Maxima workbook for Principles of NMR Spectroscopy
Chapter 17: Introduction to the Density Matrix
Section 17.1: Density matrix for a population of isolated spin-1/2 nuclei

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. 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 individual, uncoupled spins 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("1spinLib.mac");
```

(%o1) $/Users/davidg/.maxima/1spinLib.mac$

The macro library includes the definition of a matrix to represent a general density matrix for a population of isolated spins 1/2

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

$$(\%o2)\quad \begin{pmatrix} avCaConjCa & avCaConjCb \\ avCbConjCa & avCbConjCb \end{pmatrix}$$

The four elements of this matrix are just names meant to represent the averages of the products of coefficients and complex conjugates of coefficients defining the wavefunctions of the spins making up the population.
Note that in the text, these averages are indicated by an over score, but in wxMaxima, over scores are used to indicate complex conjugates.

2 17.1 The density matrix for a population of spin-1/2 nuclei

2.1 17.1.1 Average Magnetization Components from a Mixed Population

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The representation of an arbitrary wavefunction for a spin-1/2

```
(%i3) k_psi;
```

$$(\%o3)\quad \begin{pmatrix} ca \\ cb \end{pmatrix}$$

Functions introduced earlier for calculating the average magnetization components for a population of spins, all with the same wavefunction,

```
(%i4) meanPsi(Ix,k_psi);
```

$$(\%o4)\quad \frac{\overline{ca}\cdot cb+ca\cdot\overline{cb}}{2}$$

```
(%i5) meanPsi(Iy,k_psi);
```

$$(\%o5)\quad \frac{i\cdot ca\cdot\overline{cb}-i\cdot\overline{ca}\cdot cb}{2}$$

```
(%i6) meanPsi(Iz,k_psi);
```

$$(\%o6)\quad -\frac{cb\cdot\overline{cb}-ca\cdot\overline{ca}}{2}$$

Calculation of average magnetization for a population defined by a density matrix

The general form of the density matrix for a population of spin-1/2 nuclei.

```
(%i7) rhogen;
```

(%o7) $$\begin{pmatrix} avCaConjCa & avCaConjCb \\ avCbConjCa & avCbConjCb \end{pmatrix}$$

The names shown above for the density matrix elements are only labels. avCaConjCa, for instance, represents the average of the product of the coefficient ca and the complex conjugate of ca for each spin, averaged over the population.

The Ix, Iy and Iz operator matrices are the same as the ones used for the wavefunction, when the wavefunction is represented as a column vector.

```
(%i8) Ix;
```

(%o8) $$\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$$

```
(%i9) Iy;
```

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

```
(%i10) Iz;
```

(%o10) $$\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

To calculate the average Ix magnetization from the density matrix, multiply the density matrix by the Ix matrix and take the trace.

```
(%i11) Ix.rhogen;
```

(%o11) $$\begin{pmatrix} \frac{avCbConjCa}{2} & \frac{avCbConjCb}{2} \\ \frac{avCaConjCa}{2} & \frac{avCaConjCb}{2} \end{pmatrix}$$

mattrace is a Maxima function for calculating the trace of any square matrix.

```
(%i12) mattrace(%);
```

(%o12) $$\frac{avCbConjCa}{2} + \frac{avCaConjCb}{2}$$

For the other two magnetization components

```
(%i13) mattrace(Iy.rhogen);
```

(%o13) $$\frac{i \cdot avCaConjCb}{2} - \frac{i \cdot avCbConjCa}{2}$$

```
(%i14) mattrace(Iz.rhogen);
```

(%o14) $$\frac{avCaConjCa}{2}-\frac{avCbConjCb}{2}$$

2.2 17.1.2 Effects of pulses on the density matrix

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In Chapter 12, rules were derived for calculating the effect of an x-pulse of angle a on an individual wavefunction. This rule is expressed in a function defined in 1spinLib.mac

For an arbitrary wavefunction defined by the coefficients ca and cb

```
(%i15) k_psi;
```

(%o15) $$\begin{pmatrix} ca \\ cb \end{pmatrix}$$

```
(%i16) psiPulseX(k_psi,a);
```

(%o16) $$\begin{pmatrix} \cos\left(\frac{a}{2}\right)\cdot ca - i\cdot \sin\left(\frac{a}{2}\right)\cdot cb \\ \cos\left(\frac{a}{2}\right)\cdot cb - i\cdot \sin\left(\frac{a}{2}\right)\cdot ca \end{pmatrix}$$

The rotation matrix and its inverse for rotation about the x-axis.

```
(%i17) Rx(a);
```

(%o17) $$\begin{pmatrix} \cos\left(\frac{a}{2}\right) & -i\cdot \sin\left(\frac{a}{2}\right) \\ -i\cdot \sin\left(\frac{a}{2}\right) & \cos\left(\frac{a}{2}\right) \end{pmatrix}$$

```
(%i18) RxInv(a);
```

(%o18) $$\begin{pmatrix} \cos\left(\frac{a}{2}\right) & i\cdot \sin\left(\frac{a}{2}\right) \\ i\cdot \sin\left(\frac{a}{2}\right) & \cos\left(\frac{a}{2}\right) \end{pmatrix}$$

Demonstration that Rx(a) and RxInv(a) are inverses of one another

```
(%i19) Rx(a).RxInv(a);
```

(%o19) $$\begin{pmatrix} \sin\left(\frac{a}{2}\right)^2+\cos\left(\frac{a}{2}\right)^2 & 0 \\ 0 & \sin\left(\frac{a}{2}\right)^2+\cos\left(\frac{a}{2}\right)^2 \end{pmatrix}$$

```
(%i20) trigrat(%);
```

(%o20) $$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Rotation matrix and its inverse for a pi/2 pulse along the x-axis.

```
(%i21) Rx(%pi/2);
```

(%o21)
$$\begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

```
(%i22) RxInv(%pi/2);
```

(%o22)
$$\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

Calculation of the effect of a pi/2 pulse to a population represented by the general form of the density matrix.

```
(%i23) Rx(%pi/2).rhogen;
```

(%o23)
$$\begin{pmatrix} \frac{avCaConjCa}{\sqrt{2}} - \frac{i \cdot avCbConjCa}{\sqrt{2}} & \frac{avCaConjCb}{\sqrt{2}} - \frac{i \cdot avCbConjCb}{\sqrt{2}} \\ \frac{avCbConjCa}{\sqrt{2}} - \frac{i \cdot avCaConjCa}{\sqrt{2}} & \frac{avCbConjCb}{\sqrt{2}} - \frac{i \cdot avCaConjCb}{\sqrt{2}} \end{pmatrix}$$

```
(%i24) (Rx(%pi/2).rhogen).RxInv(%pi/2);
```

(%o24)
$$\begin{pmatrix} \frac{i \cdot \left(\frac{avCaConjCb}{\sqrt{2}} - \frac{i \cdot avCbConjCb}{\sqrt{2}} \right)}{\sqrt{2}} + \frac{\frac{avCaConjCa}{\sqrt{2}} - \frac{i \cdot avCbConjCa}{\sqrt{2}}}{\sqrt{2}} & \frac{\frac{avCaConjCb}{\sqrt{2}} - \frac{i \cdot avCbConjCb}{\sqrt{2}}}{\sqrt{2}} + \frac{i \cdot \left(\frac{avCaConjCa}{\sqrt{2}} - \frac{i \cdot avCbConjCa}{\sqrt{2}} \right)}{\sqrt{2}} \\ \frac{i \cdot \left(\frac{avCbConjCb}{\sqrt{2}} - \frac{i \cdot avCaConjCb}{\sqrt{2}} \right)}{\sqrt{2}} + \frac{\frac{avCbConjCa}{\sqrt{2}} - \frac{i \cdot avCaConjCa}{\sqrt{2}}}{\sqrt{2}} & \frac{\frac{avCbConjCb}{\sqrt{2}} - \frac{i \cdot avCaConjCb}{\sqrt{2}}}{\sqrt{2}} + \frac{i \cdot \left(\frac{avCbConjCa}{\sqrt{2}} - \frac{i \cdot avCaConjCa}{\sqrt{2}} \right)}{\sqrt{2}} \end{pmatrix}$$

```
(%i25) ratsimp(%);
```

(%o25)
$$\begin{pmatrix} \frac{avCaConjCa + i \cdot avCaConjCb - i \cdot avCbConjCa + avCbConjCb}{2} & -\frac{-i \cdot avCaConjCa - avCaConjCb - avCbConjCa + i \cdot avCbConjCb}{2} \\ \frac{-i \cdot avCaConjCa + avCaConjCb + avCbConjCa + i \cdot avCbConjCb}{2} & \frac{avCaConjCa - i \cdot avCaConjCb + i \cdot avCbConjCa + avCbConjCb}{2} \end{pmatrix}$$

Rotation matrices for pulses along the y-axis.

```
(%i26) Ry(a);
```

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

```
(%i27) RyInv(a);
```

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

```
(%i28) Ry(a).RyInv(a);
```

(%o28) $$\begin{pmatrix} \sin\left(\frac{a}{2}\right)^2 + \cos\left(\frac{a}{2}\right)^2 & 0 \\ 0 & \sin\left(\frac{a}{2}\right)^2 + \cos\left(\frac{a}{2}\right)^2 \end{pmatrix}$$

```
(%i29) trigrat(%);
```

(%o29) $$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

The 1spinLib.mac file also includes special functions for calculating the effects of pulses on the density matrix

```
(%i30) fundef(rhoPulseX);
```

(%o30) $\mathrm{rhoPulseX}\,(\rho, a) := \mathrm{Rx}\,(a)\,.\rho.\mathrm{RxInv}\,(a)$

```
(%i31) fundef(rhoPulseY);
```

(%o31) $\mathrm{rhoPulseY}\,(\rho, a) := \mathrm{Ry}\,(a)\,.\rho.\mathrm{RyInv}\,(a)$

```
(%i32) fundef(rhoPi2X);
```

(%o32) $\mathrm{rhoPi2X}\,(\rho) := \mathrm{rhoPulseX}\left(\rho, \frac{\pi}{2}\right)$

```
(%i33) fundef(rhoPiX);
```

(%o33) $\mathrm{rhoPiX}\,(\rho) := \mathrm{rhoPulseX}\,(\rho, \pi)$

```
(%i34) fundef(rhoPi2Y);
```

(%o34) $\mathrm{rhoPi2Y}\,(\rho) := \mathrm{rhoPulseY}\left(\rho, \frac{\pi}{2}\right)$

```
(%i35) fundef(rhoPiY);
```

(%o35) $\mathrm{rhoPiY}\,(\rho) := \mathrm{rhoPulseY}\,(\rho, \pi)$

2.3 17.1.3 Time evolution of the density matrix

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The unitary time evolution matrix and its inverse

```
(%i36) Uh(t,nu);
```

(%o36) $$\begin{pmatrix} e^{-i\cdot\pi\cdot\nu\cdot t} & 0 \\ 0 & e^{i\cdot\pi\cdot\nu\cdot t} \end{pmatrix}$$

```
(%i37) UhInv(t,nu);
```

(%o37) $\begin{pmatrix} e^{i\cdot\pi\cdot\nu\cdot t} & 0 \\ 0 & e^{-i\cdot\pi\cdot\nu\cdot t} \end{pmatrix}$

```
(%i38) Uh(t,nu).UhInv(t,nu);
```

(%o38) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

Calculation of the effects of time evolution on the general form of the density matrix.

```
(%i39) Uh(t,nu).rhogen.UhInv(t,nu);
```

(%o39) $\begin{pmatrix} avCaConjCa & e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot avCaConjCb \\ e^{2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot avCbConjCa & avCbConjCb \end{pmatrix}$

The 1spinLib.mac file also contains a function to calculate the time evolution of the density matrix

```
(%i40) fundef(rhoTime);
```

(%o40) $\mathrm{rhoTime}\,(\rho,t) := \mathrm{Uh}\,(t,\nu)\,.\rho.\mathrm{UhInv}\,(t,\nu)$

```
(%i41) rhoTime(rhogen,t);
```

(%o41) $\begin{pmatrix} avCaConjCa & e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot avCaConjCb \\ e^{2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot avCbConjCa & avCbConjCb \end{pmatrix}$

2.4 17.1.4 Density matrix at equilibrium

The 1spinLib.mac file defines a matrix representing the equilibrium state, in terms of the Boltzmann population difference, deltaP

```
(%i42) rhoEq;
```

(%o42) $\begin{pmatrix} \frac{deltaP}{2} & 0 \\ 0 & -\frac{deltaP}{2} \end{pmatrix}$

This is the simplified representation that does not include the identity matrix. The justification for deleting the identity matrix from the representation of the equilibrium density matrix is provided below, where it is shown that the identity matrix is unaffected by pulses or time evolution, and that the average magnetization components calculated for the identity matrix are zero.

Rotation operators applied to the identity matrix

```
(%i43) ident;
```

(%o43) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

(%i44) Rx(a).ident.RxInv(a);

(%o44) $$\begin{pmatrix} \sin\left(\frac{a}{2}\right)^2+\cos\left(\frac{a}{2}\right)^2 & 0 \\ 0 & \sin\left(\frac{a}{2}\right)^2+\cos\left(\frac{a}{2}\right)^2 \end{pmatrix}$$

(%i45) trigrat(%);

(%o45) $$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

(%i46) Ry(a).ident.RyInv(a);

(%o46) $$\begin{pmatrix} \sin\left(\frac{a}{2}\right)^2+\cos\left(\frac{a}{2}\right)^2 & 0 \\ 0 & \sin\left(\frac{a}{2}\right)^2+\cos\left(\frac{a}{2}\right)^2 \end{pmatrix}$$

(%i47) trigrat(%);

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

Time evolution of identity matrix

(%i48) Uh(t,nu).ident.UhInv(t,nu);

(%o48) $$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Magnetization operators applied to the identity matrix

(%i49) Ix.ident;

(%o49) $$\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$$

(%i50) Iy.ident;

(%o50) $$\begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix}$$

(%i51) Iz.ident;

(%o51) $$\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

Magnetization components of identity matrix

```
(%i52) mattrace(Ix.ident);
```

(%o52) 0

```
(%i53) mattrace(Iy.ident);
```

(%o53) 0

```
(%i54) mattrace(Iz.ident);
```

(%o54) 0

```
(%i55) allMagRho(ident);
```

$< Ix >= \ 0 < Iy >= \ 0 < Iz >= \ 0$

(%o55)

Magnetization components of equilibrium density matrix

```
(%i56) rhoEq;
```

(%o56) $\begin{pmatrix} \frac{deltaP}{2} & 0 \\ 0 & -\frac{deltaP}{2} \end{pmatrix}$

```
(%i57) mattrace(Ix.rhoEq);
```

(%o57) 0

```
(%i58) mattrace(Iy.rhoEq);
```

(%o58) 0

```
(%i59) mattrace(Iz.rhoEq);
```

(%o59) $\frac{deltaP}{2}$

```
(%i60) allMagRho(rhoEq);
```

$< Ix >= \ 0 < Iy >= \ 0 < Iz >= \ \frac{deltaP}{2}$

(%o60)

2.5 17.1.5 Density matrix description of 1-pulse experiment

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Starting equilibrium density matrix

```
(%i61) rhoEq;
```

(%o61) $\begin{pmatrix} \frac{deltaP}{2} & 0 \\ 0 & -\frac{deltaP}{2} \end{pmatrix}$

```
(%i62) allMagRho(rhoEq);
```

$$< Ix >= \ 0 < Iy >= \ 0 < Iz >= \ \frac{deltaP}{2}$$

(%o62)

pi/2 y-pulse applied to the equilibrium density matrix

```
(%i63) rho_pi2y:Ry(%pi/2).rhoEq.RyInv(%pi/2);
```

(%o63) $\begin{pmatrix} 0 & \frac{deltaP}{2} \\ \frac{deltaP}{2} & 0 \end{pmatrix}$

```
(%i64) Ix.rho_pi2y;
```

(%o64) $\begin{pmatrix} \frac{deltaP}{4} & 0 \\ 0 & \frac{deltaP}{4} \end{pmatrix}$

```
(%i65) mattrace(%);
```

(%o65) $\frac{deltaP}{2}$

```
(%i66) Iy.rho_pi2y;
```

(%o66) $\begin{pmatrix} -\frac{i\cdot deltaP}{4} & 0 \\ 0 & \frac{i\cdot deltaP}{4} \end{pmatrix}$

```
(%i67) mattrace(%);
```

(%o67) 0

```
(%i68) allMagRho(rho_pi2y);
```

$$< Ix >= \ \frac{deltaP}{2} < Iy >= \ 0 < Iz >= \ 0$$

(%o68)

Time evolution following pi/2 y pulse to equilibrium state

```
(%i69) rho_pi2y.UhInv(t,nu);
```

(%o69) $$\begin{pmatrix} 0 & \frac{e^{-i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{2} \\ \frac{e^{i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{2} & 0 \end{pmatrix}$$

```
(%i70) Uh(t,nu).rho_pi2y.UhInv(t,nu);
```

(%o70) $$\begin{pmatrix} 0 & \frac{e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{2} \\ \frac{e^{2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{2} & 0 \end{pmatrix}$$

```
(%i71) rhot:Uh(t,nu).rho_pi2y.UhInv(t,nu);
```

(%o71) $$\begin{pmatrix} 0 & \frac{e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{2} \\ \frac{e^{2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{2} & 0 \end{pmatrix}$$

```
(%i72) Ix.rhot;
```

(%o72) $$\begin{pmatrix} \frac{e^{2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{4} & 0 \\ 0 & \frac{e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{4} \end{pmatrix}$$

```
(%i73) mattrace(Ix.rhot);
```

(%o73) $$\frac{e^{2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{4}+\frac{e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{4}$$

```
(%i74) rectform(%);
```

(%o74) $$\frac{\cos\left(2\cdot\pi\cdot\nu\cdot t\right)\cdot deltaP}{2}$$

```
(%i75) Iy.rhot;
```

(%o75) $$\begin{pmatrix} -\frac{i\cdot e^{2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{4} & 0 \\ 0 & \frac{i\cdot e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{4} \end{pmatrix}$$

```
(%i76) mattrace(Iy.rhot);
```

(%o76) $$\frac{i\cdot e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{4}-\frac{i\cdot e^{2\cdot i\cdot\pi\cdot\nu\cdot t}\cdot deltaP}{4}$$

```
(%i77) rectform(%);
```

(%o77) $$\frac{\sin\left(2\cdot\pi\cdot\nu\cdot t\right)\cdot deltaP}{2}$$

```
(%i78) ;allMagRho(rhot);
```

$$< Ix >= \frac{\cos\left(2\cdot\pi\cdot\nu\cdot t\right)\cdot deltaP}{2} < Iy >= \frac{\sin\left(2\cdot\pi\cdot\nu\cdot t\right)\cdot deltaP}{2} < Iz >= 0$$

(%o78)

2.6 17.1.6 Interpretation of the Density Matrix Elements:“Populations” and “Coherences”

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pi/2 y pulse applied to the equilibrium density matrix

```
(%i79) rhoEq;
```

(%o79) $$\begin{pmatrix} \frac{deltaP}{2} & 0 \\ 0 & -\frac{deltaP}{2} \end{pmatrix}$$

```
(%i80) rhoPi2Y(rhoEq);
```

(%o80) $$\begin{pmatrix} 0 & \frac{deltaP}{2} \\ \frac{deltaP}{2} & 0 \end{pmatrix}$$

A second pi/2 y pulse

```
(%i81) rhoPi2Y(%);
```

(%o81) $$\begin{pmatrix} -\frac{deltaP}{2} & 0 \\ 0 & \frac{deltaP}{2} \end{pmatrix}$$

```
(%i82) allMagRho(%);
```

$$< Ix >= \ 0 < Iy >= \ 0 < Iz >= \ -\frac{deltaP}{2}$$

(%o82)

This represents a reversal of the original z-magnetization.

Relationships between complex numbers and their conjugates

```
(%i83) declare(c1,complex);
```

(%o83) $done$

```
(%i84) conjugate(c1);
```

(%o84) $\overline{c1}$

```
(%i85) declare(c2,complex);
```

(%o85) $done$

```
(%i86) conjugate(c2);
```

(%o86) $\overline{c2}$

```
(%i87) c1*conjugate(c2);
```

(%o87) $c1 \cdot \overline{c2}$

```
(%i88) conjugate(c2*conjugate(c1));
```

(%o88) $c1 \cdot \overline{c2}$

pi/2 y-pulse to equilibrium density matrix

```
(%i89) rhoPi2Y(rhoEq);
```

(%o89) $\begin{pmatrix} 0 & \frac{deltaP}{2} \\ \frac{deltaP}{2} & 0 \end{pmatrix}$

pi/2 x-pulse to equilibrium density matrix

```
(%i90) rhoPi2X(rhoEq);
```

(%o90) $\begin{pmatrix} 0 & \frac{i \cdot deltaP}{2} \\ -\frac{i \cdot deltaP}{2} & 0 \end{pmatrix}$

Density matrix for the case of two subpopulations of equal size. Magnetization of both populations lies in transverse plane. The magnetization of one subpopulation points along the x'-axis and the magnetization of the other subpopulation points along the y'-axis

A wavefunction with magnetization along the x'-axis

```
(%i91) k_1:ket(1/sqrt(2),1/sqrt(2));
```

(%o91) $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$

```
(%i92) allMagPsi(k_1);
```

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

(%o92)

A wavefunction with magnetization along the y'-axis

```
(%i93) k_2:ket(1/sqrt(2),%i/sqrt(2));
```

(%o93) $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \end{pmatrix}$

```
(%i94) allMagPsi(k_2);
```

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

(%o94)

The elements of the density matrix with equal populations of the two wavefunctions:
ave(ca x ca*) = ((1/sqrt(2))*(1/sqrt(2))+ (1/sqrt(2))*(1/sqrt(2)))/2 = 1/2 ave(ca x cb*) = ((1/sqrt(2))*(1/sqrt(2))+ ((1/sqrt(2))*(-i/sqrt(2)))/2 = (1-i)/4 ave(cb x ca*) = ((1/sqrt(2))*(1/sqrt(2))+ ((i/sqrt(2))*(1/sqrt(2)))/2 = (1+i)/4 ave(cb x cb*) = ((1/sqrt(2))*(1/sqrt(2))+ ((i/sqrt(2))*(-i/sqrt(2)))/2 = (1+1)/4 = 1/2

```
(%i95) rho:matrix([1/2,(1-%i)/4],[(1+%i)/4,1/2]);
```

(%o95) $\begin{pmatrix} \frac{1}{2} & \frac{1-i}{4} \\ \frac{1+i}{4} & \frac{1}{2} \end{pmatrix}$

```
(%i96) allMagRho(rho);
```

$$< Ix >= \frac{1}{4} < Iy >= \frac{1}{4} < Iz >= 0$$

(%o96)

A single wavefunction that represents magnetization pointing midway between the x'- and y'-axis can be calculated by starting with the lalpha> wavefunction, applying a pi/2 y-pulse and then an evolution time equal to 1/8*1/nu

```
(%i97) k_xy:psiTime(psiPi2Y(k_a), 1/(8*nu));
```

(%o97) $\begin{pmatrix} \frac{e^{-\frac{i\cdot\pi}{8}}}{\sqrt{2}} \\ \frac{e^{\frac{i\cdot\pi}{8}}}{\sqrt{2}} \end{pmatrix}$

The individual elements of a matrix can be accessed by their indices, with the row specified first and the column second.

```
(%i98) k_xy[1,1];
```

(%o98) $\frac{e^{-\frac{i\cdot\pi}{8}}}{\sqrt{2}}$

```
(%i99) k_xy[2,1];
```

(%o99) $\frac{e^{\frac{i\cdot\pi}{8}}}{\sqrt{2}}$

The density matrix can then be defined from the elements of the wavefunction column vector:

(%i100) rho_xy:matrix([k_xy[1,1]*conj(k_xy[1,1]),k_xy[1,1]*conj(k_xy[2,1])],
[k_xy[2,1]*conj(k_xy[1,1]),k_xy[2,1]*conj(k_xy[2,1])]);

(%o100) $$\begin{pmatrix} \frac{1}{2} & \frac{\frac{1}{\sqrt{2}}-\frac{i}{\sqrt{2}}}{2} \\ \frac{\frac{1}{\sqrt{2}}+\frac{i}{\sqrt{2}}}{2} & \frac{1}{2} \end{pmatrix}$$

The 1spinLib.mac file contains a function to calculate the density matrix for a homogeneous population from the wavefunction of that population.

(%i101) rho(k_xy);

(%o101) $$\begin{pmatrix} \frac{1}{2} & \frac{\frac{1}{\sqrt{2}}-\frac{i}{\sqrt{2}}}{2} \\ \frac{\frac{1}{\sqrt{2}}+\frac{i}{\sqrt{2}}}{2} & \frac{1}{2} \end{pmatrix}$$

(%i102) allMagRho(rho_xy);

$$< Ix >= \frac{1}{2^{\frac{3}{2}}} < Iy >= \frac{1}{2^{\frac{3}{2}}} < Iz >= 0$$

(%o102)

As shown in the text, the average magnetization from the homogeneous population is greater than that of the mixed population.

A population of three equal subpopulations with magnetization pointed along the x'-, y'- and -x'-axes.
The wavefunctions can be generated from the Ialpha> wavefunction with appropriate pulses.

(%i103) k_1:psiPi2Y(k_a);

(%o103) $$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

(%i104) allMagPsi(k_1);

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

(%o104)

(%i105) k_2:psiPulseX(k_a,-%pi/2);

(%o105) $$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \end{pmatrix}$$

(%i106) allMagPsi(k_2);

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

(%o106)

(%i107) `k_3:psiPulseY(k_a,-%pi/2);`

$$(\%o107) \quad \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$$

(%i108) `allMagPsi(k_3);`

$$< Ix >= \ -\frac{1}{2} < Iy >= \ 0 < Iz >= \ 0$$

(%o108)

Elements of the density matrix

(%i109) `rho11:(k_1[1,1]*conj(k_1[1,1])+k_2[1,1]*conj(k_2[1,1])+k_3[1,1]*conj(k_3[1,1]))/3;`

$$(\%o109) \quad \frac{1}{2}$$

(%i110) `rho12:(k_1[1,1]*conj(k_1[2,1])+k_2[1,1]*conj(k_2[2,1])+k_3[1,1]*conj(k_3[2,1]))/3;`

$$(\%o110) \quad -\frac{i}{6}$$

(%i111) `rho21:(k_1[2,1]*conj(k_1[1,1])+k_2[2,1]*conj(k_2[1,1])+k_3[2,1]*conj(k_3[1,1]))/3;`

$$(\%o111) \quad \frac{i}{6}$$

(%i112) `rho22:(k_1[2,1]*conj(k_1[2,1])+k_2[2,1]*conj(k_2[2,1])+k_3[2,1]*conj(k_3[2,1]))/3;`

$$(\%o112) \quad \frac{1}{2}$$

(%i113) `rho3:matrix([rho11,rho12],[rho21,rho22]);`

$$(\%o113) \quad \begin{pmatrix} \frac{1}{2} & -\frac{i}{6} \\ \frac{i}{6} & \frac{1}{2} \end{pmatrix}$$

(%i114) `allMagRho(rho3);`

$$< Ix >= \ 0 < Iy >= \ \frac{1}{6} < Iz >= \ 0$$

(%o114)

Created with wxMaxima.