Maxima workbook for Principles of NMR Spectroscopy Chapter 15: Two-dimensional spectra based on scalar coupling: COSY and TOCSY experiments

1 Introduction

This wxMaxima workbook is an electronic supplement to to the book Principles of NMR Spectroscopy: An Illustrated Guide, David P. Goldenberg, University Science Books, (c) 2016.
This and related files are available for download through links at: http://uscibooks.com/goldenberg.htm
wxMaxima is a graphical user interface to the computer algebra system (CAS) Maxima. General information about Maxima and wxMaxima, along with free versions of the programs, can be found at: http://maxima.sourceforge.net/ and http://andrejv.github.io/wxmaxima/
Before attempting to use this workbook, users are strongly encouraged to read and experiment with the introductory workbook, gettingStarted.wxmx, and the workbooks for Chapters 11-14

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This chapter describes the two-dimensional heteronuclear and homonuclear COSY experiments and the homonuclear TOCSY experiment. This notebook, however, only deals with the COSY experiments, because the TOCSY experiment does not satisfy the weak coupling limit, making its analysis much more difficult.
The worksheet uses the definitions found in 2spinLib.mac. These definitions, where appropriate, assume the weak- coupling limit.

```
(%i1) load("2spinLib.mac")$
```

Removing the $ symbol at the end of the command below and executing the command will output a list of all of the functions defined by the 2spinLib.mac library, and the packages it loads.

```
(%i2) functions$
```

2 15.1 A simplified heteronuclear COSY experiment

Page 426

2.1 Starting with the |alpha alpha> state

Page 426

```
(%i3) k_aa;
```

(%o3) $\begin{pmatrix}1\\0\\0\\0\end{pmatrix}$

The initial pulse is a pi/2 y pulse applied to the S-magnetization

```
(%i4) k_hetCosyaa1:psiPi2YS(k_aa);
```

(%o4) $$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \\ 0 \end{pmatrix}$$

```
(%i5) allMagPsi(k_hetCosyaa1);
```

$< Ix >=\ 0$
$< Iy >=\ 0$
$< Iz >=\ \frac{1}{2}$
$< Sx >=\ \frac{1}{2}$
$< Sy >=\ 0$
$< Sz >=\ 0$

(%o5)

Fig 15.3

The first pulse is followed by the incremented delay time, with duration t1

```
(%i6) k_hetCosyaa2:psiTime(k_hetCosyaa1,t1);
```

(%o6) $$\begin{pmatrix} \frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{\sqrt{2}} \\ \frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{\sqrt{2}} \\ 0 \\ 0 \end{pmatrix}$$

```
(%i7) allMagPsi(k_hetCosyaa2);
```

$< Ix >=\ 0$
$< Iy >=\ 0$
$< Iz >=\ \frac{1}{2}$
$< Sx >=\ \frac{\cos\left(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J\right)}{2}$
$< Sy >=\ \frac{\sin\left(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J\right)}{2}$
$< Sz >=\ 0$

(%o7)

```
(%i8) allCorrPsi(k_hetCosyaa2);
```

$< IxSx >=\ 0$
$< IxSy >=\ 0$
$< IxSz >=\ 0$
$< IySx >=\ 0$
$< IySy >=\ 0$
$< IySz >=\ 0$
$< IzSx >=\ \frac{\cos\left(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J\right)}{4}$
$< IzSy >=\ \frac{\sin\left(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J\right)}{4}$
$< IzSz >=\ 0$

(%o8)

The t1 interval is followed by a non-selective pi/2 y pulse

(%i9) k_hetCosyaa3:psiPi2Y(k_hetCosyaa2);

(%o9)
$$\begin{pmatrix} \frac{\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{2}-\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{2}}{\sqrt{2}} \\ \frac{\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{2}+\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{2}}{\sqrt{2}} \\ \frac{\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{2}-\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{2}}{\sqrt{2}} \\ \frac{\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{2}+\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{2}}{\sqrt{2}} \end{pmatrix}$$

(%i10) allMagPsi(k_hetCosyaa3);

$$< Ix >= \frac{1}{2}$$
$$< Iy >= 0$$
$$< Iz >= 0$$
$$< Sx >= 0$$
$$< Sy >= \frac{\sin\left(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J\right)}{2}$$
$$< Sz >= -\frac{\cos\left(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J\right)}{2}$$

(%o10)

(%i11) allCorrPsi(k_hetCosyaa3);

$$< IxSx >= 0$$
$$< IxSy >= \frac{\sin\left(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J\right)}{4}$$
$$< IxSz >= -\frac{\cos\left(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J\right)}{4}$$
$$< IySx >= 0$$
$$< IySy >= 0$$
$$< IySz >= 0$$
$$< IzSx >= 0$$
$$< IzSy >= 0$$
$$< IzSz >= 0$$

(%o11)

The time evolution of the wavefunction during the data acquisition period is

(%i12) k_hetCosyaat2:psiTime(k_hetCosyaa3,t2);

(%o12)
$$\begin{pmatrix} \frac{\left(\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{2}-\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{2}\right)\cdot e^{-i\cdot\pi\cdot t2\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{\sqrt{2}} \\ \frac{e^{-i\cdot\pi\cdot t2\cdot\left(-\frac{J}{2}+nuI-nuS\right)}\cdot\left(\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{2}+\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{2}\right)}{\sqrt{2}} \\ \frac{e^{-i\cdot\pi\cdot t2\cdot\left(-\frac{J}{2}-nuI+nuS\right)}\cdot\left(\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{2}-\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{2}\right)}{\sqrt{2}} \\ \frac{e^{-i\cdot\pi\cdot t2\cdot\left(\frac{J}{2}-nuI-nuS\right)}\cdot\left(\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{2}+\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{2}\right)}{\sqrt{2}} \end{pmatrix}$$

```
(%i13) allMagPsi(k_hetCosyaat2);
```

$$< Ix >= -\frac{-2 \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) - 2 \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right) + \cos\left(2 \cdot \pi \cdot t1 \cdot nuS - 2 \cdot \pi \cdot t2 \cdot nuI + (\pi \cdot t1 - \pi \cdot t2) \cdot\right.}{}$$

$$< Iy >= -\frac{-2 \cdot \sin\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) - 2 \cdot \sin\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right) - \sin\left(2 \cdot \pi \cdot t1 \cdot nuS - 2 \cdot \pi \cdot t2 \cdot nuI + (\pi \cdot t1 - \pi \cdot t2) \cdot\right.}{}$$

$$< Iz >= 0$$

$$< Sx >= \frac{-\cos\left((2 \cdot \pi \cdot t2 - 2 \cdot \pi \cdot t1) \cdot nuS + (-\pi \cdot t1 - \pi \cdot t2) \cdot J\right) - \cos\left((2 \cdot \pi \cdot t2 - 2 \cdot \pi \cdot t1) \cdot nuS + (\pi \cdot t2 - \pi \cdot t1) \cdot J\right) + \cos\left((2 \cdot \pi \cdot t1\right.}{8}$$

$$< Sy >= \frac{-\sin\left((2 \cdot \pi \cdot t2 - 2 \cdot \pi \cdot t1) \cdot nuS + (-\pi \cdot t1 - \pi \cdot t2) \cdot J\right) - \sin\left((2 \cdot \pi \cdot t2 - 2 \cdot \pi \cdot t1) \cdot nuS + (\pi \cdot t2 - \pi \cdot t1) \cdot J\right) + \sin\left((2 \cdot \pi \cdot t1 +\right.}{8}$$

$$< Sz >= -\frac{\cos\left(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J\right)}{2}$$

(%o13)

The output from the allMagPsi function is rather involved, but we can use the result to show how the resulting signal changes as the t1 interval is incremented. We assign the result for Ix to a symbol, and then separate out the terms related to t1

```
(%i14) Ix_hetCosyaa:meanPsi(Ix,k_hetCosyaat2);
```

(%o14) $$-\frac{-2 \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) - 2 \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right) + \cos\left(2 \cdot \pi \cdot t1 \cdot nuS - 2 \cdot \pi \cdot t2 \cdot nuI + (\pi \cdot t1 - \pi \cdot t2\right.}{}$$

```
(%i15) expand(%);
```

(%o15) $$-\frac{\cos\left(2 \cdot \pi \cdot t1 \cdot nuS + 2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J + \pi \cdot t1 \cdot J\right)}{8} + \frac{\cos\left(2 \cdot \pi \cdot t1 \cdot nuS + 2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J + \pi \cdot t1 \cdot J\right)}{8} + \text{co}$$

```
(%i16) trigexpand(%);
```

```
\mathrm{\tt (\%o16) }\quad -\frac{\mathrm{cos}\left( \pi \cdot \mathit{t1}\cdot J\right) \cdot \mathrm{cos}\left( \pi \cdot \mathit{t2}\
```

```
(%i17) ratsimp(%);
```

(%o17) $$-\frac{-\cos\left(\pi \cdot t2 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI\right) - \cos\left(\pi \cdot t1 \cdot J\right) \cdot \sin\left(\pi \cdot t2 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t2 \cdot nuI\right) \cdot \cos\left(2 \cdot \pi \cdot t1 \cdot nuS\right) + \sin\left(\pi \cdot t1 \cdot J\right)}{2}$$

there are four terms containing t1: sin(pi*t1*), sin(2*t1*nuS), cos(pi*t1*j) and cos(2*pi*t1*nuS) To keep these from being mixed back into the terms for t2, we temporarily substitute them with arbitrary symbols

```
(%i18) Ix_hetCosyaa:subst([sin(%pi*t1*J)=a, sin(2*%pi*t1*nuS)=b, cos(%pi*t1*J)=c,cos(2*%pi*t1*nuS)=d],%);
```

(%o18) $$-\frac{-\cos\left(\pi \cdot t2 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI\right) + a \cdot b \cdot \sin\left(\pi \cdot t2 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t2 \cdot nuI\right) - c \cdot d \cdot \sin\left(\pi \cdot t2 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t2 \cdot nuI\right)}{2}$$

```
(%i19) Ix_hetCosyaa:ratsimp(Ix_hetCosyaa4);
```

(%o19) $Ix\_hetCosyaa4$

Now combine the trig terms back using trig reduce

```
(%i20) Ix_hetCosyaa:trigreduce(Ix_hetCosyaa4);
```

(%o20) $Ix\_hetCosyaa4$

for (-c*d+a*b+1)

```
(%i21) -cos(%pi*t1*J)*cos(2*%pi*t1*nuS)+sin(%pi*t1*J)*sin(2*%pi*t1*nuS)+1;
```

(%o21) $\sin\left(\pi \cdot t1 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t1 \cdot nuS\right) - \cos\left(\pi \cdot t1 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t1 \cdot nuS\right) + 1$

```
(%i22) trigreduce(%);
```

(%o22) $1 - \cos\left(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J\right)$

for (c*d-a*b+1)

```
(%i23) cos(%pi*t1*J)*cos(2*%pi*t1*nuS)-sin(%pi*t1*J)*sin(2*%pi*t1*nuS)+1;
```

(%o23) $-\sin(\pi \cdot t1 \cdot J) \cdot \sin(2 \cdot \pi \cdot t1 \cdot nuS) + \cos(\pi \cdot t1 \cdot J) \cdot \cos(2 \cdot \pi \cdot t1 \cdot nuS) + 1$

```
(%i24) trigreduce(%);
```

(%o24) $\cos(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J) + 1$

Substitute these back

```
(%i25) Ix_hetCosyaa;
```

(%o25) *Ix_hetCosyaa4*

```
(%i26) Ix_hetCosyaa:subst([(-c*d+a*b+1)=(1-cos(2*%pi*t1*nuS+%pi*t1*J)), (c*d-a*b+1)=
       (cos(2*%pi*t1*nuS+%pi*t1*J)+1)],Ix_hetCosyaa5);
```

(%o26) *Ix_hetCosyaa5*

This confirms that the two frequency components generated during t2 are modulated by the evolution of the S-magnetization during the t1 period.

With t1=0

```
(%i27) subst(t1=0,Ix_hetCosyaa);
```

(%o27) *Ix_hetCosyaa5*

With t1 set to 1/(4*(nuS+J/2)). The immediate result of this is rather ugly, but trig reduce simplifies it to show that the two I-spin frequencies make equal contributions.

```
(%i28) subst(t1=1/(4*(nuS+J/2)),Ix_hetCosyaa);
```

(%o28) *Ix_hetCosyaa5*

```
(%i29) trigreduce(%);
```

(%o29) *Ix_hetCosyaa5*

With t1 set to 1/(2*(nuS+J/2)). The immediate output is suppressed, but the $ can be removed to see it.

```
(%i30) subst(t1=1/(2*(nuS+J/2)),Ix_hetCosyaa)$
(%i31) trigreduce(%);
```

(%o31) *Ix_hetCosyaa5*

With t1 set to 3/(4*(nuS+J/2)). The immediate output is suppressed, but the $ can be removed to see it.

```
(%i32) subst(t1=3/(4*(nuS+J/2)),Ix_hetCosyaa)$
(%i33) trigreduce(%);
```

(%o33) *Ix_hetCosyaa5*

With t1 set to 1/(nuS+J/2) The immediate output is suppressed, but the $ can be removed to see it.

```
(%i34) subst(t1=1/((nuS+J/2)),Ix_hetCosyaa)$
(%i35) trigreduce(%);
```

(%o35) *Ix_hetCosyaa5*

These results show that the relative contributions of the two I-spin frequencies vary cyclically with the duration of the t1 period, in this case, according to the frequency nuS1 = nuS + J/2.

Fig. 15.4

2.2 15.1.2 Starting with the |beta alpha> state

To automate the calculation of the wavefunctions for the other starting states, we define a function describing the effects of the preparation period on the initial wavefunction

```
(%i36) psiHetCosy(k,t1):=psiPi2Y(psiTime(psiPi2YS(k),t1));
```

(%o36) $\mathrm{psiHetCosy}(k, t1) := \mathrm{psiPi2Y}(\mathrm{psiTime}(\mathrm{psiPi2YS}(k), t1))$

```
(%i37) psiHetCosy(k_ba,t1);
```

(%o37)
$$\begin{pmatrix} -\frac{\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{2}-\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{2}}{\sqrt{2}} \\ -\frac{\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{2}+\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{2}}{\sqrt{2}} \\ \frac{\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{2}-\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{2}}{\sqrt{2}} \\ \frac{\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{2}+\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{2}}{\sqrt{2}} \end{pmatrix}$$

```
(%i38) allMagPsi(%);
```

$$< Ix >= -\frac{1}{2}$$
$$< Iy >= 0$$
$$< Iz >= 0$$
$$< Sx >= 0$$
$$< Sy >= \frac{\sin\left(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J\right)}{2}$$
$$< Sz >= -\frac{\cos\left(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J\right)}{2}$$

(%o38)

The evolution of the wavefunction during the data acquisition period

```
(%i39) k_hetCosybat2:psiTime(psiHetCosy(k_ba,t1),t2);
```

(%o39)
$$\begin{pmatrix} -\frac{\left(\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{2}-\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{2}\right)\cdot e^{-i\cdot\pi\cdot t2\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{\sqrt{2}} \\ -\frac{e^{-i\cdot\pi\cdot t2\cdot\left(-\frac{J}{2}+nuI-nuS\right)}\cdot\left(\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{2}+\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{2}\right)}{\sqrt{2}} \\ \frac{\left(\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{2}-\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{2}\right)\cdot e^{-i\cdot\pi\cdot t2\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{\sqrt{2}} \\ \frac{e^{-i\cdot\pi\cdot t2\cdot\left(\frac{J}{2}-nuI-nuS\right)}\cdot\left(\frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{2}+\frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{2}\right)}{\sqrt{2}} \end{pmatrix}$$

The evolution of the magnetization components

```
(%i40) allMagPsi(k_hetCosybat2);
```

$< Ix >= \frac{-2\cdot\cos(2\cdot\pi\cdot t2\cdot nuI-\pi\cdot t2\cdot J)-2\cdot\cos(2\cdot\pi\cdot t2\cdot nuI+\pi\cdot t2\cdot J)+\cos(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t2\cdot nuI+(-\pi\cdot t1-\pi\cdot t2)\cdot}{}$

$< Iy >= \frac{-2\cdot\sin(2\cdot\pi\cdot t2\cdot nuI-\pi\cdot t2\cdot J)-2\cdot\sin(2\cdot\pi\cdot t2\cdot nuI+\pi\cdot t2\cdot J)-\sin(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t2\cdot nuI+(-\pi\cdot t1-\pi\cdot t2)\cdot J}{}$

$< Iz >= 0$

$< Sx >= \frac{-\cos((2\cdot\pi\cdot t2-2\cdot\pi\cdot t1)\cdot nuS+(\pi\cdot t1-\pi\cdot t2)\cdot J)-\cos((2\cdot\pi\cdot t2-2\cdot\pi\cdot t1)\cdot nuS+(\pi\cdot t1+\pi\cdot t2)\cdot J)+\cos((2\cdot\pi\cdot t1+}{8}$

$< Sy >= \frac{-\sin((2\cdot\pi\cdot t2-2\cdot\pi\cdot t1)\cdot nuS+(\pi\cdot t1-\pi\cdot t2)\cdot J)-\sin((2\cdot\pi\cdot t2-2\cdot\pi\cdot t1)\cdot nuS+(\pi\cdot t1+\pi\cdot t2)\cdot J)+\sin((2\cdot\pi\cdot t1+}{8}$

$< Sz >= -\frac{\cos(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)}{2}$

(%o40)

The results for the I-magnetization components can be simplified by following the same strategy as shown for the results starting with k_aa

2.3 15.1.3 Starting with the |alpha beta> or |beta beta> states

Page 432

The quantum mechanical calculations are carried out in the same way as shown for the two other starting states.

3 15.2 The homonuclear COSY experiment

Page 435

Start with a non-selective pi/2 y-pulse to the k_aa state.

```
(%i41) k_aa;
```

(%o41) $\begin{pmatrix}1\\0\\0\\0\end{pmatrix}$

```
(%i42) k_hhCosyaa1:psiPi2Y(k_aa);
```

(%o42) $\begin{pmatrix}\frac{1}{2}\\\frac{1}{2}\\\frac{1}{2}\\\frac{1}{2}\end{pmatrix}$

```
(%i43) allMagPsi(k_hhCosyaa1);
```

$< Ix >= \frac{1}{2}$

$< Iy >= 0$

$< Iz >= 0$

$< Sx >= \frac{1}{2}$

$< Sy >= 0$

$< Sz >= 0$

(%o43)

The incremented t1 evolution period

```
(%i44) k_hhCosyaa2:psiTime(k_hhCosyaa1,t1);
```

(%o44) $$\begin{pmatrix} \frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{2} \\ \frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{2} \\ \frac{e^{-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{2} \\ \frac{e^{-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{2} \end{pmatrix}$$

```
(%i45) allMagPsi(k_hhCosyaa2);
```

$$< Ix >= \frac{\cos(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)+\cos(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)}{4}$$

$$< Iy >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)+\sin(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)}{4}$$

$$< Iz >= 0$$

$$< Sx >= \frac{\cos(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)+\cos(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)}{4}$$

$$< Sy >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)+\sin(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)}{4}$$

$$< Sz >= 0$$

(%o45)

Fig. 15.14

The second non-selective pi/2 y-pulse

```
(%i46) k_hhCosyaa3:psiPi2Y(k_hhCosyaa2)$
(%i47) allMagPsi(k_hhCosyaa3);
```

$$< Ix >= 0$$

$$< Iy >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)+\sin(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)}{4}$$

$$< Iz >= -\frac{\cos(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)+\cos(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)}{4}$$

$$< Sx >= 0$$

$$< Sy >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)+\sin(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)}{4}$$

$$< Sz >= -\frac{\cos(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)+\cos(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)}{4}$$

(%o47)

Fig. 15.15

The expressions generated by Maxima for the time-dependent magnetization components during the t2 data-acquisition period are each very long and complicated. For instance, the expression for Iy is:

```
(%i48) Iy_hhcosy:meanPsi(Iy,psiTime(k_hhCosyaa3,t2));
```

(%o48) $$-\frac{\sin((2\cdot\pi\cdot t2-2\cdot\pi\cdot t1)\cdot nuI+(-\pi\cdot t1-\pi\cdot t2)\cdot J)+\sin((2\cdot\pi\cdot t2-2\cdot\pi\cdot t1)\cdot nuI+(\pi\cdot t1-\pi\cdot t2)\cdot J)+\sin((2\cdot\pi\cdot t2}{}$$

Going from here to the expression in the text takes some doing, but it can be done!

```
(%i49) Iy_hhcosy1:expand(Iy_hhcosy);
```

(%o49) $$-\frac{\sin(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t2\cdot nuI+2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t2\cdot J)}{16}+\frac{\sin(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t2\cdot nuI+2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t2}{16}$$

```
(%i50) Iy_hhcosy2:ratsimp(trigexpand(Iy_hhcosy1));
```

(%o50) $$\frac{\cos(\pi \cdot t1 \cdot J) \cdot \cos(\pi \cdot t2 \cdot J) \cdot \sin(2 \cdot \pi \cdot t1 \cdot nuI) \cdot \cos(2 \cdot \pi \cdot t2 \cdot nuI) + \sin(\pi \cdot t2 \cdot J) \cdot \sin(2 \cdot \pi \cdot t1 \cdot nuI) \cdot \sin(2 \cdot \pi \cdot t2 \cdot nuI) \cdot}{2}$$

As shown above for the results for the heteronuclear COSY experiment, we separate out the terms for t1 by making substitutions: sin(%pi*t1*J) =a sin(2*%pi*t1*nuS)=b sin(2*%pi*t1*nuI)=c cos(2*%pi*t1*nuS)=d cos(%pi*t1*J)=e

```
(%i51) Iy_hhcosy3:subst([sin(%pi*t1*J)
       =a,sin(2*%pi*t1*nuS)=b,sin(2*%pi*t1*nuI)=c,cos(2*%pi*t1*nuS)=d,cos(%pi*t1*J)=e],Iy_hhcosy2);
```

(%o51) $$\frac{c \cdot e \cdot \cos(\pi \cdot t2 \cdot J) \cdot \cos(2 \cdot \pi \cdot t2 \cdot nuI) + a \cdot b \cdot \sin(\pi \cdot t2 \cdot J) \cdot \cos(2 \cdot \pi \cdot t2 \cdot nuI) + c \cdot d \cdot \sin(\pi \cdot t2 \cdot J) \cdot \sin(2 \cdot \pi \cdot t2 \cdot nuI)}{2}$$

```
(%i52) Iy_hhcosy4:trigreduce(Iy_hhcosy3);
```

(%o52) $$\frac{(c \cdot e + c \cdot d) \cdot \cos(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J) - a \cdot b \cdot \sin(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J) + (c \cdot e - c \cdot d) \cdot \cos(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot}{4}$$

Before trying to substitute things back, we want to convert the trig products into sums. To simplify the substitution expression, we define the substitutions and assign them to symbols.
a*b

```
(%i53) sin(%pi*t1*J)*sin(2*%pi*t1*nuS);
```

(%o53) $$\sin(\pi \cdot t1 \cdot J) \cdot \sin(2 \cdot \pi \cdot t1 \cdot nuS)$$

```
(%i54) trigreduce(%);
```

(%o54) $$\frac{\cos(2 \cdot \pi \cdot t1 \cdot nuS - \pi \cdot t1 \cdot J)}{2} - \frac{\cos(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J)}{2}$$

```
(%i55) ratsimp(%);
```

(%o55) $$-\frac{\cos(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J) - \cos(2 \cdot \pi \cdot t1 \cdot nuS - \pi \cdot t1 \cdot J)}{2}$$

```
(%i56) sub1:a*b=%;
```

(%o56) $$a \cdot b = -\frac{\cos(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J) - \cos(2 \cdot \pi \cdot t1 \cdot nuS - \pi \cdot t1 \cdot J)}{2}$$

c*e-c*d

```
(%i57) sin(2*%pi*t1*nuI)*cos(%pi*t1*J)    -sin(2*%pi*t1*nuI)*cos(2*%pi*t1*nuS);
```

(%o57) $$\cos(\pi \cdot t1 \cdot J) \cdot \sin(2 \cdot \pi \cdot t1 \cdot nuI) - \sin(2 \cdot \pi \cdot t1 \cdot nuI) \cdot \cos(2 \cdot \pi \cdot t1 \cdot nuS)$$

```
(%i58) trigreduce(%);
```

(%o58) $$-\frac{\sin(2 \cdot \pi \cdot t1 \cdot nuS + 2 \cdot \pi \cdot t1 \cdot nuI)}{2} + \frac{\sin(2 \cdot \pi \cdot t1 \cdot nuS - 2 \cdot \pi \cdot t1 \cdot nuI)}{2} + \frac{\sin(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot t1 \cdot J)}{2} + \frac{\sin(2 \cdot \pi \cdot t1 \cdot}{}$$

```
(%i59) ratsimp(%);
```

(%o59) $$-\frac{-\sin(2 \cdot \pi \cdot t1 \cdot nuI - \pi \cdot t1 \cdot J) - \sin(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot t1 \cdot J) - \sin(2 \cdot \pi \cdot t1 \cdot nuS - 2 \cdot \pi \cdot t1 \cdot nuI) + \sin(2 \cdot \pi \cdot t1 \cdot nuS +}{2}$$

```
(%i60) sub2:(c*e-c*d)=%;
```

(%o60) $$c \cdot e - c \cdot d = -\frac{-\sin(2 \cdot \pi \cdot t1 \cdot nuI - \pi \cdot t1 \cdot J) - \sin(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot t1 \cdot J) - \sin(2 \cdot \pi \cdot t1 \cdot nuS - 2 \cdot \pi \cdot t1 \cdot nuI) + \sin(2 \cdot}{2}$$

c*e+c*d

```
(%i61) sin(2*%pi*t1*nuI)*cos(%pi*t1*J)+sin(2*%pi*t1*nuI)*cos(2*%pi*t1*nuS);
```

(%o61) $$\sin(2 \cdot \pi \cdot t1 \cdot nuI) \cdot \cos(2 \cdot \pi \cdot t1 \cdot nuS) + \cos(\pi \cdot t1 \cdot J) \cdot \sin(2 \cdot \pi \cdot t1 \cdot nuI)$$

```
(%i62) trigreduce(%);
```

(%o62) $\frac{\sin(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t1\cdot nuI)}{2}-\frac{\sin(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)}{2}+\frac{\sin(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)}{2}+\frac{\sin(2\cdot\pi\cdot t1\cdot nu}{2}$

```
(%i63) ratsimp(%);
```

(%o63) $\frac{\sin(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)+\sin(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)-\sin(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)+\sin(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi}{2}$

```
(%i64) sub3:(c*e+c*d)=%;
```

(%o64) $c\cdot e+c\cdot d=\frac{\sin(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)+\sin(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)-\sin(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)+\sin(2\cdot\pi\cdot t}{2}$

Now, doing the substitution

```
(%i65) Iy_hhcosy4;
```

(%o65) $\frac{(c\cdot e+c\cdot d)\cdot\cos(2\cdot\pi\cdot t2\cdot nuI-\pi\cdot t2\cdot J)-a\cdot b\cdot\sin(2\cdot\pi\cdot t2\cdot nuI-\pi\cdot t2\cdot J)+(c\cdot e-c\cdot d)\cdot\cos(2\cdot\pi\cdot t2\cdot nuI+\pi\cdot t2\cdot}{4}$

```
(%i66) Iy_hhcosy5:subst([sub1,sub2,sub3],Iy_hhcosy4);
```

(%o66) $\frac{-a\cdot b\cdot\sin(2\cdot\pi\cdot t2\cdot nuI-\pi\cdot t2\cdot J)+a\cdot b\cdot\sin(2\cdot\pi\cdot t2\cdot nuI+\pi\cdot t2\cdot J)-\frac{\cos(2\cdot\pi\cdot t2\cdot nuI+\pi\cdot t2\cdot J)\cdot(-\sin(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)-\sin(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)}{2}}{}$

This doesn't't quite work! The reason is that a*b is not recognized as an "atom" in Maxima, that is as a fundamental part of the expression. The parts of an expression can be identified, and used in other expressions, using the part function. This function takes two arguments, an expression and an integer identifying the part

```
(%i67) part(Iy_hhcosy4,1);
```

(%o67) $a\cdot b\cdot\sin(2\cdot\pi\cdot t2\cdot nuI+\pi\cdot t2\cdot J)+(c\cdot e-c\cdot d)\cdot\cos(2\cdot\pi\cdot t2\cdot nuI+\pi\cdot t2\cdot J)-a\cdot b\cdot\sin(2\cdot\pi\cdot t2\cdot nuI-\pi\cdot t2\cdot J)+(c\cdot$

```
(%i68) part(Iy_hhcosy4,2);
```

(%o68) 4

The first part can be broken down further

```
(%i69) part(part(Iy_hhcosy4,1),1);
```

(%o69) $a\cdot b\cdot\sin(2\cdot\pi\cdot t2\cdot nuI+\pi\cdot t2\cdot J)$

This can also be written in a more compact form by providing additional arguments to part, each identifying a part index of the preceding part:

```
(%i70) part(Iy_hhcosy4,1,1);
```

(%o70) $(c\cdot e+c\cdot d)\cdot\cos(2\cdot\pi\cdot t2\cdot nuI-\pi\cdot t2\cdot J)$

This can be taken apart further

```
(%i71) part(Iy_hhcosy4,1,1,1);
```

(%o71) $c\cdot e+c\cdot d$

The term b is:

```
(%i72) part(Iy_hhcosy4,1,1,2);
```

(%o72) $\cos(2\cdot\pi\cdot t2\cdot nuI-\pi\cdot t2\cdot J)$

This shows us what the problem is: a and b are separate atoms. One way to solve this problem is to use the ratsubst function, which is similar to subst, but incorporates some algebraic knowledge. The use of ratsubst is also somewhat more restrictive than subst and must be used in the form:
ratsubst(a,b,c) which results in the substitution of a for b in c.
Going back to the form from the previous substitution

```
(%i73) Iy_hhcosy5;
```

(%o73) $$-a \cdot b \cdot \sin\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) + a \cdot b \cdot \sin\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right) - \frac{\cos(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J) \cdot (-\sin(2 \cdot \pi \cdot t1 \cdot nuI - \pi \cdot t1 \cdot J) - \sin(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot t1 \cdot J)}{2}$$

The substitution that is left to make was defined previously as sub1

```
(%i74) sub1;
```

(%o74) $$a \cdot b = -\frac{\cos\left(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J\right) - \cos\left(2 \cdot \pi \cdot t1 \cdot nuS - \pi \cdot t1 \cdot J\right)}{2}$$

Using ratsubst to make the substitution

```
(%i75) Iy_hhcosy6:ratsubst(-(cos(2*%pi*t1*nuS+%pi*t1*J)-cos(2*%pi*t1*nuS-%pi*t1*J))/2,a*b,Iy_hhcosy5);
```

(%o75) $$-\frac{\left(-\sin\left(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot t1 \cdot J\right) - \sin\left(2 \cdot \pi \cdot t1 \cdot nuI - \pi \cdot t1 \cdot J\right)\right) \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) + \left(-\sin\left(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot\right.\right.}{}$$

```
(%i76) Iy_hhcosy7:expand(Iy_hhcosy6);
```

(%o76) $$-\frac{\cos\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t1 \cdot nuS + 2 \cdot \pi \cdot t1 \cdot nuI\right)}{8} + \frac{\cos\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t1 \cdot nuS + 2\right.}{8}$$

This is basically the same as the form shown as Eq. 15.2, and we can use the part function to pull it apart and reassemble it in that form
For line a

```
(%i77) part(Iy_hhcosy7,9) + part(Iy_hhcosy7,10);
```

(%o77) $$\frac{\sin\left(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot t1 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right)}{8} + \frac{\sin\left(2 \cdot \pi \cdot t1 \cdot nuI - \pi \cdot t1 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right)}{8}$$

```
(%i78) factor(%);
```

(%o78) $$\frac{\left(\sin\left(\pi \cdot t1 \cdot (2 \cdot nuI - J)\right) + \sin\left(\pi \cdot t1 \cdot (2 \cdot nuI + J)\right)\right) \cdot \cos\left(\pi \cdot t2 \cdot (2 \cdot nuI + J)\right)}{8}$$

line b

```
(%i79) part(Iy_hhcosy7,11)+part(Iy_hhcosy7,12);
```

(%o79) $$\frac{\sin\left(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot t1 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right)}{8} + \frac{\sin\left(2 \cdot \pi \cdot t1 \cdot nuI - \pi \cdot t1 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right)}{8}$$

```
(%i80) factor(%);
```

(%o80) $$\frac{\cos\left(\pi \cdot t2 \cdot (2 \cdot nuI - J)\right) \cdot \left(\sin\left(\pi \cdot t1 \cdot (2 \cdot nuI - J)\right) + \sin\left(\pi \cdot t1 \cdot (2 \cdot nuI + J)\right)\right)}{8}$$

line c

```
(%i81) part(Iy_hhcosy7,5) + part(Iy_hhcosy7,7);
```

(%o81) $$\frac{\sin\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t1 \cdot nuS - \pi \cdot t1 \cdot J\right)}{8} - \frac{\sin\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J\right)}{8}$$

```
(%i82) factor(%);
```

(%o82) $$-\frac{\sin\left(\pi \cdot t2 \cdot (2 \cdot nuI + J)\right) \cdot \left(\cos\left(\pi \cdot t1 \cdot (2 \cdot nuS + J)\right) - \cos\left(\pi \cdot t1 \cdot (2 \cdot nuS - J)\right)\right)}{8}$$

line d

```
(%i83) part(Iy_hhcosy7,6) + part(Iy_hhcosy7,8);
```

(%o83) $$\frac{\sin\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J\right)}{8} - \frac{\sin\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) \cdot \cos\left(2 \cdot \pi \cdot t1 \cdot nuS - \pi \cdot t1 \cdot J\right)}{8}$$

```
(%i84) factor(%);
```

(%o84) $$\frac{\sin\left(\pi \cdot t1 \cdot (2 \cdot nuI - J)\right) \cdot \left(\cos\left(\pi \cdot t1 \cdot (2 \cdot nuS + J)\right) - \cos\left(\pi \cdot t1 \cdot (2 \cdot nuS - J)\right)\right)}{8}$$

line e

```
(%i85) part(Iy_hhcosy7,3) + part(Iy_hhcosy7,1);
```

(%o85) $$\frac{\cos\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t1 \cdot nuS - 2 \cdot \pi \cdot t1 \cdot nuI\right)}{8} - \frac{\cos\left(2 \cdot \pi \cdot t2 \cdot nuI + \pi \cdot t2 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t1 \cdot nuS + 2 \cdot \pi\right.}{8}$$

```
(%i86) factor(%);
```

(%o86) $$-\frac{\cos\left(\pi \cdot t2 \cdot (2 \cdot nuI + J)\right) \cdot \left(\sin\left(2 \cdot \pi \cdot t1 \cdot (nuS + nuI)\right) - \sin\left(2 \cdot \pi \cdot t1 \cdot (nuS - nuI)\right)\right)}{8}$$

line f

```
(%i87) part(Iy_hhcosy7,4) + part(Iy_hhcosy7,2);
```

(%o87) $$\frac{\cos\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t1 \cdot nuS + 2 \cdot \pi \cdot t1 \cdot nuI\right)}{8} - \frac{\cos\left(2 \cdot \pi \cdot t2 \cdot nuI - \pi \cdot t2 \cdot J\right) \cdot \sin\left(2 \cdot \pi \cdot t1 \cdot nuS - 2 \cdot \pi\right.}{8}$$

```
(%i88) factor(%);
```

(%o88) $$\frac{\cos\left(\pi \cdot t2 \cdot (2 \cdot nuI - J)\right) \cdot \left(\sin\left(2 \cdot \pi \cdot t1 \cdot (nuS + nuI)\right) - \sin\left(2 \cdot \pi \cdot t1 \cdot (nuS - nuI)\right)\right)}{8}$$

3.1 15.2.1 Origin of the anti-phase COSY components

Page 437

The magnetization components and correlations that are present at the end of the t1 evolution period, before the second pulse.

```
(%i89) allMagPsi(k_hhCosyaa2);
```

$$< Ix >= \frac{\cos\left(2 \cdot \pi \cdot t1 \cdot nuI - \pi \cdot t1 \cdot J\right) + \cos\left(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot t1 \cdot J\right)}{4}$$

$$< Iy >= \frac{\sin\left(2 \cdot \pi \cdot t1 \cdot nuI - \pi \cdot t1 \cdot J\right) + \sin\left(2 \cdot \pi \cdot t1 \cdot nuI + \pi \cdot t1 \cdot J\right)}{4}$$

$$< Iz >= 0$$

$$< Sx >= \frac{\cos\left(2 \cdot \pi \cdot t1 \cdot nuS - \pi \cdot t1 \cdot J\right) + \cos\left(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J\right)}{4}$$

$$< Sy >= \frac{\sin\left(2 \cdot \pi \cdot t1 \cdot nuS - \pi \cdot t1 \cdot J\right) + \sin\left(2 \cdot \pi \cdot t1 \cdot nuS + \pi \cdot t1 \cdot J\right)}{4}$$

$$< Sz >= 0$$

(%o89)

```
(%i90) allCorrPsi(k_hhCosyaa2);
```

$$< IxSx >= \frac{\cos(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)+\cos(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t1\cdot nuI)}{8}$$
$$< IxSy >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)+\sin(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t1\cdot nuI)}{8}$$
$$< IxSz >= \frac{\cos(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)-\cos(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)}{8}$$
$$< IySx >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t1\cdot nuI)-\sin(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)}{8}$$
$$< IySy >= -\frac{\cos(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t1\cdot nuI)-\cos(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)}{8}$$
$$< IySz >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)-\sin(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)}{8}$$
$$< IzSx >= \frac{\cos(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)-\cos(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)}{8}$$
$$< IzSy >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)-\sin(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)}{8}$$
$$< IzSz >= 0$$

(%o90)

Figs. 15.16 and 15.17

After the second pulse:

```
(%i91) allMagPsi(k_hhCosyaa3);
```

$$< Ix >= 0$$
$$< Iy >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)+\sin(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)}{4}$$
$$< Iz >= -\frac{\cos(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)+\cos(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)}{4}$$
$$< Sx >= 0$$
$$< Sy >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)+\sin(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)}{4}$$
$$< Sz >= -\frac{\cos(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)+\cos(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)}{4}$$

(%o91)

```
(%i92) allCorrPsi(k_hhCosyaa3);
```

$$< IxSx >= 0$$
$$< IxSy >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)-\sin(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)}{8}$$
$$< IxSz >= -\frac{\cos(2\cdot\pi\cdot t1\cdot nuS+\pi\cdot t1\cdot J)-\cos(2\cdot\pi\cdot t1\cdot nuS-\pi\cdot t1\cdot J)}{8}$$
$$< IySx >= \frac{\sin(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)-\sin(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)}{8}$$
$$< IySy >= -\frac{\cos(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t1\cdot nuI)-\cos(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)}{8}$$
$$< IySz >= -\frac{\sin(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t1\cdot nuI)-\sin(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)}{8}$$
$$< IzSx >= -\frac{\cos(2\cdot\pi\cdot t1\cdot nuI+\pi\cdot t1\cdot J)-\cos(2\cdot\pi\cdot t1\cdot nuI-\pi\cdot t1\cdot J)}{8}$$
$$< IzSy >= -\frac{\sin(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)+\sin(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t1\cdot nuI)}{8}$$
$$< IzSz >= \frac{\cos(2\cdot\pi\cdot t1\cdot nuS-2\cdot\pi\cdot t1\cdot nuI)+\cos(2\cdot\pi\cdot t1\cdot nuS+2\cdot\pi\cdot t1\cdot nuI)}{8}$$

(%o92)

Fig. 15.18

Of the components listed above, Sz, IxSz, Sy and IxSy are the ones that come from the Sx magnetization present after the first pulse. The IxSz component will evolve into observable I-magnetization during the data-acquisition period. The magnitude of this component is determined by nuS and the length of the t1 evolution period, but it's evolution frequencies during the data-acquisition period are nuI+J/2 and nuI-J/2.
