j-}\right)\\
&\mathrm{DQ}_y^{(ij)} \equiv \tfrac{1}{2}\left(2I_{ix}I_{jy} + 2I_{iy}I_{jx}\right) \equiv \tfrac{1}{2i}\left(I_{i+}I_{j+} - I_{i-}I_{j-}\right)\\
&\text{zero quantum, } p = 0\\
&\mathrm{ZQ}_x^{(ij)} \equiv \tfrac{1}{2}\left(2I_{ix}I_{jx} + 2I_{iy}I_{jy}\right) \equiv \tfrac{1}{2}\left(I_{i+}I_{j-} + I_{i-}I_{j+}\right)\\
&\mathrm{ZQ}_y^{(ij)} \equiv \tfrac{1}{2}\left(2I_{iy}I_{jx} - 2I_{ix}I_{jy}\right) \equiv \tfrac{1}{2i}\left(I_{i+}I_{j-} - I_{i-}I_{j+}\right)
\end{aligned}$$

2.9.2 Evolution of multiple -quantum terms

2.9.2.1 Evolution under offsets

The double- and zero-quantum operators evolve under offsets in a way which is entirely analogous to the evolution of I_x and I_y under free precession except that the frequencies of evolution are $(\Omega_i + \Omega_j)$ and $(\Omega_i - \Omega_j)$ respectively:

$$\begin{aligned}
\mathrm{DQ}_x^{(ij)} &\xrightarrow{\Omega_i t I_{iz} + \Omega_j t I_{jz}} \cos\left(\Omega_i + \Omega_j\right)t\,\mathrm{DQ}_x^{(ij)} + \sin\left(\Omega_i + \Omega_j\right)t\,\mathrm{DQ}_y^{(ij)}\\
\mathrm{DQ}_y^{(ij)} &\xrightarrow{\Omega_i t I_{iz} + \Omega_j t I_{jz}} \cos\left(\Omega_i + \Omega_j\right)t\,\mathrm{DQ}_y^{(ij)} - \sin\left(\Omega_i + \Omega_j\right)t\,\mathrm{DQ}_x^{(ij)}\\
\mathrm{ZQ}_x^{(ij)} &\xrightarrow{\Omega_i t I_{iz} + \Omega_j t I_{jz}} \cos\left(\Omega_i - \Omega_j\right)t\,\mathrm{ZQ}_x^{(ij)} + \sin\left(\Omega_i - \Omega_j\right)t\,\mathrm{ZQ}_y^{(ij)}\\
\mathrm{ZQ}_y^{(ij)} &\xrightarrow{\Omega_i t I_{iz} + \Omega_j t I_{jz}} \cos\left(\Omega_i - \Omega_j\right)t\,\mathrm{ZQ}_y^{(ij)} - \sin\left(\Omega_i - \Omega_j\right)t\,\mathrm{ZQ}_x^{(ij)}
\end{aligned}$$

2.9.2.2 *Evolution under couplings*

Multiple quantum coherence between spins *i* and *j* does not evolve under the influence of the coupling between the two active spins, *i* and *j*.

Double- and zero-quantum operators evolve under passive couplings in a way which is entirely analogous to the evolution of I_x and I_y; the resulting multiple quantum terms can be described as being anti-phase with respect to the effective couplings:

$$\begin{aligned}
\mathrm{DQ}_x^{(ij)} &\longrightarrow \cos \pi J_{\mathrm{DQ,eff}} t\ \mathrm{DQ}_x^{(ij)} + \cos \pi J_{\mathrm{DQ,eff}} t\ 2I_{kz}\mathrm{DQ}_y^{(ij)} \\
\mathrm{DQ}_y^{(ij)} &\longrightarrow \cos \pi J_{\mathrm{DQ,eff}} t\ \mathrm{DQ}_y^{(ij)} - \sin \pi J_{\mathrm{DQ,eff}} t\ 2I_{kz}\mathrm{DQ}_x^{(ij)} \\
\mathrm{ZQ}_x^{(ij)} &\longrightarrow \cos \pi J_{\mathrm{ZQ,eff}} t\ \mathrm{ZQ}_x^{(ij)} + \sin \pi J_{\mathrm{ZQ,eff}} t\ 2I_{kz}\mathrm{ZQ}_y^{(ij)} \\
\mathrm{ZQ}_y^{(ij)} &\longrightarrow \cos \pi J_{\mathrm{ZQ,eff}} t\ \mathrm{ZQ}_y^{(ij)} - \sin \pi J_{\mathrm{ZQ,eff}} t\ 2I_{kz}\mathrm{ZQ}_x^{(ij)}
\end{aligned}$$

$J_{\mathrm{DQ,eff}}$ is the sum of the couplings between spin *i* and all other spins *plus* the sum of the couplings between spin *j* and all other spins. $J_{\mathrm{ZQ,eff}}$ is the sum of the couplings between spin *i* and all other spins *minus* the sum of the couplings between spin *j* and all other spins.

For example in a three-spin system the zero-quantum coherence between spins 1 and 2, anti-phase with respect to spin 3, evolves according to

$$\begin{aligned}
&2I_{3z}\mathrm{ZQ}_y^{(12)} \longrightarrow \cos \pi J_{\mathrm{ZQ,eff}} t\ 2I_{3z}\mathrm{ZQ}_y^{(12)} - \sin \pi J_{\mathrm{ZQ,eff}} t\ \mathrm{ZQ}_x^{(12)} \\
&\text{where } J_{\mathrm{ZQ,eff}} = J_{12} - J_{23}
\end{aligned}$$

Further details of multiple-quantum evolution can be found in section 5.3 of Ernst, Bodenhausen and Wokaun *Principles of NMR in One and Two Dimensions* (Oxford University Press, 1987).