Maxima workbook for Principles of NMR Spectroscopy
Chapter 17: Introduction to the Density Matrix
Section 17.2: The density matrix for two scalar-coupled spins

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 the earlier chapters. This software is distributed under the conditions of the BSD license and without any guarantees or warranties. Please send comments, including bug reports, to this address:

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Chapter 17 introduces the density matrix for spin-1/2 nuclei. The first section deals with a population of isolated spins, without scalar coupling, whereas the second section deals with a population of weakly-coupled spin pairs. Because separate Maxima libraries (1spinLib.mac and 2spinLib.mac) are used for the two kinds of systems, separate workbooks are provided for the two sections of Chapter 17

The library used previously for quantum mechanical calculations for coupled spin pairs also contains functions for density matrix calculations for populations of uncoupled spins.
Functions with names beginning with "psi" are generally used for wavefunction calculations, whereas function names beginning with "rho" are associated with density matrix calculations.

```
(%i1) load("/Users/davidg/Dropbox/homedir/maxima/2spinLib.mac");
```

(%o1) /Users/davidg/Dropbox/homedir/maxima/2spinLib.mac

2 The Density Matrix for Two Scalar-Couple Spins

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The macro library includes the definition of a matrix to represent a general density matrix for a population of coupled spin pairs

```
(%i2) rhogen;
```

(%o2) $$\begin{pmatrix} avCaaConjCaa & avCaaConjCab & avCaaConjCba & avCaaConjCbb \\ avCabConjCaa & avCabConjCab & avCabConjCba & avCabConjCbb \\ avCbaConjCaa & avCbaConjCab & avCbaConjCba & avCbaConjCbb \\ avCbbConjCaa & avCbbConjCab & avCbbConjCba & avCbbConjCbb \end{pmatrix}$$

2.1 17.2.1 Magnetization operator matrices

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The matrix used to calculate the average z-magnetization of the I-spin is:

```
(%i3) Iz;
```

(%o3) $$\begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}$$

The average magnetization is calculated by multiplying the density matrix by the operator matrix and then taking the trace of the resulting matrix.

```
(%i4) Iz.rhogen;
```

(%o4) $$\begin{pmatrix} \frac{avCaaConjCaa}{2} & \frac{avCaaConjCab}{2} & \frac{avCaaConjCba}{2} & \frac{avCaaConjCbb}{2} \\ \frac{avCabConjCaa}{2} & \frac{avCabConjCab}{2} & \frac{avCabConjCba}{2} & \frac{avCabConjCbb}{2} \\ -\frac{avCbaConjCaa}{2} & -\frac{avCbaConjCab}{2} & -\frac{avCbaConjCba}{2} & -\frac{avCbaConjCbb}{2} \\ -\frac{avCbbConjCaa}{2} & -\frac{avCbbConjCab}{2} & -\frac{avCbbConjCba}{2} & -\frac{avCbbConjCbb}{2} \end{pmatrix}$$

```
(%i5) mattrace(%);
```

(%o5) $$-\frac{avCbbConjCbb}{2} - \frac{avCbaConjCba}{2} + \frac{avCabConjCab}{2} + \frac{avCaaConjCaa}{2}$$

The operator matrix for calculating the z-magnetization of the S-spin.

```
(%i6) Sz;
```

(%o6) $$\begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}$$

```
(%i7) Sz.rhogen;
```

(%o7) $$\begin{pmatrix} \frac{avCaaConjCaa}{2} & \frac{avCaaConjCab}{2} & \frac{avCaaConjCba}{2} & \frac{avCaaConjCbb}{2} \\ -\frac{avCabConjCaa}{2} & -\frac{avCabConjCab}{2} & -\frac{avCabConjCba}{2} & -\frac{avCabConjCbb}{2} \\ \frac{avCbaConjCaa}{2} & \frac{avCbaConjCab}{2} & \frac{avCbaConjCba}{2} & \frac{avCbaConjCbb}{2} \\ -\frac{avCbbConjCaa}{2} & -\frac{avCbbConjCab}{2} & -\frac{avCbbConjCba}{2} & -\frac{avCbbConjCbb}{2} \end{pmatrix}$$

```
(%i8) mattrace(%);
```

(%o8) $$-\frac{avCbbConjCbb}{2} + \frac{avCbaConjCba}{2} - \frac{avCabConjCab}{2} + \frac{avCaaConjCaa}{2}$$

The other operator matrices are listed below.

```
(%i9) Ix;
```

(%o9) $$\begin{pmatrix} 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \end{pmatrix}$$

```
(%i10) Ix.rhogen;
```

(%o10) $$\begin{pmatrix} \frac{avCbaConjCaa}{2} & \frac{avCbaConjCab}{2} & \frac{avCbaConjCba}{2} & \frac{avCbaConjCbb}{2} \\ \frac{avCbbConjCaa}{2} & \frac{avCbbConjCab}{2} & \frac{avCbbConjCba}{2} & \frac{avCbbConjCbb}{2} \\ \frac{avCaaConjCaa}{2} & \frac{avCaaConjCab}{2} & \frac{avCaaConjCba}{2} & \frac{avCaaConjCbb}{2} \\ \frac{avCabConjCaa}{2} & \frac{avCabConjCab}{2} & \frac{avCabConjCba}{2} & \frac{avCabConjCbb}{2} \end{pmatrix}$$

(%i11) mattrace(%);

(%o11) $$\frac{avCbbConjCab}{2} + \frac{avCbaConjCaa}{2} + \frac{avCabConjCbb}{2} + \frac{avCaaConjCba}{2}$$

(%i12) Iy;

(%o12) $$\begin{pmatrix} 0 & 0 & -\frac{i}{2} & 0 \\ 0 & 0 & 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 & 0 & 0 \\ 0 & \frac{i}{2} & 0 & 0 \end{pmatrix}$$

(%i13) Iy.rhogen;

(%o13) $$\begin{pmatrix} -\frac{i \cdot avCbaConjCaa}{2} & -\frac{i \cdot avCbaConjCab}{2} & -\frac{i \cdot avCbaConjCba}{2} & -\frac{i \cdot avCbaConjCbb}{2} \\ -\frac{i \cdot avCbbConjCaa}{2} & -\frac{i \cdot avCbbConjCab}{2} & -\frac{i \cdot avCbbConjCba}{2} & -\frac{i \cdot avCbbConjCbb}{2} \\ \frac{i \cdot avCaaConjCaa}{2} & \frac{i \cdot avCaaConjCab}{2} & \frac{i \cdot avCaaConjCba}{2} & \frac{i \cdot avCaaConjCbb}{2} \\ \frac{i \cdot avCabConjCaa}{2} & \frac{i \cdot avCabConjCab}{2} & \frac{i \cdot avCabConjCba}{2} & \frac{i \cdot avCabConjCbb}{2} \end{pmatrix}$$

(%i14) mattrace(%);

(%o14) $$-\frac{i \cdot avCbbConjCab}{2} - \frac{i \cdot avCbaConjCaa}{2} + \frac{i \cdot avCabConjCbb}{2} + \frac{i \cdot avCaaConjCba}{2}$$

(%i15) Sx;

(%o15) $$\begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix}$$

(%i16) Sx.rhogen;

(%o16) $$\begin{pmatrix} \frac{avCabConjCaa}{2} & \frac{avCabConjCab}{2} & \frac{avCabConjCba}{2} & \frac{avCabConjCbb}{2} \\ \frac{avCaaConjCaa}{2} & \frac{avCaaConjCab}{2} & \frac{avCaaConjCba}{2} & \frac{avCaaConjCbb}{2} \\ \frac{avCbbConjCaa}{2} & \frac{avCbbConjCab}{2} & \frac{avCbbConjCba}{2} & \frac{avCbbConjCbb}{2} \\ \frac{avCbaConjCaa}{2} & \frac{avCbaConjCab}{2} & \frac{avCbaConjCba}{2} & \frac{avCbaConjCbb}{2} \end{pmatrix}$$

(%i17) mattrace(%);

(%o17) $$\frac{avCbbConjCba}{2} + \frac{avCbaConjCbb}{2} + \frac{avCabConjCaa}{2} + \frac{avCaaConjCab}{2}$$

(%i18) Sy;

(%o18) $$\begin{pmatrix} 0 & -\frac{i}{2} & 0 & 0 \\ \frac{i}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{i}{2} \\ 0 & 0 & \frac{i}{2} & 0 \end{pmatrix}$$

(%i19) Sy.rhogen;

$$(\%o19)\quad \begin{pmatrix} -\frac{i\cdot avCabConjCaa}{2} & -\frac{i\cdot avCabConjCab}{2} & -\frac{i\cdot avCabConjCba}{2} & -\frac{i\cdot avCabConjCbb}{2} \\ \frac{i\cdot avCaaConjCaa}{2} & \frac{i\cdot avCaaConjCab}{2} & \frac{i\cdot avCaaConjCba}{2} & \frac{i\cdot avCaaConjCbb}{2} \\ -\frac{i\cdot avCbbConjCaa}{2} & -\frac{i\cdot avCbbConjCab}{2} & -\frac{i\cdot avCbbConjCba}{2} & -\frac{i\cdot avCbbConjCbb}{2} \\ \frac{i\cdot avCbaConjCaa}{2} & \frac{i\cdot avCbaConjCab}{2} & \frac{i\cdot avCbaConjCba}{2} & \frac{i\cdot avCbaConjCbb}{2} \end{pmatrix}$$

(%i20) mattrace(%);

$$(\%o20)\quad -\frac{i\cdot avCbbConjCba}{2}+\frac{i\cdot avCbaConjCbb}{2}-\frac{i\cdot avCabConjCaa}{2}+\frac{i\cdot avCaaConjCab}{2}$$

2.2 17.2.2 The equilibrium density matrix

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The equilibrium density matrix is defined in 2spinLib.mac, in terms of the equilibrium population differences for the two spins.

(%i21) rhoEq;

$$(\%o21)\quad \begin{pmatrix} \frac{deltaPS}{4}+\frac{deltaPI}{4} & 0 & 0 & 0 \\ 0 & \frac{deltaPI}{4}-\frac{deltaPS}{4} & 0 & 0 \\ 0 & 0 & \frac{deltaPS}{4}-\frac{deltaPI}{4} & 0 \\ 0 & 0 & 0 & -\frac{deltaPS}{4}-\frac{deltaPI}{4} \end{pmatrix}$$

The equilibrium Iz and Sz magnetization components are calculated from the density matrix using the Iz and Sz operator matrices

(%i22) mattrace(Iz.rhoEq);

$$(\%o22)\quad \frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}+\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}$$

(%i23) ratsimp(%);

$$(\%o23)\quad \frac{deltaPI}{2}$$

(%i24) mattrace(Sz.rhoEq);

$$(\%o24)\quad \frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}-\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}$$

(%i25) ratsimp(%);

$$(\%o25)\quad \frac{deltaPS}{2}$$

2.3 17.2.3 Effects of pulses on the density matrix

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The rotation matrix and its inverse for a y-pulse of angle a applied to the I-spin

(%i26) RIy(a);

$$(\%o26)\quad \begin{pmatrix} \cos\left(\frac{a}{2}\right) & 0 & -\sin\left(\frac{a}{2}\right) & 0 \\ 0 & \cos\left(\frac{a}{2}\right) & 0 & -\sin\left(\frac{a}{2}\right) \\ \sin\left(\frac{a}{2}\right) & 0 & \cos\left(\frac{a}{2}\right) & 0 \\ 0 & \sin\left(\frac{a}{2}\right) & 0 & \cos\left(\frac{a}{2}\right) \end{pmatrix}$$

```
(%i27) RIyInv(a);
```

$$(\%o27)\quad \begin{pmatrix} \cos\left(\frac{a}{2}\right) & 0 & \sin\left(\frac{a}{2}\right) & 0 \\ 0 & \cos\left(\frac{a}{2}\right) & 0 & \sin\left(\frac{a}{2}\right) \\ -\sin\left(\frac{a}{2}\right) & 0 & \cos\left(\frac{a}{2}\right) & 0 \\ 0 & -\sin\left(\frac{a}{2}\right) & 0 & \cos\left(\frac{a}{2}\right) \end{pmatrix}$$

Matrices for a pi/2 y-pulse to the I-spin

```
(%i28) RIy(%pi/2);
```

$$(\%o28)\quad \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{pmatrix}$$

```
(%i29) RIyInv(%pi/2);
```

$$(\%o29)\quad \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{pmatrix}$$

Application of a pi/2 y-pulse to the I-spin, to the equilibrium state:

```
(%i30) RIy(%pi/2).rhoEq.RIyInv(%pi/2);
```

$$(\%o30)\quad \begin{pmatrix} \frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2} & 0 & \frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2} & 0 \\ 0 & \frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2} & 0 & \frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2} \\ \frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2} & 0 & \frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2} & 0 \\ 0 & \frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2} & 0 & \frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2} \end{pmatrix}$$

```
(%i31) ratsimp(%);
```

$$(\%o31)\quad \begin{pmatrix} \frac{deltaPS}{4} & 0 & \frac{deltaPI}{4} & 0 \\ 0 & -\frac{deltaPS}{4} & 0 & \frac{deltaPI}{4} \\ \frac{deltaPI}{4} & 0 & \frac{deltaPS}{4} & 0 \\ 0 & \frac{deltaPI}{4} & 0 & -\frac{deltaPS}{4} \end{pmatrix}$$

The 2spinLib.mac file also includes functions to calculate the density matrix following different pulses applied to a state represented by an initial density matrix. The calculation shown above can also be carried out as:

```
(%i32) rhoPi2YI(rhoEq);
```

(%o32) $$\begin{pmatrix} \frac{deltaPS}{4} & 0 & \frac{deltaPI}{4} & 0 \\ 0 & -\frac{deltaPS}{4} & 0 & \frac{deltaPI}{4} \\ \frac{deltaPI}{4} & 0 & \frac{deltaPS}{4} & 0 \\ 0 & \frac{deltaPI}{4} & 0 & -\frac{deltaPS}{4} \end{pmatrix}$$

The all of the average magnetization components can be calculated as:

```
(%i33) allMagRho(%);
```

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

(%o33)

Matrices for a pi/2 x-pulse to the S-spin

```
(%i34) RSx(%pi/2);
```

(%o34) $$\begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} & 0 & 0 \\ -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} \\ 0 & 0 & -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

```
(%i35) RSxInv(%pi/2);
```

(%o35) $$\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & 0 & 0 \\ \frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ 0 & 0 & \frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

The density matrix following a pi/2 x-pulse to the S-spin, starting with the equilibrium state

```
(%i36) RSx(%pi/2).rhoEq.RSxInv(%pi/2);
```

(%o36) $$\begin{pmatrix} \frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2} & \frac{i\cdot\left(\frac{deltaPI}{4}+\frac{deltaPS}{4}\right)}{2}-\frac{i\cdot\left(\frac{deltaPI}{4}-\frac{deltaPS}{4}\right)}{2} & 0 & 0 \\ \frac{i\cdot\left(\frac{deltaPI}{4}-\frac{deltaPS}{4}\right)}{2}-\frac{i\cdot\left(\frac{deltaPI}{4}+\frac{deltaPS}{4}\right)}{2} & \frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2} & 0 & 0 \\ 0 & 0 & \frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}+\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2} & \frac{i\cdot\left(\frac{deltaPS}{4}-\frac{deltaPI}{4}\right)}{2}-\frac{i\cdot\left(-\frac{deltaPI}{4}\ldots\right.}{2} \\ 0 & 0 & \frac{i\cdot\left(-\frac{deltaPI}{4}-\frac{deltaPS}{4}\right)}{2}-\frac{i\cdot\left(\frac{deltaPS}{4}-\frac{deltaPI}{4}\right)}{2} & \frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}+\frac{-\frac{deltaPI}{4}-\ldots}{2} \end{pmatrix}$$

```
(%i37) ratsimp(%);
```

(%o37) $$\begin{pmatrix} \frac{deltaPI}{4} & \frac{i\cdot deltaPS}{4} & 0 & 0 \\ -\frac{i\cdot deltaPS}{4} & \frac{deltaPI}{4} & 0 & 0 \\ 0 & 0 & -\frac{deltaPI}{4} & \frac{i\cdot deltaPS}{4} \\ 0 & 0 & -\frac{i\cdot deltaPS}{4} & -\frac{deltaPI}{4} \end{pmatrix}$$

```
(%i38) allMagRho(%);
```

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

(%o38)

The effects of a non-selective pulse are calculated by first calculating the effects of one pulse on the density matrix, followed by the other pulse
In the example below, the matrix multiplications for the first pulse are nested in parentheses.

(%i39) `RSy(%pi/2).(RIy(%pi/2).rhoEq.RIyInv(%pi/2)).RSyInv(%pi/2);`

(%o39)
$$\begin{pmatrix} \frac{\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}+\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}}{2}+\frac{\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} & \frac{\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}+\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}}{2}-\frac{\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} \\ \frac{\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}+\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}}{2}-\frac{\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} & \frac{\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}+\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}}{2}+\frac{\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} \\ \frac{\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}}{2}+\frac{\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} & \frac{\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}}{2}-\frac{\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} \\ \frac{\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}}{2}-\frac{\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} & \frac{\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}}{2}+\frac{\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} \end{pmatrix}$$

(%i40) `ratsimp(%);`

(%o40)
$$\begin{pmatrix} 0 & \frac{deltaPS}{4} & \frac{deltaPI}{4} & 0 \\ \frac{deltaPS}{4} & 0 & 0 & \frac{deltaPI}{4} \\ \frac{deltaPI}{4} & 0 & 0 & \frac{deltaPS}{4} \\ 0 & \frac{deltaPI}{4} & \frac{deltaPS}{4} & 0 \end{pmatrix}$$

The calculations can be carried out in either order:

(%i41) `RIy(%pi/2).(RSy(%pi/2).rhoEq.RSyInv(%pi/2)).RIyInv(%pi/2);`

(%o41)
$$\begin{pmatrix} \frac{\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}}{2}+\frac{\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}}{2} & \frac{\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2}+\frac{\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} \\ \frac{\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2}+\frac{\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} & \frac{\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}}{2}+\frac{\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}}{2} \\ \frac{\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}}{2}-\frac{\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}}{2} & \frac{\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2}-\frac{\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} \\ \frac{\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}-\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2}-\frac{\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}-\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}}{2} & \frac{\frac{\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPI}{4}+\frac{deltaPS}{4}}{2}}{2}-\frac{\frac{-\frac{deltaPI}{4}-\frac{deltaPS}{4}}{2}+\frac{\frac{deltaPS}{4}-\frac{deltaPI}{4}}{2}}{2} \end{pmatrix}$$

(%i42) `ratsimp(%);`

(%o42)
$$\begin{pmatrix} 0 & \frac{deltaPS}{4} & \frac{deltaPI}{4} & 0 \\ \frac{deltaPS}{4} & 0 & 0 & \frac{deltaPI}{4} \\ \frac{deltaPI}{4} & 0 & 0 & \frac{deltaPS}{4} \\ 0 & \frac{deltaPI}{4} & \frac{deltaPS}{4} & 0 \end{pmatrix}$$

There is also a function to calculate the effects of a non-selective pi/2 y-pulse

(%i43) `rhoPi2Y(rhoEq);`

(%o43)
$$\begin{pmatrix} 0 & \frac{deltaPS}{4} & \frac{deltaPI}{4} & 0 \\ \frac{deltaPS}{4} & 0 & 0 & \frac{deltaPI}{4} \\ \frac{deltaPI}{4} & 0 & 0 & \frac{deltaPS}{4} \\ 0 & \frac{deltaPI}{4} & \frac{deltaPS}{4} & 0 \end{pmatrix}$$

The resulting magnetization components are as expected:

(%i44) `allMagRho(%);`

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

(%o44)

2.4 17.2.4 Time evolution of the two-spin density matrix

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The time evolution matrix for two weakly-coupled spins

```
(%i45) Uh(t,nuI,nuS,J);
```

(%o45)
$$\begin{pmatrix} e^{-i\cdot\pi\cdot t\cdot\left(\frac{J}{2}+nuI+nuS\right)} & 0 & 0 & 0 \\ 0 & e^{-i\cdot\pi\cdot t\cdot\left(-\frac{J}{2}+nuI-nuS\right)} & 0 & 0 \\ 0 & 0 & e^{-i\cdot\pi\cdot t\cdot\left(-\frac{J}{2}-nuI+nuS\right)} & 0 \\ 0 & 0 & 0 & e^{-i\cdot\pi\cdot t\cdot\left(\frac{J}{2}-nuI-nuS\right)} \end{pmatrix}$$

The inverse of the time-evolution matrix

```
(%i46) UhInv(t,nuI,nuS,J);
```

(%o46)
$$\begin{pmatrix} e^{i\cdot\pi\cdot t\cdot\left(\frac{J}{2}+nuI+nuS\right)} & 0 & 0 & 0 \\ 0 & e^{i\cdot\pi\cdot t\cdot\left(-\frac{J}{2}+nuI-nuS\right)} & 0 & 0 \\ 0 & 0 & e^{i\cdot\pi\cdot t\cdot\left(-\frac{J}{2}-nuI+nuS\right)} & 0 \\ 0 & 0 & 0 & e^{i\cdot\pi\cdot t\cdot\left(\frac{J}{2}-nuI-nuS\right)} \end{pmatrix}$$

Demonstration that the matrices are inverses of one another

```
(%i47) Uh(t,nuI,nuS,J).UhInv(t,nuI,nuS,J);
```

(%o47)
$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Starting with a density matrix following a pi/2 y-pulse to the I-spin, starting from the equilibrium state

```
(%i48) rho1:rhoPi2YI(rhoEq);
```

(%o48)
$$\begin{pmatrix} \frac{deltaPS}{4} & 0 & \frac{deltaPI}{4} & 0 \\ 0 & -\frac{deltaPS}{4} & 0 & \frac{deltaPI}{4} \\ \frac{deltaPI}{4} & 0 & \frac{deltaPS}{4} & 0 \\ 0 & \frac{deltaPI}{4} & 0 & -\frac{deltaPS}{4} \end{pmatrix}$$

Time evolution of this density matrix is calculated as:

```
(%i49) rho1t:Uh(t,nuI,nuS,J).rho1.UhInv(t,nuI,nuS,J);
```

(%o49)
$$\begin{pmatrix} \frac{deltaPS}{4} & 0 & \frac{deltaPI\cdot e^{i\cdot\pi\cdot t\cdot\left(nuS-nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{4} & 0 \\ 0 & -\frac{deltaPS}{4} & 0 & \frac{deltaPI\cdot e^{i\cdot\pi\cdot t\cdot\left(-nuS-nuI+\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(-\frac{J}{2}+nuI-nuS\right)}}{4} \\ \frac{deltaPI\cdot e^{i\cdot\pi\cdot t\cdot\left(nuS+nuI+\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{4} & 0 & \frac{deltaPS}{4} & 0 \\ 0 & \frac{deltaPI\cdot e^{i\cdot\pi\cdot t\cdot\left(-nuS+nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{4} & 0 & -\frac{deltaPS}{4} \end{pmatrix}$$

```
(%i50) ratsimp(%);
```

(%o50)
$$\begin{pmatrix} \frac{deltaPS}{4} & 0 & \frac{deltaPI \cdot e^{-i\cdot\pi\cdot t\cdot J-2\cdot i\cdot\pi\cdot t\cdot nuI}}{4} & 0 \\ 0 & -\frac{deltaPS}{4} & 0 & \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot J-2\cdot i\cdot\pi\cdot t\cdot nuI}}{4} \\ \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot J+2\cdot i\cdot\pi\cdot t\cdot nuI}}{4} & 0 & \frac{deltaPS}{4} & 0 \\ 0 & \frac{deltaPI \cdot e^{2\cdot i\cdot\pi\cdot t\cdot nuI-i\cdot\pi\cdot t\cdot J}}{4} & 0 & -\frac{deltaPS}{4} \end{pmatrix}$$

This can also be calculated using the rhoTime function in the 2spinLib.mac file.

(%i51) rhoTime(rho1,t);

(%o51)
$$\begin{pmatrix} \frac{deltaPS}{4} & 0 & \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot\left(nuS-nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{4} & 0 \\ 0 & -\frac{deltaPS}{4} & 0 & \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot\left(-nuS-nuI+\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(-\frac{J}{2}+nuI-nuS\right.}}{4} \\ \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot\left(nuS+nuI+\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{4} & 0 & \frac{deltaPS}{4} & 0 \\ 0 & \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot\left(-nuS+nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{4} & 0 & -\frac{deltaPS}{4} \end{pmatrix}$$

(%i52) ratsimp(%);

(%o52)
$$\begin{pmatrix} \frac{deltaPS}{4} & 0 & \frac{deltaPI \cdot e^{-i\cdot\pi\cdot t\cdot J-2\cdot i\cdot\pi\cdot t\cdot nuI}}{4} & 0 \\ 0 & -\frac{deltaPS}{4} & 0 & \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot J-2\cdot i\cdot\pi\cdot t\cdot nuI}}{4} \\ \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot J+2\cdot i\cdot\pi\cdot t\cdot nuI}}{4} & 0 & \frac{deltaPS}{4} & 0 \\ 0 & \frac{deltaPI \cdot e^{2\cdot i\cdot\pi\cdot t\cdot nuI-i\cdot\pi\cdot t\cdot J}}{4} & 0 & -\frac{deltaPS}{4} \end{pmatrix}$$

Calculation of the Ix magnetization component as a function of time

(%i53) mattrace(Ix.rho1t);

(%o53)
$$\frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot\left(nuS+nuI+\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(-\frac{J}{2}-nuI+nuS\right)}}{8} + \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot\left(nuS-nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(\frac{J}{2}+nuI+nuS\right)}}{8} + \frac{deltaPI \cdot e^{i\cdot\pi\cdot t\cdot\left(-nuS+nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t\cdot\left(\frac{J}{2}-nuI-nuS\right)}}{8}$$

(%i54) trigrat(%);

(%o54)
$$\frac{deltaPI \cdot \cos(2\cdot\pi\cdot t\cdot nuI-\pi\cdot t\cdot J)+deltaPI \cdot \cos(2\cdot\pi\cdot t\cdot nuI+\pi\cdot t\cdot J)}{4}$$

Calculation of all of the magnetization components

(%i55) allMagRho(rho1t);

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

(%o55)

Time evolution of density matrix following a non-selective pulse, as in the COSY experiment

(%i56) rho2:rhoPi2Y(rhoEq);

(%o56)
$$\begin{pmatrix} 0 & \frac{deltaPS}{4} & \frac{deltaPI}{4} & 0 \\ \frac{deltaPS}{4} & 0 & 0 & \frac{deltaPI}{4} \\ \frac{deltaPI}{4} & 0 & 0 & \frac{deltaPS}{4} \\ 0 & \frac{deltaPI}{4} & \frac{deltaPS}{4} & 0 \end{pmatrix}$$

(%i57) allMagRho(rho1);

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

(%o57)

Time evolution after non-selective pi/2 y-pulse.

```
(%i58) rho2t:rhoTime(rho2,t1);
```

$$(\%o58)\quad \begin{pmatrix} 0 & \frac{\mathit{deltaPS}\cdot e^{i\cdot\pi\cdot t1\cdot\left(-\mathit{nuS}+\mathit{nuI}-\frac{J}{2}\right)-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+\mathit{nuI}+\mathit{nuS}\right)}}{4} & \frac{\mathit{deltaPI}\cdot e^{i\cdot\pi\cdot t1\cdot\left(\mathit{nuS}-\mathit{nuI}-\frac{J}{2}\right)-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}+\mathit{nuI}+\mathit{nuS}\right)}}{4} & 0 \\ \frac{\mathit{deltaPS}\cdot e^{i\cdot\pi\cdot t1\cdot\left(\mathit{nuS}+\mathit{nuI}+\frac{J}{2}\right)-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}+\mathit{nuI}-\mathit{nuS}\right)}}{4} & 0 & 0 & \frac{\mathit{deltaPI}\cdot e^{i\cdot\pi\cdot t1\cdot\left(-\mathit{nuS}-\mathit{nuI}+\frac{J}{2}\right)-i\cdot\pi\cdot t1\cdot\left(-\ldots\right.}}{4} \\ \frac{\mathit{deltaPI}\cdot e^{i\cdot\pi\cdot t1\cdot\left(\mathit{nuS}+\mathit{nuI}+\frac{J}{2}\right)-i\cdot\pi\cdot t1\cdot\left(-\frac{J}{2}-\mathit{nuI}+\mathit{nuS}\right)}}{4} & 0 & 0 & \frac{\mathit{deltaPS}\cdot e^{i\cdot\pi\cdot t1\cdot\left(-\mathit{nuS}-\mathit{nuI}+\frac{J}{2}\right)-i\cdot\pi\cdot t1\cdot\left(-\ldots\right.}}{4} \\ 0 & \frac{\mathit{deltaPI}\cdot e^{i\cdot\pi\cdot t1\cdot\left(-\mathit{nuS}+\mathit{nuI}-\frac{J}{2}\right)-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-\mathit{nuI}-\mathit{nuS}\right)}}{4} & \frac{\mathit{deltaPS}\cdot e^{i\cdot\pi\cdot t1\cdot\left(\mathit{nuS}-\mathit{nuI}-\frac{J}{2}\right)-i\cdot\pi\cdot t1\cdot\left(\frac{J}{2}-\mathit{nuI}-\mathit{nuS}\right)}}{4} & 0 \end{pmatrix}$$

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

$$(\%o59)\quad \begin{pmatrix} 0 & \frac{\mathit{deltaPS}\cdot e^{-i\cdot\pi\cdot t1\cdot J-2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuS}}}{4} & \frac{\mathit{deltaPI}\cdot e^{-i\cdot\pi\cdot t1\cdot J-2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuI}}}{4} & 0 \\ \frac{\mathit{deltaPS}\cdot e^{i\cdot\pi\cdot t1\cdot J+2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuS}}}{4} & 0 & 0 & \frac{\mathit{deltaPI}\cdot e^{i\cdot\pi\cdot t1\cdot J-2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuI}}}{4} \\ \frac{\mathit{deltaPI}\cdot e^{i\cdot\pi\cdot t1\cdot J+2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuI}}}{4} & 0 & 0 & \frac{\mathit{deltaPS}\cdot e^{i\cdot\pi\cdot t1\cdot J-2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuS}}}{4} \\ 0 & \frac{\mathit{deltaPI}\cdot e^{2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuI}-i\cdot\pi\cdot t1\cdot J}}{4} & \frac{\mathit{deltaPS}\cdot e^{2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuS}-i\cdot\pi\cdot t1\cdot J}}{4} & 0 \end{pmatrix}$$

All of the magnetization components

```
(%i60) allMagRho(rho2t);
```

$$< Ix >= \frac{\mathit{deltaPI}\cdot\left(\cos\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}-\pi\cdot t1\cdot J\right)+\cos\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}+\pi\cdot t1\cdot J\right)\right)}{4} < Iy >= \frac{\mathit{deltaPI}\cdot\left(\sin\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}-\pi\cdot t1\cdot J\right)+\mathrm{si}\ldots\right.}{4}$$

(%o60)

Application of a second pulse following the evolution period, t1

```
(%i61) rho3:rhoPi2Y(rho2t);
```

```
\mathrm{\tt (\%o61) }\quad \begin{pmatrix}-\frac{{{e}^{-i\cdot \pi \cdot \mathit{t1}\cdot J-2\cdot i\cdot \pi \cdot \mathit{t1}\cdot \ma
```

```
(%i62) ratsimp(%);
```

```
\mathrm{\tt (\%o62) }\quad \begin{pmatrix}-\frac{{{e}^{-i\cdot \pi \cdot \mathit{t1}\cdot J-2\cdot i\cdot \pi \cdot \mathit{t1}\cdot \ma
```

The element from the upper left corner of the density matrix:

```
(%i63) rho3[1,1];
```

$$(\%o63)\quad -\frac{e^{-i\cdot\pi\cdot t1\cdot J-2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuI}-2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuS}}\cdot\left(\left(\mathit{deltaPS}\cdot e^{2\cdot i\cdot\pi\cdot t1\cdot J}+\mathit{deltaPS}\right)\cdot e^{2\cdot i\cdot\pi\cdot t1\cdot \mathit{nuI}}+\left(\left(\mathit{deltaPI}+\mathit{deltaPI}\cdot e^{2\cdot i\cdot\pi\cdot t1\cdot J}\right)\cdot e^{4\cdot i\cdot\pi\cdot t1\cdot \mathit{nuI}}+\mathit{deltaPI}\ldots\right.\right.}{16}$$

```
(%i64) trigrat(rho3[1,1]);
```

$$(\%o64)\quad -\frac{\mathit{deltaPI}\cdot\cos\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}-\pi\cdot t1\cdot J\right)+\mathit{deltaPI}\cdot\cos\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}+\pi\cdot t1\cdot J\right)+\mathit{deltaPS}\cdot\cos\left(2\cdot\pi\cdot t1\cdot \mathit{nuS}-\pi\cdot t1\cdot J\right)+\ldots}{8}$$

The element from the upper right corner of the density matrix

```
(%i65) trigrat(rho3[1,4]);
```

$$(\%o65)\quad -\frac{i\cdot\left(-\mathit{deltaPI}\cdot\sin\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}-\pi\cdot t1\cdot J\right)+\mathit{deltaPI}\cdot\sin\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}+\pi\cdot t1\cdot J\right)-\mathit{deltaPS}\cdot\sin\left(2\cdot\pi\cdot t1\cdot \mathit{nuS}-\pi\cdot t1\cdot\ldots\right.\right.}{8}$$

```
(%i66) allMagRho(rho3);
```

$$< Ix >= 0 < Iy >= \frac{\mathit{deltaPI}\cdot\left(\sin\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}-\pi\cdot t1\cdot J\right)+\sin\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}+\pi\cdot t1\cdot J\right)\right)}{4} < Iz >= -\frac{\mathit{deltaPI}\cdot\left(\cos\left(2\cdot\pi\cdot t1\cdot \mathit{nuI}-\ldots\right.\right.}{4}$$

(%o66)

A symbolic, abbreviated representation of the density matrix following the second pulse

```
(%i67) rho3abbr:matrix([d11,d12,d13,d14],[d21,d22,d23,d24],[d31,d32,d33,d34],[d41,d42,d43,d44]);
```

$$(\%o67)\quad \begin{pmatrix} d11 & d12 & d13 & d14 \\ d21 & d22 & d23 & d24 \\ d31 & d32 & d33 & d34 \\ d41 & d42 & d43 & d44 \end{pmatrix}$$

Time evolution of the density matrix after the second pulse

```
(%i68) rhoTime(rho3abbr,t2);
```

$$(\%o68)\quad \begin{pmatrix} d11 & d12\cdot e^{i\cdot\pi\cdot t2\cdot\left(-nuS+nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t2\cdot\left(\frac{J}{2}+nuI+nuS\right)} & d13\cdot e^{i\cdot\pi\cdot t2\cdot\left(nuS-nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t2\cdot\left(\frac{J}{2}+nuI+nuS\right)} \\ d21\cdot e^{i\cdot\pi\cdot t2\cdot\left(nuS+nuI+\frac{J}{2}\right)-i\cdot\pi\cdot t2\cdot\left(-\frac{J}{2}+nuI-nuS\right)} & d22 & d23\cdot e^{i\cdot\pi\cdot t2\cdot\left(nuS-nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t2\cdot\left(-\frac{J}{2}+nuI-nuS\right)} \\ d31\cdot e^{i\cdot\pi\cdot t2\cdot\left(nuS+nuI+\frac{J}{2}\right)-i\cdot\pi\cdot t2\cdot\left(-\frac{J}{2}-nuI+nuS\right)} & d32\cdot e^{i\cdot\pi\cdot t2\cdot\left(-nuS+nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t2\cdot\left(-\frac{J}{2}-nuI+nuS\right)} & d33 \\ d41\cdot e^{i\cdot\pi\cdot t2\cdot\left(nuS+nuI+\frac{J}{2}\right)-i\cdot\pi\cdot t2\cdot\left(\frac{J}{2}-nuI-nuS\right)} & d42\cdot e^{i\cdot\pi\cdot t2\cdot\left(-nuS+nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t2\cdot\left(\frac{J}{2}-nuI-nuS\right)} & d43\cdot e^{i\cdot\pi\cdot t2\cdot\left(nuS-nuI-\frac{J}{2}\right)-i\cdot\pi\cdot t2\cdot\left(\frac{J}{2}-nuI-nuS\right)} \end{pmatrix}$$

```
(%i69) ratsimp(%);
```

$$(\%o69)\quad \begin{pmatrix} d11 & d12\cdot e^{-i\cdot\pi\cdot t2\cdot J-2\cdot i\cdot\pi\cdot t2\cdot nuS} & d13\cdot e^{-i\cdot\pi\cdot t2\cdot J-2\cdot i\cdot\pi\cdot t2\cdot nuI} & d14\cdot e^{-2\cdot i\cdot\pi\cdot t2\cdot nuI-2\cdot i\cdot\pi\cdot t2\cdot nuS} \\ d21\cdot e^{i\cdot\pi\cdot t2\cdot J+2\cdot i\cdot\pi\cdot t2\cdot nuS} & d22 & d23\cdot e^{2\cdot i\cdot\pi\cdot t2\cdot nuS-2\cdot i\cdot\pi\cdot t2\cdot nuI} & d24\cdot e^{i\cdot\pi\cdot t2\cdot J-2\cdot i\cdot\pi\cdot t2\cdot nuI} \\ d31\cdot e^{i\cdot\pi\cdot t2\cdot J+2\cdot i\cdot\pi\cdot t2\cdot nuI} & d32\cdot e^{2\cdot i\cdot\pi\cdot t2\cdot nuI-2\cdot i\cdot\pi\cdot t2\cdot nuS} & d33 & d34\cdot e^{i\cdot\pi\cdot t2\cdot J-2\cdot i\cdot\pi\cdot t2\cdot nuS} \\ d41\cdot e^{2\cdot i\cdot\pi\cdot t2\cdot nuI+2\cdot i\cdot\pi\cdot t2\cdot nuS} & d42\cdot e^{2\cdot i\cdot\pi\cdot t2\cdot nuI-i\cdot\pi\cdot t2\cdot J} & d43\cdot e^{2\cdot i\cdot\pi\cdot t2\cdot nuS-i\cdot\pi\cdot t2\cdot J} & d44 \end{pmatrix}$$

The diagonal elements are not affected by the second evolution period, but all of the other density matrix elements are.
The elements on the skew diagonal (from the lower left to the upper right) contain frequency terms that are the sum and difference of nuI and nuS.
