Tutorial Phase Cycling

Contents

1 Introduction

The advantage arising from the use of phase cycles can be seen by comparing the COSY and DQF COSY spectrum for a two-spin system.

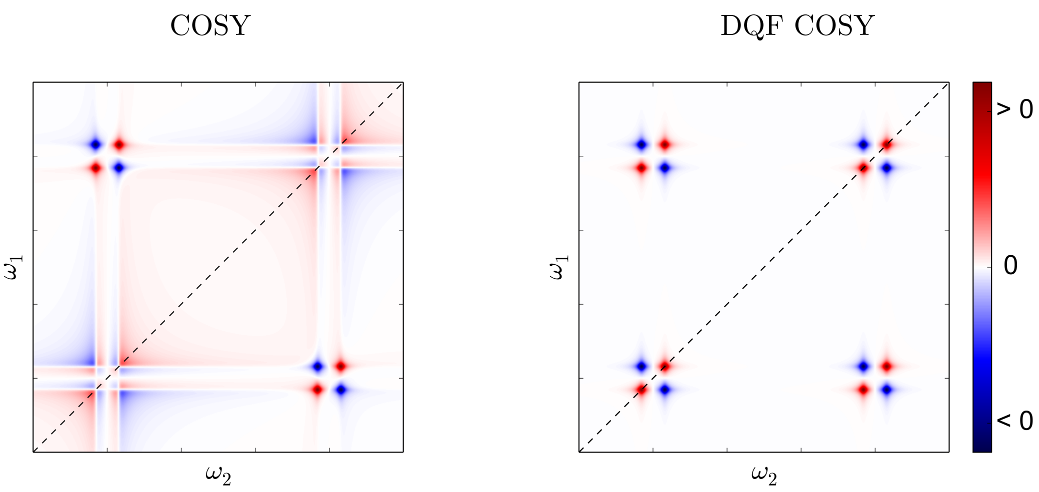


Figure 1: Comparison of COSY spectrum (left) and DQF COSY spectrum (right).

The COSY spectrum shows a double dispersion lineshape for the diagonal-peak multiplets. Such peaks are rather broad and dominate the spectrum. Thus, such a lineshape is undesirable for high resolution spectroscopy.

In the DQF COSY spectrum the double dispersion lineshape is not present. Both cross-peak multiplets and diagonal-peak multiplets have an absorption mode lineshape. This results in less overlap in realistic spectra with many resonances.

The DQF COSY spectrum can be obtained by filtering all the observed signals through a state of a certain ***coherence***. (For the DQF COSY experiment it is a state of ***double-quantum coherence***; hence the name **D**ouble-**Q**uantum **F**iltered **COSY**.)

In general, the selection of specific ***coherences*** is often desired in NMR experiments. This selection can be achieved by a method called ***phase cycling***.

Gaining a deeper insight into the working principles of phase cycling is the purpose of this tutorial. The ***D***iscrete ***R***epresentation of ***OP***erators for ***S***pin systems (***DROPS***) via ***SpinDrops*** will be used to illustrate the idea of these experiments.[1]

[1]A. Garon, R. Zeier and S. J. Glaser, Phys. Rev. A 91, 042122 (2015)

2 Coherence Order p

2.1 Raising and Lowering Operators in Place of $\hat{\mathbf{I}}_x$ and $\hat{\mathbf{I}}_y$ Operators

The product operators $\hat{\mathrm{I}}_{\mathrm{x}}$ and $\hat{\mathrm{I}}_{\mathrm{y}}$ correspond to transverse magnetization.

$\hat{\mathrm{I}}_{\mathrm{x}}$ $\hat{\mathrm{I}}_{\mathrm{y}}$

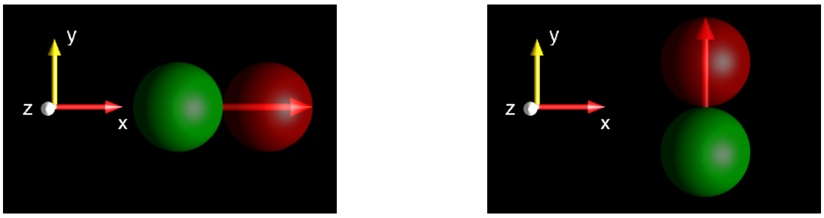


Figure 2: $\hat{\mathrm{I}}_{\mathrm{x}}$ operator (left) and $\hat{\mathrm{I}}_{\mathrm{y}}$ operator (right) in DROPS.

For the classification of coherence orders these operators will be expressed in terms of the so-called ***raising operator*** $\hat{\mathrm{I}}^{+}$ and ***lowering operator*** $\hat{\mathrm{I}}^{-}$. By definition, the coherence order of $p(\hat{\mathrm{I}}^{+})$=+1 and $p(\hat{\mathrm{I}}^{-})$=−1.

$\hat{\mathrm{I}}^{+}$ $\hat{\mathrm{I}}^{-}$

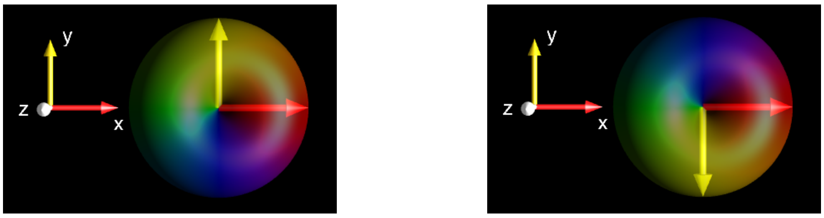


Figure 3: $\hat{\mathrm{I}}^{+}$ operator (left) and $\hat{\mathrm{I}}^{-}$ operator (right) in DROPS.

The definition of $\hat{I}^+$ is

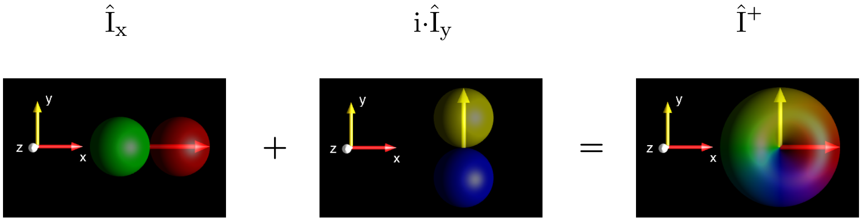


Figure 4: Visual representation for the definition of the raising operator: $\hat{I}_x + i\hat{I}_y = \hat{I}^+$

Note the colors of the operators $\hat{I}_x$ and $i{\cdot}\hat{I}_y$ and the distribution of the colors in the raising operator $\hat{I}^+$.

Similarly, the definition of $\hat{I}^-$ is

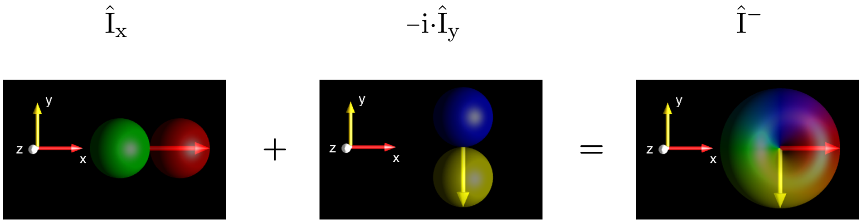


Figure 5: Visual representation for the definition of the lowering operator: $\hat{I}_x - i\hat{I}_y = \hat{I}^-$

A clear distinction between raising operator $\hat{I}^+$ and lowering operator $\hat{I}^-$ can be made. For the raising operator, the rainbow color gradient (red, yellow, green, blue) is counter-clockwise. For the lowering operator, on the other hand, this color gradient is clockwise.

In addition to the representation in DROPS, Figure 4 and 5 illustrate the representation of operators in terms of vectors (red and yellow arrows). Linear cartesian spin operators (e.g. $\hat{I}_x$) can be represented as three-dimensional real vectors. These vectors are represented by red arrows within SpinDrops. Imaginary vectors (e.g. $i{\cdot}\hat{I}_y$) are represented by yellow arrows.

According to these definitions, the operators for the transverse magnetization $\hat{\mathrm{I}}_{\mathrm{x}}$ and $\hat{\mathrm{I}}_{\mathrm{y}}$ can be expressed in terms of the raising operator $\hat{\mathrm{I}}^{+}$ and lowering operators $\hat{\mathrm{I}}^{-}$.

$\frac{1}{2}\hat{\mathrm{I}}^{+}$ $\quad$ $\frac{1}{2}\hat{\mathrm{I}}^{-}$ $\quad$ $\hat{\mathrm{I}}_{\mathrm{x}}$

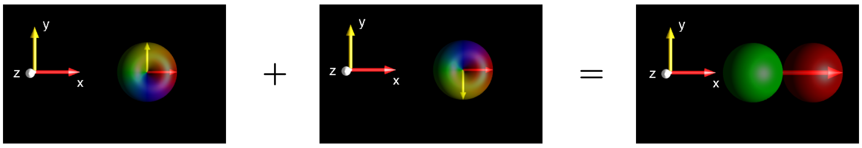


Figure 6: Visual representation for $\hat{\mathrm{I}}_{\mathrm{x}}$ in terms of $\hat{\mathrm{I}}^{+}$ and $\hat{\mathrm{I}}^{-}$: $\frac{1}{2}(\hat{\mathrm{I}}^{+} + \hat{\mathrm{I}}^{-}) = \hat{\mathrm{I}}_{\mathrm{x}}$

$\frac{1}{2i}\hat{\mathrm{I}}^{+}$ $\quad$ $-\frac{1}{2i}\hat{\mathrm{I}}^{-}$ $\quad$ $\hat{\mathrm{I}}_{\mathrm{y}}$

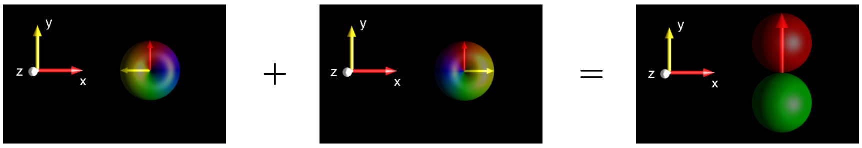


Figure 7: Visual representation for $\hat{\mathrm{I}}_{\mathrm{y}}$ in terms of $\hat{\mathrm{I}}^{+}$ and $\hat{\mathrm{I}}^{-}$: $\frac{1}{2i}(\hat{\mathrm{I}}^{+} - \hat{\mathrm{I}}^{-}) = \hat{\mathrm{I}}_{\mathrm{y}}$

Note that the red and green areas accumulate. The yellow and blue areas, on the other hand, cancel each other. This is due to the fact that they are of opposite sign. Remember that the color code is as follows:

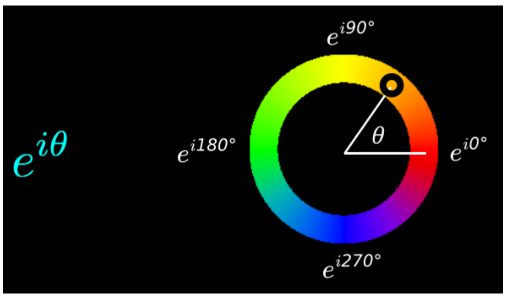


Figure 8: SpinDrops color code

$$
\begin{array}{llll}
\text{red} & \equiv e^{i0°} & = & 1 \\
\text{yellow} & \equiv e^{i90°} & = & i \\
\text{green} & \equiv e^{i180°} & = & -1 \\
\text{blue} & \equiv e^{i270°} & = & -i
\end{array}
$$

Exercise:

Verify the expressions for the transverse magnetizations in terms of raising and lowering operator. The separation of an operator into its part of different coherences can be achieved very easily within SpinDrops.

Choose:

- ***Spin System*** $\ggg$ ***1-Spin***
- ***Initial State*** $\ggg$ ***I1x (or I1y)***
- ***Options*** $\ggg$ ***Separation*** $\ggg$ ***Coh. Order p***
  Make sure the experiment timeline is at t=0.

After you have chosen ***Coh. Order p*** you will see the separation of the operator. The part of the state ($\hat{\mathrm{I}}_{\mathrm{x}}$ or $\hat{\mathrm{I}}_{\mathrm{y}}$) that corresponds to the positive coherence order p=+1 is illustrated above the xy-plane. The negative part of the coherence order, p=−1, can be seen underneath this plane.

In order to return to the usual representation, choose:

- ***Options*** $\ggg$ ***Separation*** $\ggg$ ***Standard***

2.2 Definition of Coherence Order p

Section 2.1 introduced the raising operator $\hat{\mathrm{I}}^{+}$ and the lowering operator $\hat{\mathrm{I}}^{-}$. It has been stated that the raising operator has a coherence order of $p(\hat{\imath}^{+})=+1$, and the lowering operator has a coherence order of $p(\hat{\imath}^{-})=-1$. Now it's time to discuss what the coherence order actually is.

The coherence order p is based on what happens to a particular state $\hat{\mathrm{p}}$ (e.g. an operator or product operator) when a z-rotation through an angle Φ is applied. If the operator only acquires a phase of $(-\boldsymbol{p}\cdot\Phi)$, the operator is said to have coherence order $\boldsymbol{p}$.[2]

This definition can be expressed in the following symbolic representation:

$$\hat{p}^{(\boldsymbol{p})} \xrightarrow{\textit{rotate by } \Phi \textit{ about z-axis}} \hat{p}^{(\boldsymbol{p})} \cdot e^{-i\cdot\boldsymbol{p}\cdot\Phi}$$

(Note: Since the operator $\hat{\mathrm{I}}_{\mathrm{z}}$ is not affected by any rotation about the z-axis, we see immediately that $\hat{\mathrm{I}}_{\mathrm{z}}$ corresponds to a coherence order of $p=0$.)

[2] based on J. Keeler, *Understanding NMR Spectroscopy*, 2nd ed. (Wiley,Chichester, 2010).

In order to get a better understanding of coherence orders and the corresponding definition, let's have a look at a concrete example.

A good starting point is to take the raising operator $\hat{\mathrm{I}}^{+}$ as our initial state. It has been stated that this operator corresponds to a coherence order of p=+1. Now that we know how the coherence order is defined, we can try to verify this statement. For that reason, we let this state evolve under a z-rotation through an angle Φ.

First we will use the definition of the raising operator $\hat{\mathrm{I}}^{+}$ to split it into the transverse magnetizations $\hat{\mathrm{I}}_{\mathrm{x}}$ and $\hat{\mathrm{I}}_{\mathrm{y}}$.

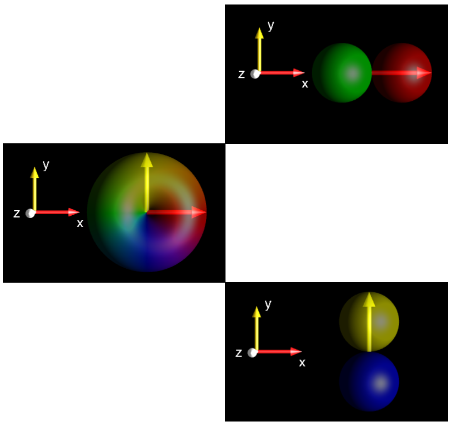


Figure 9: Evolution of $\hat{\mathrm{I}}^{+}$ under z-rotation of angle Φ:
a) Splitting of $\hat{\mathrm{I}}^{+}$ into its $\hat{\mathrm{I}}_{\mathrm{x}}$- and $\hat{\mathrm{I}}_{\mathrm{y}}$-components

We can evolve the transverse magnetizations $\hat{I}_x$ and $\hat{I}_y$ in the usual manner. For the visualization we will use an angle Φ of 45°.
(However, any angle would result in the same value for the coherence order p)

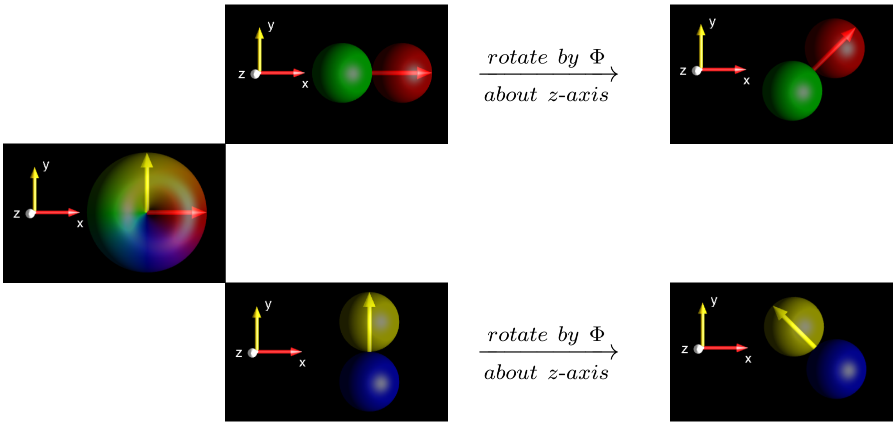


Figure 10: Evolution of $\hat{I}^+$ under z-rotation of angle Φ:
a) Splitting of $\hat{I}^+$ into its $\hat{I}_x$- and $\hat{I}_y$-components
b) Evolution of the $\hat{I}_x$- and $\hat{I}_y$-components

As you might have expected, the transverse magnetizations will simply rotate by an angle Φ (here 45°).

Merging the evolved transverse magnetizations results in the initial raising operator $\hat{I}^+$. However, under the z-rotation of angle Φ, the raising operator has acquired a phase. The raising operators before and after the rotation about the z-axis are illustrated in Figure 11.

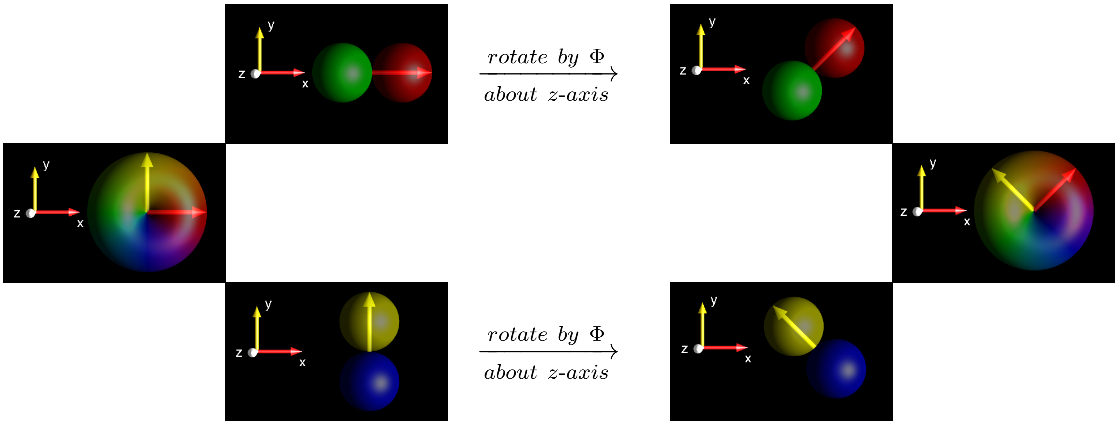


Figure 11: Evolution of $\hat{I}^+$ under z-rotation of angle Φ:
a) Splitting of $\hat{I}^+$ into its $\hat{I}_x$- and $\hat{I}_y$-components
b) Evolution of the $\hat{I}_x$- and $\hat{I}_y$-components
c) Recombine the $\hat{I}_x$- and $\hat{I}_y$-components

You can test the effect of a z-rotation of angle Φ on the raising operator $\hat{I}^+$ on your own. Therefore choose:

- ***Spin System*** ⋙ ***1-Spin***
- ***Initial State*** ⋙ ***I1(+)***
- ***Pulse Sequence*** ⋙ ***Rotation*** ⋙ ***z Rotation***
  and select one of the predefined angles.

Alternatively, you can use a delay time to realize an arbitrary rotation about the z-axis. However, you have to take care of the relation between your delay time and the offset frequency of your spin. Following the procedure below leads to a rotation by an eighth of a full turn, i.e. an angle of 45°.

- ***Spin System*** ⋙ ***1-Spin***
- ***Spin System*** ⋙ ***Parameters***
  and set the offset frequency ν_1 *to 1 Hz.*
- ***Initial State*** ⋙ ***I1(+)***
- ***Options*** ⋙ ***Preferences...***
  and make sure that ***Advanced Sequence Editor*** *is not selected.*
- ***Pulse Sequence*** ⋙ ***Edit Sequences...***
  and set only one entry with a delay time of 125 ms ($= \frac{1}{8}$ *s).*

For any angle Φ the raising operator acquires a phase of $(-p \cdot \Phi)$=$(-\,[+\mathbf{1}]\cdot\Phi)$. This can be seen by fixing a certain point of the raising operator before the rotation, e.g. a point located in the red area. During the rotation, the color at this point changes continuously from red $\equiv e^{i0°}$ (at Φ=0°) to blue $\equiv e^{i270°} = e^{-i90°}$ (at Φ=90°) to green $\equiv e^{\pm i180°}$ (at Φ=180°) and so on (dependent on the choice of the rotational angle Φ).

Using the definition of the coherence order p

$$\hat{p}^{(p)} \xrightarrow{\textit{rotate by } \Phi \textit{ about z-axis}} \hat{p}^{(p)} \cdot e^{-i \cdot p \cdot \Phi}$$

we have shown that the raising operator $\hat{\mathrm{I}}^{+}$ corresponds to a coherence order p of +1.

Mathematical development:

$$
\begin{aligned}
\hat{\mathrm{I}}^{+} = \hat{\mathrm{I}}_{\mathrm{x}} + i\hat{\mathrm{I}}_{\mathrm{y}} \quad \xrightarrow{\Phi\hat{\mathrm{I}}_{\mathrm{z}}} \quad & \hat{\mathrm{I}}_{\mathrm{x}}\cos\Phi + \hat{\mathrm{I}}_{\mathrm{y}}\sin\Phi + i(\hat{\mathrm{I}}_{\mathrm{y}}\cos\Phi - \hat{\mathrm{I}}_{\mathrm{x}}\sin\Phi) && (1)\\
=& (\hat{\mathrm{I}}_{\mathrm{x}} + i\hat{\mathrm{I}}_{\mathrm{y}})\cos\Phi - i(\hat{\mathrm{I}}_{\mathrm{x}} + i\hat{\mathrm{I}}_{\mathrm{y}})\sin\Phi && (2)\\
=& (\hat{\mathrm{I}}_{\mathrm{x}} + i\hat{\mathrm{I}}_{\mathrm{y}})(\cos\Phi - i\sin\Phi) && (3)\\
=& \hat{\mathrm{I}}^{+}e^{-i\Phi} && (4)
\end{aligned}
$$

In (1) we use the definition of the raising operator

$$\hat{\mathrm{I}}^{+} = \hat{\mathrm{I}}_{\mathrm{x}} + i\hat{\mathrm{I}}_{\mathrm{y}}$$

and let these two terms evolve under z-rotation through an angle Φ according to the theory of angular momentum operators. Closed form solutions for the evolution of angular momentum operators within experiments can be found in NMR-textbooks[3].

To go from (3) to (4), again the definition of the raising operator $\hat{\mathrm{I}}^{+}$ is used, as well as Euler's formula

$$\cos\Phi - i\sin\Phi = e^{-i\Phi}$$

[3] e.g. J. Keeler, *Understanding NMR Spectroscopy*, 2nd ed. (Wiley,Chichester, 2010)

Exercise:

What do you expect happens to the lowering operator $\hat{\mathrm{I}}^{-}$ under a z-rotation through an angle of 90°?

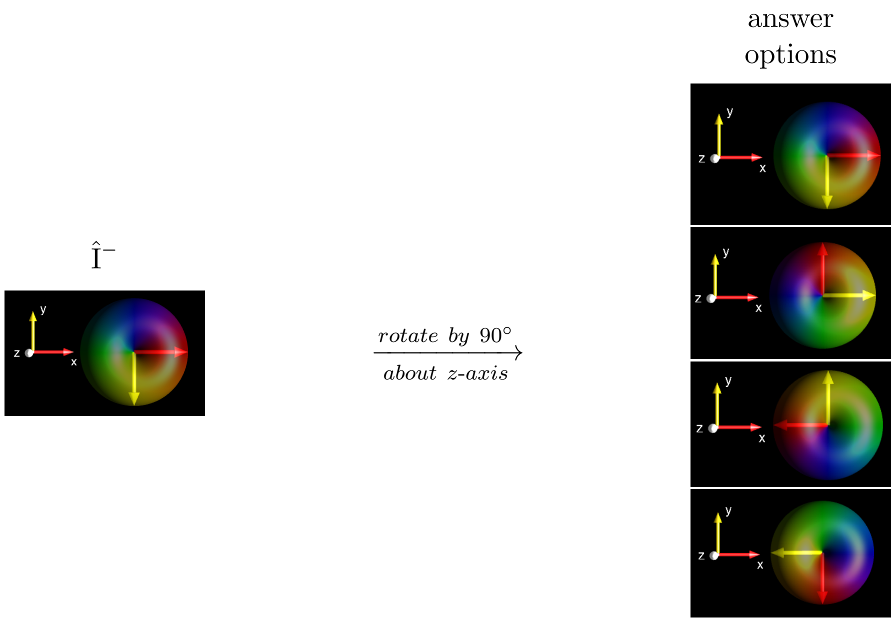


Figure 12: Operator $\hat{\mathrm{I}}^{-}$ (left) and four answer options (right) for its representation after a z-rotation through an angle of 90°.

Check if your expectation is correct. In order to do this, choose:

- ***Spin System ⋙ 1-Spin***
- ***Initial State ⋙ I1(-)***
- ***Pulse Sequence ⋙ Rotation ⋙ z Rotation ⋙ 90°(z)***

Alternatively, you can simulate a delay of time $\frac{1}{4\nu}$, with ν being the offset frequency of your spin. For example:

- ***Spin System*** ⋙ ***1-Spin***
- ***Spin System*** ⋙ ***Parameters***
  and set ν_1*=1 Hz.*
- ***Initial State*** ⋙ ***I1(-)***
- ***Options*** ⋙ ***Preferences...***
  and make sure that ***Advanced Sequence Editor*** *is not selected.*
- ***Pulse Sequence*** ⋙ ***Edit Sequence...***
  and set only one entry with a delay time of 250 ms.

Press the play button and compare the result with your expectation.

Explanation:

Since the lowering operator $\hat{\mathrm{I}}^-$ corresponds to a coherence order of -1, the rotation through an angle Φ=90° leads to a phase of $(-p \cdot \Phi)$=$(-[\mathbf{-1}]\cdot 90°)$= 90°. Using the same approach as for the raising operator, we fix a point located in the red area of the lowering operator before the rotation has been carried out. Due to the coherence order of -1, this point will correspond to a yellow area after the rotation of Φ=90° has been carried out. Thus, in contrast to the raising operator the change in color is in the opposite direction.

In addition, we can also find the solution very easily by using the following approach. The rotation of 90° results in a phase of $(-p \cdot \Phi)$=$(-[\mathbf{-1}]\cdot 90°)$ for the lowering operator $\hat{\mathrm{I}}^-$. However, a phase of $(-[\mathbf{-1}]\cdot 90°) \;\widehat{=}\; e^{i90°} = e^{i\cdot\frac{\pi}{2}} = i$. This means, we simply have to multiply our initial state $\hat{\mathrm{I}}^-$ with a value of i to find the correct solution. In order to do this, we refer to the color coding shown below:

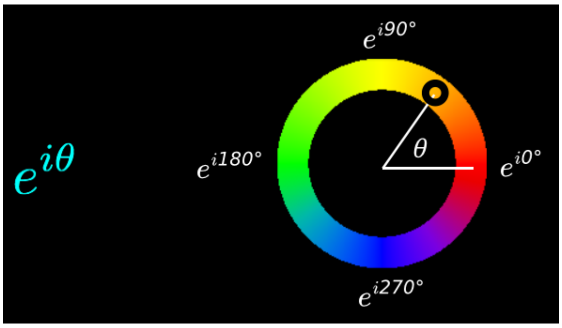


Figure 13: SpinDrops color code

The multiplication will have the following effect:

$$\begin{aligned}
\text{red} \equiv 1 \quad &\xrightarrow{\textit{multiply with } i} \quad 1 \cdot i = i \equiv \text{yellow} \\
\text{yellow} \equiv i \quad &\xrightarrow{\textit{multiply with } i} \quad i \cdot i = -1 \equiv \text{green} \\
\text{green} \equiv -1 \quad &\xrightarrow{\textit{multiply with } i} \quad -1 \cdot i = -i \equiv \text{blue} \\
\text{blue} \equiv -i \quad &\xrightarrow{\textit{multiply with } i} \quad -i \cdot i = 1 \equiv \text{red}
\end{aligned}$$

2.3 Zero- and Multiple-Quantum Coherences

So far we have seen that the operators $\hat{\mathrm{I}}_\mathrm{x}$ and $\hat{\mathrm{I}}_\mathrm{y}$ can be split into parts with coherence order p=+1 and p=−1. Such operators are said to represent ***single-quantum coherence***. Beyond those also ***multiple-quantum coherences*** (with e.g. p=±2) or ***zero-quantum coherences*** (with p=0) can appear.

For example, create $2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{x}}$ as the initial state, and view its coherence orders:

- ***Spin System*** $\ggg$ ***2-Spin***
- ***Initial State*** $\ggg$ ***Edit Initial State...***
  and then create the state $2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{x}}$.

  Dependent on your settings under
  Options $\ggg$ ***Preferences...***
  there are two ways:

  1. ***Edit Operator by String*** *inactive:*
     Create the following state.

Terms		Real Part	Imag. Part
x	x	1	0
Add		Delete	Clear All

  2. ***Edit Operator by String*** *active:*
     Enter `2I1xI2x` *as your* ***Product Op. Expression***
     and confirm with ***OK***.

- ***Options*** $\ggg$ ***Separation*** $\ggg$ ***Coh. Order p***

Exercise:

What are the coherence orders that constitute the state $2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{x}}$? Do you have an idea why these coherence orders appear?

Hint: Use the definition of $\hat{\mathrm{I}}_{i\mathrm{x}}$ *(i=1,2) in terms of the raising and lowering operator and multiply the terms.*

Mathematical development:

$$2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{x}} = 2\left[\frac{1}{2}(\hat{\mathrm{I}}_1^+ + \hat{\mathrm{I}}_1^-)\frac{1}{2}(\hat{\mathrm{I}}_2^+ + \hat{\mathrm{I}}_2^-)\right] \tag{1}$$

$$\begin{array}{rccccccc} = \frac{1}{2}[\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ & + & \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^- & + & \hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^- & + & \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^+] \\ p = +2 & & p = -2 & & p = 0 & & p = 0 \end{array} \tag{2}$$

In (1) we replace the $\hat{\mathrm{I}}_{ix}$ (i=1,2) operators by using the following definition

$$\hat{\mathrm{I}}_{\mathrm{ix}} = \frac{1}{2}(\hat{\mathrm{I}}_\mathrm{i}^+ + \hat{\mathrm{I}}_\mathrm{i}^-)$$

The operator $\hat{\mathrm{I}}_1^+$ corresponds to coherence order p=+1. The same holds true for $\hat{\mathrm{I}}_2^+$. Let's now focus on the term $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$. In order to determine the coherence order of this term, the effect of a z-rotation of angle Φ is examined.

$$\begin{aligned} \hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ \quad \xrightarrow{\Phi\hat{\mathrm{I}}_\mathrm{z}} \quad & (\hat{\mathrm{I}}_1^+ e^{-i\cdot 1\cdot\Phi})\cdot(\hat{\mathrm{I}}_2^+ e^{-i\cdot 1\cdot\Phi}) \\ =& \hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ e^{-i\cdot(1+1)\cdot\Phi} \\ =& \hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ e^{-i\cdot 2\cdot\Phi} \end{aligned}$$

The coherence order of $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ is determined according to its definition in subsection 2.2. The coherence order for the term $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ is then simply the sum of the coherence orders of the individual operators. Thus, the coherence order for $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ is p=+2. Similarly, the coherence order of $\hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^-$ is p=−2.
It follows that the remaining two terms $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^-$ and $\hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^+$ both have a coherence order of p=0.

The representation with separated coherence orders shows exactly the result from above. One operator at p=+2 (second line above the xy-plane), one operator at p=−2 (second line below the xy-plane) and a combination of two operators, each with p=0 (at the line located in the xy-plane). Thus, we can see that the product operator $2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{x}}$ consists of parts with double-quantum coherence and zero-quantum coherence.

$2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{x}}$

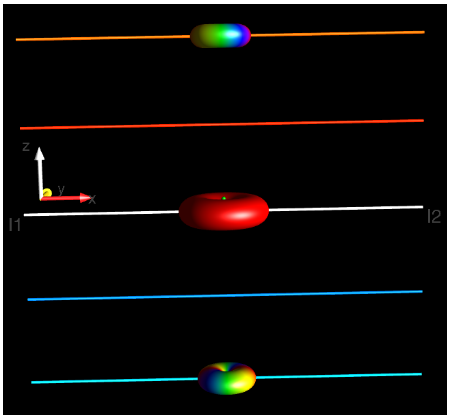


Figure 14: Coherence-order-separated representation of $2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{x}}$.

Exercise:

We have already seen how a state with p=+1 evolves under a z-rotation of an angle Φ. Now we focus on a state with p=+2. Figure 15 illustrates the $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ operator.
Try to predict the phase acquired by this operator resulting from a z-rotation through an angle of 45°. Focus on a red area of the operator prior to the z-rotation. Which color corresponds to this area after the z-rotation? What is the difference compared to the operator $\hat{\mathrm{I}}^+$ with p=+1?

$\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$

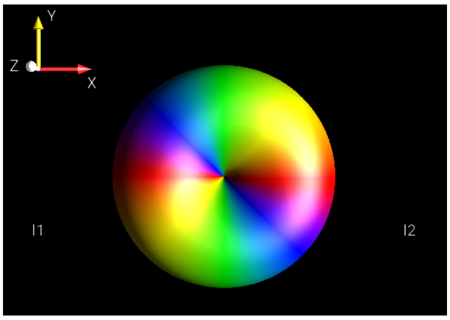


Figure 15: Operator $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$

Explanation:

The $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ operator corresponds to a coherence order of +2. The rotation through an angle of Φ=45° is illustrated in Figure 16 and leads to a phase of $(-p \cdot \Phi)$=(– [+**2**]·45°)=–90°, which is equivalent to $e^{-i90^\circ}=e^{-i\cdot\frac{\pi}{2}}=-i$. This means, we have to multiply our initial state with a value of $-i$ to find the correct solution. Since a red area corresponds to a value of 1, the z-rotation changes this area according to $1\cdot(-i)=-i$. Thus, after the z-rotation this area is blue. This is in contrast to the z-rotation through an angle of 45° with initial state $\hat{\mathrm{I}}^+$. Figure 11 shows that the area after the rotation corresponds to a color halfway between red and blue. Thus, the change in phase resulting from a z-rotation through an angle Φ is twice as fast for $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ with p=+2 compared to $\hat{\mathrm{I}}^+$ with p=+1.

$\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ $\qquad\qquad$ $-i\cdot\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$

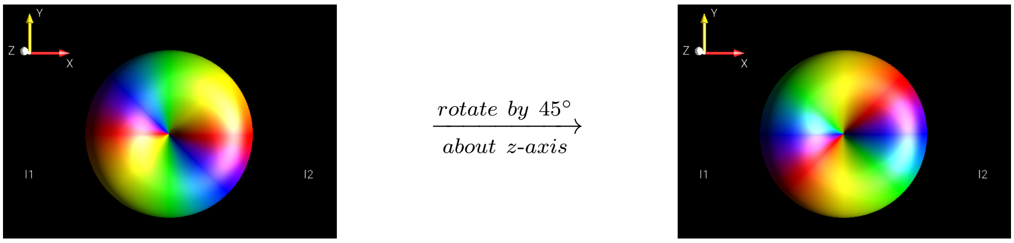


Figure 16: Operator $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ before (left) and after z-rotation through an angle of 45° (right).

You can test the z-rotation with initial state $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ on your own. The following procedure leads to a rotation through an angle of 45°.

- ***Spin System*** ⋙ ***2-Spin***
- ***Spin System*** ⋙ ***Parameters***
  and set the offset frequencies ν_1 *and* ν_2 *to 1 Hz,*
  and the coupling J_{12} *to zero.*
- ***Initial State*** ⋙ ***MQ(+/-ops.)*** ⋙ ***2Q(I1,I2)*** ⋙ ***I1(+)*I2(+)***
- ***Options*** ⋙ ***Preferences...***
  and make sure that ***Advanced Sequence Editor*** *is not selected.*
- ***Pulse Sequence*** ⋙ ***Edit Sequences...***
  and set only one entry with a delay time of 125 ms ($=\frac{1}{8}$ *s*).

2.4 Coherence Orders and Pulses

Experiments consist of pulses and delays. Coherence orders can be changed by pulses, while they remain constant during a delay.

In order to see the effect of a pulse, let's apply a 90°_x pulse to the operator $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$. Therefore, choose:

- ***Spin System*** $\ggg$ ***2-Spin***
- ***Initial State*** $\ggg$ ***MQ(+/-ops.)*** $\ggg$ ***2Q(I1,I2)*** $\ggg$ ***I1(+)*I2(+)***
- ***Options*** $\ggg$ ***Separation*** $\ggg$ ***Coh. Order p***
- ***Pulse Sequence*** $\ggg$ ***Rotation*** $\ggg$ ***90° Pulse*** $\ggg$ ***90°(x)***

The initial operator $\hat{I}_1^+\hat{I}_2^+$ corresponds to p=+2. Thus, prior to applying the pulse we see only this coherence order. When we press the play button to apply the 90°_x pulse additional coherences start to appear at the expense of our initial coherence order. In our case, the 90°_x pulse leads to a state which has contributions from all coherence orders between +2 and −2.
The initial and final states are shown below.

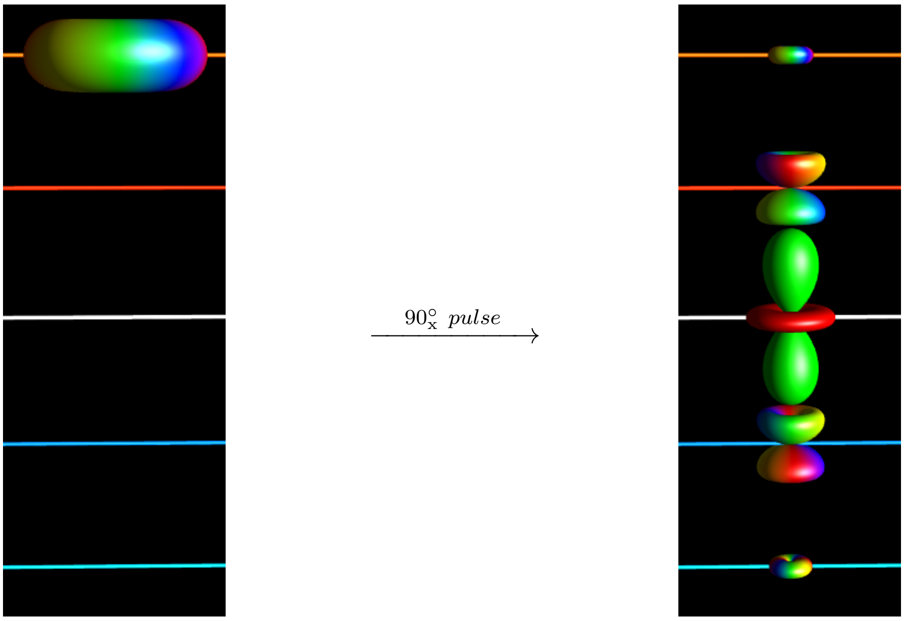


Figure 17: Operator $\hat{I}_1^+\hat{I}_2^+$ (left) and the corresponding state after a 90°_x pulse.

3 The Principles of Phase Cycling

By using phase cycles it is possible to select certain ***coherence pathways*** and reject the others. We will now explore such a selection process in more detail.

When selecting coherence pathways via phase cycling not only one but several experiments will be carried out. In order to avoid confusion, we will call the individual experiments ***sub-experiments*** (or ***scans***). They have to be distinguished from the term ***experiment*** which will be used to represent the sum of all the sub-experiments.

3.1 The Summation Process

In order to become more familiar with the summation process, let's have a look at some examples.

Imagine you have performed two sub-experiments and you want to combine them in order to obtain the final outcome. This situation is illustrated below for $\hat{\mathrm{I}}_\mathrm{z}$ operators with different scaling factors.

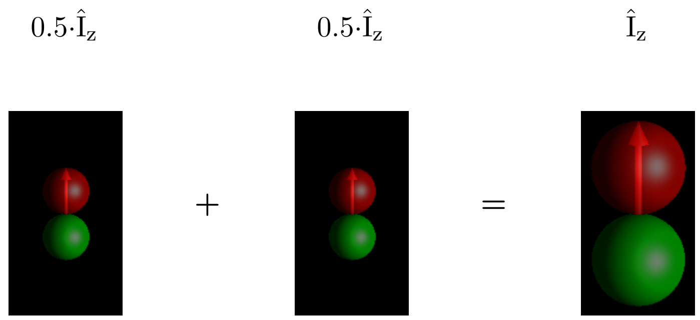


Figure 18: Results of two sub-experiments and their sum.

There is no restriction to the number of sub-experiments. The illustration below shows the summation process using the results of four sub-experiments.

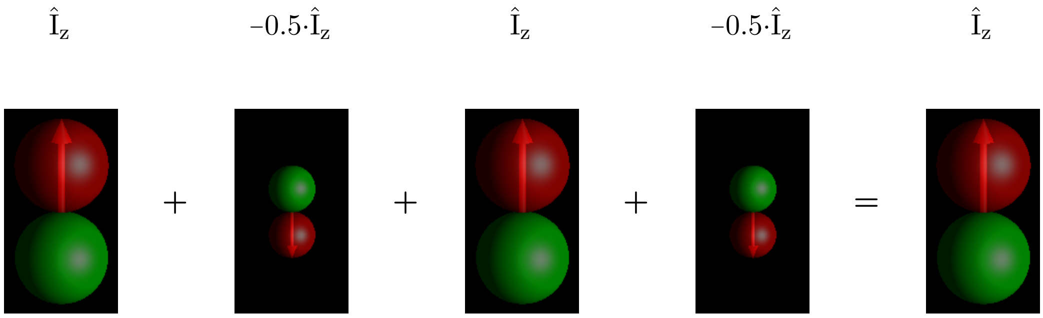


Figure 19: Results of four sub-experiments and their sum.

Within a phase cycling procedure the focus is on the individual coherence orders. We have already seen that SpinDrops allows for a representation with separated coherence orders. Summing sub-experiments in the coherence-separated representation does not differ from the example just given. However, we have to do the summation process for one coherence order after another. The following exercise explores summation.

Exercise:

The illustration in Figure 20 shows the results of two sub-experiments. For each of them, coherence orders p=+1 (top), p=0 (centre) and p=−1 (bottom) are shown. Try to predict the outcome when summing the results of the two sub-experiments.
(Hint: Focus on the color distribution. Areas with opposite sign will cancel each other)

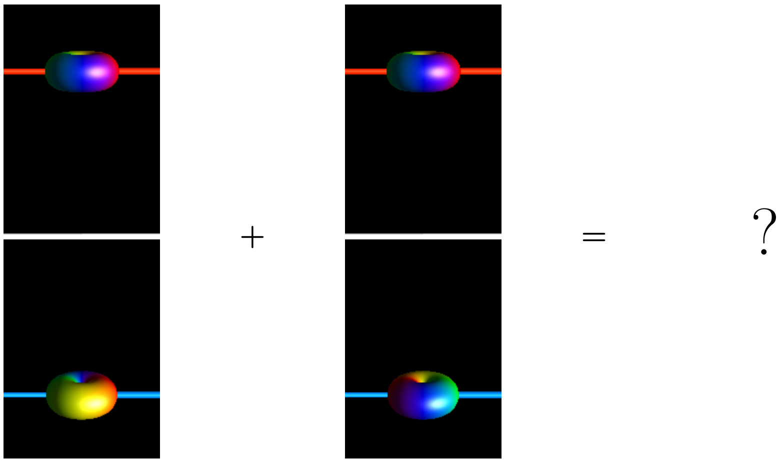


Figure 20: Coherence-separated representation for the results of two sub-experiments.

Explanation:

The summation process within the coherence-separated representation is illustrated below. In order to find the final outcome, we will start with coherence order p=+1. In both sub-experiments this coherence order is populated via $\hat{\mathrm{I}}^{+}$, so the sum corresponds to $2{\cdot}\hat{\mathrm{I}}^{+}$. Coherence order p=0, on the other hand, is not populated in both cases. Thus, we can not expect to find a populated coherence order p=0 when adding up the partial results. Coherence order p=−1 is of greater interest. Here we have $\hat{\mathrm{I}}^{-}$ for the first case and $-\hat{\mathrm{I}}^{-}$ for the second case. Therefore, the summation process zeros p=−1. This example demonstrates that although coherence orders are populated they may cancel each other when summing up the results of the sub-experiments.

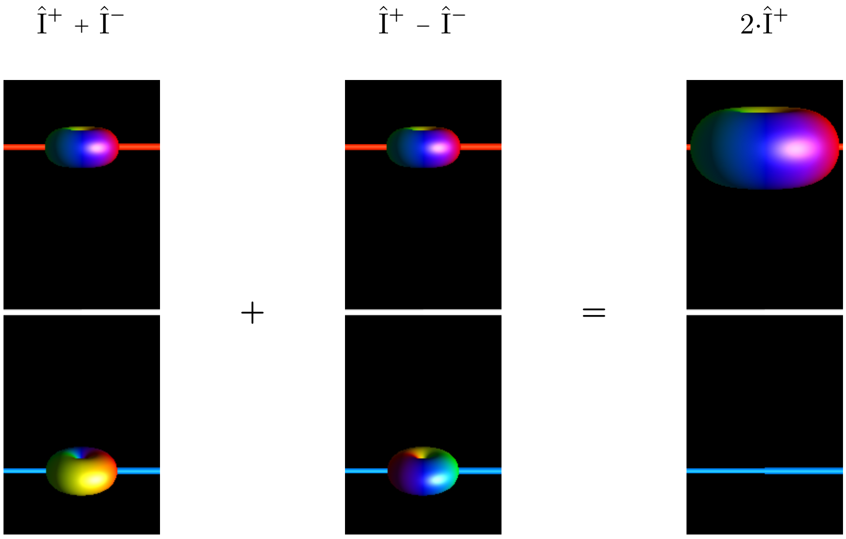


Figure 21: Coherence-separated representation for the results of two sub-experiments and their sum.

3.2 The Phase of Coherences

Within a phase cycling procedure the applied pulse sequence in each sub-experiment is exactly the same, but for specific pulses there will be a shift of $\Delta\Phi$ in the phase. Shifting the phase of a pulse means that its rotation axis is rotated in the xy-plane, e.g. a 90°_x pulse shifted by $\Delta\Phi$=90° is a 90°_y pulse.

In order to become more familiar with such experiments, let's focus on a concrete example. Our initial state will be $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ (coherence order p_0=+2) and 90° pulses will be applied to that state. We will have four sub-experiments with a single 90°_x, 90°_y, $90^\circ_\mathrm{-x}$ or $90^\circ_\mathrm{-y}$ pulse, respectively. These pulses will lead to a population of various coherence orders (denoted with p_1).

Prepare the system as follows:

- ***Spin System*** ⋙ ***2-Spin***
- ***Initial State*** ⋙ ***MQ(+/-ops.)*** ⋙ ***2Q(I1,I2)*** ⋙ ***I1(+)*I2(+)***
- ***Options*** ⋙ ***Separation*** ⋙ ***Coh. Order p***
- ***Pulse Sequence*** ⋙ ***Tutorials*** ⋙ ***Phase Cycling*** ⋙ ***1.Coherence Phase***

Selecting the pulse sequence ***1.Coherence Phase*** will cause a change in the screen layout within SpinDrops. On the left side you will find the individual sub-experiments. This example has four of them. From top to bottom the pulse in each sub-experiment is shifted by 90°. On the right side is the sum of all the sub-experiments.

sub-experiments experiment

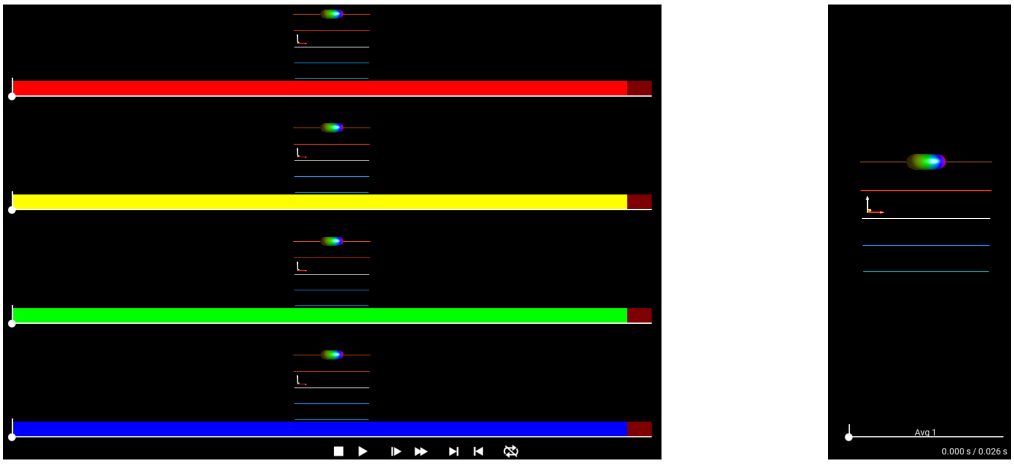


Figure 22: SpinDrops layout for phase cycling experiments; *1.Coherence Phase* at the beginning of the experiment with initial state $\hat{I}_1^+\hat{I}_2^+$.

In general it holds true that if the pulse causes a change in coherence, shifting its phase will result in a shift of the phase of the resulting coherence. We will now focus on the results of the individual sub-experiments and verify this statement. Let's start with coherence order p_1=+2 which is the same as our initial coherence order. As can be seen from Figure 23, shifting pulse phases has no effect on the phase of the final state if initial and final coherence order are the same.

90°_x 90°_y $90^\circ_\mathrm{-x}$ $90^\circ_\mathrm{-y}$

p=+2

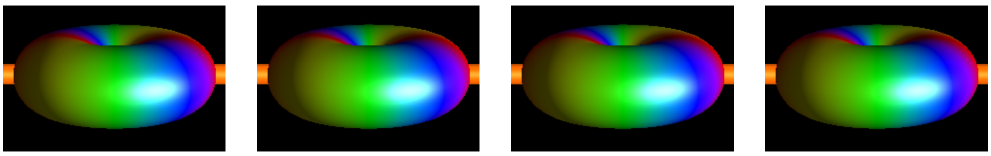


Figure 23: Experiment *1.Coherence Phase* with initial state $\hat{I}_1^+\hat{I}_2^+$, coherence order p_1=+2 after a 90°_x, 90°_y, $90^\circ_\mathrm{-x}$ and $90^\circ_\mathrm{-y}$ pulse.

Let's now focus on the pathway from our initial coherence order p_0=+2 to the coherence order p_1=+1. The results are shown in Figure 24.

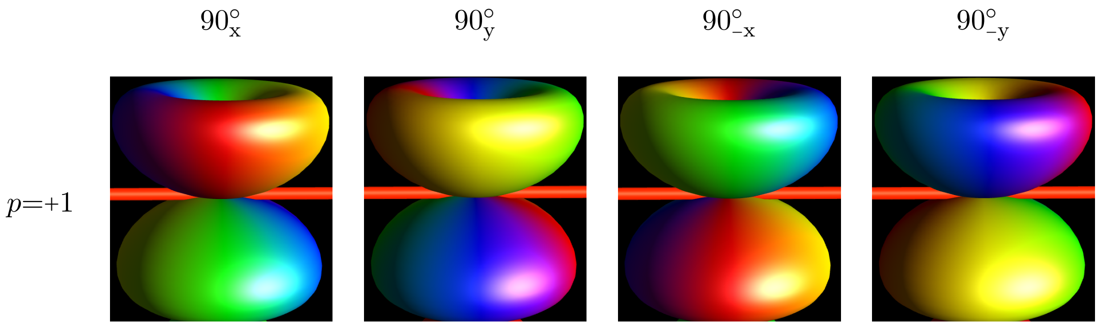


Figure 24: As Figure 23, but for coherence order p_1=+1.

When looking at the phase of the individual coherences, we can see that a shift of the phase of the pulse by 90° results in a shift of the phase of the resulting coherence by 90° (i.e. multiplication by $e^{i90^\circ} = i$). Remember that the color code is as follows:

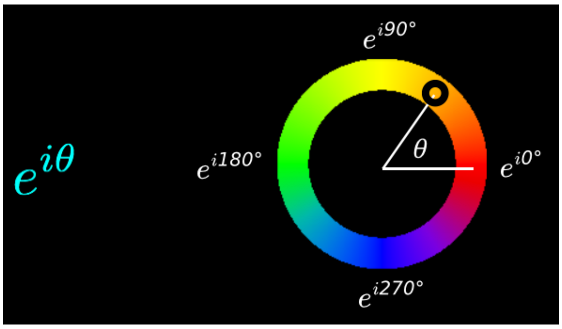


Figure 25: SpinDrops color code

Now let's see what happens for a transition from p_0=+2 to p_1=0. The results from our four sub-experiments at coherence order p_1=0 are illustrated in Figure 26.

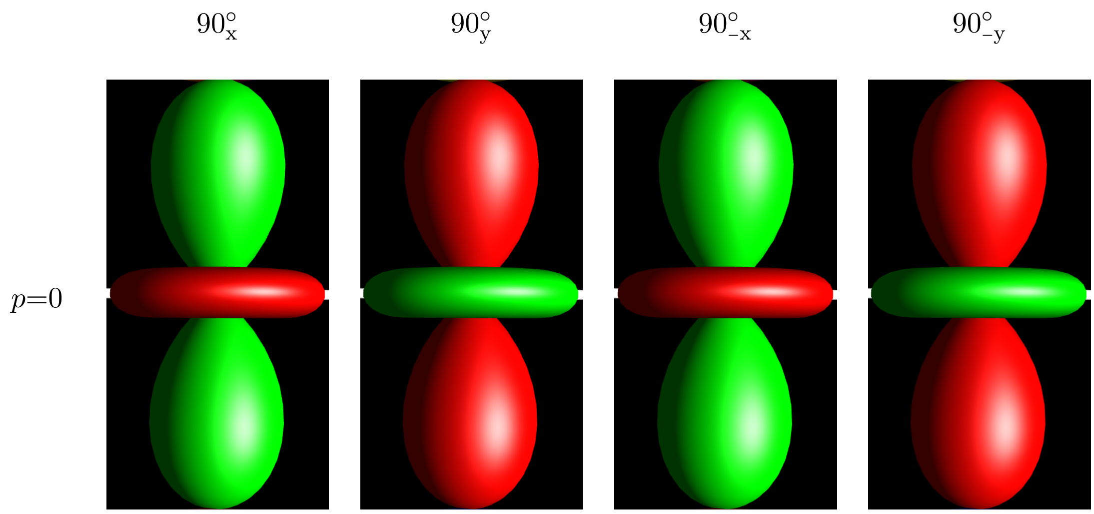


Figure 26: As Figure 23, but for coherence order p_1=0.

When looking at the phase of the individual coherences, we can see that a shift of the phase of the pulse by 90° results in a shift of the phase of the coherence by 180° (i.e. multiplication by $e^{i180^\circ} = -1$).
Consequently, the coherence also acquires a phase shift. However, the phase acquired by the coherence with p=0 is different compared to the coherence with p=+1.

Phase cycling is based on the property that transitions from an initial coherence p_0 to different final coherences p_1 result in different phase shifts of the final coherence.

This behavior can be used to distinguish between different coherence pathways and is a key ingredient for the selection of certain coherences.

Comparing the acquired phase shifts from the example indicates a systematic behavior. In fact, ***shifting the phase of a pulse*** that causes a change in coherence order from p_0 to p_1 ***results in a phase of (−$\Delta p \Delta \Phi$) of the resulting coherence***. Δp (=p_1−p_0) is the change of the coherence order and $\Delta\Phi$ is the change of the phase of the applied pulse.

Exercise:

Having this knowledge about the acquired phase, let's come back to our example system $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$ (coherence order p_0=+2). Focus now on the coherence p_1=−1 after a 90°_x pulse. It is shown below:

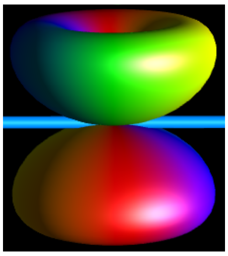


Figure 27: Experiment *1.Coherence Phase* with initial state $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$, coherence order p_1=−1 after a 90°_x pulse.

Try to predict the acquired phase and the color distribution of this coherence after a 90°_y pulse, i.e. after shifting the initial 90°_x pulse by $\Delta\Phi$=90°. After that do the same for a $90^\circ_{-\mathrm{x}}$ and $90^\circ_{-\mathrm{y}}$ pulse.

Mathematical development:

The change in coherence for a transition from p_0=+2 to p_1=−1 is

$$\Delta p = p_1 - p_0 = -1 - (+2) = -3$$

The shift of the phase of the pulse (relative to the 90°_{x} pulse) is

$$\begin{array}{lll}
90^\circ_{\mathrm{x}} \text{ pulse} & \rightarrow 90^\circ_{\mathrm{y}} \text{ pulse} & \Rightarrow \Delta\Phi = 90^\circ \\
90^\circ_{\mathrm{x}} \text{ pulse} & \rightarrow 90^\circ_{\mathrm{-x}} \text{ pulse} & \Rightarrow \Delta\Phi = 180^\circ \\
90^\circ_{\mathrm{x}} \text{ pulse} & \rightarrow 90^\circ_{\mathrm{-y}} \text{ pulse} & \Rightarrow \Delta\Phi = 270^\circ
\end{array}$$

The coherence acquires a phase of $(-\Delta p \Delta\Phi)$. Thus

$$\begin{array}{lllllll}
\Delta\Phi = 90^\circ & \Rightarrow & (-(-3)\cdot 90^\circ) = 270^\circ & \xrightarrow{\textit{map to } 360^\circ\textit{-range}} & 270^\circ & \Rightarrow & e^{i270^\circ} = -i \\
\Delta\Phi = 180^\circ & \Rightarrow & (-(-3)\cdot 180^\circ) = 540^\circ & \xrightarrow{\textit{map to } 360^\circ\textit{-range}} & 180^\circ & \Rightarrow & e^{i180^\circ} = -1 \\
\Delta\Phi = 270^\circ & \Rightarrow & (-(-3)\cdot 270^\circ) = 810^\circ & \xrightarrow{\textit{map to } 360^\circ\textit{-range}} & 90^\circ & \Rightarrow & e^{i90^\circ} = i
\end{array}$$

Now you have to remember the color wheel and multiply each "color" (i.e. phase factor of the coherence) with the calculated phase factors from above. This will lead to the following result:

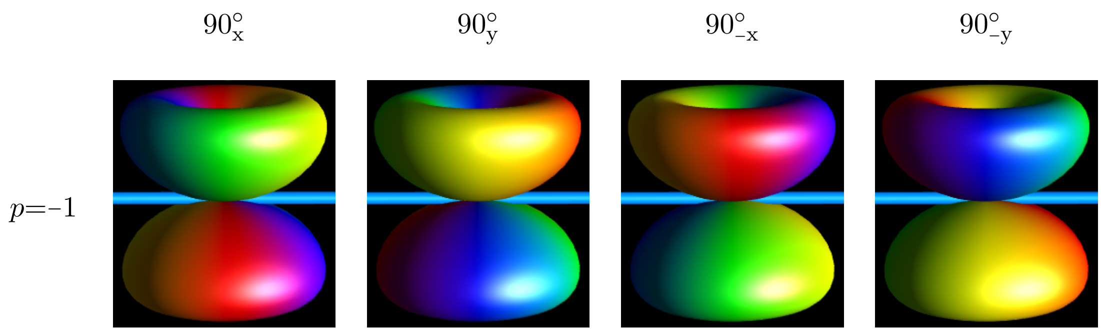


Figure 28: As Figure 23, but for coherence order p_1=−1.

The pathway from our initial coherence order p_0=+2 to the coherence order p_1=−2 corresponds to Δp=−4. Since the pulse applied in the individual sub-experiments is shifted by a multiple of 90°, the phase of the coherence is shifted by a multiple of 360°. The results are shown below:

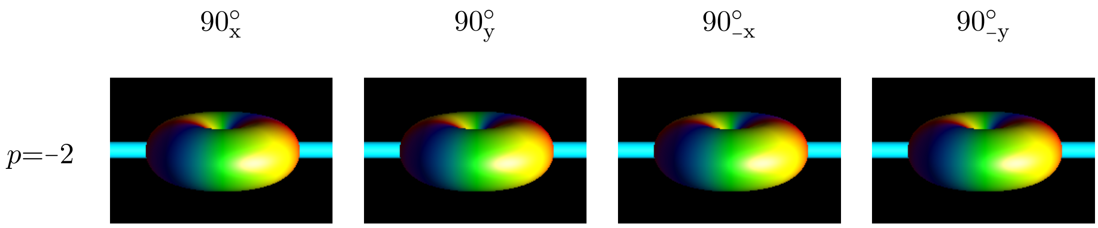


Figure 29: As Figure 23, but for coherence order p_1=−2.

To consider the final result of our experiment, we sum the results from our sub-experiments. This means our focus is now on the right side of the SpinDrops screen. This part of the screen is illustrated in the Figure 30.

The results at coherence orders p=+2 and p=−2 are the same at each sub-experiment. Thus, for the final outcome of our experiment we will have an accumulation at these coherence orders.

The situation is different for the other coherence orders. The graphic reveals vanishing results for each of them. However, it is not immediately obvious why the sum of the sub-experiments leads to this result.

In the next part of the tutorial we will have a closer look of these situations.

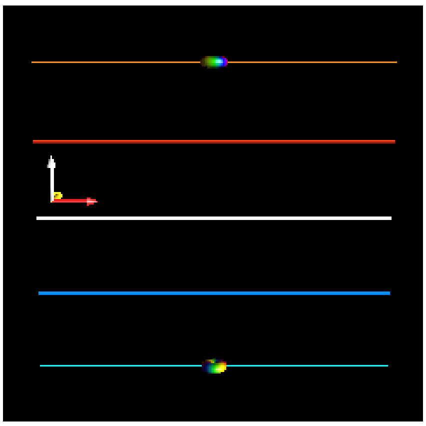


Figure 30: Final result of the experiment *1.Coherence Phase* with initial state $\hat{I}_1^+\hat{I}_2^+$.

3.3 Coherence Pathway Selection via Phase Cycling

3.3.1 Selection of a Single Pathway

So far, we know that different pathways of the coherence result in different phases of the coherence. However, it is still not clear how this will help us to select a certain coherence pathway and reject others.

Let's stick with our example from above and the transition from p_0=+2 to p_1=−1. We now want to combine the results from our four sub-experiments (with 90°_{x}, 90°_{y}, $90^\circ_{\mathrm{-x}}$ and $90^\circ_{\mathrm{-y}}$ pulse), in such a way that individual coherences will add constructively.
Simply adding the four final coherences creates a vanishing result. This is due to the fact that the phase of our coherence after a 90°_{x} pulse is exactly the opposite of our coherence after a $90^\circ_{\mathrm{-x}}$ pulse. The same is true for a 90°_{y} and a $90^\circ_{\mathrm{-y}}$ pulse. The summation for the pairs that cancel each other are illustrated below.

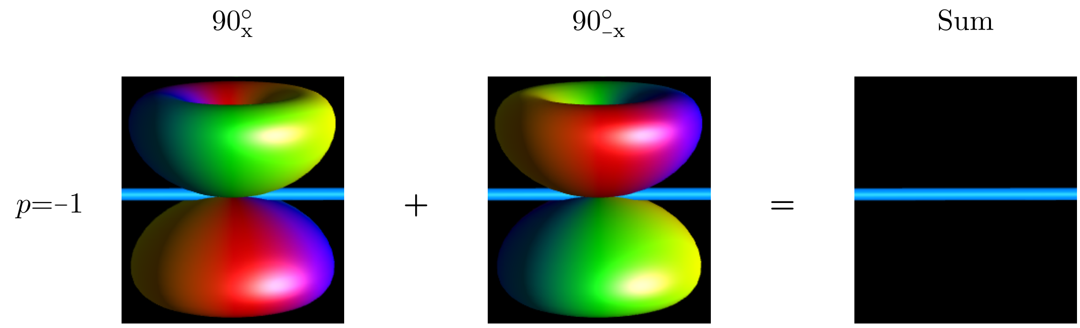


Figure 31: Experiment *1.Coherence Phase* with initial state $\hat{I}_1^+\hat{I}_2^+$, coherence order p_1=−1 after the 90°_{x} and the $90^\circ_{\mathrm{-x}}$ pulse and the sum of these terms.

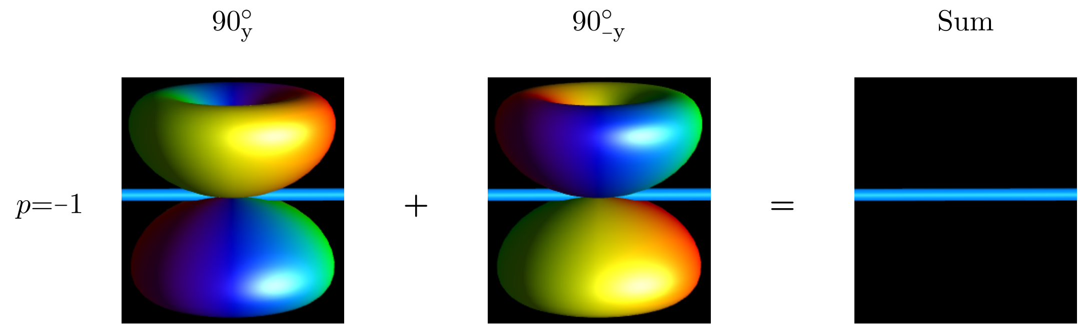


Figure 32: Experiment *1.Coherence Phase* with initial state $\hat{I}_1^+\hat{I}_2^+$, coherence order p_1=−1 after the 90°_{y} and the $90^\circ_{\mathrm{-y}}$ pulse and the sum of these terms.

Thus, if we want the results to add up, we need to modify the phases of the individual coherences before the summation. This modification is performed by using the so-called ***receiver phase***. In order to understand the principle of phase cycling, it is sufficient for us to know that the receiver phase is under our control and we can use it to cause a phase shift to the results of a certain sub-experiment.

We will now take advantage of the receiver phase to modify the phase of the coherences after the individual sub-experiments (i.e. after the 90°_x, 90°_y, $90^\circ_\mathrm{-x}$ and $90^\circ_\mathrm{-y}$ pulses). In order to have a situation in which the individual coherences for p_1=–1 will add up, we use the following receiver phases for the individual sub-experiments:

$$
\begin{array}{rclrcr}
90^\circ_\mathrm{x}\ \text{pulse} & \Rightarrow & \text{receiver phase} & = 0^\circ & \equiv \text{multiplication by} & e^{i0^\circ} = 1 \\
90^\circ_\mathrm{y}\ \text{pulse} & \Rightarrow & \text{receiver phase} & = -270^\circ & \equiv \text{multiplication by} & e^{i(-270^\circ)} = i \\
90^\circ_\mathrm{-x}\ \text{pulse} & \Rightarrow & \text{receiver phase} & = -180^\circ & \equiv \text{multiplication by} & e^{i(-180^\circ)} = -1 \\
90^\circ_\mathrm{-y}\ \text{pulse} & \Rightarrow & \text{receiver phase} & = -90^\circ & \equiv \text{multiplication by} & e^{i(-90^\circ)} = -i
\end{array}
$$

You can prepare the experiment including these receiver phases on your own by selecting:

- ***Spin System*** ⋙ ***2-Spin***
- ***Initial State*** ⋙ ***MQ(+/-ops.)*** ⋙ ***2Q(I1,I2)*** ⋙ ***I1(+)*I2(+)***
- ***Options*** ⋙ ***Separation*** ⋙ ***Coh. Order p***
- ***Pulse Sequence*** ⋙ ***Tutorial*** ⋙ ***Phase Cycling*** ⋙ ***2.Pathway Selection***

Note the difference with respect to the *1.Coherence Phase* experiment: the receiver phases are illustrated as partially transparent element at the and of each pulse sequence. The color indicates the value for the receiver phase using the usual color coding.

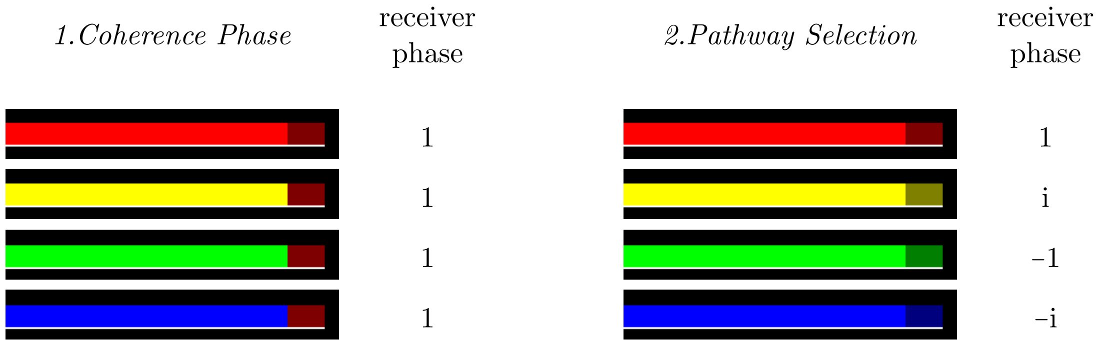


Figure 33: Illustration of receiver phases within SpinDrops.

It is important to point out that for ***real experiments*** the sub-experiments are carried our first and the receiver phase is applied ***afterwards***. Therefore, the left side of the screen within SpinDrops will show you exactly the same for the *1.Coherence Phase* and the *2.Pathway Selection* experiment. However, in order to obtain the sum of the sub-experiments on the right side, the receiver phase is applied, altering the outcome of the overall experiment.

In order to ***grasp the effect of phase cycling*** procedures, it is useful to take the receiver phase into account ***during*** individual sub-experiments. This can be achieved within SpinDrops. Choose:

- ***Options*** ⋙ ***Preferences...***
  and enable ***Apply RX Phase****.*

Having the possibility to see the effect of the receiver phase during sub-experiments is a very helpful feature that will be used for the rest of the tutorial.

Let's now come back to the *2.Pathway Selection* experiment. Using the receiver phases of the *2.Pathway Selection* experiment, we simply turn back the phase shifts gained by the use of different pulse phases with respect to the transition from coherence p_0=+2 to coherence p_1=−1. Thus, the coherences with p_1=−1 will add up. The graphic below compares the situation obtained with the *1.Coherence Phase* (without additional receiver phase) with the results from the *2.Pathway Selection* experiment.

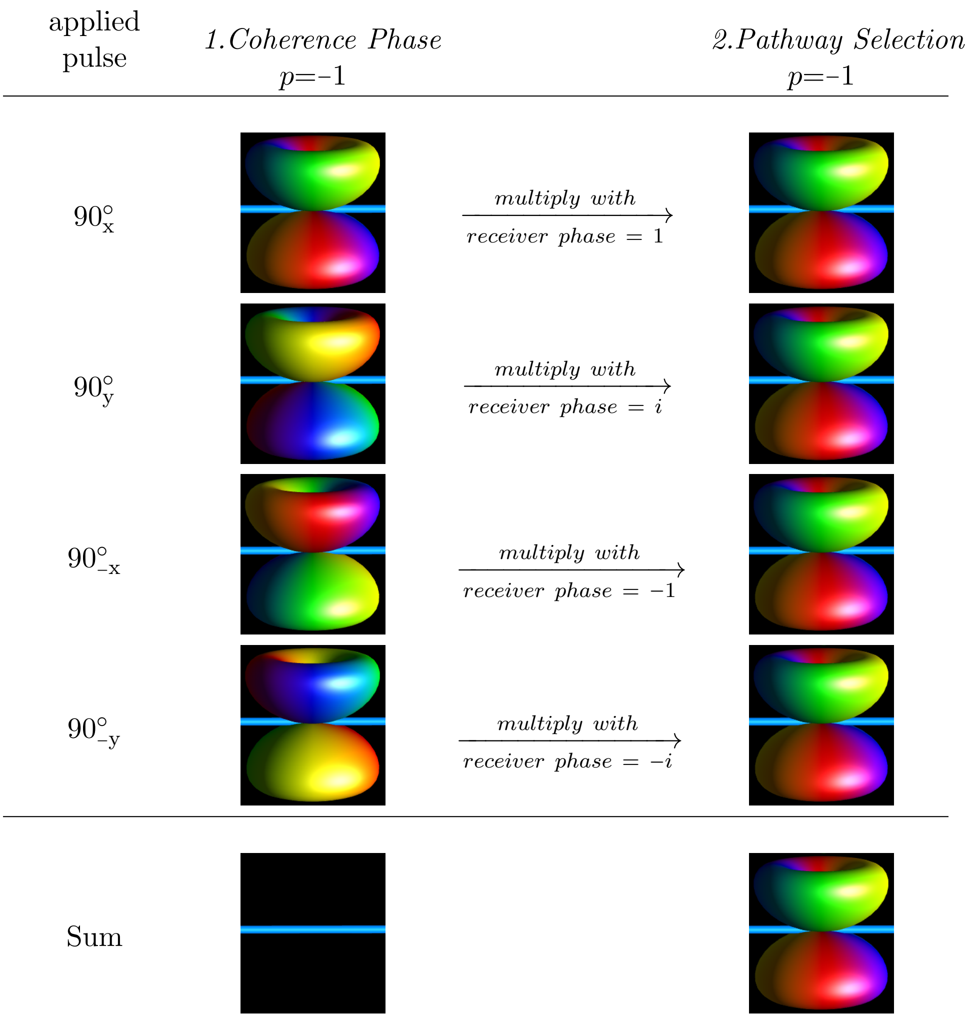


Figure 34: Experiments *1.Coherence Phase* (left) and *2.Pathway Selection* (right) with initial state $\hat{I}_1^+\hat{I}_2^+$, coherence order p_1=−1 after a 90°_x, 90°_y, 90°_{-x} and 90°_{-y} pulse and the sum of the individual terms.

As you can see on the right side of the SpinDrops screen, all the other coherences in this example will cancel. This can also be obtained from Figure 35. It shows the entire outcome from our four sub-experiments modified by the corresponding receiver phase. When adding the results, areas of opposite sign will cancel each other. Consequently, we have vanishing results for all coherence orders, except for p=−1. Thus, we have achieved our goal of selecting a certain coherence pathway.

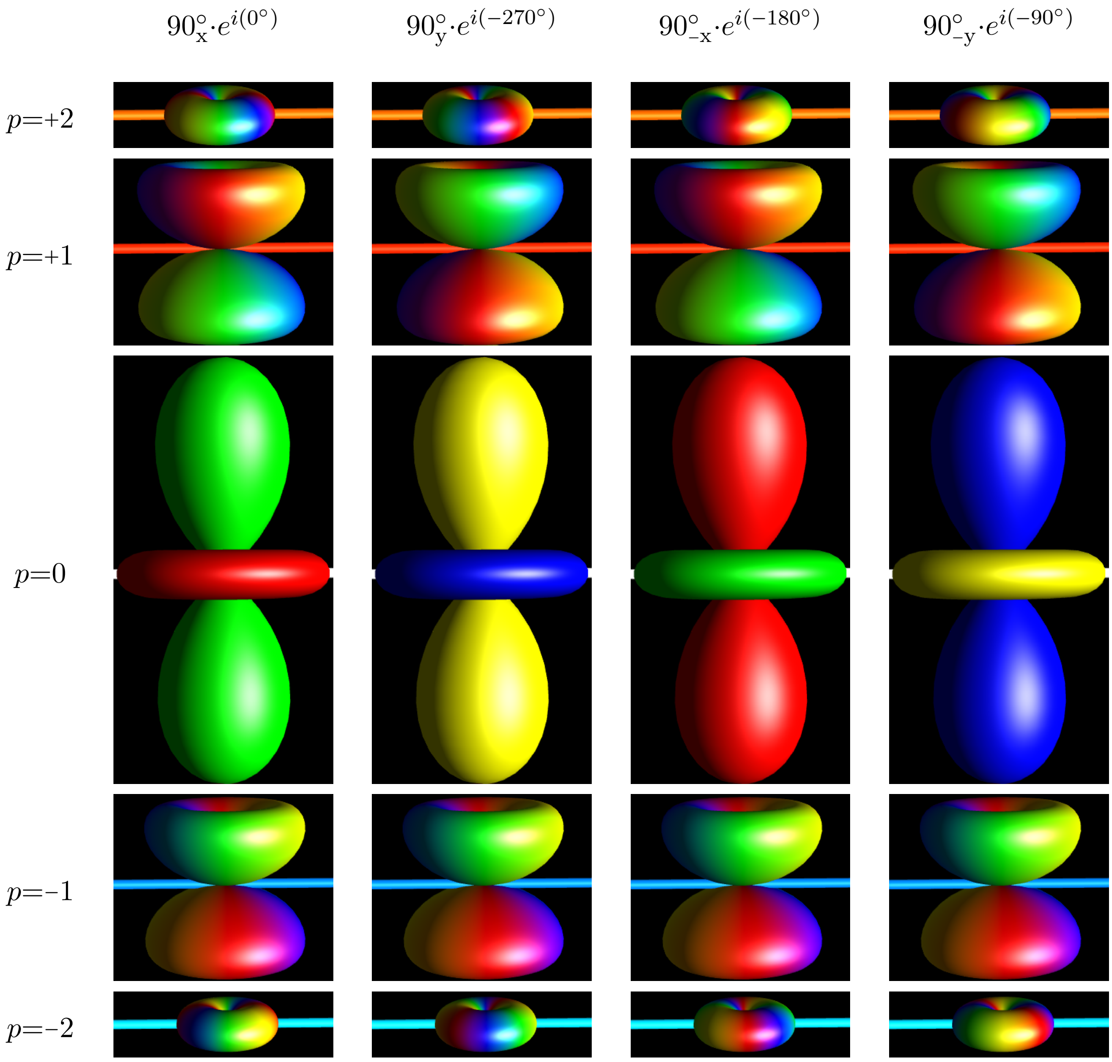


Figure 35: Experiment *2.Pathway Selection* with initial state $\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+$, coherence representation after a 90°_{x}, 90°_{y}, $90^\circ_{\mathrm{-x}}$ and $90^\circ_{\mathrm{-y}}$ pulse. The results of the four sub-experiments are modified by a receiver phase to select the transition to p_1=−1.

3.3.2 Selection of Multiple Pathways

In general, however, not all other coherences must cancel out while only one coherence order remains. What remains is a discrete set of coherence orders.

In the example above our goal was to select the coherence transitions from p_0=+2 to p_1=−1 (i.e. Δp=−3). To achieve this goal, we decided to apply a four-step phase cycle, i.e. we performed four experiments and applied a 90°_x, a 90°_y, a $90^\circ_{-\mathrm{x}}$ and a $90^\circ_{-\mathrm{y}}$ pulse, respectively. Thus, in each experiment we shifted the phase of the pulse by 90°.
The general formula describing a given Δp and a shift of the phase of the pulse by 90° result in the coherence acquiring a phase of

$$(-\Delta p \Delta\Phi) \quad \Rightarrow \quad e^{-i\Delta p\Delta\Phi} \equiv e^{-i\Delta p\cdot\frac{\pi}{2}}.$$ [4]

Equivalent to our selected pathway, all coherences that acquire the same phase will also add up. For a ***four-step*** cycle, this case appears for coherence transitions that differ from our selected one (e.g. from Δp=−3) by a ***multiple of four***, e.g.:

$$\begin{aligned}(-(\Delta p{+}4)\Delta\Phi) \Rightarrow \quad & e^{-i(\Delta p+4)\Delta\Phi} \equiv e^{-i(\Delta p+4)\frac{\pi}{2}} \\ &= e^{-i\Delta p\cdot\frac{\pi}{2}} e^{i4\frac{\pi}{2}} = e^{-i\Delta p\cdot\frac{\pi}{2}} e^{i2\pi} \\ &= e^{-i\Delta p\cdot\frac{\pi}{2}} \cdot 1 = e^{-i\Delta p\cdot\frac{\pi}{2}}\end{aligned}$$

And more generally speaking:

For a N-step cycle the increment of the phase of the pulse corresponds to $\frac{360^\circ}{N} = \frac{2\pi}{N}$. The selection of a particular coherence transition with Δp (achieved by values for the receiver phase that compensate for the phase shift of the selected coherence order) leads to the selection of a discrete set with coherence transitions Δp+nN (n $\in \mathbb{N}$).

However, we do not have to care about all of these coherence transitions. The reason for this is that high orders of multiple-quantum coherences become very unlikely. The generation of multiple-quantum coherence of order m would require a significant coupling of a spin to m−1 other spins. In practice it is usually sufficient to take triple-quantum as the maximum coherence order into consideration.

[4] according to J. Keeler, *Understanding NMR Spectroscopy*, 2nd ed. (Wiley,Chichester, 2010).

As an example for the selection of multiple coherence pathways, let's stick with our $\hat{I}_1^+\hat{I}_2^+$ operator and the transition from p_0=+2 to p_1=−1 (i.e. Δp=−3), but with a two-step cycle (i.e. N=2). In order to prepare the experiment, choose:

- ***Spin System ⋙ 2-Spin***
- ***Initial State ⋙ MQ(+/-ops.) ⋙ 2Q(I1,I2) ⋙ I1(+)*I2(+)***
- ***Options ⋙ Separation ⋙ Coh. Order p***
- ***Pulse Sequence ⋙ Tutorial ⋙ Phase Cycling ⋙ 3.Multiple Pathways***

Since we now know that we actually do not select a single transition Δp, but an entire set with Δp+nN (n $\in \mathbb{N}$), we can assume that coherences other than p_1=−1 will also remain after the phase cycling procedure.

The coherence p_1=+1 will also remain as a consequence of the coherence transition with Δp =−3+1·2 = −1 ($\equiv \Delta p$+nN).

Actually, we have already performed the necessary sub-experiments in the previous section. We simply have to take the results obtained for the 90°_x and the $90^\circ_\mathrm{-x}$ pulse (already multiplied with the corresponding receiver phases, [0°, −180°]). However, we now only add up these two results instead of the four results obtained earlier.

The *3.Multiple Pathways* experiment shows exactly this situation. The summation process is illustrated below. Indeed, only the coherence pathways with Δp=−1 (from p_0=+2 to p_1=+1) and Δp=−3 (from p_0=+2 to p_1=−1) will add up and are therefore "selected". All other coherences that belong to different coherence pathways, however, will be cancelled due to the phase cycling procedure.

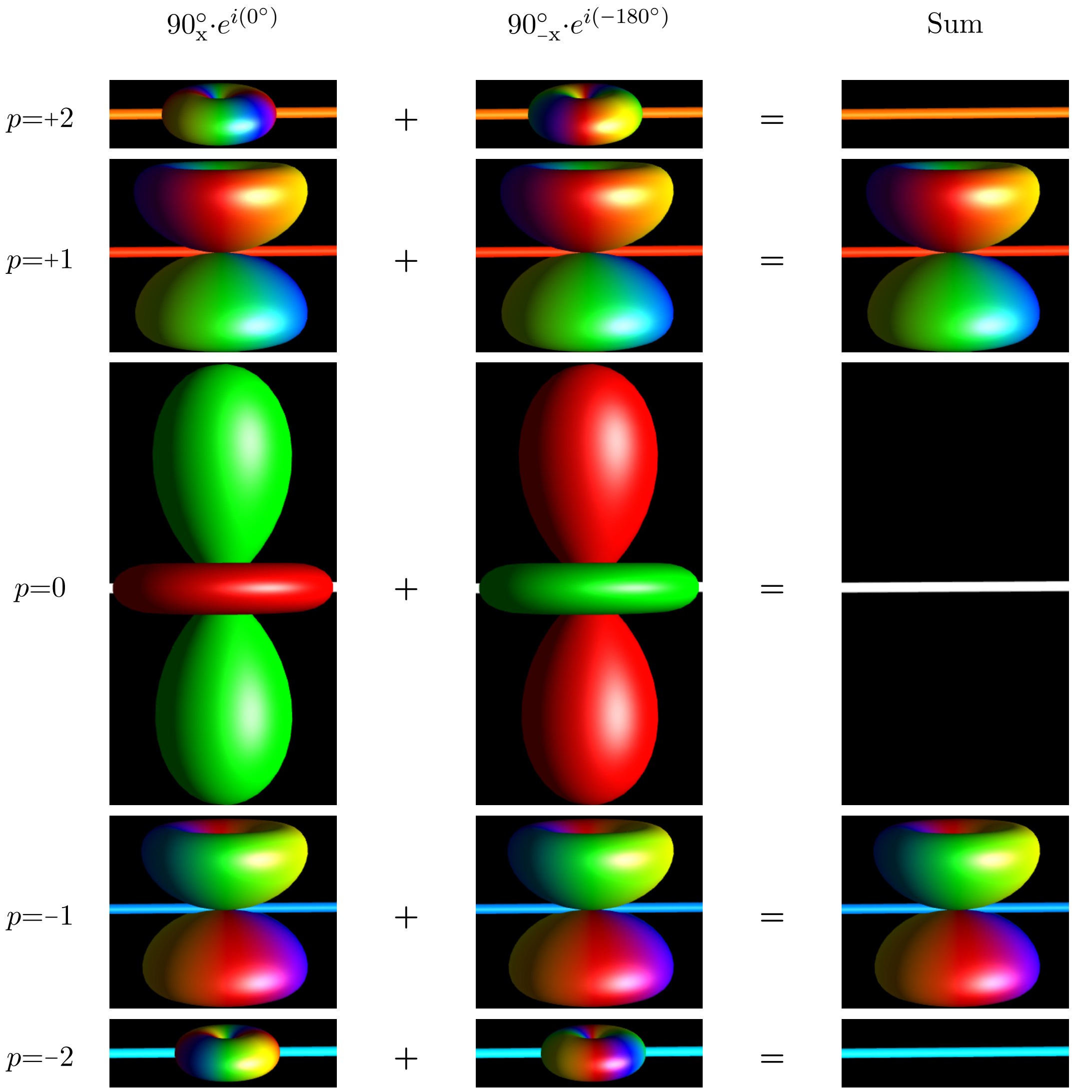
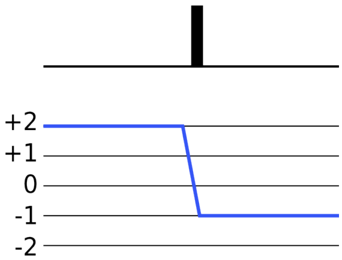


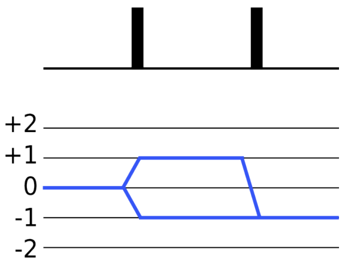
Figure 36: Experiment *3.Multiple Pathways* with initial state $\hat{I}_1^+\hat{I}_2^+$, coherence representation after a 90°_x and 90°_{-x} pulse. The results of the two sub-experiments are modified by the receiver phases, [0°, −180°], to select the transitions to p_1=+1 and −1.

3.3.3 Coherence Transfer Pathways

By using phase cycles we can select specific coherences and can then consider only those terms. Underneath graphics for pulse sequences you often find illustrations that show the desired coherences at each stage of the experiment. These illustrations are called ***C**oherence **T**ransfer **P**athways* (**CTP**). Examples for such CTPs are shown below:



Pulse sequence (top) and
CTP with a single pathway from
coherence order p_0=+2 to p_1=−1 (bottom)



Pulse sequence (top) and
CTP with multiple pathways (bottom)

When looking at the CTP of pulse sequences, you will find that the last pulse usually leads to a coherence transfer to $p{=}{-}1$. The reason for this is that only $p{=}{-}1$ is observable. Thus, it is the only coherence of interest for us at the end of an experiment.
What we ultimately observe are the x- and y-magnetizations (both correspond to $p{=}{\pm}1$). However, those are usually combined into a complex time-domain signal

$$S(t) \propto [M_x(t) + iM_y(t)]$$

and it can be shown that (due to the way of combining the signals) this is equivalent to detecting only the coherence order $p{=}{-}1$.
Other coherence orders will not be observed, so we can neglect them.

3.4 Combining Phase Cycles

In pulse sequences we have usually more than just one single pulse. And we may want to select different coherence pathways at different stages of our pulse sequence.

Consider the following example:

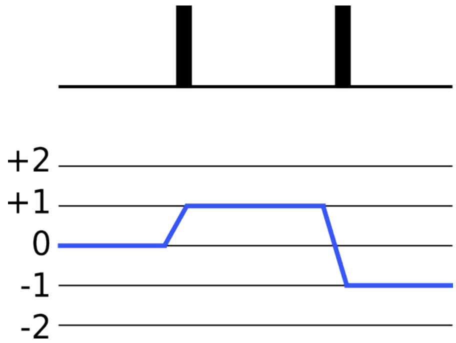


Figure 37: Pulse sequence (top) with two pulses (denoted with I and II) and CTP with a selected coherence transition Δp_{I}=+1 at pulse I and Δp_{II}=−2 at pulse II (bottom).

In this example, the coherence transition with Δp_{I}=+1 is desired for the first pulse. In order to achieve this transition, we can use a phase cycling procedure with a four-step cycle. (Remember, using a two-step cycle would additionally select the coherence transition with Δp_{I}=−1.)
For the second pulse the desired coherence transition is Δp_{II}=−2. The question is, what is required to carry out such a selection? The answer is simple: We can use again a phase cycling procedure with a four-step cycle. However, the two applied phase cycling procedures have to be independent of one another.
For us, this means primarily one thing: ***more sub-experiments***! For the ***2*** phase cycles, each performed by using a cycle with ***4*** steps, we have to perform $\boldsymbol{4^2}$ sub-experiments. That is because for every phase shift of pulse II (in order to select Δp_{II}=−2) we have to perform 4 sub-experiments to select Δp_{I}=+1 at pulse I.
(Note: Since only coherence order p=−1 is detected and other coherences will not be observed, there is actually no need to select the final transition to p=−1. This will be discussed in more detail later on. Nevertheless, phase cycling procedures will be applied to both pulses since the aim of this subsection is to understand the combination of phase cycles.)

In order to see how the combination of phase cycles works, we look at a concrete example. Therefore, choose the following settings:

- ***Spin System*** $\ggg$ ***2-Spin***
- ***Spin System*** $\ggg$ ***Parameters***
  and set the first offset frequency ν_1 *to 1 Hz*
  and the coupling J_{12} *to 1 Hz.*
  (offset frequency ν_2 *is irrelevant for our experiment)*
- ***Initial State*** $\ggg$ ***I1z***
- ***Options*** $\ggg$ ***Separation*** $\ggg$ ***Coh. Order p***
- ***Pulse Sequence*** $\ggg$ ***Tutorial*** $\ggg$ ***Phase Cycling*** $\ggg$ ***4.Combine Cycles***
  Note: The delay time between the pulses in the sub-experiments is $\frac{1}{2 \cdot J12} = 500\,ms$.
  It will be used for subsequent calculations.

Pressing the play button reveals that the first pulse creates coherence orders p_1=±1 and the second pulse leads to a population of different coherence orders for the individual sub-experiments. We will now use the combination of phase cycles to track a specific coherence pathway. Therefore, we will perform 16 sub-experiments. In order to avoid confusion arising from the rather larger number of sub-experiments, it is useful to split them in groups of four and treat them separately. Each group (denoted with A, B, C, D) comprises four sub-experiments.

Group A:

The first four sub-experiments select the coherence transition with Δp_{I}=+1. Therefore, we shift the phase of the first pulse by 90° at each of the four sub-experiments. We can say the phase of the first pulse goes through the sequence [0°, 90°, 180°, 270°]. The pulse in the first sub-experiment will be a 90°_{x} pulse. The phase shifts in the sequence are relative to this pulse.

The receiver phase for the sub-experiments consists of contributions that account for shifting the phase of the two pulses (I and II). These contributions will be denoted with RX_{I} for pulse I and RX_{II} for pulse II. Hence, the receiver phase corresponds to $RX_{\mathrm{I}} + RX_{\mathrm{II}}$. For the transition Δp_{I}=+1 our coherence acquires a phase $(-\Delta p_{\mathrm{I}}\Delta\Phi)$, i.e. [0°, -90°, -180°, -270°]. To select the transition Δp_{I}=+1 with pulse I, the contribution RX_{I} is [0°, 90°, 180°, 270°]. Pulse II is not shifted within group A sub-experiments. Thus, the contribution RX_{II} is [0°, 0°, 0°, 0°] and the receiver phase is [0° + 0°, 90° + 0°, 180° + 0°, 270° + 0°]=[0°, 90°, 180°, 270°]. The receiver phase for group A sub-experiments is therefore equivalent to the contributions due to RX_{I}. Using these values for the receiver phase ensures that coherences with p_1=+1 will add up, while those with p_1=−1 will cancel.
Figure 38 illustrates this behaviour by showing the individual states immediately after the first pulse, modified by the corresponding receiver phase. Remember, for real experiments, the receiver phase is actually applied to the individual sub-experiments before summation. However, having ***Apply RX Phase*** active within SpinDrops shows the effect of the receiver phase in the sub-experiments. In this way, the images of Figure 38 can be reproduced within SpinDrops by setting the time immediately after the first pulse. The four sub-experiments of group A correspond the sub-experiments shown in the first row within SpinDrops.

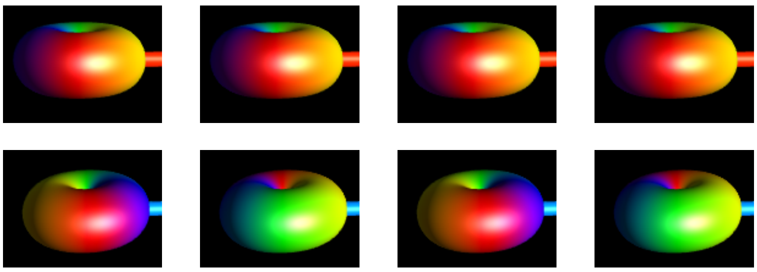


Figure 38: Experiment *4.Combine Cycles* with initial state $\hat{\mathrm{I}}_{1\mathrm{z}}$, coherence orders p_1=+1 and −1 after a 90°_{x}, 90°_{y}, $90^\circ_{\mathrm{-x}}$ and $90^\circ_{\mathrm{-y}}$ pulse. The results of the four sub-experiments are modified by the receiver phases, [0°, 90°, 180°, 270°], to select the transition Δp_{I}=+1.

Of course, our pulse sequence is not finished after the first pulse. Let's assume we finish the sub-experiments of group A with the second pulse being a 90°_x pulse for each. In case of having performed only these four sub-experiments, Figure 39 would be the final result of our experiment. It shows that adding the final results from our four sub-experiments will not lead to a vanishing term at any coherence order. Thus, although we selected Δp_I=+1 at the first pulse, we were not yet able to select a coherence transitions with Δp_II=−2 at the second pulse.

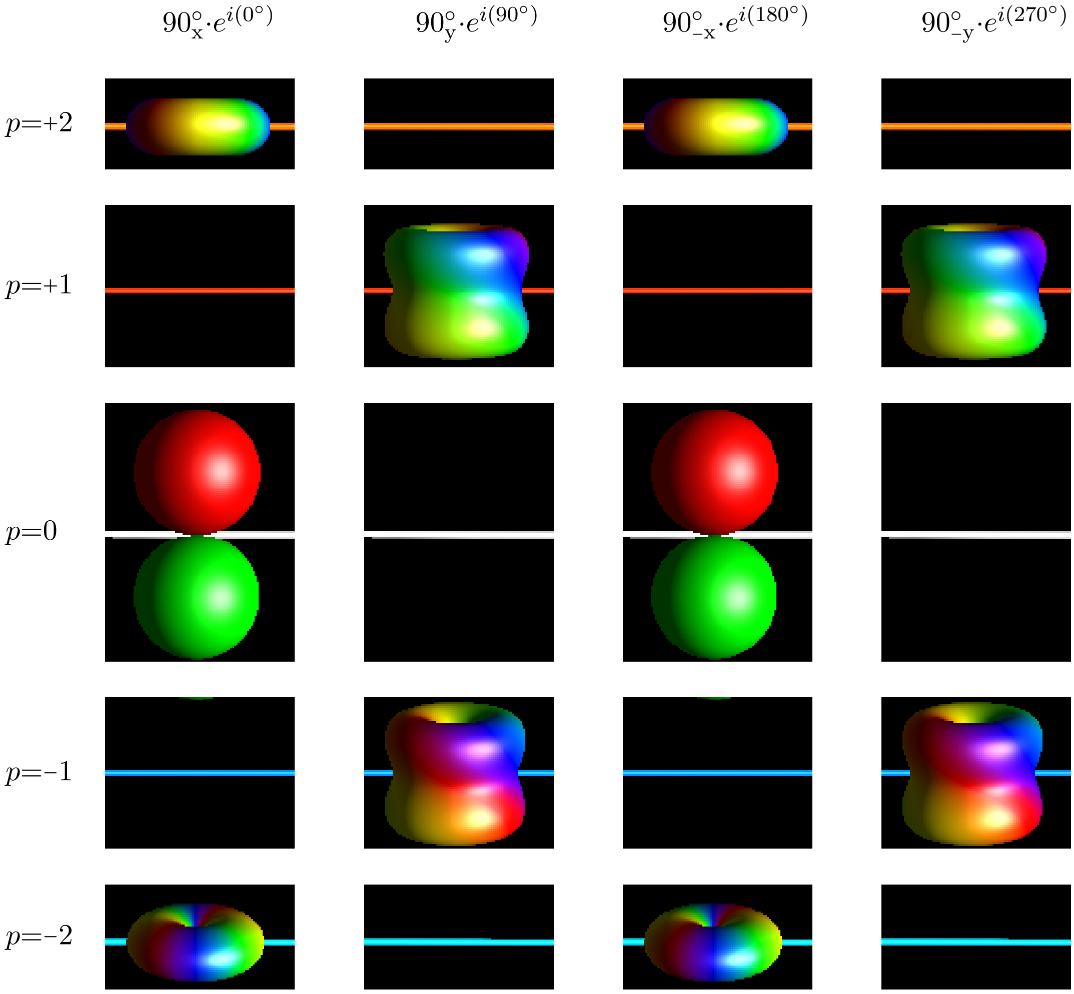


Figure 39: Experiment *4.Combine Cycles* with initial state $\hat{\mathrm{I}}_{1z}$, coherence representation after the applied pulse sequences of only group A sub-experiments. The results of the four sub-experiments are modified by the receiver phases, [0°, 90°, 180°, 270°], to select the transition Δp_I=+1 at the first pulse.

In order to select a coherence transition with Δp_{II}=−2 with the second pulse, we apply a phase cycling procedure to that pulse.

Group B:

For this reason, we will now shift the phase of the second pulse by 90° relative to the 90°_x pulse used for the sub-experiments of group A.
However, we still have to take care to select the transition with Δp_{I}=+1 at the first pulse. Consequently, we have to perform the four sub-experiments necessary to select this transition. For this reason, we go again through the sequence [0°, 90°, 180°, 270°] for the first pulse, while the second pulse remains at a constant shift of 90° relative to a 90°_x pulse.
The receiver phase for these four sub-experiments can not be the same as in group A since we have shifted the phase of the second pulse. We have to take this into account. In order to do so, we simply have to add the contribution RX_{II} needed to select Δp_{II}=−2 at the second pulse to the sequence for the receiver phase used in group A. Since we have a phase shift at the second pulse of $\Delta\Phi$=90°, the phase in coherence will be $(-\Delta p_{\text{II}}\Delta\Phi) \equiv (-[-2]\cdot 90^\circ) = 180^\circ$. The contribution RX_{II} that we need in this situation is therefore −180°. The overall receiver phase for our four sub-experiments in group B is therefore [0° − 180°, 90° − 180°, 180° − 180°, 270° − 180°] ≡ [180°, 270°, 0°, 90°].
Group B corresponds to the second row of sub-experiments of the *4.Combine Cycles* experiment within SpinDrops.

Group C:

In order to continue with our phase cycling procedure at the second pulse, we will use a pulse phase for the second pulse of 180° instead of 90° used in group B. Of course, we still have to select the transition with Δp_{I}=+1 at the first pulse. Thus, we have to perform the required four sub-experiments.
For the receiver phase, we can again use the sequence from group A and add the contribution RX_{II} required to select Δp_{II}=−2 at the second pulse. Since we have to add a value of $(\Delta p_{\text{II}}\Delta\Phi) \equiv ([-2]\cdot 180^\circ) = -360^\circ \equiv 0^\circ$, this boils down to exactly the same sequence for the receiver phase used in group A.
Group C corresponds to the third row of sub-experiments.

Group D:

Similarly, the last four sub-experiments are carried out with a pulse phase of the second pulse of 270° and a receiver phase similar to the one for group B.
The last row in the *4.Combine Cycles* experiment shows the sub-experiments of group D.

We will now take a look at the different coherences orders after the 16 sub-experiments. Since we made sure to have only p_1=+1 after the first pulse and the goal is to select Δp_{II}=−2 for the second pulse, the coherence order p_2=−1 is the only one which should not cancel out completely.

Let's first focus on coherence order p_2=+2. Summation of these 16 results leads to its complete cancellation. This can be seen by focusing on one column after another and noticing that each pair of operators cancels.

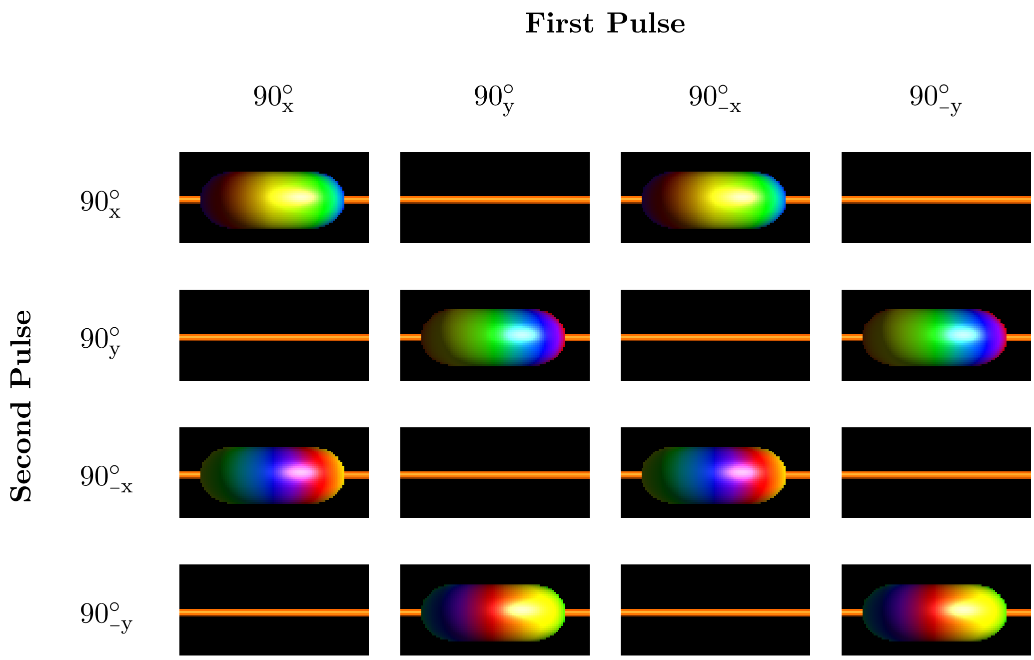


Figure 40: Experiment *4.Combine Cycles* with initial state $\hat{\mathrm{I}}_{1z}$, coherence order p_2=+2 after the applied pulse sequences of the 16 sub-experiments. The results of the 16 sub-experiments are modified by a receiver phase to select the transition Δp_{I}=+1 at the first pulse and Δp_{II}=−2 at the second pulse.

For the coherence order p_2=+1 the summation of all 16 results also leads to a complete cancellation. One way to see this is to look at the table below and sum up successively all the elements along imaginary diagonal lines.

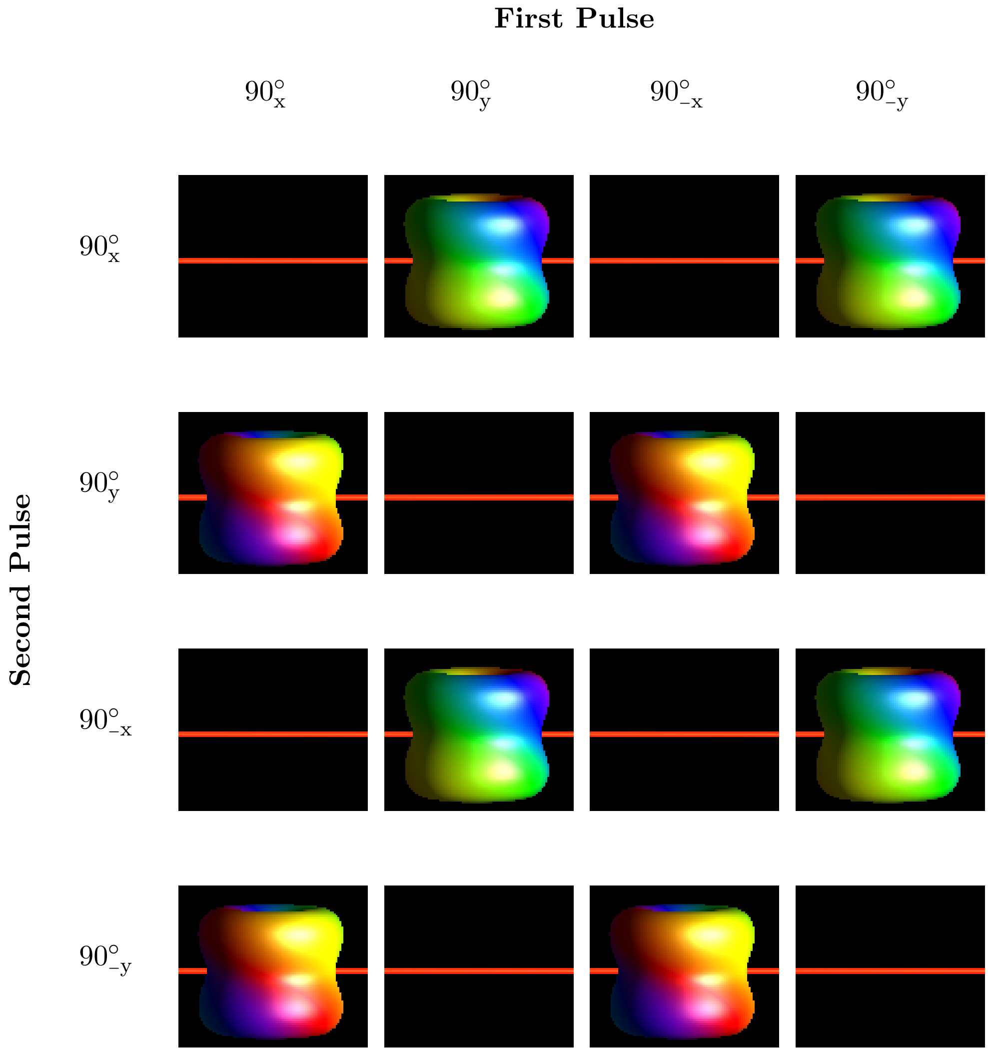


Figure 41: As Figure 40, but for coherence order p_2=+1.

Adding the contributions from successive columns shows that the terms for coherence order p_2=0 will cancel.

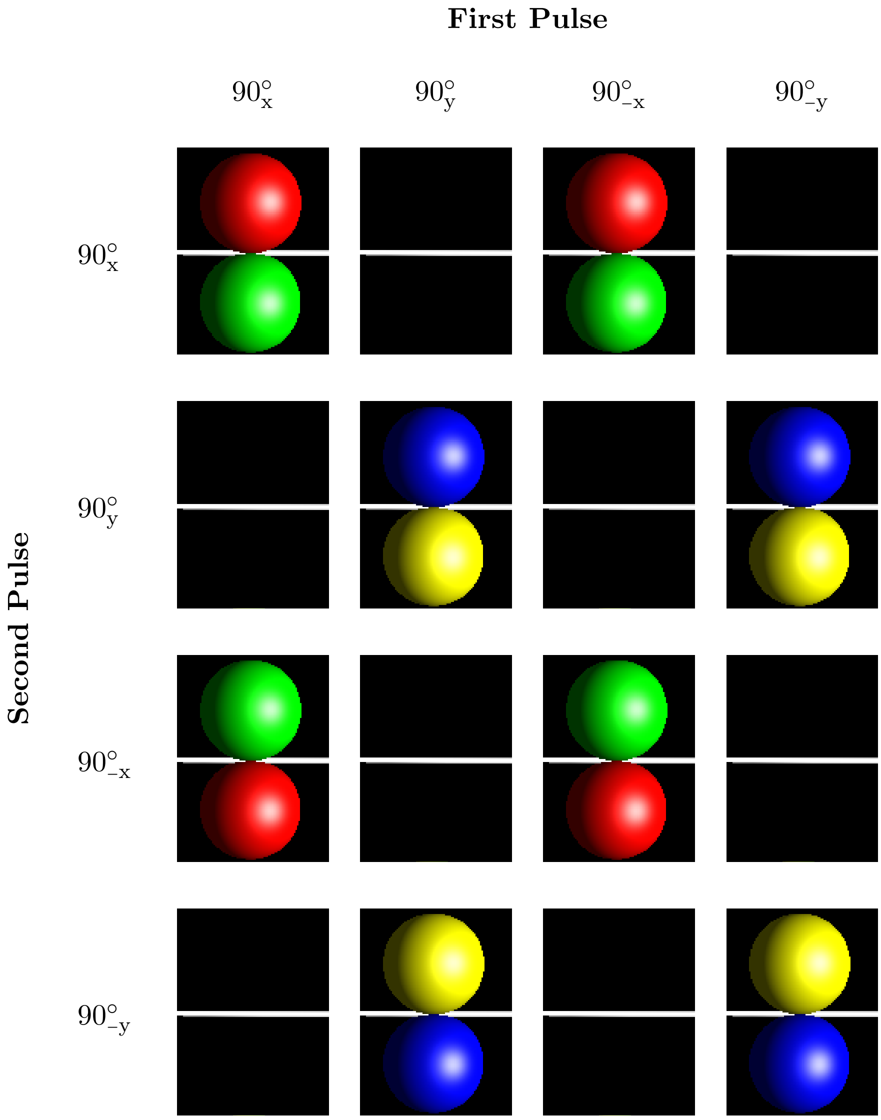


Figure 42: As Figure 40, but for coherence order p_2=0.

The most important coherence for us is of order p_2=−1. Due to our selected coherence pathway, it should remain after the phase cycling procedure.
Half of the results illustrated in Figure 43 show a vanishing outcome and will therefore not contribute to the final result of our experiment. The other half, however, shows exactly the same pattern for each of the sub-experiments. Thus, we will have an accumulation of these coherences.

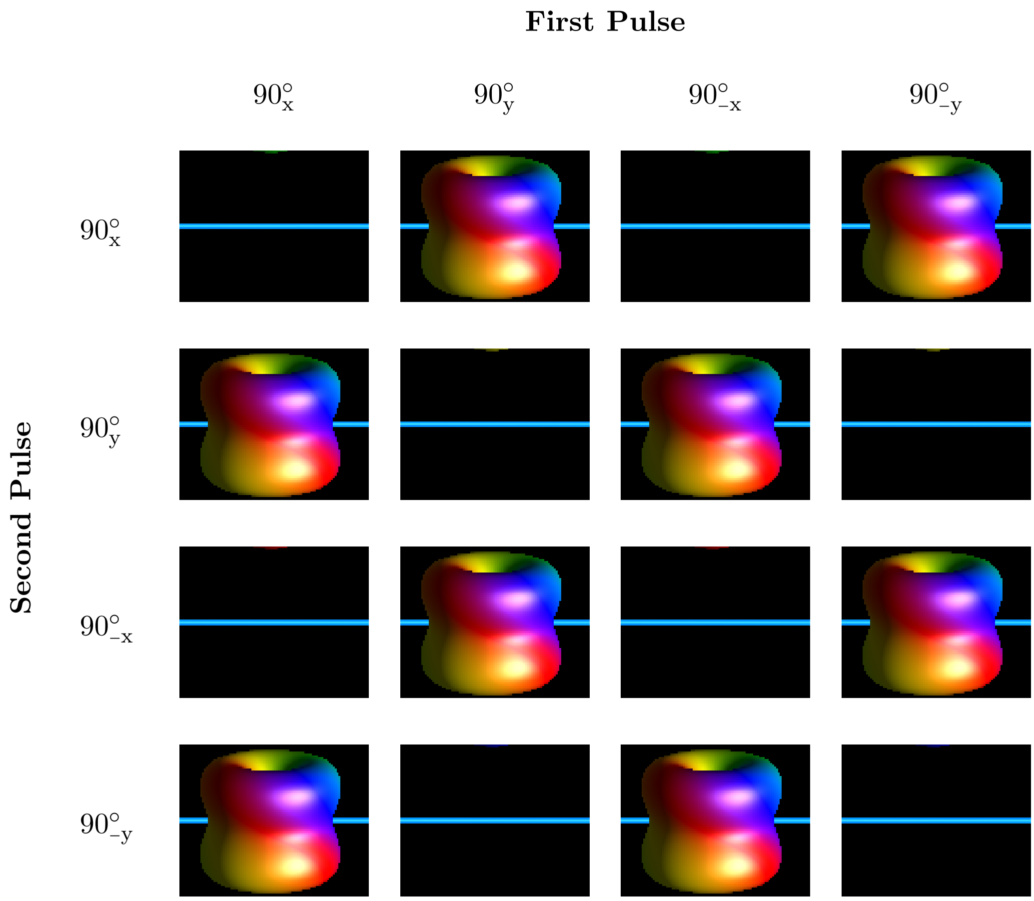


Figure 43: As Figure 40, but for coherence order p_2=−1.

For the sake of completeness, let's take a look at the coherence order p_2=−2. Here it is again easy to see that the summation of all terms will lead to a complete cancellation. You simply have to focus again on successive columns.

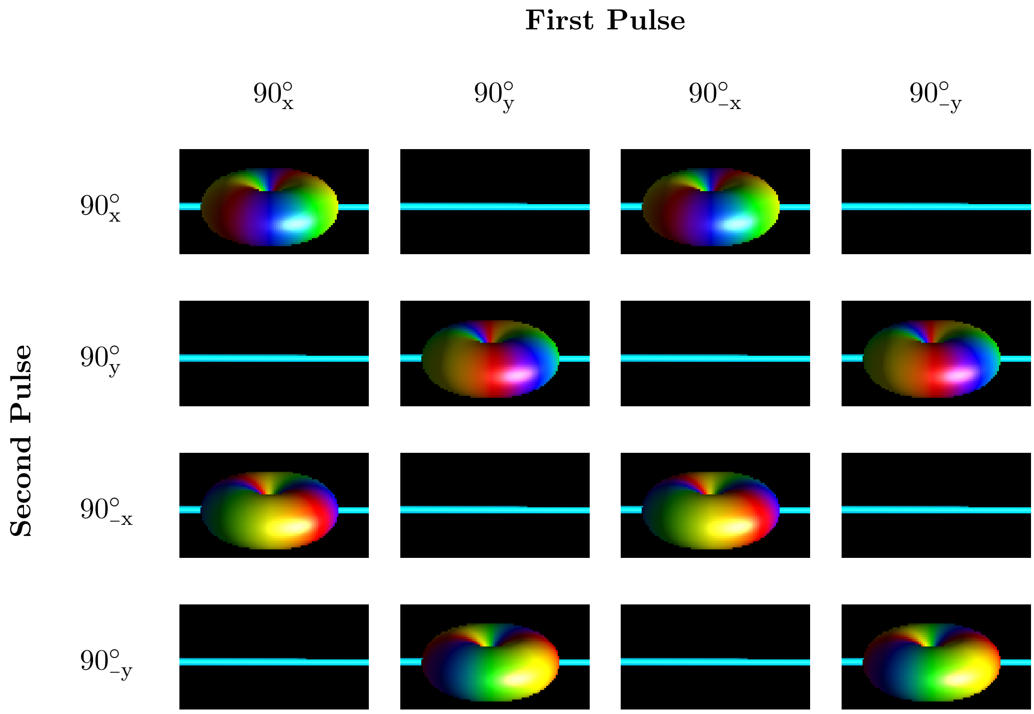


Figure 44: As Figure 40, but for coherence order p_2=−2.

Mathematical development of the *4.Combine Cycles* experiment:

$$\hat{H} = (2\pi\nu_1)\hat{\mathrm{I}}_{1z} + (2\pi\nu_2)\hat{\mathrm{I}}_{2z} + (\pi J)2\hat{\mathrm{I}}_{1z}\hat{\mathrm{I}}_{2z} \tag{1}$$

$$\rho_0 = \hat{\mathrm{I}}_{1z} \tag{2}$$

Effect of the first 90°$_x$ pulse:

$$\hat{\mathrm{I}}_{1z} \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1x}} -\hat{\mathrm{I}}_{1y} \tag{3}$$

$$-\hat{\mathrm{I}}_{1y} = -\frac{1}{2i}(\hat{\mathrm{I}}_1^+ - \hat{\mathrm{I}}_1^-) \xrightarrow[i.e.\ p=+1]{filter\ \Delta p_{\mathrm{I}}=+1} -\frac{1}{2i}\hat{\mathrm{I}}_1^+ \tag{4}$$

In equation (4) we used the definition of $\hat{\mathrm{I}}_{1y}$ in terms of the raising and lowering operator. Due to our filtering via phase cycling, the $\hat{\mathrm{I}}_1^+$ term is the only one of interest to us and we can ignore the other term.
In the following, the filtering process in equation (4) will be investigated in more detail. We recognize that in each of the groups (A,B,C,D) the phase of the first pulse goes through the sequence [0°, 90°, 180°, 270°]. Furthermore, the receiver phase of each sub-experiment contains a contribution that accounts for the shift of the first pulse, RX_{I}, and causes a transition from p_0=0 to p_1=+1. This means the contribution RX_{I} that accounts for the first pulse goes through the sequence [0°, 90°, 180°, 270°] in each of the four groups. Since the phase cycling procedure to select the desired coherence transition with the first pulse is identical in each group, we can reduce our attention to the four sub-experiments of just one them.

$$\hat{\mathrm{I}}_{1z} \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1x}} -\hat{\mathrm{I}}_{1y} \quad \xrightarrow[RX_{\mathrm{I}}\ =\ 1]{multiply\ with} -\hat{\mathrm{I}}_{1y} \quad = -\left(\frac{1}{2i}(\hat{\mathrm{I}}_1^+ - \hat{\mathrm{I}}_1^-)\right) = -\frac{1}{2i}\hat{\mathrm{I}}_1^+ + \frac{1}{2i}\hat{\mathrm{I}}_1^- \tag{5}$$

$$\hat{\mathrm{I}}_{1z} \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1y}} \hat{\mathrm{I}}_{1x} \quad \xrightarrow[RX_{\mathrm{I}}\ =\ i]{multiply\ with} i\cdot\hat{\mathrm{I}}_{1x} \quad = i\cdot\left(\frac{1}{2}(\hat{\mathrm{I}}_1^+ + \hat{\mathrm{I}}_1^-)\right) = -\frac{1}{2i}\hat{\mathrm{I}}_1^+ - \frac{1}{2i}\hat{\mathrm{I}}_1^- \tag{6}$$

$$\hat{\mathrm{I}}_{1z} \xrightarrow{-(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1x}} \hat{\mathrm{I}}_{1y} \quad \xrightarrow[RX_{\mathrm{I}}\ =\ -1]{multiply\ with} \hat{\mathrm{I}}_{1y} \quad = -1\cdot\left(\frac{1}{2i}(\hat{\mathrm{I}}_1^+ - \hat{\mathrm{I}}_1^-)\right) = -\frac{1}{2i}\hat{\mathrm{I}}_1^+ + \frac{1}{2i}\hat{\mathrm{I}}_1^- \tag{7}$$

$$\hat{\mathrm{I}}_{1z} \xrightarrow{-(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1y}} -\hat{\mathrm{I}}_{1x} \quad \xrightarrow[RX_{\mathrm{I}}\ =\ -i]{multiply\ with} i\cdot\hat{\mathrm{I}}_{1x} \quad = i\cdot\left(\frac{1}{2}(\hat{\mathrm{I}}_1^+ + \hat{\mathrm{I}}_1^-)\right) = -\frac{1}{2i}\hat{\mathrm{I}}_1^+ - \frac{1}{2i}\hat{\mathrm{I}}_1^- \tag{8}$$

The results from equation (5)-(8) show that the $\hat{\mathrm{I}}_1^+$ terms survive the phase cycling procedure while the $\hat{\mathrm{I}}_1^-$ terms cancel.

Thus, after the first pulse we have: $-\frac{1}{2i}\hat{\mathrm{I}}_1^+$

Free evolution:

Since all the terms in the Hamiltonian commute, we can look at the evolution under individual terms successively.

Effect of the $(2\pi\nu_1)\hat{\mathrm{I}}_{1\mathrm{z}}$ term:

$$-\frac{1}{2i}\hat{\mathrm{I}}_1^+ \xrightarrow{(2\pi\nu_1 t)\cdot\hat{\mathrm{I}}_{1\mathrm{z}}} -\frac{1}{2i}\hat{\mathrm{I}}_1^+ \cdot e^{-i(2\pi\nu_1 t)} \tag{9}$$

$$\begin{aligned} -\frac{1}{2i}\hat{\mathrm{I}}_1^+ \cdot e^{-i(2\pi\nu_1 t)} &= -\frac{1}{2i}\hat{\mathrm{I}}_1^+ \cdot (\cos(2\pi\nu_1 t) - i\sin(2\pi\nu_1 t)) && (10)\\ &= -\frac{1}{2i}\hat{\mathrm{I}}_1^+ \cdot (-1 - i\cdot 0) && (11)\\ &= \frac{1}{2i}\hat{\mathrm{I}}_1^+ && (12) \end{aligned}$$

In equation (9), the definition of the coherence order is used to evaluate the evolution of $\hat{\mathrm{I}}_1^+$. In equation (10)-(12) we made use of Euler's formula and substituted the parameters for ν_1=1 Hz and t=$\frac{1}{2\cdot J12}=\frac{1}{2\cdot 1\,Hz}$=500 ms:

$$\begin{aligned} e^{-i(2\pi\nu_1 t)} &= \cos(2\pi\nu_1 t) - i\sin(2\pi\nu_1 t)\\ \cos(2\pi\nu_1 t) &= \cos(\pi) = -1\\ \sin(2\pi\nu_1 t) &= \sin(\pi) = 0 \end{aligned}$$

Effect of the $(\pi J)2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{z}}$ term:

In order to evaluate the effect of the $(\pi J)2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{z}}$ term, we replace $\hat{\mathrm{I}}_1^+$ in equation (13) by its definition in terms of $\hat{\mathrm{I}}_{1\mathrm{x}}$ and $\hat{\mathrm{I}}_{1\mathrm{y}}$:

$$\frac{1}{2i}\hat{\mathrm{I}}_1^+ = \frac{1}{2i}(\hat{\mathrm{I}}_{1\mathrm{x}} + i\hat{\mathrm{I}}_{1\mathrm{y}}) = \frac{1}{2i}\hat{\mathrm{I}}_{1\mathrm{x}} + \frac{1}{2}\hat{\mathrm{I}}_{1\mathrm{y}} \tag{13}$$

Now we follow each term separately:

$$\frac{1}{2i}\hat{\mathrm{I}}_{1\mathrm{x}} \xrightarrow{(\pi Jt)\cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{z}}} \frac{1}{2i}\Big(\hat{\mathrm{I}}_{1\mathrm{x}}\cos(\pi Jt) + 2\hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{z}}\sin(\pi Jt)\Big) = \frac{1}{2i}\cdot 2\hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{z}} \tag{14}$$

$$\frac{1}{2}\hat{\mathrm{I}}_{1\mathrm{y}} \xrightarrow{(\pi Jt)\cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{z}}} \frac{1}{2}\Big(\hat{\mathrm{I}}_{1\mathrm{y}}\cos(\pi Jt) - 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{z}}\sin(\pi Jt)\Big) = -\frac{1}{2}\cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{z}} \tag{15}$$

Thus,

$$\frac{1}{2i}\hat{\mathrm{I}}_1^+ \xrightarrow{(\pi Jt)\cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{z}}} \frac{1}{2i}\cdot 2\hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{z}} - \frac{1}{2}\cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{z}} \tag{16}$$

Equation (14) describes the evolution of the $\hat{\mathrm{I}}_{1\mathrm{x}}$ term, while equation (15) describes the evolution of the $\hat{\mathrm{I}}_{1\mathrm{y}}$ term. In both, we substitute t = $\frac{1}{2\cdot J12}$ and recognize that

$$\cos(\pi Jt) = \cos(\frac{\pi}{2}) = 0$$
$$\sin(\pi Jt) = \sin(\frac{\pi}{2}) = 1$$

Knowing the evolution of the individual terms, we are now able the write the effect of $(\pi J)2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{z}}$ on $\frac{1}{2i}\hat{\mathrm{I}}_1^+$ which is shown in equation (16).

After the delay time our outcome is described by: $\dfrac{1}{2i}\cdot 2\hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{z}} - \dfrac{1}{2}\cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{z}}$

Effect of the second 90°$_x$ pulse:

$$\frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{z}} \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1\mathrm{x}} + (\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{2\mathrm{x}}} -\frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{y}} \tag{17}$$

$$-\frac{1}{2} \cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{z}} \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1\mathrm{x}} + (\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{2\mathrm{x}}} \frac{1}{2} \cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} \tag{18}$$

Thus,

$$\frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{z}} - \frac{1}{2} \cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{z}} \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1\mathrm{x}} + (\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{2\mathrm{x}}} -\frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{y}} + \frac{1}{2} \cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} \tag{19}$$

In equation (17) and (18) we apply the 90°$_\mathrm{x}$ pulses to each term of our state separately. The result is then summarized in equation (19).
The important point is now that we also applied a phase cycling procedure to the second pulse. Due to this procedure only the coherence order p=−1 will be of interest to us and we ignore all other terms.
In order to figure out which term remains after the phase cycling, we have to write all the transverse magnetizations in term of the raising and lowering operators. We will first focus on the $-\frac{1}{2i}\cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{y}}$ term:

$$-\frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{y}} = -\frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}} \left(\frac{1}{2i}(\hat{\mathrm{I}}_2^+ - \hat{\mathrm{I}}_2^-)\right) = -\frac{1}{2i} \cdot \frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^+ + \frac{1}{2i} \cdot \frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^-$$
$$-\frac{1}{2i} \cdot \frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^+ + \frac{1}{2i} \cdot \frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^- \xrightarrow[i.e.\ p=-1]{filter\ \Delta p_{\mathrm{II}}=-2} \frac{1}{2i} \cdot \frac{1}{2i} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^- = -\frac{1}{4} \cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^-$$

The $\frac{1}{2}\cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}}$ term contains no parts with coherence order p=−1:

$$\begin{aligned}\frac{1}{2} \cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} &= \frac{1}{2} \cdot 2\left(\frac{1}{2}(\hat{\mathrm{I}}_1^+ + \hat{\mathrm{I}}_1^-) \cdot (\frac{1}{2i}(\hat{\mathrm{I}}_2^+ - \hat{\mathrm{I}}_2^-))\right) \\ &= \frac{1}{4i} \cdot \left(\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ - \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^- - \hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^- + \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^+\right)\end{aligned}$$

We can see that $2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}}$ contains only zero- and double-quantum terms.
(Generally speaking, all $2\hat{\mathrm{I}}_{1\mathrm{i}}\hat{\mathrm{I}}_{2\mathrm{j}}$ terms (i,j = x or y) are mixtures of zero- and double-quantum coherence)

Equation (20) illustrates the effect of the filtering achieved by the second pulse.

$$-\frac{1}{2i}\cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{y}} + \frac{1}{2}\cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} \xrightarrow[i.e.\ p=-1]{filter\ \Delta p_{\mathrm{II}}=-2} \frac{1}{2i}\cdot\frac{1}{2i}\cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2}^{-} = -\frac{1}{4}\cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2}^{-} \quad (20)$$

The result of our entire experiment is therefore: $-\frac{1}{4}\cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2}^{-}$

This is exactly the same result obtained with our visual inspection of the phase cycling procedure:

$-\frac{1}{4}\cdot 2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2}^{-}$

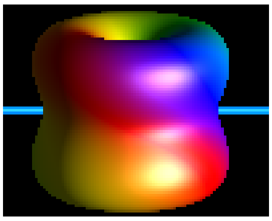


Figure 45: Final result of the *4.Combine Cycles* experiment with initial state $\hat{\mathrm{I}}_{1\mathrm{z}}$.

3.5 Reducing the Number of Phase Cycling Sub-Experiments

The number of necessary experiments grows exponentially when using the 'brute force' approach described in subsection 3.4. The following subsection introduces strategies to reduce this large number.

3.5.1 Pulse Applied to Equilibrium Magnetization

An important property of a pulse applied to equilibrium magnetization (e.g. $\hat{I}_{1z}$ with coherence order zero) is that it can only result in coherences of order ±1. In order to understand this, we have to recognize that a pulse applied to $\hat{I}_{1z}$ can only generate $\hat{I}_{1x}$ or $\hat{I}_{1y}$ (both have equal mixtures of p=+1 and p=−1).
(Note: multiple-quantum coherence is created by applying a pulse to an anti-phase state)

For many pulse sequences, the generation of coherence orders p=±1 from equilibrium magnetization is desired. Thus, applying a phase cycle to the first pulse is often not necessary.

3.5.2 The Final Pulse

The task of the last pulse in a pulse sequence is usually to cause a transition to the observable coherence p=−1. There is no need to consider other pathways since we simply can not detect them.
Imagine we achieved the desired coherences just prior to this final pulse. Then there is no need to select the final transition to p=−1. The corresponding phase cycle would cancel the transitions to all other coherences, except for the transition to p=−1. However, because we can not detect the other coherences, adding these phase cycles would not change the result of our experiment. (Comparing this with subsection 3.4 shows that the phase cycling procedure at the last pulse was not necessary.)

3.5.3 High-Order Multiple-Quantum Coherences

As mentioned earlier, there is no need to consider all possible coherence orders. The generation of coherences with order greater than triple-quantum is usually very unlikely since it requires significant coupling of one spin to more than three other spins.

3.5.4 Grouping Pulses Together

So far, we applied phase cycles to individual pulses in order to select particular coherence pathways. However, it is also possible to group pulses together and apply a phase cycling procedure to the entire group. The only thing we have to do is to shift all the pulses in the group by the same phase at the individual steps in a phase cycling procedure. Thus, there is no need to apply phase cycles to each pulse in the group separately.

4 The DQF COSY Experiment

DQF COSY is a two-dimensional experiment which is often used in practice. The spectra from a COSY and a DQF COSY experiment were shown at the beginning of this tutorial. The DQF COSY spectrum offers benefits compared to the COSY spectrum and is obtained via phase cycling.
Since we now know about phase cycling, we are able to understand the process of double-quantum filtering during the DQF COSY experiment.

The pulse sequence of a DQF COSY experiment and the desired CTP are shown below:

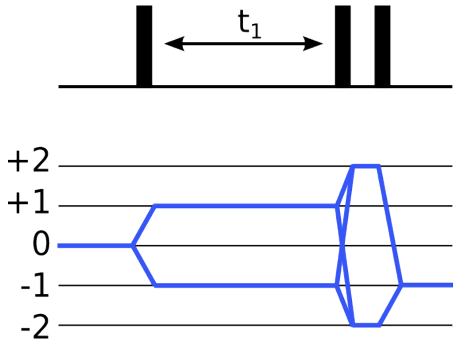


Figure 46: DQF COSY pulse sequence (top) and a Coherence Transfer Pathway (bottom).

The CTP shows only the desired pathway. However, there are more coherences present at the individual stages of a single sub-experiment. The CTP that is shown will be obtained via phase cycling. It illustrates that the signals will be filtered through a stage of double-quantum coherence between the second and third pulse.

Exercise:

Try to figure out the minimum number of phase cycles we will need to obtain the CTP above. At which pulses do we need to apply a phase cycling procedure and what is the number of steps for each phase cycle?

Option 1:

The CTP we are going the select can be achieved with only one 4-Step-Cycle.
Our CTP shows multiple pathways. Fortunately, the phase cycling procedure has the ability to select multiple pathways at the same time. The pathways we need correspond to a transition from the initial coherence order p_0=0 to the coherence orders p_2=±2 after the second pulse (i.e. $\Delta p_{\mathrm{I+II}}$=±2 for this group of pulses). Since the Δp values differ by four, we can select both pathways by using a 4-Step-Cycle. Thus, the CTP can be obtained by grouping together the first two pulses, and then cycle them together to select the desired transition.
The final pulse causes the transition to the observable coherence order p_3=−1. A second phase cycle at the final pulse is not necessary. There is no need to cycle the transition from the already selected coherence orders p_2=±2 to p_3=−1 since the coherence order p_3=−1 is the only observable coherence anyway. Cancelling the transition to other coherence orders via phase cycling would not change the outcome of the experiment.

Option 2:

There is an alternative approach leading also to the desired CTP. It also uses a single 4-Step-Cycle. The phase cycling procedure is applied to the third pulse.
To understand this, consider the final coherence p_3=−1 at the end of our pulse sequence. This is the only observable coherence. Our task is to guide the coherences p_2=+2 and p_2=−2 to this final coherence. Again, we can use the property of the phase cycling procedure to select multiple pathways at the same time. The pathways we need correspond to a transition with Δp_{III}=−3 for the coherence order p_2=+2 and a transition with Δp_{III}=+1 for coherence order p_2=−2. The Δp values differ again by a value of four. Thus, we select both pathways by using a 4-Step-Cycle.
Selecting these transitions comes with the benefit that p_2=+2 and p_2=−2 are the only coherence orders we need to consider during the second and the third pulse.
In addition, there is no need to select the coherences p_1=+1 and p_1=−1 during the first and the second pulse. The reason for this is that we start with equilibrium magnetization and the first pulse can only result in coherence order p_1=±1.

We will now illustrate the first procedure.

In order to go through the sequence, we have to prepare our system:

- ***Spin System ⋙ 2-Spin***
- ***Spin System ⋙ 2-Spin ⋙ Parameters***
  and set the first offset frequency ν_1 to 1 Hz,
  set the second offset frequency ν_2 to −1 Hz
  and the coupling J_{12} to 1 Hz.
- ***Initial State ⋙ I1z***
- ***Options ⋙ Separation ⋙ Coh. Order p***
- ***Pulse Sequence ⋙ Tutorial ⋙ Phase Cycling ⋙ 5.DQF COSY***
  Note: The delay time between first and second pulse
  in the sub-experiments is $365\,ms$.
  It will be used for subsequent calculations.

We want to apply a 4-Step-Cycle to a group that contains the first two pulses in our pulse sequence. Since it is a 4-Step-Cycle, the phase shift of the pulses go through the sequence [0°, 90°, 180°, 270°].
One of the desired coherence transitions is $\Delta p_{\mathrm{I+II}}$=−2. In section 3.2 we have seen how the phases acquired by individual coherences can be calculated. The phase acquired by the coherence is $(-\Delta p_{\mathrm{I+II}}\Delta\Phi) \equiv (-[-2]\Delta\Phi)$, i.e. the phase goes through the sequence [0°, 180°, 360°, 540°], or mapped to the [0°,360°] range [0°, 180°, 0°, 180°].
The receiver phase is therefore [0°, −180°, 0°, −180°]. Mapped these to the [0°,360°] range we have again [0°, 180°, 0°, 180°].
In section 3.3.2 we have seen that phase cycling selects an entire set of coherence transitions. Since we have a 4-Step-Cycle, we have not only selected the transition with $\Delta p_{\mathrm{I+II}}$=−2, but additionally $\Delta p_{\mathrm{I+II}}$=−2+1·4=+2 ($\equiv \Delta p$+nN). Thus, the setup for our 4-Step-Cycle is complete and we can start to perform the experiment.

During the first sub-experiment of our 4-Step-Cycle the involved pulses are 90°_x pulses. Let's consider the effect of them on our initial state.
Therefore, we start with equilibrium magnetization on spin one, i.e. $\hat{I}_{1z}$, and apply a 90°_x pulse.

$\hat{I}_{1z}$ $\qquad$ $-\hat{I}_{1y} = -\frac{1}{2i}\hat{I}_1^+ + \frac{1}{2i}\hat{I}_1^-$

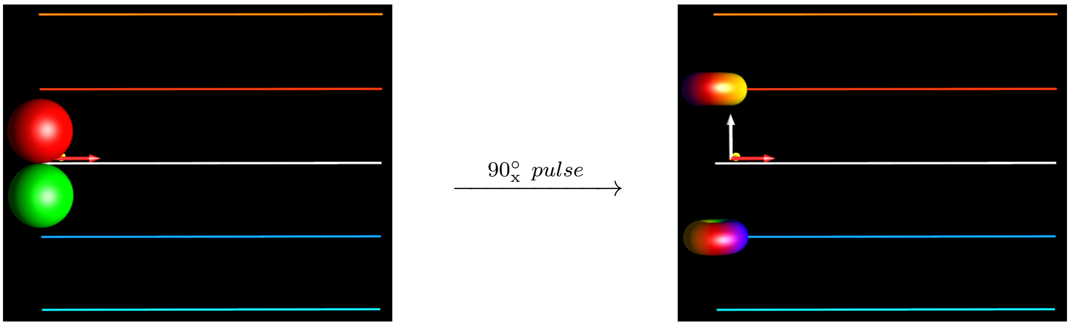


Figure 47: Experiment *5.DQF COSY* with initial state $\hat{I}_{1z}$, initial state (left) and state after the first 90°_x pulse (right).

Now, we let this state evolve during the delay time t_1.

$-\hat{I}_{1y} = -\frac{1}{2i}\hat{I}_1^+ + \frac{1}{2i}\hat{I}_1^-$ $\qquad$ State after t_1

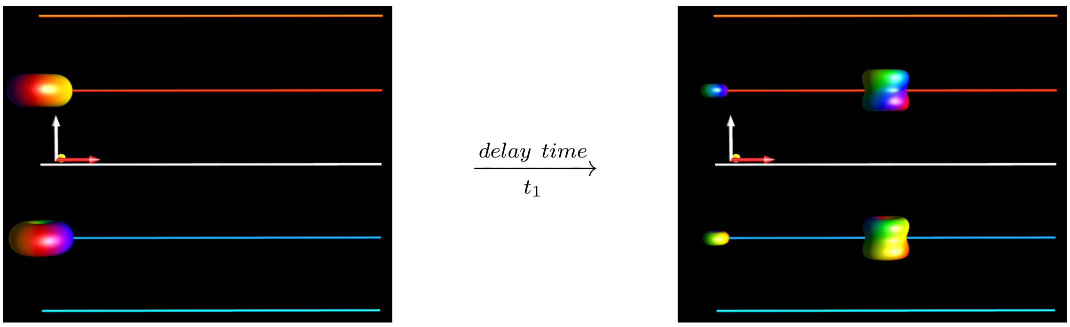


Figure 48: Experiment *5.DQF COSY* with initial state $\hat{I}_{1z}$, state after first 90°_x pulse (left) and after delay time t_1 (right).

The state after the delay time t_1 is a superposition of a few operators.
(Note: You can see them listed explicitly via *Options* ⋙ *List Prod. Ops.* within SpinDrops)

The second 90°_{x} pulse has the following effect.

State after t_1 State after 2^{nd} 90°_{x} pulse

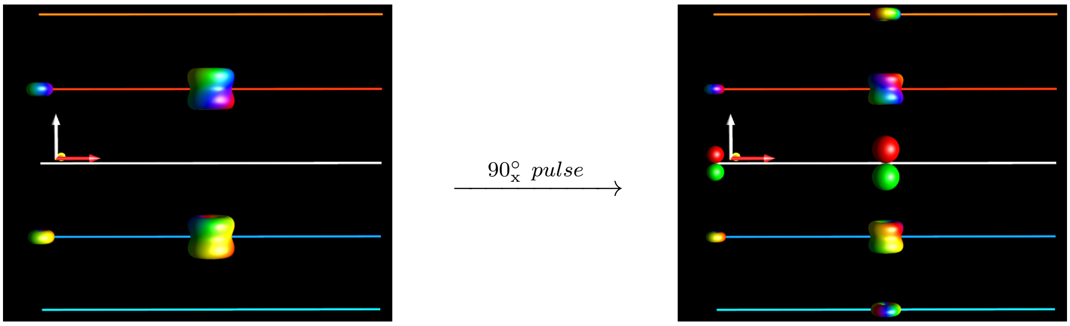


Figure 49: Experiment *5.DQF COSY* with initial state $\hat{I}_{1z}$, state after delay time t_1 (left) and after second 90°_{x} pulse (right).

This is the result from the first sub-experiment of our phase cycling procedure. We still have to perform sub-experiments with 90°_{y}, $90^\circ_{\mathrm{-x}}$, $90^\circ_{\mathrm{-y}}$ pulses as the first two pulses in the sequence. In order to track the coherences during the phase cycling procedure, we also have to take the individual receiver phases into account.
(Actually, the receiver phase is applied to the individual sub-experiments before summation. However, in order to understand the effect of the phase cycling procedure, we will take the receiver phase into consideration in the DROPS images.)

After performing the sub-experiments, the results are added together. Therefore, let's consider the situation after the first two pulses. We will focus on one coherence order after another.

For the coherence order p_2=+2 we expect accumulating results. The corresponding droplets are shown in Figure 50 and fulfill our expectation.

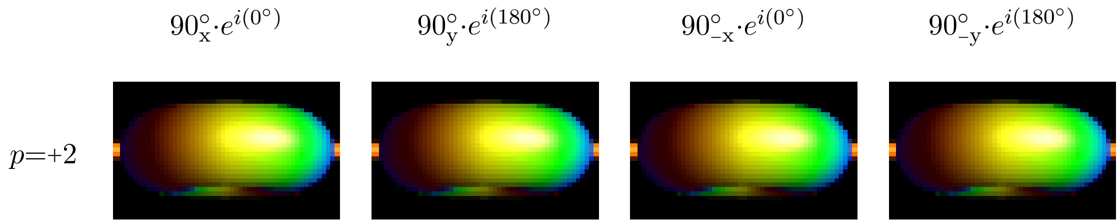


Figure 50: Experiment *5.DQF COSY* with initial state $\hat{\mathrm{I}}_{1\mathrm{z}}$, coherence order p_2=+2 after the applied pulse sequences of the four sub-experiments. The results of the four sub-experiments are modified by a receiver phase to select the transition $\Delta p_{\mathrm{I+II}}$=±2 at the first two pulses.

The terms at coherence order p_2=+1 will cancel out completely. This can be seen by adding the results from the first and the third sub-experiments, which will cancel each other. The same is true for the second and fourth sub-experiment.

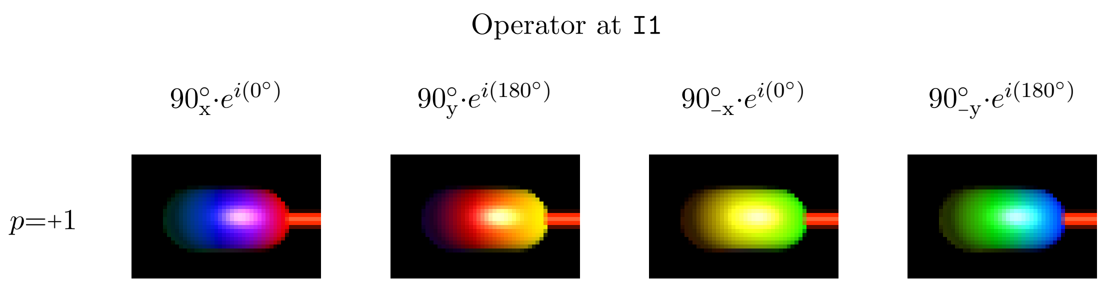


Figure 51: As Figure 50, but for droplets located at `I1` with coherence order p_2=+1.

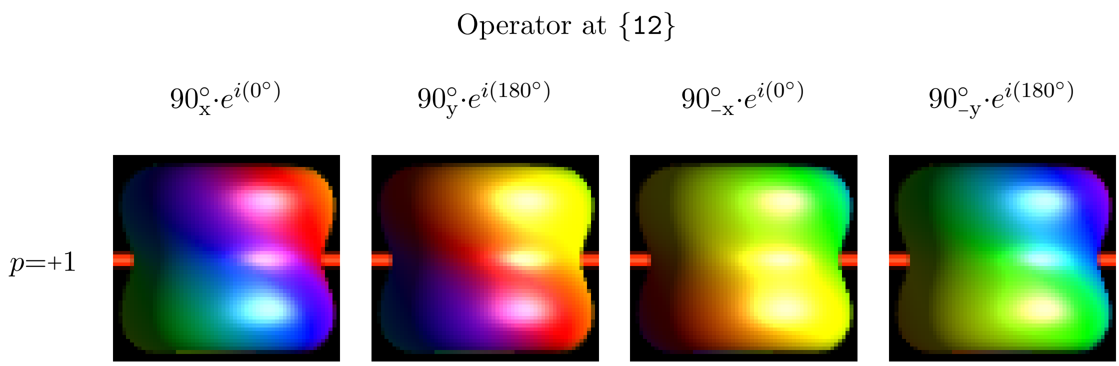


Figure 52: As Figure 50, but for droplets located at {`12`} with coherence order p_2=+1.

The terms at coherence order p_2=0 will also be cancelled out due to the phase cycling procedure.

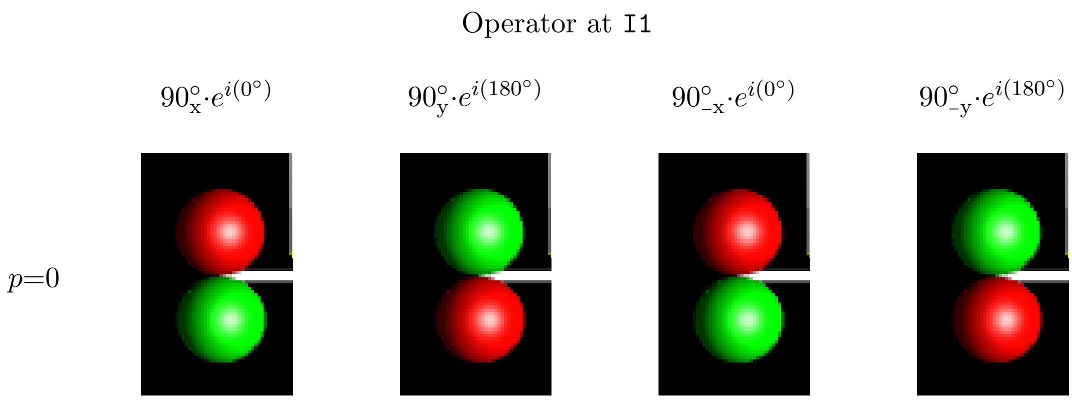


Figure 53: As Figure 50, but for droplets located at `I1` with coherence order p_2=0.

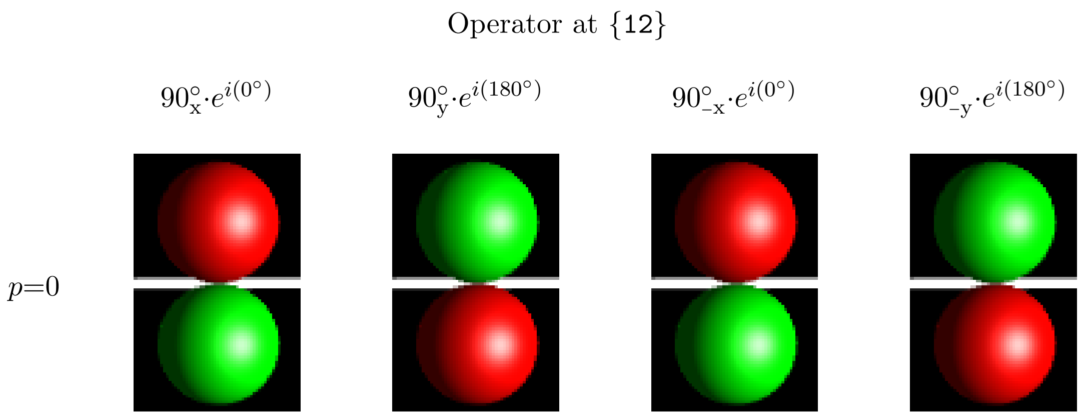


Figure 54: As Figure 50, but for droplets located at {`12`} with coherence order p_2=0.

The same is true for coherence order p_2=−1. Similar to coherence order p_2=+1, the results from the first sub-experiment cancels with the third sub-experiment, and the result from the second sub-experiment cancels with the fourth sub-experiment.

Operator at `I1`

$90^\circ_{\mathrm{x}}\cdot e^{i(0^\circ)}$ $90^\circ_{\mathrm{y}}\cdot e^{i(180^\circ)}$ $90^\circ_{-\mathrm{x}}\cdot e^{i(0^\circ)}$ $90^\circ_{-\mathrm{y}}\cdot e^{i(180^\circ)}$

p=−1

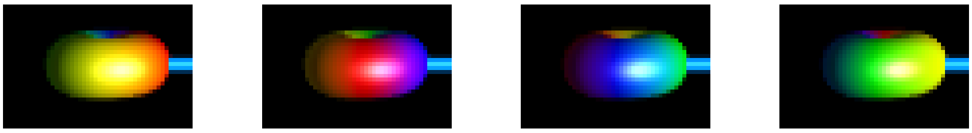


Figure 55: As Figure 50, but for droplets located at `I1` with coherence order p_2=−1.

Operator at {`12`}

$90^\circ_{\mathrm{x}}\cdot e^{i(0^\circ)}$ $90^\circ_{\mathrm{y}}\cdot e^{i(180^\circ)}$ $90^\circ_{-\mathrm{x}}\cdot e^{i(0^\circ)}$ $90^\circ_{-\mathrm{y}}\cdot e^{i(180^\circ)}$

p=−1

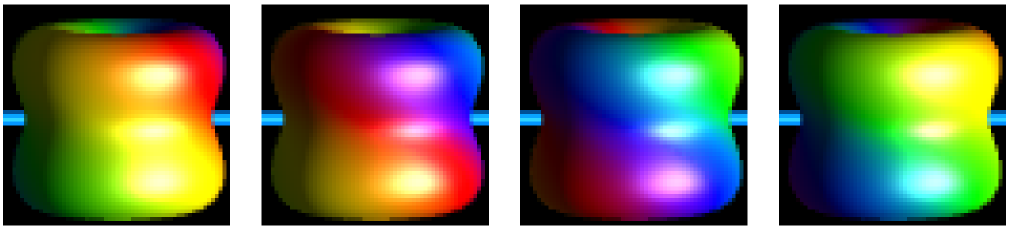


Figure 56: As Figure 50, but for droplets located at {`12`} with coherence order p_2=−1.

Coherence order p_2=−2 is again a coherence selected by our phase cycling procedure. Thus, we expect again to have accumulating results.

$90^\circ_{\mathrm{x}} \cdot e^{i(0^\circ)}$ $90^\circ_{\mathrm{y}} \cdot e^{i(180^\circ)}$ $90^\circ_{-\mathrm{x}} \cdot e^{i(0^\circ)}$ $90^\circ_{-\mathrm{y}} \cdot e^{i(180^\circ)}$

p=−2

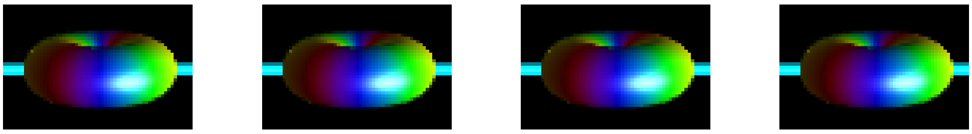


Figure 57: As Figure 50, but for droplets located at {12} with coherence order p_2=−2.

Since the phase cycling procedure is acting as desired, the last thing we have to do is to apply the last 90°_{x} pulse. The effect of this pulse is illustrated below:

double-quantum filtered result before 90°_{x} pulse

double-quantum filtered result after 90°_{x} pulse

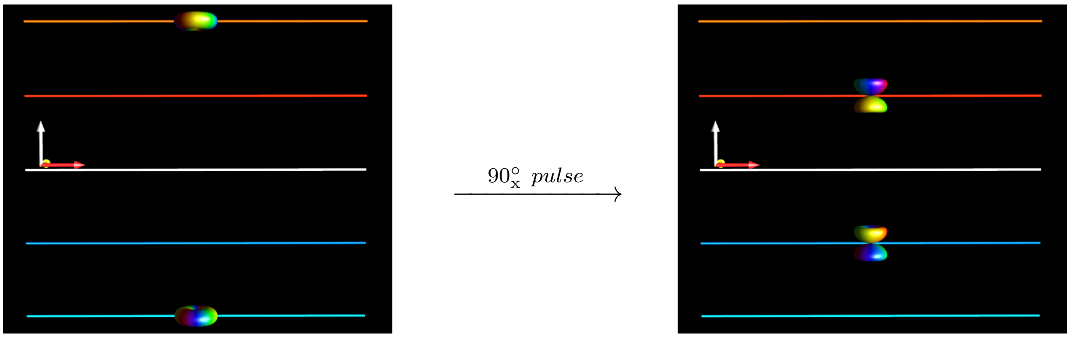


Figure 58: Experiment *5.DQF COSY* with initial state $\hat{\mathrm{I}}_{1\mathrm{z}}$, filtered result after selecting the transition $\Delta p_{\mathrm{I+II}}$=±2 at the first two pulses via phase cycling (left) and after third 90°_{x} pulse (right).

The only coherence order of interest to us is the one with p_3=−1 since this is the only one which can be observed. With this, our DQF COSY experiment is finished.

Mathematical development of the *5.DQF COSY* experiment:

$$\hat{H} = (2\pi\nu_1)\hat{\mathrm{I}}_{1\mathrm{z}} + (2\pi\nu_2)\hat{\mathrm{I}}_{2\mathrm{z}} + (\pi J)2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{z}} \tag{1}$$

$$\rho_0 = \hat{\mathrm{I}}_{1\mathrm{z}} \tag{2}$$

Effect of the first 90$^\circ_x$ pulse:

$$\hat{\mathrm{I}}_{1\mathrm{z}} \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1\mathrm{x}}} -\hat{\mathrm{I}}_{1\mathrm{y}} \tag{3}$$

Free evolution:

Since all the terms in the Hamiltonian commute, we can look at the individual terms successively.

Effect of the $(2\pi\nu_1)\hat{\mathrm{I}}_{1\mathrm{z}}$ term:

$$-\hat{\mathrm{I}}_{1\mathrm{y}} \xrightarrow{(2\pi\nu_1 t_1)\cdot\hat{\mathrm{I}}_{1\mathrm{z}}} -\hat{\mathrm{I}}_{1\mathrm{y}}\cos(2\pi\nu_1 t_1) + \hat{\mathrm{I}}_{1\mathrm{x}}\sin(2\pi\nu_1 t_1) \tag{4}$$

Effect of the $(\pi J)2\hat{\mathrm{I}}_{1z}\hat{\mathrm{I}}_{2z}$ term:

In order to evaluate the effect of the $(\pi J)2\hat{\mathrm{I}}_{1z}\hat{\mathrm{I}}_{2z}$ term, we focus separately on the $\hat{\mathrm{I}}_{1y}$ and the $\hat{\mathrm{I}}_{1x}$ term and then combine the results.

$$
\begin{aligned}
-\hat{\mathrm{I}}_{1y}\cos(2\pi\nu_1 t_1) \xrightarrow{(\pi J t_1)\cdot 2\hat{\mathrm{I}}_{1z}\hat{\mathrm{I}}_{2z}} \quad & -\hat{\mathrm{I}}_{1y}\cos(2\pi\nu_1 t_1)\cos(\pi J t_1) \\
& + 2\hat{\mathrm{I}}_{1x}\hat{\mathrm{I}}_{2z}\cos(2\pi\nu_1 t_1)\sin(\pi J t_1)
\end{aligned} \tag{5}
$$

$$
\begin{aligned}
\hat{\mathrm{I}}_{1x}\sin(2\pi\nu_1 t_1) \xrightarrow{(\pi J t_1)\cdot 2\hat{\mathrm{I}}_{1z}\hat{\mathrm{I}}_{2z}} \quad & \hat{\mathrm{I}}_{1x}\sin(2\pi\nu_1 t_1)\cos(\pi J t_1) \\
& + 2\hat{\mathrm{I}}_{1y}\hat{\mathrm{I}}_{2z}\sin(2\pi\nu_1 t_1)\sin(\pi J t_1)
\end{aligned} \tag{6}
$$

$$
\begin{aligned}
-\hat{\mathrm{I}}_{1y}\cos(2\pi\nu_1 t_1) + \hat{\mathrm{I}}_{1x}\sin(2\pi\nu_1) \xrightarrow{(\pi J t_1)\cdot 2\hat{\mathrm{I}}_{1z}\hat{\mathrm{I}}_{2z}} \quad & -\hat{\mathrm{I}}_{1y}\cos(2\pi\nu_1 t_1)\cos(\pi J t_1) \\
& + 2\hat{\mathrm{I}}_{1x}\hat{\mathrm{I}}_{2z}\cos(2\pi\nu_1 t_1)\sin(\pi J t_1) \\
& + \hat{\mathrm{I}}_{1x}\sin(2\pi\nu_1 t_1)\cos(\pi J t_1) \\
& + 2\hat{\mathrm{I}}_{1y}\hat{\mathrm{I}}_{2z}\sin(2\pi\nu_1 t_1)\sin(\pi J t_1)
\end{aligned} \tag{7}
$$

Equation (5) describes the evolution of the $\hat{\mathrm{I}}_{1y}$ term, while equation (6) describes the evolution of the $\hat{\mathrm{I}}_{1x}$ term.
Knowing the evolution of the individual terms, we are now able the write the effect of $(\pi J)2\hat{\mathrm{I}}_{1z}\hat{\mathrm{I}}_{2z}$ which is shown in equation (7).

$$
\begin{aligned}
\text{The result after the delay time is:} \quad & -\hat{\mathrm{I}}_{1y}\cos(2\pi\nu_1 t_1)\cos(\pi J t_1) \\
& + 2\hat{\mathrm{I}}_{1x}\hat{\mathrm{I}}_{2z}\cos(2\pi\nu_1 t_1)\sin(\pi J t_1) \\
& + \hat{\mathrm{I}}_{1x}\sin(2\pi\nu_1 t_1)\cos(\pi J t_1) \\
& + 2\hat{\mathrm{I}}_{1y}\hat{\mathrm{I}}_{2z}\sin(2\pi\nu_1 t_1)\sin(\pi J t_1)
\end{aligned}
$$

Effect of the second 90$^\circ_x$ pulse:

$$-\hat{\mathrm{I}}_{1\mathrm{y}}\cos(2\pi\nu_1 t_1)\cos(\pi J t_1) \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1\mathrm{x}}\ +\ (\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{2\mathrm{x}}} -\hat{\mathrm{I}}_{1\mathrm{z}}\cos(2\pi\nu_1 t_1)\cos(\pi J t_1) \quad (8)$$

$$2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{z}}\cos(2\pi\nu_1 t_1)\sin(\pi J t_1) \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1\mathrm{x}}\ +\ (\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{2\mathrm{x}}} -2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}}\cos(2\pi\nu_1 t_1)\sin(\pi J t_1) \quad (9)$$

$$\hat{\mathrm{I}}_{1\mathrm{x}}\sin(2\pi\nu_1 t_1)\cos(\pi J t_1) \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1\mathrm{x}}\ +\ (\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{2\mathrm{x}}} \hat{\mathrm{I}}_{1\mathrm{x}}\sin(2\pi\nu_1 t_1)\cos(\pi J t_1) \quad (10)$$

$$2\hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{z}}\sin(2\pi\nu_1 t_1)\sin(\pi J t_1) \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1\mathrm{x}}\ +\ (\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{2\mathrm{x}}} -2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{y}}\sin(2\pi\nu_1 t_1)\sin(\pi J t_1) \quad (11)$$

In equation (8) - (11) we apply the 90$^\circ_\mathrm{x}$ pulses to each term of our state separately.

After the second 90$^\circ_\mathrm{x}$ pulse the result is:

$$\begin{aligned}
&-\hat{\mathrm{I}}_{1\mathrm{z}}\cos(2\pi\nu_1 t_1)\cos(\pi J t_1)\\
&-2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}}\cos(2\pi\nu_1 t_1)\sin(\pi J t_1)\\
&+\hat{\mathrm{I}}_{1\mathrm{x}}\sin(2\pi\nu_1 t_1)\cos(\pi J t_1)\\
&-2\hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{y}}\sin(2\pi\nu_1 t_1)\sin(\pi J t_1)
\end{aligned}$$

Due to phase cycling, only terms with p_2=±2 will survive. Only these coherence orders will be of interest to us and we ignore all other terms. Thus, we have to figure out which terms of our current state fulfill this condition.
We can ignore the $\hat{\mathrm{I}}_{1\mathrm{z}}$-term since it corresponds to coherence order p_2=0.
The $\hat{\mathrm{I}}_{1\mathrm{x}}$ and the $2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}}$ terms are of coherence order p_2=±1 and therefore also not of interest to us.
In fact, it is only the $2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}}$ term which contains double-quantum coherence.
(Remember: all $2\hat{\mathrm{I}}_{1\mathrm{i}}\hat{\mathrm{I}}_{2\mathrm{j}}$ terms (i,j = x or y) are mixtures of zero- and double-quantum coherence)

$$-2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}}\cos(2\pi\nu_1 t_1)\sin(\pi J t_1) = \alpha\cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} \quad (12)$$

$$\alpha\cdot 2\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} = \alpha\cdot\frac{1}{2i}(\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ - \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^- - \hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^- + \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^+) \quad (13)$$

$$\alpha\cdot\frac{1}{2i}(\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ - \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^- - \hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^- + \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^+) \xrightarrow[i.e.\ p=\pm 2]{filter\ \Delta p_{\mathrm{I}+\mathrm{II}}=\pm 2} \frac{\alpha}{2i}(\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ - \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^-) \quad (14)$$

In equation (12) we replaced the t_1-dependent trigonometric terms with α for clarity. Equation (13) - (14) illustrate the effect of our filtering process.

The result after the phase cycling procedure is: $\alpha \cdot \frac{1}{2i}(\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ - \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^-)$

Effect of the third 90°$_x$ pulse:

In order to apply the third 90°_x pulse, we rewrite our result in terms of transverse magnetizations.

$$
\begin{aligned}
&\alpha \cdot \frac{1}{2i}(\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_2^+ - \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_2^-) \\
&= \alpha \cdot \frac{1}{2i}\Big((\hat{\mathrm{I}}_{1\mathrm{x}} + i\hat{\mathrm{I}}_{1\mathrm{y}})(\hat{\mathrm{I}}_{2\mathrm{x}} + i\hat{\mathrm{I}}_{2\mathrm{y}}) - (\hat{\mathrm{I}}_{1\mathrm{x}} - i\hat{\mathrm{I}}_{1\mathrm{y}})(\hat{\mathrm{I}}_{2\mathrm{x}} - i\hat{\mathrm{I}}_{2\mathrm{y}})\Big) \\
&= \alpha \cdot \frac{1}{2i}(\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{x}} + i\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} + i\hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{x}} - \hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{y}} - \hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{x}} + i\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} + i\hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{x}} + \hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{y}}) \\
&= \alpha \cdot (\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} + \hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{x}})
\end{aligned}
$$

Now we can easily apply the third 90°_x pulse.

$$
\alpha \cdot (\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{y}} + \hat{\mathrm{I}}_{1\mathrm{y}}\hat{\mathrm{I}}_{2\mathrm{x}}) \xrightarrow{(\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{1\mathrm{x}} \,+\, (\frac{\pi}{2})\cdot\hat{\mathrm{I}}_{2\mathrm{x}}} \alpha \cdot (\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{x}}) \tag{15}
$$

In order to compare the result with our visual inspection, we have to go to the representation in terms of raising and lowering operator one last time.

$$
\begin{aligned}
\alpha \cdot (\hat{\mathrm{I}}_{1\mathrm{x}}\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_{2\mathrm{x}}) &= \alpha \cdot \left(\frac{1}{2}(\hat{\mathrm{I}}_1^+ + \hat{\mathrm{I}}_1^-)\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_{1\mathrm{z}}\frac{1}{2}(\hat{\mathrm{I}}_2^+ + \hat{\mathrm{I}}_2^-)\right) \\
&= \alpha \cdot \frac{1}{2} \cdot \left(\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^+ + \hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^-\right)
\end{aligned}
$$

Finally, we take this result, restore α and rearranged the resulting terms.

$$
\begin{aligned}
&\alpha \cdot \frac{1}{2} \cdot \left(\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^+ + \hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^-\right) \\
&= \left(\hat{\mathrm{I}}_1^+\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^+ + \hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^-\right) \cdot (-\frac{1}{2})\cos(2\pi\nu_1 t_1)\sin(\pi J t_1)
\end{aligned} \tag{16}
$$

The result of our entire experiment is therefore:

$$\begin{aligned}\left(\hat{I}_1^+\hat{I}_{2z} + \hat{I}_1^-\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^+ + \hat{I}_{1z}\hat{I}_2^-\right) \cdot (-\frac{1}{2})\cos(2\pi\nu_1 t_1)\sin(\pi J t_1)\\ = (\hat{I}_{1x}\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_{2x}) \cdot (-\frac{1}{2})\cos(2\pi\nu_1 t_1)\sin(\pi J t_1)\end{aligned}$$

Substituting the values for the offset frequency (ν_1=1 Hz), the coupling constant (J_{12}=1 Hz) and the delay time (t=365 ms) shows that this is the same result obtained with our visual inspection of the DQF COSY experiment.

$0.3\cdot(\hat{I}_1^+\hat{I}_{2z} + \hat{I}_1^-\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^+ + \hat{I}_{1z}\hat{I}_2^-)$

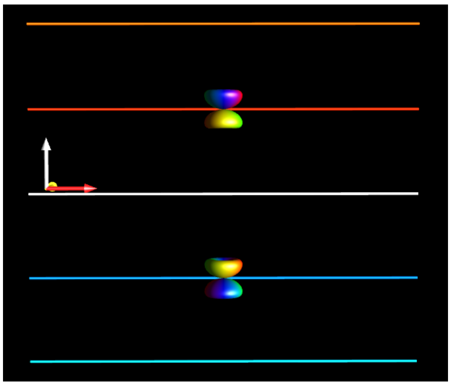


Figure 59: Final result of the *5.DQF COSY* experiment with initial state $\hat{I}_{1z}$.

Since only coherence order p_3=–1 is observable, it is the only coherence order we have to consider.

$$0.3{\cdot}(\hat{\mathrm{I}}_1^-\hat{\mathrm{I}}_{2\mathrm{z}} + \hat{\mathrm{I}}_{1\mathrm{z}}\hat{\mathrm{I}}_2^-)$$

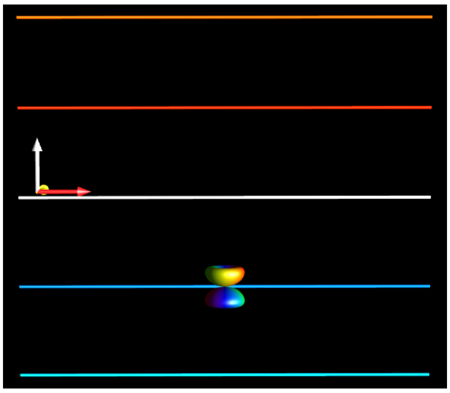


Figure 60: Final result of the *5.DQF COSY* experiment with initial state $\hat{\mathrm{I}}_{1\mathrm{z}}$, coherence order p_3=–1.

Final remark:

With the help of this tutorial, we are now able to understand filtering process as used in the DQF COSY experiment. The occurrence of a much nicer looking spectrum in a DQF COSY experiment compared to a simple COSY experiment was not discussed. In fact, this can be explained by a closer inspection of lineshapes measured with NMR experiments. Nevertheless, we would like to point out that both of the resulting anti-phase terms of our DQF COSY experiment have the same modulation in t_1 and both appear along the x-axis (i.e. no mixtures of $\hat{I}_{kx}$ and $\hat{I}_{ky}$). This allows the generation of a spectrum with double absorption mode lineshapes for all lines in the spectrum. In a simple COSY experiment this is not possible.