Chapter 18. Basis set for the density matrix and the product operator formalism. Part 1. Single-spin populations

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 18 introduces the idea of using a basis set composed of operator matrices to represent the density matrix. The first section deals with a population of isolated spins, without scalar coupling, whereas the rest of the chapter 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 parts 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.

```
--> load("1spinLib.mac")$
```

2 18.1 A basis set for a single-spin population

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The operator matrices for the x-, y- and z-magnetization components for isolated spin-1/2 nuclei.

```
--> Ix;
```

(%o2) $\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$

```
--> Iy;
```

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

```
--> Iz;
```

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

The operator matrices are orthogonal, which is shown by demonstrating that the trace of each pair-wise product is zero.

```
--> mattrace(Ix.Iy);
```

(%o5) 0

```
--> mattrace(Ix.Iz);
```

(%o6) 0

```
--> mattrace(Iy.Iz);
```

(%o7) 0

The fourth matrix making up the basis set is the identity matrix

```
--> ident;
```

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

The identity matrix is also orthogonal to all of the operator matrices

```
--> mattrace(ident.Ix);
```

(%o9) 0

```
--> mattrace(ident.Iy);
```

(%o10) 0

```
--> mattrace(ident.Iz);
```

(%o11) 0

2.1 18.1.1 Magnetization components

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Define an arbitrary density matrix as a linear combination of Ix, Iy, Iz and the identity matrix

```
--> rho1:cx*Ix+cy*Iy+cz*Iz+c1*ident;
```

(%o12) $\begin{pmatrix} \frac{cz}{2}+c1 & \frac{cx}{2}-\frac{i\cdot cy}{2} \\ \frac{i\cdot cy}{2}+\frac{cx}{2} & c1-\frac{cz}{2} \end{pmatrix}$

The 1spinLib.mac file defines a function, opBasisRep, that takes an arbitrary density matrix and prints it as the linear combination.

```
--> opBasisRep(rho1);
```

$(cx)*Ix \; + \; (cy)*Iy \; + \; (cz)*Iz$

(%o13)

Note that the representation does not include a component representing the identity matrix. This is because, the identity matrix component does not contribute to any observable measurement, as shown later in the chapter.

Calculate the x-magnetization for the density matrix

```
--> Ix.rho1;
```

(%o14) $\begin{pmatrix} \frac{\frac{cx}{2}+\frac{i\cdot cy}{2}}{2} & \frac{c1-\frac{cz}{2}}{2} \\ \frac{c1+\frac{cz}{2}}{2} & \frac{\frac{cx}{2}-\frac{i\cdot cy}{2}}{2} \end{pmatrix}$

```
--> mattrace(Ix.rho1);
```

(%o15) $\frac{\frac{cx}{2}+\frac{i\cdot cy}{2}}{2}+\frac{\frac{cx}{2}-\frac{i\cdot cy}{2}}{2}$

```
--> ratsimp(%);
```

(%o16) $$\frac{cx}{2}$$

All of the magnetization components can be calculated using the allMagRho command in 1spinLib.mac

```
--> allMagRho(rho1);
```

$$< Ix >= \frac{cx}{2} < Iy >= \frac{cy}{2} < Iz >= \frac{cz}{2}$$

(%o17)

The magnetization components are simply the coefficients divided by two.

2.2 18.1.2 Pulses

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The rotation matrices for a pulse along the x'-axis

```
--> Rx(a);
```

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

```
--> RxInv(a);
```

(%o19) $$\begin{pmatrix} \cos\left(\frac{a}{2}\right) & i\cdot\sin\left(\frac{a}{2}\right) \\ i\cdot\sin\left(\frac{a}{2}\right) & \cos\left(\frac{a}{2}\right) \end{pmatrix}$$

An x-pulse of angle a applied to the density matrix represented as a linear combination of Ix, Iy, Iz and the identity matrix

```
--> Rx(a).rho1.RxInv(a);
```

(%o20) $$\begin{pmatrix} \cos\left(\frac{a}{2}\right)\cdot\left(i\cdot\sin\left(\frac{a}{2}\right)\cdot\left(\frac{cx}{2}-\frac{i\cdot cy}{2}\right)+\cos\left(\frac{a}{2}\right)\cdot\left(\frac{cz}{2}+c1\right)\right)-i\cdot\sin\left(\frac{a}{2}\right)\cdot\left(\cos\left(\frac{a}{2}\right)\cdot\left(\frac{i\cdot cy}{2}+\frac{cx}{2}\right)+i\cdot\sin\left(\frac{a}{2}\right)\cdot\left(c1-\frac{cz}{2}\right)\right) & \mathrm{co} \\ \cos\left(\frac{a}{2}\right)\cdot\left(\cos\left(\frac{a}{2}\right)\cdot\left(\frac{i\cdot cy}{2}+\frac{cx}{2}\right)+i\cdot\sin\left(\frac{a}{2}\right)\cdot\left(c1-\frac{cz}{2}\right)\right)-i\cdot\sin\left(\frac{a}{2}\right)\cdot\left(i\cdot\sin\left(\frac{a}{2}\right)\cdot\left(\frac{cx}{2}-\frac{i\cdot cy}{2}\right)+\cos\left(\frac{a}{2}\right)\cdot\left(\frac{cz}{2}+c1\right)\right) & \mathrm{co} \end{pmatrix}$$

```
--> trigrat(%);
```

(%o21) $$\begin{pmatrix} \frac{2\cdot c1+\sin(a)\cdot cy+\cos(a)\cdot cz}{2} & \frac{cx+i\cdot(\sin(a)\cdot cz-\cos(a)\cdot cy)}{2} \\ -\frac{i\cdot(\sin(a)\cdot cz-\cos(a)\cdot cy)-cx}{2} & -\frac{-2\cdot c1+\sin(a)\cdot cy+\cos(a)\cdot cz}{2} \end{pmatrix}$$

The opBasisRep function can be used to show the basis representation after the pulse

```
--> opBasisRep(Rx(a).rho1.RxInv(a));
```

$$(cx)*Ix\ +\ (\cos(a)\cdot cy-\sin(a)\cdot cz)*Iy\ +\ (\cos(a)\cdot cz+\sin(a)\cdot cy)*Iz$$

(%o22)

For just the Ix component

```
--> Rx(a).Ix.RxInv(a);
```

(%o23) $$\begin{pmatrix} 0 & \frac{\sin\left(\frac{a}{2}\right)^2}{2}+\frac{\cos\left(\frac{a}{2}\right)^2}{2} \\ \frac{\sin\left(\frac{a}{2}\right)^2}{2}+\frac{\cos\left(\frac{a}{2}\right)^2}{2} & 0 \end{pmatrix}$$

```
--> trigrat(%);
```

(%o24) $\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$

```
--> opBasisRep(%);
```

$(1) * Ix + (0) * Iy + (0) * Iz$

(%o25)

The Iy component

```
--> Rx(a).Iy.RxInv(a);
```

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

```
--> trigrat(%);
```

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

```
--> opBasisRep(%);
```

$(0) * Ix + (\cos(a)) * Iy + (\sin(a)) * Iz$

(%o28)

The z-component

```
--> Rx(a).Iz.RxInv(a);
```

(%o29) $\begin{pmatrix} \frac{\cos\left(\frac{a}{2}\right)^2}{2} - \frac{\sin\left(\frac{a}{2}\right)^2}{2} & i \cdot \cos\left(\frac{a}{2}\right) \cdot \sin\left(\frac{a}{2}\right) \\ -i \cdot \cos\left(\frac{a}{2}\right) \cdot \sin\left(\frac{a}{2}\right) & \frac{\sin\left(\frac{a}{2}\right)^2}{2} - \frac{\cos\left(\frac{a}{2}\right)^2}{2} \end{pmatrix}$

```
--> trigrat(%);
```

(%o30) $\begin{pmatrix} \frac{\cos(a)}{2} & \frac{i \cdot \sin(a)}{2} \\ -\frac{i \cdot \sin(a)}{2} & -\frac{\cos(a)}{2} \end{pmatrix}$

```
--> opBasisRep(%);
```

$(0) * Ix + (-\sin(a)) * Iy + (\cos(a)) * Iz$

(%o31)

Pulses along the y'-axis

Applied to Ix

```
--> Ry(a).Ix.RyInv(a);
```

(%o32) $\begin{pmatrix} -\cos\left(\frac{a}{2}\right) \cdot \sin\left(\frac{a}{2}\right) & \frac{\cos\left(\frac{a}{2}\right)^2}{2} - \frac{\sin\left(\frac{a}{2}\right)^2}{2} \\ \frac{\cos\left(\frac{a}{2}\right)^2}{2} - \frac{\sin\left(\frac{a}{2}\right)^2}{2} & \cos\left(\frac{a}{2}\right) \cdot \sin\left(\frac{a}{2}\right) \end{pmatrix}$

```
--> trigrat(%);
```

(%o33) $\begin{pmatrix} -\frac{\sin(a)}{2} & \frac{\cos(a)}{2} \\ \frac{\cos(a)}{2} & \frac{\sin(a)}{2} \end{pmatrix}$

```
--> opBasisRep(%);
```

$(\cos(a)) * Ix + (0) * Iy + (-\sin(a)) * Iz$

(%o34)

Applied to Iy

```
--> Ry(a).Iy.RyInv(a);
```

(%o35) $\begin{pmatrix} 0 & -\frac{i\cdot\sin\left(\frac{a}{2}\right)^2}{2}-\frac{i\cdot\cos\left(\frac{a}{2}\right)^2}{2} \\ \frac{i\cdot\sin\left(\frac{a}{2}\right)^2}{2}+\frac{i\cdot\cos\left(\frac{a}{2}\right)^2}{2} & 0 \end{pmatrix}$

```
--> trigrat(%);
```

(%o36) $\begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix}$

```
--> opBasisRep(%);
```

$(0) * Ix + (1) * Iy + (0) * Iz$

(%o37)

Applied to Iz

```
--> Ry(a).Iz.RyInv(a);
```

(%o38) $\begin{pmatrix} \frac{\cos\left(\frac{a}{2}\right)^2}{2}-\frac{\sin\left(\frac{a}{2}\right)^2}{2} & \cos\left(\frac{a}{2}\right)\cdot\sin\left(\frac{a}{2}\right) \\ \cos\left(\frac{a}{2}\right)\cdot\sin\left(\frac{a}{2}\right) & \frac{\sin\left(\frac{a}{2}\right)^2}{2}-\frac{\cos\left(\frac{a}{2}\right)^2}{2} \end{pmatrix}$

```
--> trigrat(%);
```

(%o39) $\begin{pmatrix} \frac{\cos(a)}{2} & \frac{\sin(a)}{2} \\ \frac{\sin(a)}{2} & -\frac{\cos(a)}{2} \end{pmatrix}$

```
--> opBasisRep(%);
```

$(\sin(a)) * Ix + (0) * Iy + (\cos(a)) * Iz$

(%o40)

2.3 18.1.3 Time evolution

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The unitary time-evolution matrix and its inverse

```
--> Uh(t,nu);
```

(%o41) $\begin{pmatrix} e^{-i\cdot\pi\cdot\nu\cdot t} & 0 \\ 0 & e^{i\cdot\pi\cdot\nu\cdot t} \end{pmatrix}$

```
--> UhInv(t,nu);
```

(%o42) $\begin{pmatrix} e^{i\cdot\pi\cdot\nu\cdot t} & 0 \\ 0 & e^{-i\cdot\pi\cdot\nu\cdot t} \end{pmatrix}$

Evolution of the component beginning as Ix

```
--> Ix;
```

(%o43) $\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$

```
--> Uh(t,nu).Ix.UhInv(t,nu);
```

(%o44) $\begin{pmatrix} 0 & \frac{e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}}{2} \\ \frac{e^{2\cdot i\cdot\pi\cdot\nu\cdot t}}{2} & 0 \end{pmatrix}$

```
--> rectform(%);
```

(%o45) $\begin{pmatrix} 0 & \frac{\cos(2\cdot\pi\cdot\nu\cdot t)}{2} - \frac{i\cdot\sin(2\cdot\pi\cdot\nu\cdot t)}{2} \\ \frac{i\cdot\sin(2\cdot\pi\cdot\nu\cdot t)}{2} + \frac{\cos(2\cdot\pi\cdot\nu\cdot t)}{2} & 0 \end{pmatrix}$

```
--> opBasisRep(%);
```

$(\cos(2\cdot\pi\cdot\nu\cdot t)) * Ix + (\sin(2\cdot\pi\cdot\nu\cdot t)) * Iy + (0) * Iz$

(%o46)

Evolution of Iy

```
--> Iy;
```

(%o47) $\begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix}$

```
--> Uh(t,nu).Iy.UhInv(t,nu);
```

(%o48) $\begin{pmatrix} 0 & -\frac{i\cdot e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}}{2} \\ \frac{i\cdot e^{2\cdot i\cdot\pi\cdot\nu\cdot t}}{2} & 0 \end{pmatrix}$

```
--> opBasisRep(%);
```

$(-\sin(2\cdot\pi\cdot\nu\cdot t)) * Ix + (\cos(2\cdot\pi\cdot\nu\cdot t)) * Iy + (0) * Iz$

(%o49)

Evolution of Iz

```
--> Uh(t,nu).Iz.UhInv(t,nu);
```

(%o50) $\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$

```
--> opBasisRep(%);
```

$(0) * Ix + (0) * Iy + (1) * Iz$

(%o51)

Effects of pulses and time evolution on identity matrix

```
--> ident;
```

(%o52) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

```
--> Rx(a).ident.RxInv(a);
```

(%o53) $\begin{pmatrix} \sin\left(\frac{a}{2}\right)^2 + \cos\left(\frac{a}{2}\right)^2 & 0 \\ 0 & \sin\left(\frac{a}{2}\right)^2 + \cos\left(\frac{a}{2}\right)^2 \end{pmatrix}$

```
--> trigrat(%);
```

(%o54) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

```
--> Ry(a).ident.RyInv(a);
```

(%o55) $\begin{pmatrix} \sin\left(\frac{a}{2}\right)^2+\cos\left(\frac{a}{2}\right)^2 & 0 \\ 0 & \sin\left(\frac{a}{2}\right)^2+\cos\left(\frac{a}{2}\right)^2 \end{pmatrix}$

```
--> trigrat(%);
```

(%o56) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

```
--> Uh(t,nu).ident.UhInv(t,nu);
```

(%o57) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

pi/2 x-pulse applied to an arbitrary density matrix represented as a linear combination of Ix, Iy, Iz and the identity matrix.

```
--> rho1;
```

(%o58) $\begin{pmatrix} \frac{cz}{2}+c1 & \frac{cx}{2}-\frac{i\cdot cy}{2} \\ \frac{i\cdot cy}{2}+\frac{cx}{2} & c1-\frac{cz}{2} \end{pmatrix}$

```
--> opBasisRep(rho1);
```

$(cx)*Ix\ +\ (cy)*Iy\ +\ (cz)*Iz$

(%o59)

```
--> opBasisRep(Rx(%pi/2).rho1.RxInv(%pi/2));
```

$(cx)*Ix\ +\ (-cz)*Iy\ +\ (cy)*Iz$

(%o60)

2.4 18.1.4 Equilibrium and a single-pulse experiment

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The equilibrium density matrix

```
--> rhoEq;
```

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

```
--> opBasisRep(rhoEq);
```

$(0)*Ix\ +\ (0)*Iy\ +\ (deltaP)*Iz$

(%o62)

```
--> rhoPi2Y(Iz);
```

(%o63) $\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$

```
--> opBasisRep(%);
```

$(1) * Ix + (0) * Iy + (0) * Iz$

(%o64)

```
--> rhoTime(Ix,t);
```

(%o65) $$\begin{pmatrix} 0 & \frac{e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}}{2} \\ \frac{e^{2\cdot i\cdot\pi\cdot\nu\cdot t}}{2} & 0 \end{pmatrix}$$

```
--> opBasisRep(%);
```

$(\cos(2\cdot\pi\cdot\nu\cdot t)) * Ix + (\sin(2\cdot\pi\cdot\nu\cdot t)) * Iy + (0) * Iz$

(%o66)

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