

# Mathematica supplement for

## "A Physical Interpretation of the Product Operator Formalism"

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### Introduction to the supplement

This supplement is intended to provide the mathematical details and examples that have been left out of the main paper, as well as to provide a means for the reader to carry out additional calculations.

The definitions and equations used for this notebook are provided in two Mathematica package files. For the system composed of a single isolated spin, the "oneSpinLib" package is used, while a separate package "twoSpinLib" is used for calculations involving a scalar-coupled spin pair. These packages are not needed to read the notebook, but are necessary to carry out calculations. The library files must be placed in an appropriate location where Mathematica will look for them. I suggest creating a directory "NMR" in the Applications directory in \$BaseDirectory. (this is /Library/Mathematica on Mac OS X) or in \$UserBaseDirectory (~/.Library/Mathematica on Mac OS X).

If installed in one of these locations, the packages are loaded with the commands:

```
<< NMR`oneSpinLib`
```

or

```
<< NMR`twoSpinLib`
```

Because some of the same names are used for different functions in the two libraries, one set must be cleared before the other is loaded. This is done with:

```
Remove["NMR`oneSpinLib`*"]
```

or

```
Remove["NMR`twoSpinLib`*"]
```

Each of the packages includes two sets of functions, one for calculations involving wavefunctions representing pure populations and the other for calculations involving density matrices, which can represent either pure populations or mixtures of spins with different wavefunctions. Functions involving wavefunctions are identified with "psi" as part of the name, while functions involving density matrices are identified with "rho".

There are at least two other Mathematica notebooks available for carrying out product-operator calculations:

Prod\_Op\_Cart.nb by John Shriver

POMA.nb by Peter Guntert.

Both of these can be obtained at: <http://www.nmr.chem.uu.nl/~hsu/NMR/POMA/poma.html>

The two notebooks cited above implement the product operator formalism using symbolic manipulations. The packages for this notebook, on the other hand, uses matrix representations of the wavefunctions, operators and the density matrix to calculate the effects of pulses and evolution periods. The operators are used to calculate the average observable magnetization components and correlations, as described in the text.

Like the accompanying manuscript, this notebook and the associated packages assumes a "left-hand rule" for the effects of pulses and precession. This is contrary to the convention of Sorensen et al. (Progress in NMR Spectroscopy 16, 163-192 (1983)), but it is consistent with most vector representations of NMR experiments, where, for instance, a positive pulse along the x-axis rotates z-magnetization towards the y-axis.

## ■ Some Mathematica conventions

Because they have to be interpreted by a machine, the expressions used in Mathematica must follow rather strict rules of syntax. One aspect that is particularly important in using this notebook is the convention for parentheses and brackets:

1. Parentheses are used only to group the parts of an algebraic expression, for instance  $(a+b)(c+d)$
2. Square brackets are used to enclose the arguments of a function, either built in Mathematica functions or user-defined functions. For instance  $\text{Sin}[x]$ . The names of Mathematica's built in functions always begin with a capital letter, and it is considered good form to begin the names of user functions with a lower case letter. I have broken this rule for symbols representing matrices or matrix functions, including the  $I_x$ ,  $I_y$  and  $I_z$  operators and the matrices for rotation and time evolution.
3. Curly brackets are used to represent lists, including vectors and matrices. For instance a two-element vector is written as:  $\{a,b\}$ , and a 2x2 matrix is written as a list of two two-element vectors, where the individual vectors are the rows:  $\{\{a,b\},\{c,d\}\}$

The output of matrices can be made to follow the normal convention by entering

```
$PrePrint = If[MatrixQ[#], MatrixForm[#], #] &
```

at the beginning of a workbook. This is included automatically in the two libraries, so that when a matrix is entered as described above, the output is in the usual row-column form:

```
In[1]:= $PrePrint = If[MatrixQ[#], MatrixForm[#], #] &
```

```
Out[1]= If[MatrixQ[##], ##, ##] &
```

```
In[2]:= {{1, 2}, {3, 4}}
```

```
Out[2]=  $\begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$ 
```

It is often convenient to be able to access the result of a previous calculation. The symbol "%" always represents to result of the last calculation, and can be entered into a new calculation. For instance:

```
In[3]:= 6 ^ 2
```

```
Out[3]= 36
```

```
In[4]:= %
```

```
Out[4]= 36
```

```
In[5]:= Sqrt[%]
```

```
Out[5]= 6
```

Mathematica has a number of built in functions to simplify algebraic expressions or apply trigonometric identities. If the program generates something in one form, one of these functions can be used to try to simplify it or change it to more useful form:

```
In[6]:= Sin[2 nuI π t] Sin[2 nuS π t]
Out[6]= Sin[2 nuI π t] Sin[2 nuS π t]

In[7]:= TrigReduce[%]
Out[7]=  $\frac{1}{2} (\cos[2 \text{nuI} \pi t - 2 \text{nuS} \pi t] - \cos[2 \text{nuI} \pi t + 2 \text{nuS} \pi t])$ 
```

Previous results can also be referred to by line number:

```
In[8]:= Out[6]
Out[8]= Sin[2 nuI π t] Sin[2 nuS π t]
```

Or

```
In[9]:= %4
Out[9]= 36
```

Substitutions can be incorporated into expressions as shown below:

```
In[10]:= x + y
Out[10]= x + y

In[11]:= x + y /. x -> 5
Out[11]= 5 + y
```

A multiple substitution

```
In[12]:= x + y /. {x -> 5, y -> 6}
Out[12]= 11
```

These substitutions do not assign values to the symbols x and y:

```
In[13]:= x
Out[13]= X

In[14]:= y
Out[14]= Y
```

---

## Wavefunctions and operators for an isolated spin

### ■ Loading the one-spin library

```
In[15]:=
In[16]:= Remove["NMR`oneSpinLib`*"]
In[17]:= << NMR`oneSpinLib`
```

The objects defined by the library can be listed with the Names function

```
In[18]:= Names["NMR`oneSpinLib`*"]
```

```
Out[18]= {a, allMagPsi, allMagRho, ca, cb, deltaP, H, Hinv, Ix, Iy, Iz, meanPsi,
  meanRho, nu, op, psi, psiA, psiB, psiGen, psiPi2x, psiPi2y, psiPix, psiPiy,
  psiPulseX, psiPulseY, psiTime, rho, rhoEq, rhoGen, rhoPi2x, rhoPi2y, rhoPix,
  rhoPiy, rhoPulseX, rhoPulseY, rhoPulseY, rhoTime, Rinvx, Rinvy, Rx, Ry, t}
```

For information about an object, type "?name". For instance:

```
In[19]:= ? allMagPsi
```

allMagPsi[psi] writes output with all three magnetization components when applied to a wavefunction psi

## ■ Wavefunctions

In the text, wavefunctions are written in the Dirac notation, so that the general form of a wavefunction for a single spin is written as:

$$|\Psi\rangle = c\alpha |\alpha\rangle + c\beta |\beta\rangle$$

For calculations with Mathematica, it is more convenient to use a vector representation of the wavefunctions, and matrices for operators.

For a single spin, the wavefunction is a vector with two elements, corresponding to the complex coefficients for the  $|\alpha\rangle$  and  $|\beta\rangle$  basis wavefunctions. The oneSpinLib package defines the general form of a wavefunction:

```
In[20]:= psiGen
```

```
Out[20]= {ca, cb}
```

Note that in Mathematica, vectors are written as a list of elements enclosed in curly braces. There is no distinction between row and column vectors. The basis wavefunctions,  $|\alpha\rangle$  and  $|\beta\rangle$ , are defined as:

```
In[21]:= psiA
```

```
Out[21]= {1, 0}
```

```
In[22]:= psiB
```

```
Out[22]= {0, 1}
```

## ■ Operators

Operators are represented by matrices, and the action of the operator on a wavefunction is calculated by multiplying the wavefunction by the operator. The three magnetization operators are:

```
In[23]:= Ix
```

$$\text{Out[23]} = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$$

```
In[24]:= Iy
```

$$\text{Out[24]} = \begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix}$$

In[25]:= **Iz**

$$\text{Out[25]} = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

Vector and matrix multiplication are entered by placing a period between the arguments, as shown below for some examples of the action of the operators;

In[26]:= **Ix.psiA**

$$\text{Out[26]} = \left\{ 0, \frac{1}{2} \right\}$$

In[27]:= **Iy.psiA**

$$\text{Out[27]} = \left\{ 0, \frac{i}{2} \right\}$$

In[28]:= **Iz.psiA**

$$\text{Out[28]} = \left\{ \frac{1}{2}, 0 \right\}$$

Notice that the result of multiplying psiA by Iz is the original vector times a constant, 1/2. This defines psiA as an eigenfunction (or eigenvector) of Iz, and the eigenvalue, 1/2, represents the value of the observable, Iz, that will always be produced by the measurement. psiB is the other eigenfunction of Iz:

In[29]:= **Iz.psiB**

$$\text{Out[29]} = \left\{ 0, -\frac{1}{2} \right\}$$

In this case, the eigenvalue is -1/2. Mathematica can find the eigenfunctions and eigenvalues for any operator defined by a square matrix:

In[30]:= **Eigensystem[Iz]**

$$\text{Out[30]} = \left\{ \left\{ -\frac{1}{2}, \frac{1}{2} \right\}, \left\{ \{0, 1\}, \{1, 0\} \right\} \right\}$$

The first part of the result is a list of the two eigenvalues, and the second part is a list of the two eigenvectors. For the other two magnetization operators:

In[31]:= **Eigensystem[Ix]**

$$\text{Out[31]} = \left\{ \left\{ -\frac{1}{2}, \frac{1}{2} \right\}, \left\{ \{-1, 1\}, \{1, 1\} \right\} \right\}$$

In[32]:= **Eigensystem[Iy]**

$$\text{Out[32]} = \left\{ \left\{ -\frac{1}{2}, \frac{1}{2} \right\}, \left\{ \{i, 1\}, \{-i, 1\} \right\} \right\}$$

These forms of the eigenvectors are not normalized, as they must be in order to generate appropriate values in quantum-mechanical calculations. But, Mathematica can take care of this. For the Ix eigenfunctions:

In[33]:= **Normalize[{-1, 1}]**

$$\text{Out[33]} = \left\{ -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}$$

```
In[34]:= Normalize[{1, 1}]
```

$$\text{Out[34]} = \left\{ \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}$$

For the  $l_y$  eigenfunctions:

```
In[35]:= Normalize[{i, 1}]
```

$$\text{Out[35]} = \left\{ \frac{i}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}$$

```
In[36]:= Normalize[{-i, 1}]
```

$$\text{Out[36]} = \left\{ -\frac{i}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}$$

## ■ The average outcome of a measurement

The average value of a measurement,  $A$ , applied to a large number of particles with the same wavefunction is calculated as:

$\langle A \rangle = \langle \Psi | A | \Psi \rangle$ , as written in Dirac notation. For a system involving only spins, the bracket represents the multiplication of the result of applying  $A$  to  $|\Psi\rangle$  by the complex conjugate of the wavefunction ( $\langle \Psi |$ ). In Mathematica, the average outcome of measuring  $I_z$  for the basis wavefunction `psiA` is carried out as:

```
In[37]:= Conjugate[psiA].Iz.psiA
```

$$\text{Out[37]} = \frac{1}{2}$$

The one-spin library has a function that carries out this manipulation and simplifies the result:

```
In[38]:= meanPsi[Iz, psiA]
```

$$\text{Out[38]} = \frac{1}{2}$$

The simplification is obviously not necessary in this case, but is convenient with more complicated examples, especially those involving a wavefunction that changes with time. Be aware that the simplification rules used in this function assume that any undefined variables that define the wavefunction are real valued, except that it treats as complex the special variables, `ca` and `cb`, used to define the general form of the wavefunction. So, an expression for calculating the average value of  $I_z$  for a general wavefunction can be determined using:

```
In[39]:= meanPsi[Iz, psiGen]
```

$$\text{Out[39]} = \frac{1}{2} \text{ca Conjugate[ca]} - \frac{1}{2} \text{cb Conjugate[cb]}$$

For convenience, the library also includes a function that calculates the average values for all three of the magnetization components:

```
In[40]:= allMagPsi[psiA]
```

$$\langle I_x \rangle = 0$$

$$\langle I_y \rangle = 0$$

$$\langle I_z \rangle = \frac{1}{2}$$

In[41]:= **allMagPsi[psiB]**

$$\langle I_x \rangle = 0$$

$$\langle I_y \rangle = 0$$

$$\langle I_z \rangle = -\frac{1}{2}$$

In[42]:= **allMagPsi[psiGen]**

$$\langle I_x \rangle = \frac{1}{2} \text{cb Conjugate[ca]} + \frac{1}{2} \text{ca Conjugate[cb]}$$

$$\langle I_y \rangle = -\frac{1}{2} i \text{cb Conjugate[ca]} + \frac{1}{2} i \text{ca Conjugate[cb]}$$

$$\langle I_z \rangle = \frac{1}{2} \text{ca Conjugate[ca]} - \frac{1}{2} \text{cb Conjugate[cb]}$$

We can use these functions to confirm the properties of the eigenfunctions for  $I_x$  and  $I_y$

In[43]:= **Eigensystem[Ix]**

$$\text{Out[43]} = \left\{ \left\{ -\frac{1}{2}, \frac{1}{2} \right\}, \{ \{-1, 1\}, \{1, 1\} \} \right\}$$

In[44]:= **allMagPsi[Normalize[{-1, 1}]]**

$$\langle I_x \rangle = -\frac{1}{2}$$

$$\langle I_y \rangle = 0$$

$$\langle I_z \rangle = 0$$

In[45]:= **allMagPsi[Normalize[{1, 1}]]**

$$\langle I_x \rangle = \frac{1}{2}$$

$$\langle I_y \rangle = 0$$

$$\langle I_z \rangle = 0$$

In[46]:= **Eigensystem[Iy]**

$$\text{Out[46]} = \left\{ \left\{ -\frac{1}{2}, \frac{1}{2} \right\}, \{ \{i, 1\}, \{-i, 1\} \} \right\}$$

In[47]:= **allMagPsi[Normalize[{i, 1}]]**

$$\langle I_x \rangle = 0$$

$$\langle I_y \rangle = -\frac{1}{2}$$

$$\langle I_z \rangle = 0$$

```
In[48]:= allMagPsi[Normalize[{-i, 1}]]
```

```
<Ix> = 0
```

```
<Iy> =  $\frac{1}{2}$ 
```

```
<Iz> = 0
```

## Equilibrium population difference for a single spin

The relative concentrations of two states at thermal equilibrium are given by the Boltzmann equation:

```
In[49]:= Na / Nb == Exp[(Eb - Ea) / (kT)] == Exp[deltaE / (kT)]
```

```
Out[49]=  $\frac{N_a}{N_b} == e^{\frac{-E_a + E_b}{kT}} == e^{\text{deltaE}/kT}$ 
```

For conventional NMR experiments,  $\text{deltaE} \ll kT$ , and the Boltzmann distribution can be approximated as:

```
In[50]:= Na / Nb == 1 + deltaE / (kT)
```

```
Out[50]=  $\frac{N_a}{N_b} == 1 + \frac{\text{deltaE}}{kT}$ 
```

$N_a$  can be written in terms of  $N_b$ :

```
In[51]:= Na == Nb (1 + deltaE / (kT))
```

```
Out[51]=  $N_a == \left(1 + \frac{\text{deltaE}}{kT}\right) N_b$ 
```

The fractional population difference,  $\text{deltaP}$  is defined as:

```
In[52]:= deltaP == (Na - Nb) / (Na + Nb)
```

```
Out[52]=  $\text{deltaP} == \frac{N_a - N_b}{N_a + N_b}$ 
```

The numerator can be written as:

```
In[53]:= (Na - Nb) == Nb ((1 + deltaE / (kT)) - 1)
```

```
Out[53]=  $N_a - N_b == \frac{\text{deltaE} N_b}{kT}$ 
```

The denominator is:

```
In[54]:= Nb + Na == Nb ((1 + deltaE / (kT)) + 1)
```

```
Out[54]=  $N_a + N_b == \left(2 + \frac{\text{deltaE}}{kT}\right) N_b$ 
```

Since  $\text{deltaE}/(kT) \ll 1$ ,

```
In[55]:= Na + Nb == (2) Nb
```

```
Out[55]=  $N_a + N_b == 2 N_b$ 
```



And

$$\text{In[56]:= } \Delta P = (N_a - N_b) / (N_a + N_b) = \left( \frac{\Delta E N_b}{kT} \right) / (2 N_b)$$

$$\text{Out[56]= } \Delta P = \frac{N_a - N_b}{N_a + N_b} = \frac{\Delta E}{2 kT}$$

## Pulses and time evolution for a single spin

### ■ Pulses

Rotations along the x' and y' axis are represented as matrices. The new wavefunction is generated by multiplying the old wavefunction by the rotation matrix. For a pulse of angle  $\alpha$  along the x'-axis the matrix is:

$$\text{In[57]:= } \mathbf{R_x}[\alpha]$$

$$\text{Out[57]= } \begin{pmatrix} \cos\left[\frac{\alpha}{2}\right] & i \sin\left[\frac{\alpha}{2}\right] \\ i \sin\left[\frac{\alpha}{2}\right] & \cos\left[\frac{\alpha}{2}\right] \end{pmatrix}$$

For a pulse along the y'-axis, the matrix is:

$$\text{In[58]:= } \mathbf{R_y}[\alpha]$$

$$\text{Out[58]= } \begin{pmatrix} \cos\left[\frac{\alpha}{2}\right] & \sin\left[\frac{\alpha}{2}\right] \\ -\sin\left[\frac{\alpha}{2}\right] & \cos\left[\frac{\alpha}{2}\right] \end{pmatrix}$$

For example, a  $\pi/2$  pulse along the x'-axis applied to  $\psi_A$ :

$$\text{In[59]:= } \mathbf{R_x}[\pi / 2] . \psi_A$$

$$\text{Out[59]= } \left\{ \frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}} \right\}$$

$$\text{In[60]:= } \mathbf{allMagPsi} \left[ \left\{ \frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}} \right\} \right]$$

$$\langle I_x \rangle = 0$$

$$\langle I_y \rangle = \frac{1}{2}$$

$$\langle I_z \rangle = 0$$

confirming that the magnetization is rotated from the z-axis to the y'-axis. A pulse along the y'-axis:

$$\text{In[61]:= } \mathbf{R_y}[\pi / 2] . \psi_A$$

$$\text{Out[61]= } \left\{ \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right\}$$

$$\text{In[62]:= } \mathbf{allMagPsi} \left[ \left\{ \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right\} \right]$$

$$\langle I_x \rangle = -\frac{1}{2}$$

$$\langle I_y \rangle = 0$$

$$\langle I_z \rangle = 0$$

This shows that the rotations follow the left-hand convention.

The library also includes some functions for specific pulses:

Pulses along the x-axis:

`psiPulseX`

`psiPi2x` (a  $\pi/2$  pulse)

`psiPix`

Pulses along the y'-axis

`psiPulseY`

`psiPulsePi2y` (a  $\pi/2$  pulse)

`psiPiy`

Some more examples:

```
In[63]:= psiPulseX[psiA, Pi / 2]
```

$$\text{Out[63]} = \left\{ \frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}} \right\}$$

```
In[64]:= psiPi2x[psiA]
```

$$\text{Out[64]} = \left\{ \frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}} \right\}$$

```
In[65]:= psiPi2x[psiB]
```

$$\text{Out[65]} = \left\{ \frac{i}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}$$

```
In[66]:= psiPi2y[psiB]
```

$$\text{Out[66]} = \left\{ \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}$$

The operations for the pulses and for calculating the magnetization components don't have to be done separately:

```
In[67]:= allMagPsi[psiPi2y[psiA]]
```

$$\langle I_x \rangle = -\frac{1}{2}$$

$$\langle I_y \rangle = 0$$

$$\langle I_z \rangle = 0$$

```
In[68]:= allMagPsi[psiPi2y[psiB]]
```

$$\langle I_x \rangle = \frac{1}{2}$$

$$\langle I_y \rangle = 0$$

$$\langle I_z \rangle = 0$$

## Time evolution

Like pulses, the effects of time evolution in stationary magnetic field are calculated by matrix multiplication. In this case, it is the matrix form of the Hamiltonian operator. For the purposes of calculations, it is convenient to express the energies of the  $|a\rangle$  and  $|b\rangle$  states in terms of the frequency of radiation required to stimulate a transition:

$$\Delta E = h \nu = \gamma B / (2 \pi)$$

where  $h$  is Planck's constant, and  $\gamma$  is the gyromagnetic ratio, and  $B$  is the strength of the external magnetic field. The energies of the two states are:

$$E_a = -\gamma B / (4 \pi) = -h \nu / 2$$

$$E_b = \gamma B / (4 \pi) = h \nu / 2$$

If these equations are divided by Planck's constant, the energies are expressed in units of  $h$ . This, then, allows all of the calculated results for the time-dependent changes in the wavefunction and magnetization components to be expressed in terms of the resonance frequency,  $\nu$ .

Following this convention the Hamiltonian matrix is given by:

In[69]:= **H[t, nu]**

$$\text{Out[69]} = \begin{pmatrix} e^{i \nu \pi t} & 0 \\ 0 & e^{-i \nu \pi t} \end{pmatrix}$$

The general form of the time-dependent wavefunction is:

In[70]:= **H[t, nu].psiGen**

$$\text{Out[70]} = \{c_a e^{i \nu \pi t}, c_b e^{-i \nu \pi t}\}$$

where  $c_a$  and  $c_b$  are the complex coefficients in the starting wavefunction.

Calculate what happens following a  $\pi/2$ -x pulse to the  $\psi_A$  wavefunction:

In[71]:= **H[t, nu].psiPi2x[psiA]**

$$\text{Out[71]} = \left\{ \frac{e^{i \nu \pi t}}{\sqrt{2}}, \frac{i e^{-i \nu \pi t}}{\sqrt{2}} \right\}$$

The library also contains a function for calculating the time-dependent wavefunction: `psiTime[psi,t]`

In[72]:= **psiTime[psiPi2x[psiA], t]**

$$\text{Out[72]} = \left\{ \frac{e^{i \nu \pi t}}{\sqrt{2}}, \frac{i e^{-i \nu \pi t}}{\sqrt{2}} \right\}$$

In[73]:= **allMagPsi** $\left[\left\{\frac{e^{i \nu \pi t}}{\sqrt{2}}, \frac{i e^{-i \nu \pi t}}{\sqrt{2}}\right\}\right]$

$$\langle I_x \rangle = \frac{1}{2} \sin[2 \nu \pi t]$$

$$\langle I_y \rangle = \frac{1}{2} \cos[2 \nu \pi t]$$

$$\langle I_z \rangle = 0$$

Calculate what happens to spins in  $\psi_B$ -state after the same pulse:

```
In[74]:= psiTime[psiPi2x[psiB], t]
```

```
Out[74]=  $\left\{ \frac{i e^{i \nu \pi t}}{\sqrt{2}}, \frac{e^{-i \nu \pi t}}{\sqrt{2}} \right\}$ 
```

```
In[75]:= allMagPsi[%]
```

```
<Ix> =  $-\frac{1}{2} \sin[2 \nu \pi t]$ 
```

```
<Iy> =  $-\frac{1}{2} \cos[2 \nu \pi t]$ 
```

```
<Iz> = 0
```

The magnetization components for the spins that begin in the two state always point in opposite directions, so that the net magnetization is that of the small excess that began in the psiA state.

---

## Wavefunctions and operators for a coupled spin pair

Remove definitions from oneSpinLib and load twoSpinLib:

```
In[76]:= Remove["NMR`oneSpinLib`*"]
```

```
In[77]:= << NMR`twoSpinLib`
```

```
In[78]:= Names["NMR`twoSpinLib`*"]
```

```
Out[78]= {a, allCorPsi, allCorRho, allMagPsi, allMagRho, caa, cab, cba, cbb, deltaPi, deltaPs,
H, Hc, HcInv, Hinv, Hs, HsInv, i, Ix, IxSx, IxSy, IxSz, Iy, IySx, IySy, IySz, Iz, IzSx,
IzSy, IzSz, i$, J, meanPsi, meanRho, nuI, nuS, op, opBasisRep, opNames, opNames$,
opValues, opValues$, psi, psiAA, psiAB, psiBA, psiBB, psiGen, psiPi2Ix, psiPi2Iy,
psiPi2Sx, psiPi2Sy, psiPi2x, psiPi2y, psiPiIx, psiPiIy, psiPiSx, psiPiSy, psiPix,
psiPiy, psiPulseIx, psiPulseIy, psiPulseSx, psiPulseSy, psiPulseX, psiPulseY,
psiTime, psiTimeC, psiTimeS, rho, rhoEq, rhoGen, rhoPi2Ix, rhoPi2Iy, rhoPi2Sx,
rhoPi2Sy, rhoPi2x, rhoPi2y, rhoPiIx, rhoPiIy, rhoPiSx, rhoPiSy, rhoPix, rhoPiy,
rhoPulseIx, rhoPulseIy, rhoPulseSx, rhoPulseSy, rhoPulseX, rhoPulseY, rhoTime,
rhoTimeC, rhoTimeS, Rix, RixInv, RIy, RIyInv, RSx, RSxInv, RSy, RSyInv, Sx, Sy, Sz, t}
```

The general form of the wavefunction for a scalar coupled spin pair can be written as:

caa psiAA + cab psiAB+ cba psiBA+ cbb psiBB

with the basis set defined in vector form as:

```
In[79]:= psiAA
```

```
Out[79]= {1, 0, 0, 0}
```

```
In[80]:= psiAB
```

```
Out[80]= {0, 1, 0, 0}
```

```
In[81]:= psiBA
```

```
Out[81]= {0, 0, 1, 0}
```

```
In[82]:= psiBB
```

```
Out[82]= {0, 0, 0, 1}
```

The general form of a wavefunction can be written in vector form as:

In[83]:= **psiGen**

Out[83]= {caa, cab, cba, cbb}

There are now six magnetization operators:

In[84]:= **Ix**

$$\text{Out[84]} = \begin{pmatrix} 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \end{pmatrix}$$

In[85]:= **Iy**

$$\text{Out[85]} = \begin{pmatrix} 0 & 0 & -\frac{i}{2} & 0 \\ 0 & 0 & 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 & 0 & 0 \\ 0 & \frac{i}{2} & 0 & 0 \end{pmatrix}$$

In[86]:= **Iz**

$$\text{Out[86]} = \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}$$

In[87]:= **Sx**

$$\text{Out[87]} = \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix}$$

In[88]:= **Sy**

$$\text{Out[88]} = \begin{pmatrix} 0 & -\frac{i}{2} & 0 & 0 \\ \frac{i}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{i}{2} \\ 0 & 0 & \frac{i}{2} & 0 \end{pmatrix}$$

In[89]:= **Sz**

$$\text{Out[89]} = \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}$$

The average magnetization components are calculated by applying the operator to the wavefunction and multiplying the result by the complex conjugate of the wavefunction. For instance, to calculate the average magnetization of the I-spin along the z-axis for the psiAA state:

In[90]:= **Conjugate[psiAA].Iz.psiAA**

$$\text{Out[90]} = \frac{1}{2}$$

The twoSpinLib package includes a function to calculate all of the average magnetization components for a given wavefunction:

In[91]:= **allMagPsi[psiAA]**

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = 0$$

$$\langle I_z \rangle = \frac{1}{2} \quad \langle S_z \rangle = \frac{1}{2}$$

Thus, the psiAA wavefunction represents a state in which the magnetization of both spins is aligned with the positive z-axis.

For psiAB:

In[92]:= **allMagPsi[psiAB]**

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = 0$$

$$\langle I_z \rangle = \frac{1}{2} \quad \langle S_z \rangle = -\frac{1}{2}$$

In this case, the I magnetization is aligned with the positive z-axis and the S magnetization is aligned with the negative z-axis.

Four other wavefunctions are used extensively as examples in the text. Three of these are generated by applying pulses to some of the basis set wavefunctions. As for the one-spin case, the effects of pulses are calculated using special rotation matrices. For a pulse of angle  $a$  to the I-spin along the x-axis, the rotation matrix is:

In[93]:= **RIx[a]**

$$\text{Out[93]} = \begin{pmatrix} \cos\left[\frac{a}{2}\right] & 0 & i \sin\left[\frac{a}{2}\right] & 0 \\ 0 & \cos\left[\frac{a}{2}\right] & 0 & i \sin\left[\frac{a}{2}\right] \\ i \sin\left[\frac{a}{2}\right] & 0 & \cos\left[\frac{a}{2}\right] & 0 \\ 0 & i \sin\left[\frac{a}{2}\right] & 0 & \cos\left[\frac{a}{2}\right] \end{pmatrix}$$

The example wavefunction psiA is defined as the result of applying a  $\pi/2$  pulse along the x-axis to the S-spin of the psiAA state:

```
In[94]:= psiA = RSx[Pi / 2] . psiAA
```

$$\text{Out[94]} = \left\{ \frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}}, 0, 0 \right\}$$

```
In[95]:= allMagPsi[psiA]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = \frac{1}{2}$$

$$\langle I_z \rangle = \frac{1}{2} \quad \langle S_z \rangle = 0$$

The S magnetization is rotated to the y-axis, as expected.

The twoSpinLib package includes special functions for pi and pi/2 pulses to either spin, one of which is used below to calculate another of the example wavefunctions.

```
In[96]:= psiB = psiPi2Sx[psiBA]
```

$$\text{Out[96]} = \left\{ 0, 0, \frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}} \right\}$$

```
In[97]:= allMagPsi[psiB]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = \frac{1}{2}$$

$$\langle I_z \rangle = -\frac{1}{2} \quad \langle S_z \rangle = 0$$

A pulse to both spins is calculated by multiplying the wavefunction by one rotation matrix and then multiplying the result by the other matrix:

```
In[98]:= psiC = RIx[Pi / 2] . RSx[Pi / 2] . psiAA
```

$$\text{Out[98]} = \left\{ \frac{1}{2}, \frac{i}{2}, \frac{i}{2}, -\frac{1}{2} \right\}$$

Although matrix multiplication is not, in general, commutative, multiplications by the rotation matrices can be carried out in either order:

```
In[99]:= RSx[Pi / 2] . RIx[Pi / 2] . psiAA
```

$$\text{Out[99]} = \left\{ \frac{1}{2}, \frac{i}{2}, \frac{i}{2}, -\frac{1}{2} \right\}$$

```
In[100]:= allMagPsi[psiC]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = \frac{1}{2} \quad \langle S_y \rangle = \frac{1}{2}$$

$$\langle I_z \rangle = 0 \quad \langle S_z \rangle = 0$$

The other wavefunction used for examples in the text is psiD:

```
In[101]:= psiD = {0, 1/Sqrt[2], 1/Sqrt[2], 0}
```

$$\text{Out[101]} = \left\{ 0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right\}$$

This wavefunction is not so easy to generate from one of the basis wavefunctions, but has very interesting properties:

```
In[102]:= allMagPsi[psiD]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = 0$$

$$\langle I_z \rangle = 0 \quad \langle S_z \rangle = 0$$

There is no net magnetization in any direction! For any measurement of individual particles, the two possible outcomes, 1/2 and -1/2 will be obtained with equal probability.

## Product operators and correlations

The product operators are generated by multiplying the corresponding operator matrices:

```
In[103]:= Ix.Sx
```

$$\text{Out[103]} = \begin{pmatrix} 0 & 0 & 0 & \frac{1}{4} \\ 0 & 0 & \frac{1}{4} & 0 \\ 0 & \frac{1}{4} & 0 & 0 \\ \frac{1}{4} & 0 & 0 & 0 \end{pmatrix}$$

```
In[104]:= Ix.Sy
```

$$\text{Out[104]} = \begin{pmatrix} 0 & 0 & 0 & -\frac{i}{4} \\ 0 & 0 & \frac{i}{4} & 0 \\ 0 & -\frac{i}{4} & 0 & 0 \\ \frac{i}{4} & 0 & 0 & 0 \end{pmatrix}$$

```
In[105]:= Ix.Sz
```

$$\text{Out[105]} = \begin{pmatrix} 0 & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & -\frac{1}{4} \\ \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 \end{pmatrix}$$

```
In[106]:= Iy.Sx
```

$$\text{Out[106]} = \begin{pmatrix} 0 & 0 & 0 & -\frac{i}{4} \\ 0 & 0 & -\frac{i}{4} & 0 \\ 0 & \frac{i}{4} & 0 & 0 \\ \frac{i}{4} & 0 & 0 & 0 \end{pmatrix}$$



In[107]:= **Iy.Sy**

$$\text{Out[107]} = \begin{pmatrix} 0 & 0 & 0 & -\frac{1}{4} \\ 0 & 0 & \frac{1}{4} & 0 \\ 0 & \frac{1}{4} & 0 & 0 \\ -\frac{1}{4} & 0 & 0 & 0 \end{pmatrix}$$

In[108]:= **Iy.Sz**

$$\text{Out[108]} = \begin{pmatrix} 0 & 0 & -\frac{i}{4} & 0 \\ 0 & 0 & 0 & \frac{i}{4} \\ \frac{i}{4} & 0 & 0 & 0 \\ 0 & -\frac{i}{4} & 0 & 0 \end{pmatrix}$$

In[109]:= **Iz.Sx**

$$\text{Out[109]} = \begin{pmatrix} 0 & \frac{1}{4} & 0 & 0 \\ \frac{1}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{4} \\ 0 & 0 & -\frac{1}{4} & 0 \end{pmatrix}$$

In[110]:= **Iz.Sy**

$$\text{Out[110]} = \begin{pmatrix} 0 & -\frac{i}{4} & 0 & 0 \\ \frac{i}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{i}{4} \\ 0 & 0 & -\frac{i}{4} & 0 \end{pmatrix}$$

In[111]:= **Iz.Sz**

$$\text{Out[111]} = \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 \\ 0 & 0 & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$$

The product operator matrices are also defined in the twoSpinLib, with symbols IxSx, IxSy, etc.

The average value of the product is calculated in the same way as the average magnetization components. For instance, to calculate the average product IzSz for the psiAA wavefunction:

In[112]:= **Conjugate[psiAA].IzSz.psiAA**

$$\text{Out[112]} = \frac{1}{4}$$

A special function is provided to calculate all of the product averages for a wavefunction:

In[113]:= **allCorPsi[psiAA]**

$$\begin{aligned}
\langle I_x S_x \rangle &= 0 & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\
\langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= 0 & \langle I_y S_z \rangle &= 0 \\
\langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= 0 & \langle I_z S_z \rangle &= \frac{1}{4}
\end{aligned}$$

This result is consistent with the fact that, for this wavefunction,  $\langle I_z \rangle = \langle S_z \rangle = 1/2$ , and all of the other average magnetization components are zero.

For psiA, generated by applying a  $\pi/2$ -x pulse to the S spin:

```
In[114]:= allCorPsi[psiA]
```

$$\begin{aligned}
\langle I_x S_x \rangle &= 0 & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\
\langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= 0 & \langle I_y S_z \rangle &= 0 \\
\langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= \frac{1}{4} & \langle I_z S_z \rangle &= 0
\end{aligned}$$

The net correlation changes along with the magnetization component.

For the wavefunction psiD

```
In[115]:= allCorPsi[psiD]
```

$$\begin{aligned}
\langle I_x S_x \rangle &= \frac{1}{4} & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\
\langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= \frac{1}{4} & \langle I_y S_z \rangle &= 0 \\
\langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= 0 & \langle I_z S_z \rangle &= -\frac{1}{4}
\end{aligned}$$

Even though all of the average magnetization components are zero, there are three non-zero product averages, indicating correlations between  $I_x$  and  $S_x$ ,  $I_y$  and  $S_y$ , and  $I_z$  and  $S_z$  measured for individual spin pairs.

---

## Pulses and time evolution for a scalar-coupled spin pair

The matrices used to calculate the effects of a pulse on the wavefunction have been introduced earlier. These pulses can change the correlations associated with a wavefunction, as well as the observable magnetization. For instance, starting with the psiAA wavefunction:

### ■ Pulses

```
In[116]:= allMagPsi[psiAA]
```

$$\begin{aligned}
\langle I_x \rangle &= 0 & \langle S_x \rangle &= 0 \\
\langle I_y \rangle &= 0 & \langle S_y \rangle &= 0 \\
\langle I_z \rangle &= \frac{1}{2} & \langle S_z \rangle &= \frac{1}{2}
\end{aligned}$$

```
In[117]:= allCorPsi[psiAA]
```

$$\begin{aligned}
\langle I_x S_x \rangle &= 0 & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\
\langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= 0 & \langle I_y S_z \rangle &= 0 \\
\langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= 0 & \langle I_z S_z \rangle &= \frac{1}{4}
\end{aligned}$$

Applying a  $\pi/2$ -x pulse to the S-spin

In[118]:= **psiPi2Sx[psiAA]**

$$\text{Out[118]} = \left\{ \frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}}, 0, 0 \right\}$$

In[119]:= **allMagPsi** $\left[\left\{\frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}}, 0, 0\right\}\right]$

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = \frac{1}{2}$$

$$\langle I_z \rangle = \frac{1}{2} \quad \langle S_z \rangle = 0$$

In[120]:= **allCorPsi** $\left[\left\{\frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}}, 0, 0\right\}\right]$

$$\langle I_x S_x \rangle = 0 \quad \langle I_x S_y \rangle = 0 \quad \langle I_x S_z \rangle = 0$$

$$\langle I_y S_x \rangle = 0 \quad \langle I_y S_y \rangle = 0 \quad \langle I_y S_z \rangle = 0$$

$$\langle I_z S_x \rangle = 0 \quad \langle I_z S_y \rangle = \frac{1}{4} \quad \langle I_z S_z \rangle = 0$$

The  $I_z$  component of the  $I_z S_z$  correlation is rotated to the y-axis.

A subsequent  $\pi/2$ -x pulse to the S-spin:

In[121]:= **psiPi2Ix** $\left[\left\{\frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}}, 0, 0\right\}\right]$

$$\text{Out[121]} = \left\{ \frac{1}{2}, \frac{i}{2}, \frac{i}{2}, -\frac{1}{2} \right\}$$

In[122]:= **allMagPsi** $\left[\left\{\frac{1}{2}, \frac{i}{2}, \frac{i}{2}, -\frac{1}{2}\right\}\right]$

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = \frac{1}{2} \quad \langle S_y \rangle = \frac{1}{2}$$

$$\langle I_z \rangle = 0 \quad \langle S_z \rangle = 0$$

In[123]:= **allCorPsi** $\left[\left\{\frac{1}{2}, \frac{i}{2}, \frac{i}{2}, -\frac{1}{2}\right\}\right]$

$$\begin{aligned}
\langle I_x S_x \rangle &= 0 & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\
\langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= \frac{1}{4} & \langle I_y S_z \rangle &= 0 \\
\langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= 0 & \langle I_z S_z \rangle &= 0
\end{aligned}$$

The original  $I_z S_z$  correlation is now converted into an  $I_y S_y$  correlation.

A pulse applied to the  $\psi_{ID}$  wavefunction:

In[124]:= **psiD**

$$\text{Out[124]} = \left\{ 0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right\}$$

In[125]:= **allMagPsi[psiD]**

$$\begin{aligned}
\langle I_x \rangle &= 0 & \langle S_x \rangle &= 0 \\
\langle I_y \rangle &= 0 & \langle S_y \rangle &= 0 \\
\langle I_z \rangle &= 0 & \langle S_z \rangle &= 0
\end{aligned}$$

In[126]:= **allCorPsi[psiD]**

$$\begin{aligned}
\langle I_x S_x \rangle &= \frac{1}{4} & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\
\langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= \frac{1}{4} & \langle I_y S_z \rangle &= 0 \\
\langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= 0 & \langle I_z S_z \rangle &= -\frac{1}{4}
\end{aligned}$$

In[127]:= **psiPi2Ix[psiD]**

$$\text{Out[127]} = \left\{ \frac{i}{2}, \frac{1}{2}, \frac{1}{2}, \frac{i}{2} \right\}$$

In[128]:= **allMagPsi** $\left[\left\{\frac{i}{2}, \frac{1}{2}, \frac{1}{2}, \frac{i}{2}\right\}\right]$

$$\begin{aligned}
\langle I_x \rangle &= 0 & \langle S_x \rangle &= 0 \\
\langle I_y \rangle &= 0 & \langle S_y \rangle &= 0 \\
\langle I_z \rangle &= 0 & \langle S_z \rangle &= 0
\end{aligned}$$

There are still no net magnetization components.

In[129]:= **allCorPsi** $\left[\left\{\frac{i}{2}, \frac{1}{2}, \frac{1}{2}, \frac{i}{2}\right\}\right]$

$$\begin{aligned}
\langle I_x S_x \rangle &= \frac{1}{4} & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\
\langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= 0 & \langle I_y S_z \rangle &= -\frac{1}{4} \\
\langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= -\frac{1}{4} & \langle I_z S_z \rangle &= 0
\end{aligned}$$

The pulse along the x-axis does not affect  $I_x S_x$ , but  $-I_y S_y$  is converted to  $I_z S_y$  and  $-I_z S_z$  is converted to  $-I_y S_z$ .

## Time evolution

The time evolution in a stationary magnetic field is calculated using the Hamiltonian operator, which is represented in matrix form as:

In[130]:= **H[t, nuI, nuS, J]**

$$\text{Out[130]} = \begin{pmatrix} e^{i \left( -\frac{J}{2} + \text{nuI} + \text{nuS} \right) \pi t} & 0 & 0 & 0 \\ 0 & e^{i \left( \frac{J}{2} + \text{nuI} - \text{nuS} \right) \pi t} & 0 & 0 \\ 0 & 0 & e^{i \left( \frac{J}{2} - \text{nuI} + \text{nuS} \right) \pi t} & 0 \\ 0 & 0 & 0 & e^{i \left( -\frac{J}{2} - \text{nuI} - \text{nuS} \right) \pi t} \end{pmatrix}$$

where, nuI and nuS are the Larmor frequencies of the two spins in the absence of scalar coupling, and J is the coupling constant. In this representation, the energies of the four states are specified by the frequencies and the coupling constant. The general form of the time-dependent wavefunction is:

In[131]:= **H[t, nuI, nuS, J].psiGen**

$$\text{Out[131]} = \left\{ \text{caa} e^{i \left( -\frac{J}{2} + \text{nuI} + \text{nuS} \right) \pi t}, \text{cab} e^{i \left( \frac{J}{2} + \text{nuI} - \text{nuS} \right) \pi t}, \text{cba} e^{i \left( \frac{J}{2} - \text{nuI} + \text{nuS} \right) \pi t}, \text{cbb} e^{i \left( -\frac{J}{2} - \text{nuI} - \text{nuS} \right) \pi t} \right\}$$

where caa, cab, cba and cbb are the initial values of the complex coefficients. The calculation is incorporated into a function, psiTime, for which only the wavefunction and time are explicitly specified:

In[132]:= **psiTime[psiGen, t]**

$$\text{Out[132]} = \left\{ \text{caa} e^{i \left( -\frac{J}{2} + \text{nuI} + \text{nuS} \right) \pi t}, \text{cab} e^{i \left( \frac{J}{2} + \text{nuI} - \text{nuS} \right) \pi t}, \text{cba} e^{i \left( \frac{J}{2} - \text{nuI} + \text{nuS} \right) \pi t}, \text{cbb} e^{i \left( -\frac{J}{2} - \text{nuI} - \text{nuS} \right) \pi t} \right\}$$

### ■ Evolution of observable magnetization.

Starting with psiA:

In[133]:= **psiTime[psiA, t]**

$$\text{Out[133]} = \left\{ \frac{e^{i \left( -\frac{J}{2} + \text{nuI} + \text{nuS} \right) \pi t}}{\sqrt{2}}, \frac{i e^{i \left( \frac{J}{2} + \text{nuI} - \text{nuS} \right) \pi t}}{\sqrt{2}}, 0, 0 \right\}$$

$$\text{In[134]} := \text{allMagPsi} \left[ \left\{ \frac{e^{i \left( -\frac{J}{2} + \text{nuI} + \text{nuS} \right) \pi t}}{\sqrt{2}}, \frac{i e^{i \left( \frac{J}{2} + \text{nuI} - \text{nuS} \right) \pi t}}{\sqrt{2}}, 0, 0 \right\} \right]$$

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = -\frac{1}{2} \sin[(J - 2 \text{nuS}) \pi t]$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = \frac{1}{2} \cos[(J - 2 \text{nuS}) \pi t]$$

$$\langle I_z \rangle = \frac{1}{2} \quad \langle S_z \rangle = 0$$

Since  $\sin(-x) = -\sin(x)$ , the expression for  $\langle S_x \rangle$  can be rewritten as:  $\frac{1}{2} \sin[(2 \text{nuS} - J) \pi t]$

Since  $\cos(-x) = \cos(x)$ , the expression for  $\langle S_y \rangle$  can be rewritten as:  $\frac{1}{2} \cos[(2 \text{nuS} - J) \pi t]$

The magnetization precesses with frequency  $\text{nuS} - J/2$ .

Starting with psiB:, where  $\langle I_y \rangle = 1/2$  and  $\langle S_z \rangle = -1/2$

```
In[135]:= allMagPsi[psiTime[psiB, t]]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = \frac{1}{2} \sin[(J + 2\nu_S) \pi t]$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = \frac{1}{2} \cos[(J + 2\nu_S) \pi t]$$

$$\langle I_z \rangle = -\frac{1}{2} \quad \langle S_z \rangle = 0$$

The result is the same as for psiA, except that the frequency is now  $\nu_S + J/2$ .

Starting with psiC, where  $\langle I_y \rangle = 1/2$  and  $\langle S_y \rangle = 1/2$ , and there is no net z-magnetization for either spin:

```
In[136]:= allMagPsi[psiTime[psiC, t]]
```

$$\langle I_x \rangle = \frac{1}{2} \cos[J \pi t] \sin[2\nu_I \pi t] \quad \langle S_x \rangle = \frac{1}{2} \cos[J \pi t] \sin[2\nu_S \pi t]$$

$$\langle I_y \rangle = \frac{1}{4} (\cos[(J - 2\nu_I) \pi t] + \cos[(J + 2\nu_I) \pi t])$$

$$\langle S_y \rangle = \frac{1}{4} (\cos[(J - 2\nu_S) \pi t] + \cos[(J + 2\nu_S) \pi t])$$

$$\langle I_z \rangle = 0 \quad \langle S_z \rangle = 0$$

For the  $I_y$  and  $S_y$  components, there are two frequency components for each. The expressions for the  $I_x$  and  $S_x$  components are less clear, but can be rewritten using trigonometric identities built into the Mathematica TrigReduce function.

For  $I_x$ :

```
In[137]:= TrigReduce[1/2 Cos[J π t] Sin[2 νI π t]]
```

$$\text{Out[137]} = \frac{1}{4} (-\sin[J \pi t - 2\nu_I \pi t] + \sin[J \pi t + 2\nu_I \pi t])$$

For  $S_x$ :

```
In[138]:= TrigReduce[1/2 Cos[J π t] Sin[2 νS π t]]
```

$$\text{Out[138]} = \frac{1}{4} (-\sin[J \pi t - 2\nu_S \pi t] + \sin[J \pi t + 2\nu_S \pi t])$$

Each spin gives rise to two frequencies, separated by the coupling constant  $J$ , even though there is only a single wavefunction.

## ■ Evolution of correlations

```
In[139]:= psiA
```

$$\text{Out[139]} = \left\{ \frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}}, 0, 0 \right\}$$

In[140]:= **psiTime[psiA, t]**

$$\text{Out[140]} = \left\{ \frac{e^{i \left( -\frac{J}{2} + \text{nuI} + \text{nuS} \right) \pi t}}{\sqrt{2}}, \frac{i e^{i \left( \frac{J}{2} + \text{nuI} - \text{nuS} \right) \pi t}}{\sqrt{2}}, 0, 0 \right\}$$

In[141]:= **allCorPsi[psiTime[psiA, t]]**

$$\langle \text{IxSx} \rangle = 0 \quad \langle \text{IxSy} \rangle = 0 \quad \langle \text{IxSz} \rangle = 0$$

$$\langle \text{IySx} \rangle = 0 \quad \langle \text{IySy} \rangle = 0 \quad \langle \text{IySz} \rangle = 0$$

$$\langle \text{IzSx} \rangle = -\frac{1}{4} \sin[(J - 2 \text{nuS}) \pi t] \quad \langle \text{IzSy} \rangle = \frac{1}{4} \cos[(J - 2 \text{nuS}) \pi t] \quad \langle \text{IzSz} \rangle = 0$$

To simplify the expressions for the correlations that evolve from psiC, nuI and nuS are both set to 0.

In[142]:= **allMagPsi[psiTime[psiC, t] /. {nuI -> 0, nuS -> 0}]**

$$\langle \text{Ix} \rangle = 0 \quad \langle \text{Sx} \rangle = 0$$

$$\langle \text{Iy} \rangle = \frac{1}{2} \cos[J \pi t] \quad \langle \text{Sy} \rangle = \frac{1}{2} \cos[J \pi t]$$

$$\langle \text{Iz} \rangle = 0 \quad \langle \text{Sz} \rangle = 0$$

In[143]:= **allCorPsi[psiTime[psiC, t] /. {nuI -> 0, nuS -> 0}]**

$$\langle \text{IxSx} \rangle = 0 \quad \langle \text{IxSy} \rangle = 0 \quad \langle \text{IxSz} \rangle = -\frac{1}{4} \sin[J \pi t]$$

$$\langle \text{IySx} \rangle = 0 \quad \langle \text{IySy} \rangle = \frac{1}{4} \quad \langle \text{IySz} \rangle = 0$$

$$\langle \text{IzSx} \rangle = -\frac{1}{4} \sin[J \pi t] \quad \langle \text{IzSy} \rangle = 0 \quad \langle \text{IzSz} \rangle = 0$$

Remove the restriction that nuI=0 and nuS=0

In[144]:= **allMagPsi[psiTime[psiC, t]]**

$$\langle \text{Ix} \rangle = \frac{1}{2} \cos[J \pi t] \sin[2 \text{nuI} \pi t] \quad \langle \text{Sx} \rangle = \frac{1}{2} \cos[J \pi t] \sin[2 \text{nuS} \pi t]$$

$$\langle \text{Iy} \rangle = \frac{1}{4} (\cos[(J - 2 \text{nuI}) \pi t] + \cos[(J + 2 \text{nuI}) \pi t])$$

$$\langle \text{Sy} \rangle = \frac{1}{4} (\cos[(J - 2 \text{nuS}) \pi t] + \cos[(J + 2 \text{nuS}) \pi t])$$

$$\langle \text{Iz} \rangle = 0 \quad \langle \text{Sz} \rangle = 0$$

In[145]:= **allCorPsi[psiTime[psiC, t]]**

$$\begin{aligned}
\langle I_{xSx} \rangle &= \frac{1}{4} \sin[2 \nu I \pi t] \sin[2 \nu S \pi t] & \langle I_{xSy} \rangle &= \frac{1}{8} (\sin[2 (\nu I - \nu S) \pi t] + \sin[2 (\nu I + \nu S) \pi t]) \\
\langle I_{xSz} \rangle &= \frac{1}{8} (-\sin[(J - 2 \nu I) \pi t] - \sin[(J + 2 \nu I) \pi t]) \\
\langle I_{ySx} \rangle &= \frac{1}{8} (-\sin[2 (\nu I - \nu S) \pi t] + \sin[2 (\nu I + \nu S) \pi t]) & \langle I_{ySy} \rangle &= \\
\frac{1}{8} (\cos[2 (\nu I - \nu S) \pi t] + \cos[2 (\nu I + \nu S) \pi t]) & \langle I_{ySz} \rangle &= \frac{1}{4} \sin[J \pi t] \sin[2 \nu I \pi t] \\
\langle I_{zSx} \rangle &= \frac{1}{8} (-\sin[(J - 2 \nu S) \pi t] - \sin[(J + 2 \nu S) \pi t]) \\
\langle I_{zSy} \rangle &= \frac{1}{4} \sin[J \pi t] \sin[2 \nu S \pi t] & \langle I_{zSz} \rangle &= 0
\end{aligned}$$

The evolution of the  $I_{xSz}$ ,  $I_{ySz}$ ,  $I_{zSx}$  and  $I_{zSy}$  correlations are accounted for by the complementary evolution of the observable transverse magnetization components.

For each of the transverse correlations ( $I_{xSx}$ ,  $I_{xSy}$ ,  $I_{ySx}$  and  $I_{ySy}$ ), the average value can be represented as the product of the projections of two precessing vectors onto the corresponding axes. In some cases, though, the expressions returned by Mathematica must be re-written:

For  $I_{xSx}$

$$\text{In[146]:= } \langle I_{xSx} \rangle = \frac{1}{4} \sin[2 \nu I \pi t] \sin[2 \nu S \pi t]$$

$$\text{Out[146]= } \frac{1}{4} \langle I_{xSx} \rangle = \sin[2 \nu I \pi t] \sin[2 \nu S \pi t]$$

For  $I_{xSy}$

$$\text{In[147]:= } \langle I_{xSy} \rangle = \frac{1}{8} (\sin[2 (\nu I - \nu S) \pi t] + \sin[2 (\nu I + \nu S) \pi t])$$

$$\text{Out[147]= } \frac{1}{8} \langle I_{xSy} \rangle = (\sin[2 (\nu I - \nu S) \pi t] + \sin[2 (\nu I + \nu S) \pi t])$$

This can be rearranged using trigonometric identities

$$\text{In[148]:= } \text{TrigFactor} \left[ \frac{1}{8} (\sin[2 (\nu I - \nu S) \pi t] + \sin[2 (\nu I + \nu S) \pi t]) \right]$$

$$\text{Out[148]= } \frac{1}{4} \cos[(\nu I - \nu S) \pi t - (\nu I + \nu S) \pi t] \sin[(\nu I - \nu S) \pi t + (\nu I + \nu S) \pi t]$$

Simplifying the arguments of the cosine and sine functions

$$\text{In[149]:= } \frac{1}{4} \cos[2 \nu S \pi t] \sin[2 \nu I \pi t]$$

$$\text{Out[149]= } \frac{1}{4} \cos[2 \nu S \pi t] \sin[2 \nu I \pi t]$$

For  $I_{ySx}$ , simplify as above



$$\text{In}[150]:= \text{"<IySx> = " } \frac{1}{8} (-\text{Sin}[2 (\text{nuI} - \text{nuS}) \pi t] + \text{Sin}[2 (\text{nuI} + \text{nuS}) \pi t])$$

$$\text{Out}[150]= \frac{1}{8} \text{<IySx> = } (-\text{Sin}[2 (\text{nuI} - \text{nuS}) \pi t] + \text{Sin}[2 (\text{nuI} + \text{nuS}) \pi t])$$

$$\text{In}[151]:= \text{TrigFactor}\left[\frac{1}{8} (-\text{Sin}[2 (\text{nuI} - \text{nuS}) \pi t] + \text{Sin}[2 (\text{nuI} + \text{nuS}) \pi t])\right]$$

$$\text{Out}[151]= -\frac{1}{4} \text{Cos}[(\text{nuI} - \text{nuS}) \pi t + (\text{nuI} + \text{nuS}) \pi t] \text{Sin}[(\text{nuI} - \text{nuS}) \pi t - (\text{nuI} + \text{nuS}) \pi t]$$

$$\text{In}[152]:= \frac{1}{4} \text{Cos}[2 \text{nuI} \pi t] \text{Sin}[2 \text{nuS} \pi t]$$

$$\text{Out}[152]= \frac{1}{4} \text{Cos}[2 \text{nuI} \pi t] \text{Sin}[2 \text{nuS} \pi t]$$

For lySy

$$\text{In}[153]:= \text{"<IySy> = " } \frac{1}{8} (\text{Cos}[2 (\text{nuI} - \text{nuS}) \pi t] + \text{Cos}[2 (\text{nuI} + \text{nuS}) \pi t])$$

$$\text{Out}[153]= \frac{1}{8} \text{<IySy> = } (\text{Cos}[2 (\text{nuI} - \text{nuS}) \pi t] + \text{Cos}[2 (\text{nuI} + \text{nuS}) \pi t])$$

$$\text{In}[154]:= \text{TrigFactor}\left[\frac{1}{8} (\text{Cos}[2 (\text{nuI} - \text{nuS}) \pi t] + \text{Cos}[2 (\text{nuI} + \text{nuS}) \pi t])\right]$$

$$\text{Out}[154]= \frac{1}{4} \text{Cos}[(\text{nuI} - \text{nuS}) \pi t - (\text{nuI} + \text{nuS}) \pi t] \text{Cos}[(\text{nuI} - \text{nuS}) \pi t + (\text{nuI} + \text{nuS}) \pi t]$$

$$\text{In}[155]:= \frac{1}{4} \text{Cos}[2 \text{nuI} \pi t] \text{Cos}[2 \text{nuS} \pi t]$$

$$\text{Out}[155]= \frac{1}{4} \text{Cos}[2 \text{nuI} \pi t] \text{Cos}[2 \text{nuS} \pi t]$$

Each of the expressions for time evolution of correlations can also be written as sums of trigonometric functions  
For lxSx

$$\text{In}[156]:= \text{"<IxSx> = " } \frac{1}{4} \text{Sin}[2 \text{nuI} \pi t] \text{Sin}[2 \text{nuS} \pi t]$$

$$\text{Out}[156]= \frac{1}{4} \text{<IxSx> = } \text{Sin}[2 \text{nuI} \pi t] \text{Sin}[2 \text{nuS} \pi t]$$

$$\text{In}[157]:= \text{TrigReduce}\left[\frac{1}{4} \text{Sin}[2 \text{nuI} \pi t] \text{Sin}[2 \text{nuS} \pi t]\right]$$

$$\text{Out}[157]= \frac{1}{8} (\text{Cos}[2 \text{nuI} \pi t - 2 \text{nuS} \pi t] - \text{Cos}[2 \text{nuI} \pi t + 2 \text{nuS} \pi t])$$

$$\text{In}[158]:= \frac{1}{8} (\text{Cos}[2 (\text{nuI} - \text{nuS}) \pi t] - \text{Cos}[2 (\text{nuI} + \text{nuS}) \pi t])$$

$$\text{Out}[158]= \frac{1}{8} (\text{Cos}[2 (\text{nuI} - \text{nuS}) \pi t] - \text{Cos}[2 (\text{nuI} + \text{nuS}) \pi t])$$

For IxSy

$$\text{In[159]:= } \langle \mathbf{I_x S_y} \rangle = \frac{1}{8} (\sin[2 (\nu \mathbf{I} - \nu \mathbf{S}) \pi \mathbf{t}] + \sin[2 (\nu \mathbf{I} + \nu \mathbf{S}) \pi \mathbf{t}])$$

$$\text{Out[159]= } \frac{1}{8} \langle \mathbf{I_x S_y} \rangle = (\sin[2 (\nu \mathbf{I} - \nu \mathbf{S}) \pi \mathbf{t}] + \sin[2 (\nu \mathbf{I} + \nu \mathbf{S}) \pi \mathbf{t}])$$

In[160]:= ForIySx

$$\text{Out[160]= } \begin{pmatrix} 0 & 0 & 0 & -\frac{i \text{For}}{4} \\ 0 & 0 & -\frac{i \text{For}}{4} & 0 \\ 0 & \frac{i \text{For}}{4} & 0 & 0 \\ \frac{i \text{For}}{4} & 0 & 0 & 0 \end{pmatrix}$$

$$\text{In[161]:= } \langle \mathbf{I_y S_x} \rangle = \frac{1}{8} (-\sin[2 (\nu \mathbf{I} - \nu \mathbf{S}) \pi \mathbf{t}] + \sin[2 (\nu \mathbf{I} + \nu \mathbf{S}) \pi \mathbf{t}])$$

$$\text{Out[161]= } \frac{1}{8} \langle \mathbf{I_y S_x} \rangle = (-\sin[2 (\nu \mathbf{I} - \nu \mathbf{S}) \pi \mathbf{t}] + \sin[2 (\nu \mathbf{I} + \nu \mathbf{S}) \pi \mathbf{t}])$$

For IySy

$$\text{In[162]:= } \langle \mathbf{I_y S_y} \rangle = \frac{1}{8} (\cos[2 (\nu \mathbf{I} - \nu \mathbf{S}) \pi \mathbf{t}] + \cos[2 (\nu \mathbf{I} + \nu \mathbf{S}) \pi \mathbf{t}])$$

$$\text{Out[162]= } \frac{1}{8} \langle \mathbf{I_y S_y} \rangle = (\cos[2 (\nu \mathbf{I} - \nu \mathbf{S}) \pi \mathbf{t}] + \cos[2 (\nu \mathbf{I} + \nu \mathbf{S}) \pi \mathbf{t}])$$

## Populations of with multiple wavefunctions

### ■ Equilibrium

The relative populations of two states at thermal equilibrium are give by the Boltzmann equation:

$$N_a/N_b = \text{Exp}[-(E_a-E_b)/(k T)]$$

When the absolute value of  $\Delta E \ll k T$ , this can be approximated as:

$$N_a/N_b = 1-(E_a-E_b)/(k T)$$

Making the simplifying assumptions that:

1. The only states present for the coupled two-spin system are  $\psi_{AA}$ ,  $\psi_{AB}$ ,  $\psi_{BA}$  and  $\psi_{BB}$
2. The energy associated with the scalar coupling constant,  $J$ , does not significantly affect the populations

If the energy differences for the two transitions are  $\Delta E_I$  and  $\Delta E_S$ , then the energies of the individual states are written as:

$$E_{aa} = -(\Delta E_I + \Delta E_S)/2$$

$$E_{ab} = -(\Delta E_I - \Delta E_S)/2$$

$$E_{ba} = (\Delta E_I - \Delta E_S)/2$$

$$E_{bb} = (\Delta E_I + \Delta E_S)/2$$

The fraction of molecules in each state is:

$$N/N_t = \text{Exp}[-E/(k T)] / \text{Sum}[\text{Exp}[-E/(k T)]]$$

where the sum in the denominator is over all of the states. For small energies relative to  $k T$

$$N/N_t = (1 - E/(k T)) / \text{Sum}[1 - E/(k T)]$$

$$\text{Sum}[1 - E/(k T)] = (1 + (\Delta E_I + \Delta E_S)/2) + (1 + (\Delta E_I - \Delta E_S)/2) + (1 - (\Delta E_I - \Delta E_S)/2) + (1 - (\Delta E_I + \Delta E_S)/2) = 4$$

$$N_{aa}/N_t = (1 + (\Delta E_I + \Delta E_S)/(2 k T))/4$$

$$N_{ab}/N_t = (1 + (\Delta E_I - \Delta E_S)/(2 k T))/4$$

$$N_{ba}/N_t = (1 + (\Delta E_I - \Delta E_S)/(2 k T))/4$$

$$N_{bb}/N_t = (1 + (\Delta E_I + \Delta E_S)/(2 k T))/4$$

Define population differences as:

$$\Delta P_I = \Delta E_I/(2 k T)$$

$$\Delta P_S = \Delta E_S/(2 k T)$$

Then, the fractional populations are given by:

$$f_{aa} = N_{aa}/N_t = 1/4(1 + \Delta P_I + \Delta P_S)$$

$$f_{ab} = N_{ab}/N_t = 1/4(1 + \Delta P_I - \Delta P_S)$$

$$fba = Nba/Nt = 1/4(1 - \text{deltaPI} + \text{deltaPS})$$

$$fbb = Nbb/Nt = 1/4(1 - \text{deltaPI} - \text{deltaPS})$$

In[163]:= **f**aa = 1 / 4 (1 + deltaPI + deltaPS)

$$\text{Out[163]} = \frac{1}{4} (1 + \text{deltaPI} + \text{deltaPS})$$

In[164]:= **f**ab = 1 / 4 (1 + deltaPI - deltaPS)

$$\text{Out[164]} = \frac{1}{4} (1 + \text{deltaPI} - \text{deltaPS})$$

In[165]:= **f**ba = 1 / 4 (1 - deltaPI + deltaPS)

$$\text{Out[165]} = \frac{1}{4} (1 - \text{deltaPI} + \text{deltaPS})$$

In[166]:= **f**bb = 1 / 4 (1 - deltaPI - deltaPS)

$$\text{Out[166]} = \frac{1}{4} (1 - \text{deltaPI} - \text{deltaPS})$$

In[167]:= **f**aa + **f**ab + **f**ba + **f**bb

$$\begin{aligned} \text{Out[167]} = & \frac{1}{4} (1 - \text{deltaPI} - \text{deltaPS}) + \frac{1}{4} (1 + \text{deltaPI} - \text{deltaPS}) + \\ & \frac{1}{4} (1 - \text{deltaPI} + \text{deltaPS}) + \frac{1}{4} (1 + \text{deltaPI} + \text{deltaPS}) \end{aligned}$$

In[168]:= **Simplify[%]**

$$\text{Out[168]} = 1$$

Calculate the average Iz magnetization at equilibrium:

In[169]:= **f**aa 1 / 2 + **f**ab 1 / 2 - **f**ba 1 / 2 - **f**bb 1 / 2

$$\begin{aligned} \text{Out[169]} = & \frac{1}{8} (-1 + \text{deltaPI} - \text{deltaPS}) + \frac{1}{8} (1 + \text{deltaPI} - \text{deltaPS}) + \\ & \frac{1}{8} (-1 + \text{deltaPI} + \text{deltaPS}) + \frac{1}{8} (1 + \text{deltaPI} + \text{deltaPS}) \end{aligned}$$

In[170]:= **Simplify[%]**

$$\text{Out[170]} = \frac{\text{deltaPI}}{2}$$

Average Sz magnetization at equilibrium:

In[171]:= **f**aa 1 / 2 - **f**ab 1 / 2 + **f**ba 1 / 2 - **f**bb 1 / 2

$$\begin{aligned} \text{Out[171]} = & \frac{1}{8} (-1 - \text{deltaPI} + \text{deltaPS}) + \frac{1}{8} (1 - \text{deltaPI} + \text{deltaPS}) + \\ & \frac{1}{8} (-1 + \text{deltaPI} + \text{deltaPS}) + \frac{1}{8} (1 + \text{deltaPI} + \text{deltaPS}) \end{aligned}$$

In[172]:= **Simplify[%]**

$$\text{Out[172]} = \frac{\text{deltaPS}}{2}$$

Average product IzSz

In[173]:= **faa 1 / 4 - fab 1 / 4 - fba 1 / 4 + fbb 1 / 4**

$$\begin{aligned} \text{Out[173]} = & \frac{1}{16} (1 - \text{deltaPI} - \text{deltaPS}) + \frac{1}{16} (-1 + \text{deltaPI} - \text{deltaPS}) + \\ & \frac{1}{16} (-1 - \text{deltaPI} + \text{deltaPS}) + \frac{1}{16} (1 + \text{deltaPI} + \text{deltaPS}) \end{aligned}$$

In[174]:= **Simplify[%]**

Out[174]= 0

Average magnetization components and products following a pi/2x pulse to the S-spin. The symbols faa, fab, fba, fbb are used to represent the populations that began in the corresponding states but have now been changed by the pulse.

In[175]:= **allMagPsi[psiPi2Sx[psiAA]]**

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = \frac{1}{2}$$

$$\langle I_z \rangle = \frac{1}{2} \quad \langle S_z \rangle = 0$$

In[176]:= **allMagPsi[psiPi2Sx[psiAB]]**

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = -\frac{1}{2}$$

$$\langle I_z \rangle = \frac{1}{2} \quad \langle S_z \rangle = 0$$

In[177]:= **allMagPsi[psiPi2Sx[psiBA]]**

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = \frac{1}{2}$$

$$\langle I_z \rangle = -\frac{1}{2} \quad \langle S_z \rangle = 0$$

In[178]:= **allMagPsi[psiPi2Sx[psiBB]]**

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = -\frac{1}{2}$$

$$\langle I_z \rangle = -\frac{1}{2} \quad \langle S_z \rangle = 0$$

The average Sy magnetization

```
In[179]:= faa 1 / 2 - fab 1 / 2 + fba 1 / 2 - fbb 1 / 2
```

$$\text{Out[179]} = \frac{1}{8} (-1 - \text{deltaPI} + \text{deltaPS}) + \frac{1}{8} (1 - \text{deltaPI} + \text{deltaPS}) + \frac{1}{8} (-1 + \text{deltaPI} + \text{deltaPS}) + \frac{1}{8} (1 + \text{deltaPI} + \text{deltaPS})$$

```
In[180]:= Simplify[%]
```

$$\text{Out[180]} = \frac{\text{deltaPS}}{2}$$

Correlations following the pi/2 pulse to the S-spins

```
In[181]:= allCorPsi[psiPi2Sx[psiAA]]
```

$$\begin{aligned} \langle I_x S_x \rangle &= 0 & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\ \langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= 0 & \langle I_y S_z \rangle &= 0 \\ \langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= \frac{1}{4} & \langle I_z S_z \rangle &= 0 \end{aligned}$$

```
In[182]:= allCorPsi[psiPi2Sx[psiAB]]
```

$$\begin{aligned} \langle I_x S_x \rangle &= 0 & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\ \langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= 0 & \langle I_y S_z \rangle &= 0 \\ \langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= -\frac{1}{4} & \langle I_z S_z \rangle &= 0 \end{aligned}$$

```
In[183]:= allCorPsi[psiPi2Sx[psiBA]]
```

$$\begin{aligned} \langle I_x S_x \rangle &= 0 & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\ \langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= 0 & \langle I_y S_z \rangle &= 0 \\ \langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= -\frac{1}{4} & \langle I_z S_z \rangle &= 0 \end{aligned}$$

```
In[184]:= allCorPsi[psiPi2Sx[psiBB]]
```

$$\begin{aligned} \langle I_x S_x \rangle &= 0 & \langle I_x S_y \rangle &= 0 & \langle I_x S_z \rangle &= 0 \\ \langle I_y S_x \rangle &= 0 & \langle I_y S_y \rangle &= 0 & \langle I_y S_z \rangle &= 0 \\ \langle I_z S_x \rangle &= 0 & \langle I_z S_y \rangle &= \frac{1}{4} & \langle I_z S_z \rangle &= 0 \end{aligned}$$

The only non-zero correlation is IzSy.

The average IzSy correlation is calculated as:

```
In[185]:= faa 1 / 4 - fab 1 / 4 - fba 1 / 4 + fbb 1 / 4
```

$$\text{Out[185]} = \frac{1}{16} (1 - \text{deltaPI} - \text{deltaPS}) + \frac{1}{16} (-1 + \text{deltaPI} - \text{deltaPS}) + \frac{1}{16} (-1 - \text{deltaPI} + \text{deltaPS}) + \frac{1}{16} (1 + \text{deltaPI} + \text{deltaPS})$$

```
In[186]:= Simplify[%]
```

```
Out[186]= 0
```

Time evolution following the  $\pi/2x$  pulse to the S spin:  
For the population that begins in the  $\psi_{iAA}$  state:

```
In[187]:= allMagPsi[psiTime[psiPi2Sx[psiAA], t]]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = -\frac{1}{2} \sin[(J - 2\nu_S) \pi t]$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = \frac{1}{2} \cos[(J - 2\nu_S) \pi t]$$

$$\langle I_z \rangle = \frac{1}{2} \quad \langle S_z \rangle = 0$$

For the population that begins in the  $\psi_{iAB}$  state:

```
In[188]:= allMagPsi[psiTime[psiPi2Sx[psiAB], t]]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = \frac{1}{2} \sin[(J - 2\nu_S) \pi t]$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = -\frac{1}{2} \cos[(J - 2\nu_S) \pi t]$$

$$\langle I_z \rangle = \frac{1}{2} \quad \langle S_z \rangle = 0$$

For the population that begins in the  $\psi_{iBA}$  state:

```
In[189]:= allMagPsi[psiTime[psiPi2Sx[psiBA], t]]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = \frac{1}{2} \sin[(J + 2\nu_S) \pi t]$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = \frac{1}{2} \cos[(J + 2\nu_S) \pi t]$$

$$\langle I_z \rangle = -\frac{1}{2} \quad \langle S_z \rangle = 0$$

For the population that begins in the  $\psi_{iBB}$  state:

```
In[190]:= allMagPsi[psiTime[psiPi2Sx[psiBB], t]]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = -\frac{1}{2} \sin[(J + 2 \text{nuS}) \pi t]$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = -\frac{1}{2} \cos[(J + 2 \text{nuS}) \pi t]$$

$$\langle I_z \rangle = -\frac{1}{2} \quad \langle S_z \rangle = 0$$

The weighted average for Sy

$$\text{In[191]:= } \text{faa} \left( \frac{1}{2} \cos[(J - 2 \text{nuS}) \pi t] \right) + \text{fab} \left( -\frac{1}{2} \cos[(J - 2 \text{nuS}) \pi t] \right) + \\ \text{fba} \left( \frac{1}{2} \cos[(J + 2 \text{nuS}) \pi t] \right) + \text{fbb} \left( -\frac{1}{2} \cos[(J + 2 \text{nuS}) \pi t] \right)$$

$$\text{Out[191]= } -\frac{1}{8} (1 + \text{deltaPI} - \text{deltaPS}) \cos[(J - 2 \text{nuS}) \pi t] + \frac{1}{8} (1 + \text{deltaPI} + \text{deltaPS}) \cos[(J - 2 \text{nuS}) \pi t] - \\ \frac{1}{8} (1 - \text{deltaPI} - \text{deltaPS}) \cos[(J + 2 \text{nuS}) \pi t] + \frac{1}{8} (1 - \text{deltaPI} + \text{deltaPS}) \cos[(J + 2 \text{nuS}) \pi t]$$

In[192]:= **Simplify[%]**

$$\text{Out[192]= } \frac{1}{4} \text{deltaPS} (\cos[(J - 2 \text{nuS}) \pi t] + \cos[(J + 2 \text{nuS}) \pi t])$$

The weighted average for Sx:

$$\text{In[193]:= } \text{faa} \left( -\frac{1}{2} \sin[(J - 2 \text{nuS}) \pi t] \right) + \text{fab} \left( \frac{1}{2} \sin[(J - 2 \text{nuS}) \pi t] \right) + \\ \text{fba} \left( \frac{1}{2} \sin[(J + 2 \text{nuS}) \pi t] \right) + \text{fbb} \left( -\frac{1}{2} \sin[(J + 2 \text{nuS}) \pi t] \right)$$

$$\text{Out[193]= } \frac{1}{8} (1 + \text{deltaPI} - \text{deltaPS}) \sin[(J - 2 \text{nuS}) \pi t] - \frac{1}{8} (1 + \text{deltaPI} + \text{deltaPS}) \sin[(J - 2 \text{nuS}) \pi t] - \\ \frac{1}{8} (1 - \text{deltaPI} - \text{deltaPS}) \sin[(J + 2 \text{nuS}) \pi t] + \frac{1}{8} (1 - \text{deltaPI} + \text{deltaPS}) \sin[(J + 2 \text{nuS}) \pi t]$$

In[194]:= **Simplify[%]**

$$\text{Out[194]= } \frac{1}{2} \text{deltaPS} \cos[J \pi t] \sin[2 \text{nuS} \pi t]$$

In[195]:= **TrigReduce[%]**

$$\text{Out[195]= } \frac{1}{4} (-\text{deltaPS} \sin[J \pi t - 2 \text{nuS} \pi t] + \text{deltaPS} \sin[J \pi t + 2 \text{nuS} \pi t])$$

In[196]:= **Factor[%]**

$$\text{Out[196]= } -\frac{1}{4} \text{deltaPS} (\sin[J \pi t - 2 \text{nuS} \pi t] - \sin[J \pi t + 2 \text{nuS} \pi t])$$

The correlations also evolve with time:

In[197]:= **allCorPsi[psiTime[psiPi2Sx[psiAA], t]]**



$$\begin{aligned}
\langle IxSx \rangle &= 0 & \langle IxSy \rangle &= 0 & \langle IxSz \rangle &= 0 \\
\langle IySx \rangle &= 0 & \langle IySy \rangle &= 0 & \langle IySz \rangle &= 0 \\
\langle IzSx \rangle &= -\frac{1}{4} \sin[(J - 2 \text{nuS}) \pi t] & \langle IzSy \rangle &= \frac{1}{4} \cos[(J - 2 \text{nuS}) \pi t] & \langle IzSz \rangle &= 0
\end{aligned}$$

In[198]:= **allCorPsi**[psiTime[psiPi2Sx[psiAB], t]]

$$\begin{aligned}
\langle IxSx \rangle &= 0 & \langle IxSy \rangle &= 0 & \langle IxSz \rangle &= 0 \\
\langle IySx \rangle &= 0 & \langle IySy \rangle &= 0 & \langle IySz \rangle &= 0 \\
\langle IzSx \rangle &= \frac{1}{4} \sin[(J - 2 \text{nuS}) \pi t] & \langle IzSy \rangle &= -\frac{1}{4} \cos[(J - 2 \text{nuS}) \pi t] & \langle IzSz \rangle &= 0
\end{aligned}$$

In[199]:= **allCorPsi**[psiTime[psiPi2Sx[psiBA], t]]

$$\begin{aligned}
\langle IxSx \rangle &= 0 & \langle IxSy \rangle &= 0 & \langle IxSz \rangle &= 0 \\
\langle IySx \rangle &= 0 & \langle IySy \rangle &= 0 & \langle IySz \rangle &= 0 \\
\langle IzSx \rangle &= -\frac{1}{4} \sin[(J + 2 \text{nuS}) \pi t] & \langle IzSy \rangle &= -\frac{1}{4} \cos[(J + 2 \text{nuS}) \pi t] & \langle IzSz \rangle &= 0
\end{aligned}$$

In[200]:= **allCorPsi**[psiTime[psiPi2Sx[psiBB], t]]

$$\begin{aligned}
\langle IxSx \rangle &= 0 & \langle IxSy \rangle &= 0 & \langle IxSz \rangle &= 0 \\
\langle IySx \rangle &= 0 & \langle IySy \rangle &= 0 & \langle IySz \rangle &= 0 \\
\langle IzSx \rangle &= \frac{1}{4} \sin[(J + 2 \text{nuS}) \pi t] & \langle IzSy \rangle &= \frac{1}{4} \cos[(J + 2 \text{nuS}) \pi t] & \langle IzSz \rangle &= 0
\end{aligned}$$

Weighted average of IzSy :

$$\begin{aligned}
\text{In[201]:= } & \text{faa} \left( \frac{1}{4} \cos[(J - 2 \text{nuS}) \pi t] \right) + \text{fab} \left( -\frac{1}{4} \cos[(J - 2 \text{nuS}) \pi t] \right) + \\
& \text{fba} \left( -\frac{1}{4} \cos[(J + 2 \text{nuS}) \pi t] \right) + \text{fbb} \left( \frac{1}{4} \cos[(J + 2 \text{nuS}) \pi t] \right) \\
\text{Out[201]= } & -\frac{1}{16} (1 + \text{deltaPI} - \text{deltaPS}) \cos[(J - 2 \text{nuS}) \pi t] + \frac{1}{16} (1 + \text{deltaPI} + \text{deltaPS}) \cos[(J - 2 \text{nuS}) \pi t] + \\
& \frac{1}{16} (1 - \text{deltaPI} - \text{deltaPS}) \cos[(J + 2 \text{nuS}) \pi t] - \frac{1}{16} (1 - \text{deltaPI} + \text{deltaPS}) \cos[(J + 2 \text{nuS}) \pi t]
\end{aligned}$$

In[202]:= **Simplify**[%]

$$\text{Out[202]= } \frac{1}{4} \text{deltaPS} \sin[J \pi t] \sin[2 \text{nuS} \pi t]$$

In[203]:= **TrigReduce**[%]

$$\text{Out[203]= } \frac{1}{8} (\text{deltaPS} \cos[J \pi t - 2 \text{nuS} \pi t] - \text{deltaPS} \cos[J \pi t + 2 \text{nuS} \pi t])$$

In[204]:= **Factor**[%]

$$\text{Out[204]= } \frac{1}{8} \text{deltaPS} (\cos[J \pi t - 2 \text{nuS} \pi t] - \cos[J \pi t + 2 \text{nuS} \pi t])$$

Weighted average of IzSx:

```
In[205]:= faa  $\left(-\frac{1}{4} \sin[(J - 2 \text{nuS}) \pi t]\right) + fab \left(\frac{1}{4} \sin[(J - 2 \text{nuS}) \pi t]\right) +$   

         fba  $\left(-\frac{1}{4} \sin[(J + 2 \text{nuS}) \pi t]\right) + fbb \left(\frac{1}{4} \sin[(J + 2 \text{nuS}) \pi t]\right)$   

Out[205]=  $\frac{1}{16} (1 + \text{deltaPI} - \text{deltaPS}) \sin[(J - 2 \text{nuS}) \pi t] - \frac{1}{16} (1 + \text{deltaPI} + \text{deltaPS}) \sin[(J - 2 \text{nuS}) \pi t] +$   

 $\frac{1}{16} (1 - \text{deltaPI} - \text{deltaPS}) \sin[(J + 2 \text{nuS}) \pi t] - \frac{1}{16} (1 - \text{deltaPI} + \text{deltaPS}) \sin[(J + 2 \text{nuS}) \pi t]$ 
```

```
In[206]:= Simplify[%]
```

```
Out[206]=  $-\frac{1}{8} \text{deltaPS} (\sin[(J - 2 \text{nuS}) \pi t] + \sin[(J + 2 \text{nuS}) \pi t])$ 
```

setting nuS to zero for Sy

```
In[207]:=  $\frac{1}{4} \text{deltaPS} (\cos[(J - 2 \text{nuS}) \pi t] + \cos[(J + 2 \text{nuS}) \pi t]) /. \text{nuS} \rightarrow 0$ 
```

```
Out[207]=  $\frac{1}{2} \text{deltaPS} \cos[J \pi t]$ 
```

setting nuS to zero for IzSx:

```
In[208]:=  $-\frac{1}{8} \text{deltaPS} (\sin[(J - 2 \text{nuS}) \pi t] + \sin[(J + 2 \text{nuS}) \pi t]) /. \text{nuS} \rightarrow 0$ 
```

```
Out[208]=  $-\frac{1}{4} \text{deltaPS} \sin[J \pi t]$ 
```

Setting nuS to zero for Sx

```
In[209]:=  $-\frac{1}{4} \text{deltaPS} (\sin[J \pi t - 2 \text{nuS} \pi t] - \sin[J \pi t + 2 \text{nuS} \pi t]) /. \text{nuS} \rightarrow 0$ 
```

```
Out[209]= 0
```

Setting nuS to zero for IzSy

```
In[210]:=  $\frac{1}{8} \text{deltaPS} (\cos[J \pi t - 2 \text{nuS} \pi t] - \cos[J \pi t + 2 \text{nuS} \pi t]) /. \text{nuS} \rightarrow 0$ 
```

```
Out[210]= 0
```

---

## Density matrix for a population of single spins

```
In[211]:= Remove["NMR`twoSpinLib`*"]
```

```
<< NMR`oneSpinLib`
```

The general form of the density matrix is:

```
In[213]:= rhoGen
```

```
Out[213]=  $\begin{pmatrix} \text{ca Conjugate[ca]} & \text{ca Conjugate[cb]} \\ \text{cb Conjugate[ca]} & \text{cb Conjugate[cb]} \end{pmatrix}$ 
```

### The three operator matrices:

In[214]:= **Ix**

$$\text{Out[214]} = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$$

In[215]:= **Iy**

$$\text{Out[215]} = \begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix}$$

In[216]:= **Iz**

$$\text{Out[216]} = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

### ■ General expressions for calculating the average magnetization components:

For Ix:

In[217]:= **Tr[Ix.rhoGen]**

$$\text{Out[217]} = \frac{1}{2} \text{cb Conjugate[ca]} + \frac{1}{2} \text{ca Conjugate[cb]}$$

For Iy:

In[218]:= **Tr[Iy.rhoGen]**

$$\text{Out[218]} = -\frac{1}{2} i \text{cb Conjugate[ca]} + \frac{1}{2} i \text{ca Conjugate[cb]}$$

For Iz:

In[219]:= **Tr[Iz.rhoGen]**

$$\text{Out[219]} = \frac{1}{2} \text{ca Conjugate[ca]} - \frac{1}{2} \text{cb Conjugate[cb]}$$

The oneSpinLib package includes a function to calculate all of the magnetization components from the density matrix:

In[220]:= **allMagRho[rhoGen]**

$$\langle I_x \rangle = \frac{1}{2} (\text{cb Conjugate[ca]} + \text{ca Conjugate[cb]})$$

$$\langle I_y \rangle = -\frac{1}{2} i (\text{cb Conjugate[ca]} - \text{ca Conjugate[cb]})$$

$$\langle I_z \rangle = \frac{1}{2} (\text{ca Conjugate[ca]} - \text{cb Conjugate[cb]})$$

### The equilibrium density matrix:

In[221]:= **rhoEq**

$$\text{Out[221]} = \begin{pmatrix} \frac{\text{deltaP}}{2} & 0 \\ 0 & -\frac{\text{deltaP}}{2} \end{pmatrix}$$

The equilibrium magnetization components:

In[222]:= **allMagRho[rhoEq]**

<Ix> = 0

<Iy> = 0

<Iz> =  $\frac{\text{deltaP}}{2}$

## ■ The rotation matrices:

For rotation about the x-axis

In[223]:= **Rx[a]**

$$\text{Out[223]} = \begin{pmatrix} \cos\left[\frac{a}{2}\right] & i \sin\left[\frac{a}{2}\right] \\ i \sin\left[\frac{a}{2}\right] & \cos\left[\frac{a}{2}\right] \end{pmatrix}$$

In[224]:= **Rinvx[a]**

$$\text{Out[224]} = \begin{pmatrix} \frac{\cos\left[\frac{a}{2}\right]}{\cos^2\left[\frac{a}{2}\right] + \sin^2\left[\frac{a}{2}\right]} & -\frac{i \sin\left[\frac{a}{2}\right]}{\cos^2\left[\frac{a}{2}\right] + \sin^2\left[\frac{a}{2}\right]} \\ -\frac{i \sin\left[\frac{a}{2}\right]}{\cos^2\left[\frac{a}{2}\right] + \sin^2\left[\frac{a}{2}\right]} & \frac{\cos\left[\frac{a}{2}\right]}{\cos^2\left[\frac{a}{2}\right] + \sin^2\left[\frac{a}{2}\right]} \end{pmatrix}$$

In[225]:= **Simplify[%]**

$$\text{Out[225]} = \begin{pmatrix} \cos\left[\frac{a}{2}\right] & -i \sin\left[\frac{a}{2}\right] \\ -i \sin\left[\frac{a}{2}\right] & \cos\left[\frac{a}{2}\right] \end{pmatrix}$$

In[226]:= **Rx[Pi / 2]**

$$\text{Out[226]} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

In[227]:=

In[228]:= **Rinvx[Pi / 2]**

$$\text{Out[228]} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

For rotation about the y-axis:

In[229]:= **Ry[a]**

$$\text{Out[229]} = \begin{pmatrix} \cos\left[\frac{a}{2}\right] & \sin\left[\frac{a}{2}\right] \\ -\sin\left[\frac{a}{2}\right] & \cos\left[\frac{a}{2}\right] \end{pmatrix}$$

In[230]:= **Rinvy[a]**

$$\text{Out[230]} = \begin{pmatrix} \frac{\cos\left[\frac{a}{2}\right]}{\cos^2\left[\frac{a}{2}\right] + \sin^2\left[\frac{a}{2}\right]} & -\frac{\sin\left[\frac{a}{2}\right]}{\cos^2\left[\frac{a}{2}\right] + \sin^2\left[\frac{a}{2}\right]} \\ \frac{\sin\left[\frac{a}{2}\right]}{\cos^2\left[\frac{a}{2}\right] + \sin^2\left[\frac{a}{2}\right]} & \frac{\cos\left[\frac{a}{2}\right]}{\cos^2\left[\frac{a}{2}\right] + \sin^2\left[\frac{a}{2}\right]} \end{pmatrix}$$

In[231]:= **Simplify[%]**

$$\text{Out[231]} = \begin{pmatrix} \cos\left[\frac{a}{2}\right] & -\sin\left[\frac{a}{2}\right] \\ \sin\left[\frac{a}{2}\right] & \cos\left[\frac{a}{2}\right] \end{pmatrix}$$

## ■ The effect of a $\pi/2$ x-pulse applied to the equilibrium population

In[232]:= **Rx[Pi / 2].rhoEq.Rinvx[Pi / 2]**

$$\text{Out[232]} = \begin{pmatrix} 0 & -\frac{i \text{deltaP}}{2} \\ \frac{i \text{deltaP}}{2} & 0 \end{pmatrix}$$

In[233]:= **allMagRho[%]**

<Ix> = 0

<Iy> =  $\frac{\text{deltaP}}{2}$

<Iz> = 0

## ■ Orthogonality of the operator matrices:

In[234]:= **Ix.Iy**

$$\text{Out[234]} = \begin{pmatrix} \frac{i}{4} & 0 \\ 0 & -\frac{i}{4} \end{pmatrix}$$

In[235]:= **Tr[%]**

Out[235]= 0

In[236]:= **Ix.Iz**

$$\text{Out[236]} = \begin{pmatrix} 0 & -\frac{1}{4} \\ \frac{1}{4} & 0 \end{pmatrix}$$

In[237]:= **Tr[%]**

Out[237]= 0

In[238]:= **Iy.Iz**

$$\text{Out[238]} = \begin{pmatrix} 0 & \frac{i}{4} \\ \frac{i}{4} & 0 \end{pmatrix}$$

In[239]:= **Tr[%]**

Out[239]= 0

## ■ Self-products of the operator matrices

In[240]:= **Ix.Ix**

$$\text{Out[240]} = \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix}$$

In[241]:= **Tr[%]**

$$\text{Out[241]} = \frac{1}{2}$$

In[242]:= **Iy.Iy**

$$\text{Out[242]} = \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix}$$

In[243]:= **Tr[%]**

$$\text{Out[243]} = \frac{1}{2}$$

In[244]:= **Iz.Iz**

$$\text{Out[244]} = \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix}$$

In[245]:= **Tr[%]**

$$\text{Out[245]} = \frac{1}{2}$$

## ■ Time evolution of the density matrix

The change in the density matrix during a time period in a constant magnetic field is calculated using the Hamiltonian matrix and its inverse:

In[246]:= **H[t, nu]**

$$\text{Out[246]} = \begin{pmatrix} e^{i \text{nu } \pi \text{ t}} & 0 \\ 0 & e^{-i \text{nu } \pi \text{ t}} \end{pmatrix}$$

In[247]:= **Hinv[t, nu]**

$$\text{Out[247]} = \begin{pmatrix} e^{-i \text{nu } \pi \text{ t}} & 0 \\ 0 & e^{i \text{nu } \pi \text{ t}} \end{pmatrix}$$

For the general form of the density matrix:

```
In[248]:= H[t, nu].rhoGen.Hinv[t, nu]
```

$$\text{Out[248]=} \begin{pmatrix} \text{ca Conjugate[ca]} & \text{ca e}^{2 i \text{nu } \pi t} \text{Conjugate[cb]} \\ \text{cb e}^{-2 i \text{nu } \pi t} \text{Conjugate[ca]} & \text{cb Conjugate[cb]} \end{pmatrix}$$

Applying a  $\pi/2$ -x pulse to the equilibrium matrix, followed by a time evolution period:

```
In[249]:= Rx[Pi / 2].rhoEq.Rinvx[Pi / 2]
```

$$\text{Out[249]=} \begin{pmatrix} 0 & -\frac{i \text{deltaP}}{2} \\ \frac{i \text{deltaP}}{2} & 0 \end{pmatrix}$$

```
In[250]:= H[t, nu].%.Hinv[t, nu]
```

$$\text{Out[250]=} \begin{pmatrix} 0 & -\frac{1}{2} i \text{deltaP e}^{2 i \text{nu } \pi t} \\ \frac{1}{2} i \text{deltaP e}^{-2 i \text{nu } \pi t} & 0 \end{pmatrix}$$

Converting this to trigonometric form:

```
In[251]:= ExpToTrig[%]
```

$$\text{Out[251]=} \begin{pmatrix} 0 & -\frac{1}{2} i \text{deltaP Cos}[2 \text{nu } \pi t] + \frac{1}{2} \text{deltaP Sin}[2 \text{nu } \pi t] \\ \frac{1}{2} i \text{deltaP Cos}[2 \text{nu } \pi t] + \frac{1}{2} \text{deltaP Sin}[2 \text{nu } \pi t] & 0 \end{pmatrix}$$

This is equivalent to  $\text{deltaP}(\text{Cos}[2 \text{nu } \pi t] \text{Iy} + \text{Sin}[2 \text{nu } \pi t] \text{Ix})$

```
In[252]:= deltaP (Cos[2 nu pi t] Iy + Sin[2 nu pi t] Ix)
```

$$\text{Out[252]=} \begin{pmatrix} 0 & \text{deltaP} \left( -\frac{1}{2} i \text{Cos}[2 \text{nu } \pi t] + \frac{1}{2} \text{Sin}[2 \text{nu } \pi t] \right) \\ \text{deltaP} \left( \frac{1}{2} i \text{Cos}[2 \text{nu } \pi t] + \frac{1}{2} \text{Sin}[2 \text{nu } \pi t] \right) & 0 \end{pmatrix}$$

## Density matrix for a population of coupled spins

```
In[253]:= Remove["NMR`oneSpinLib`*"]
```

The general form of the density matrix is:

General form of the density matrix

```
In[255]:= rhoGen
```

$$\text{Out[255]=} \begin{pmatrix} \text{caa Conjugate[caa]} & \text{caa Conjugate[cab]} & \text{caa Conjugate[cba]} & \text{caa Conjugate[cbb]} \\ \text{cab Conjugate[caa]} & \text{cab Conjugate[cab]} & \text{cab Conjugate[cba]} & \text{cab Conjugate[cbb]} \\ \text{cba Conjugate[caa]} & \text{cba Conjugate[cab]} & \text{cba Conjugate[cba]} & \text{cba Conjugate[cbb]} \\ \text{cbb Conjugate[caa]} & \text{cbb Conjugate[cab]} & \text{cbb Conjugate[cba]} & \text{cbb Conjugate[cbb]} \end{pmatrix}$$

Equilibrium density matrix

In[256]:= **rhoEq**

$$\text{Out[256]} = \begin{pmatrix} \frac{\text{deltaPi}}{4} + \frac{\text{deltaPs}}{4} & 0 & 0 & 0 \\ 0 & \frac{\text{deltaPi}}{4} - \frac{\text{deltaPs}}{4} & 0 & 0 \\ 0 & 0 & -\frac{\text{deltaPi}}{4} + \frac{\text{deltaPs}}{4} & 0 \\ 0 & 0 & 0 & -\frac{\text{deltaPi}}{4} - \frac{\text{deltaPs}}{4} \end{pmatrix}$$

Compare with  $(\text{deltaPi}/2) I_z + (\text{deltaPs}/2) S_z$ In[257]:= **(deltaPi / 2) Iz + (deltaPs / 2) Sz**

$$\text{Out[257]} = \begin{pmatrix} \frac{\text{deltaPi}}{4} + \frac{\text{deltaPs}}{4} & 0 & 0 & 0 \\ 0 & \frac{\text{deltaPi}}{4} - \frac{\text{deltaPs}}{4} & 0 & 0 \\ 0 & 0 & -\frac{\text{deltaPi}}{4} + \frac{\text{deltaPs}}{4} & 0 \\ 0 & 0 & 0 & -\frac{\text{deltaPi}}{4} - \frac{\text{deltaPs}}{4} \end{pmatrix}$$

## ■ The rotation matrices :

In[258]:= **RIx[a]**

$$\text{Out[258]} = \begin{pmatrix} \cos\left[\frac{a}{2}\right] & 0 & i \sin\left[\frac{a}{2}\right] & 0 \\ 0 & \cos\left[\frac{a}{2}\right] & 0 & i \sin\left[\frac{a}{2}\right] \\ i \sin\left[\frac{a}{2}\right] & 0 & \cos\left[\frac{a}{2}\right] & 0 \\ 0 & i \sin\left[\frac{a}{2}\right] & 0 & \cos\left[\frac{a}{2}\right] \end{pmatrix}$$

In[259]:= **RIxInv[a]**

$$\text{Out[259]} = \begin{pmatrix} \cos\left[\frac{a}{2}\right] & 0 & -i \sin\left[\frac{a}{2}\right] & 0 \\ 0 & \cos\left[\frac{a}{2}\right] & 0 & -i \sin\left[\frac{a}{2}\right] \\ -i \sin\left[\frac{a}{2}\right] & 0 & \cos\left[\frac{a}{2}\right] & 0 \\ 0 & -i \sin\left[\frac{a}{2}\right] & 0 & \cos\left[\frac{a}{2}\right] \end{pmatrix}$$

In[260]:= **RSx[a]**

$$\text{Out[260]} = \begin{pmatrix} \cos\left[\frac{a}{2}\right] & i \sin\left[\frac{a}{2}\right] & 0 & 0 \\ i \sin\left[\frac{a}{2}\right] & \cos\left[\frac{a}{2}\right] & 0 & 0 \\ 0 & 0 & \cos\left[\frac{a}{2}\right] & i \sin\left[\frac{a}{2}\right] \\ 0 & 0 & i \sin\left[\frac{a}{2}\right] & \cos\left[\frac{a}{2}\right] \end{pmatrix}$$

In[261]:= **RSxInv[a]**

$$\text{Out[261]} = \begin{pmatrix} \cos\left[\frac{a}{2}\right] & -i \sin\left[\frac{a}{2}\right] & 0 & 0 \\ -i \sin\left[\frac{a}{2}\right] & \cos\left[\frac{a}{2}\right] & 0 & 0 \\ 0 & 0 & \cos\left[\frac{a}{2}\right] & -i \sin\left[\frac{a}{2}\right] \\ 0 & 0 & -i \sin\left[\frac{a}{2}\right] & \cos\left[\frac{a}{2}\right] \end{pmatrix}$$

The effects of rotations on the density matrix are calculated in the same fashion as for the 1-spin case. For a  $\pi/2$



pulse to the S-spin applied to the equilibrium state:

```
In[262]:= RIX[Pi / 2].rhoEq.RIXInv[Pi / 2];
```

```
In[263]:= Simplify[%]
```

$$\text{Out[263]} = \begin{pmatrix} \frac{\text{deltaPs}}{4} & 0 & -\frac{i \text{deltaPi}}{4} & 0 \\ 0 & -\frac{\text{deltaPs}}{4} & 0 & -\frac{i \text{deltaPi}}{4} \\ \frac{i \text{deltaPi}}{4} & 0 & \frac{\text{deltaPs}}{4} & 0 \\ 0 & \frac{i \text{deltaPi}}{4} & 0 & -\frac{\text{deltaPs}}{4} \end{pmatrix}$$

There are functions in the twoSpinLib package to calculate all of the magnetization components and correlations from the density matrix:

$$\text{In[264]} := \text{allMagRho} \left[ \begin{pmatrix} \frac{\text{deltaPs}}{4} & 0 & -\frac{i \text{deltaPi}}{4} & 0 \\ 0 & -\frac{\text{deltaPs}}{4} & 0 & -\frac{i \text{deltaPi}}{4} \\ \frac{i \text{deltaPi}}{4} & 0 & \frac{\text{deltaPs}}{4} & 0 \\ 0 & \frac{i \text{deltaPi}}{4} & 0 & -\frac{\text{deltaPs}}{4} \end{pmatrix} \right]$$

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = \frac{\text{deltaPi}}{2} \quad \langle S_y \rangle = 0$$

$$\langle I_z \rangle = 0 \quad \langle S_z \rangle = \frac{\text{deltaPs}}{2}$$

$$\text{In[265]} := \text{allCorRho} \left[ \begin{pmatrix} \frac{\text{deltaPs}}{4} & 0 & -\frac{i \text{deltaPi}}{4} & 0 \\ 0 & -\frac{\text{deltaPs}}{4} & 0 & -\frac{i \text{deltaPi}}{4} \\ \frac{i \text{deltaPi}}{4} & 0 & \frac{\text{deltaPs}}{4} & 0 \\ 0 & \frac{i \text{deltaPi}}{4} & 0 & -\frac{\text{deltaPs}}{4} \end{pmatrix} \right]$$

$$\langle I_x S_x \rangle = 0 \quad \langle I_x S_y \rangle = 0 \quad \langle I_x S_z \rangle = 0$$

$$\langle I_y S_x \rangle = 0 \quad \langle I_y S_y \rangle = 0 \quad \langle I_y S_z \rangle = 0$$

$$\langle I_z S_x \rangle = 0 \quad \langle I_z S_y \rangle = 0 \quad \langle I_z S_z \rangle = 0$$

There are also functions to calculate the effects of pulses, for instance:

```
In[266]:= rhoPi2Ix[rhoEq];
```

```
In[267]:= Simplify[%]
```

$$\text{Out[267]} = \begin{pmatrix} \frac{\text{deltaPs}}{4} & 0 & -\frac{i \text{deltaPi}}{4} & 0 \\ 0 & -\frac{\text{deltaPs}}{4} & 0 & -\frac{i \text{deltaPi}}{4} \\ \frac{i \text{deltaPi}}{4} & 0 & \frac{\text{deltaPs}}{4} & 0 \\ 0 & \frac{i \text{deltaPi}}{4} & 0 & -\frac{\text{deltaPs}}{4} \end{pmatrix}$$

## ■ Time evolution

The Hamiltonian matrix and its inverse are expressed in terms of the Larmor frequencies,  $\text{nuI}$  and  $\text{nuS}$ , and the coupling constant,  $J$ :

In[268]:= **H[t, nuI, nuS, J]**

$$\text{Out[268]} = \begin{pmatrix} e^{i \left( -\frac{J}{2} + \text{nuI} + \text{nuS} \right) \pi t} & 0 & 0 & 0 \\ 0 & e^{i \left( \frac{J}{2} + \text{nuI} - \text{nuS} \right) \pi t} & 0 & 0 \\ 0 & 0 & e^{i \left( \frac{J}{2} - \text{nuI} + \text{nuS} \right) \pi t} & 0 \\ 0 & 0 & 0 & e^{i \left( -\frac{J}{2} - \text{nuI} - \text{nuS} \right) \pi t} \end{pmatrix}$$

In[269]:= **Hinv[t, nuI, nuS, J]**

$$\text{Out[269]} = \begin{pmatrix} e^{-i \left( -\frac{J}{2} + \text{nuI} + \text{nuS} \right) \pi t} & 0 & 0 & 0 \\ 0 & e^{-\frac{1}{2} i (J+2 \text{nuI}-2 \text{nuS}) \pi t} & 0 & 0 \\ 0 & 0 & e^{-\frac{1}{2} i (J-2 \text{nuI}+2 \text{nuS}) \pi t} & 0 \\ 0 & 0 & 0 & e^{\frac{1}{2} i (J+2 (\text{nuI}+\text{nuS})) \pi t} \end{pmatrix}$$

Time evolution of the density matrix, written in its general form, is:

In[270]:= **H[t, nuI, nuS, J].rhoGen.Hinv[t, nuI, nuS, J];**

In[271]:= **Simplify[%]**

$$\text{Out[271]} = \begin{pmatrix} \text{caa Conjugate[caa]} & \text{caa } e^{-i (J-2 \text{nuS}) \pi t} \text{Conjugate[cab]} & \text{caa } e^{-i (J-2 \text{nuI}) \pi t} \text{Conjugate[cba]} \\ \text{cab } e^{i (J-2 \text{nuS}) \pi t} \text{Conjugate[caa]} & \text{cab Conjugate[cab]} & \text{cab } e^{2 i (\text{nuI}-\text{nuS}) \pi t} \text{Conjugate[cb}] \\ \text{cba } e^{i (J-2 \text{nuI}) \pi t} \text{Conjugate[caa]} & \text{cba } e^{-2 i (\text{nuI}-\text{nuS}) \pi t} \text{Conjugate[cab]} & \text{cba Conjugate[cb}] \\ \text{cbb } e^{-2 i (\text{nuI}+\text{nuS}) \pi t} \text{Conjugate[caa]} & \text{cbb } e^{-i (J+2 \text{nuI}) \pi t} \text{Conjugate[cab]} & \text{cbb } e^{-i (J+2 \text{nuS}) \pi t} \text{Conjugate[cb}] \end{pmatrix}$$

A function for calculating the time evolution of the density matrix:

In[272]:= **rhoTime[rhoGen, t];**

In[273]:= **Simplify[%]**

$$\text{Out[273]} = \begin{pmatrix} \text{caa Conjugate[caa]} & \text{caa } e^{-i (J-2 \text{nuS}) \pi t} \text{Conjugate[cab]} & \text{caa } e^{-i (J-2 \text{nuI}) \pi t} \text{Conjugate[cb}] \\ \text{cab } e^{i (J-2 \text{nuS}) \pi t} \text{Conjugate[caa]} & \text{cab Conjugate[cab]} & \text{cab } e^{2 i (\text{nuI}-\text{nuS}) \pi t} \text{Conjugate[cb}] \\ \text{cba } e^{i (J-2 \text{nuI}) \pi t} \text{Conjugate[caa]} & \text{cba } e^{-2 i (\text{nuI}-\text{nuS}) \pi t} \text{Conjugate[cab]} & \text{cba Conjugate[cb}] \\ \text{cbb } e^{-2 i (\text{nuI}+\text{nuS}) \pi t} \text{Conjugate[caa]} & \text{cbb } e^{-i (J+2 \text{nuI}) \pi t} \text{Conjugate[cab]} & \text{cbb } e^{-i (J+2 \text{nuS}) \pi t} \text{Conjugate[cb}] \end{pmatrix}$$

A simple experiment: a pulse to both I and S, followed by time evolution:

In[274]:= **rho1 = rhoPi2x[rhoEq];**

In[275]:= **Simplify[%]**

$$\text{Out[275]} = \begin{pmatrix} 0 & -\frac{i \text{deltaPs}}{4} & -\frac{i \text{deltaPi}}{4} & 0 \\ \frac{i \text{deltaPs}}{4} & 0 & 0 & -\frac{i \text{deltaPi}}{4} \\ \frac{i \text{deltaPi}}{4} & 0 & 0 & -\frac{i \text{deltaPs}}{4} \\ 0 & \frac{i \text{deltaPi}}{4} & \frac{i \text{deltaPs}}{4} & 0 \end{pmatrix}$$

```
In[276]:= allMagRho[rho1]
```

$$\langle I_x \rangle = 0 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = \frac{\text{deltaPi}}{2} \quad \langle S_y \rangle = \frac{\text{deltaPs}}{2}$$

$$\langle I_z \rangle = 0 \quad \langle S_z \rangle = 0$$

```
In[277]:= allCorRho[rho1]
```

$$\langle I_x S_x \rangle = 0 \quad \langle I_x S_y \rangle = 0 \quad \langle I_x S_z \rangle = 0$$

$$\langle I_y S_x \rangle = 0 \quad \langle I_y S_y \rangle = 0 \quad \langle I_y S_z \rangle = 0$$

$$\langle I_z S_x \rangle = 0 \quad \langle I_z S_y \rangle = 0 \quad \langle I_z S_z \rangle = 0$$

```
In[278]:= rho2 = rhoTime[rho1, t];
```

```
In[279]:= Simplify[%]
```

$$\text{Out[279]} = \begin{pmatrix} 0 & -\frac{1}{4} i \text{deltaPs} e^{-i (J-2 \text{nuS}) \pi t} & -\frac{1}{4} i \text{deltaPi} e^{-i (J-2 \text{nuI}) \pi t} & 0 \\ \frac{1}{4} i \text{deltaPs} e^{i (J-2 \text{nuS}) \pi t} & 0 & 0 & -\frac{1}{4} i \text{deltaPi} e^{i (J+2 \text{nuI}) \pi t} \\ \frac{1}{4} i \text{deltaPi} e^{i (J-2 \text{nuI}) \pi t} & 0 & 0 & -\frac{1}{4} i \text{deltaPs} e^{i (J+2 \text{nuS}) \pi t} \\ 0 & \frac{1}{4} i \text{deltaPi} e^{-i (J+2 \text{nuI}) \pi t} & \frac{1}{4} i \text{deltaPs} e^{-i (J+2 \text{nuS}) \pi t} & 0 \end{pmatrix}$$

```
In[280]:= allMagRho[rho2]
```

$$\langle I_x \rangle = \frac{1}{2} \text{deltaPi} \cos[J \pi t] \sin[2 \text{nuI} \pi t] \quad \langle S_x \rangle = \frac{1}{2} \text{deltaPs} \cos[J \pi t] \sin[2 \text{nuS} \pi t]$$

$$\langle I_y \rangle = \frac{1}{4} \text{deltaPi} (\cos[(J-2 \text{nuI}) \pi t] + \cos[(J+2 \text{nuI}) \pi t])$$

$$\langle S_y \rangle = \frac{1}{4} \text{deltaPs} (\cos[(J-2 \text{nuS}) \pi t] + \cos[(J+2 \text{nuS}) \pi t])$$

$$\langle I_z \rangle = 0 \quad \langle S_z \rangle = 0$$

```
In[281]:=
```

## ■ Representation of the density matrix as a linear combination of operator matrices

The density matrix can be represented as a linear combination of the matrices for the 6 magnetization operators and the 9 product operators, plus the identity matrix. When this is done, the contribution of each term to the observable magnetization components can easily be calculated from the coefficients of the matrices.

For instance, consider a density matrix that is composed simply of  $I_x$ . If we calculate the average magnetization components and correlations for a state represented by this density matrix:

```
In[282]:= allMagRho[Ix]
```

$$\langle I_x \rangle = 1 \quad \langle S_x \rangle = 0$$

$$\langle I_y \rangle = 0 \quad \langle S_y \rangle = 0$$

$$\langle I_z \rangle = 0 \quad \langle S_z \rangle = 0$$

```
In[283]:= allCorRho[Ix]
```

```

<IxSx> = 0      <IxSy> = 0      <IxSz> = 0
<IySx> = 0      <IySy> = 0      <IySz> = 0
<IzSx> = 0      <IzSy> = 0      <IzSz> = 0

```

The only non-zero average is  $\langle I_x \rangle = 1$ . Thus, the average is simply the coefficient of the matrix. This is not a valid result for a real state, though, which simply means that  $I_x$  is not a density matrix for a real state.

Consider a density matrix composed of  $I_x S_y$ :

```

In[284]:= allMagRho[IxSy]

<Ix> = 0      <Sx> = 0
<Iy> = 0      <Sy> = 0
<Iz> = 0      <Sz> = 0

In[285]:= allCorRho[IxSy]

<IxSx> = 0      <IxSy> =  $\frac{1}{4}$       <IxSz> = 0
<IySx> = 0      <IySy> = 0      <IySz> = 0
<IzSx> = 0      <IzSy> = 0      <IzSz> = 0

```

In this case, the average value of  $I_x S_y$  is 1/4 of the coefficient.

If we write a linear combination of  $I_x$  and  $I_x S_y$

```

In[286]:= allMagRho[Ix + IxSy]

<Ix> = 1      <Sx> = 0
<Iy> = 0      <Sy> = 0
<Iz> = 0      <Sz> = 0

In[287]:= allCorRho[Ix + IxSy]

<IxSx> = 0      <IxSy> =  $\frac{1}{4}$       <IxSz> = 0
<IySx> = 0      <IySy> = 0      <IySz> = 0
<IzSx> = 0      <IzSy> = 0      <IzSz> = 0

```

The average values are simply added together. In general, the average value for an observable magnetization component is equal to the corresponding coefficient in the operator representation, and the average value for a correlation is equal to 1/4 of the corresponding coefficient.

The twoSpinLib package includes a special function that returns the non-zero components of the operator representation for any density matrix:

```

In[288]:= opBasisRep[Ix]

1 Ix

In[289]:= opBasisRep[Ix + IxSy]

```

1Ix

1IxSy

In[290]:= **opBasisRep**[rhoEq]

$\frac{\text{deltaPi}}{2} I_z$

$\frac{\text{deltaPs}}{2} S_z$

## ■ Rules for operator basis calculations

The functions for calculating the effects of pulses and evolution periods on the density matrix can be applied to any of the operator matrices do establish the rules for their transformations.

For instance for a pulse along the x'-axis:

In[291]:= **rhoPulseIx**[Ix, a];

In[292]:= **Simplify**[%]

Out[292]= 
$$\begin{pmatrix} 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \end{pmatrix}$$

This is just the starting matrix Ix, as expected. To confirm this, use the opBasisRep function

In[293]:= **opBasisRep**[rhoPulseIx[Ix, a]]

1Ix

For the same pulse applied to Iy:

In[294]:= **opBasisRep**[rhoPulseIx[Iy, a]]

Cos[a] Iy

-Sin[a] Iz

For the analogous pulse to the S-spin:

In[295]:= **opBasisRep**[rhoPulseSx[Sy, a]]

Cos[a] Sy

-Sin[a] Sz

## Chemical-shift evolution

In[296]:= **opBasisRep**[rhoTime[Ix, t] /. {J → 0}]

Cos[2 nuI π t] Ix

-Sin[2 nuI π t] Iy

In[297]:= **opBasisRep**[rhoTime[Sx, t] /. {J → 0}]

$\text{Cos}[2 \text{nuS } \pi \text{ t}] \text{Sx}$

$-\text{Sin}[2 \text{nuS } \pi \text{ t}] \text{Sy}$

For a product operator:

In[298]:= **opBasisRep[rhoTime[IySx, t] /. {J → 0}]**

$\frac{1}{2} (\text{Sin}[2 (\text{nuI} - \text{nuS}) \pi \text{ t}] + \text{Sin}[2 (\text{nuI} + \text{nuS}) \pi \text{ t}]) \text{IxSx}$

$-\text{Sin}[2 \text{nuI } \pi \text{ t}] \text{Sin}[2 \text{nuS } \pi \text{ t}] \text{IxSy}$

$\frac{1}{2} (\text{Cos}[2 (\text{nuI} - \text{nuS}) \pi \text{ t}] + \text{Cos}[2 (\text{nuI} + \text{nuS}) \pi \text{ t}]) \text{IySx}$

$\frac{1}{2} (\text{Sin}[2 (\text{nuI} - \text{nuS}) \pi \text{ t}] - \text{Sin}[2 (\text{nuI} + \text{nuS}) \pi \text{ t}]) \text{IySy}$

Evolution under the influence of scalar coupling only

In[299]:= **opBasisRep[rhoTime[Ix, t] /. {nuI → 0, nuS → 0}]**

$\text{Cos}[J \pi \text{ t}] \text{Ix}$

$2 \text{Sin}[J \pi \text{ t}] \text{IySz}$

In[300]:= **opBasisRep[rhoTime[IxSz, t] /. {nuI → 0, nuS → 0}]**

$\frac{1}{2} \text{Sin}[J \pi \text{ t}] \text{Iy}$

$\text{Cos}[J \pi \text{ t}] \text{IxSz}$

In[301]:= **opBasisRep[rhoTime[IzSx, t] /. {nuI → 0, nuS → 0}]**

$\frac{1}{2} \text{Sin}[J \pi \text{ t}] \text{Sy}$

$\text{Cos}[J \pi \text{ t}] \text{IzSx}$

Transverse correlations do not change during scalar coupling evolution

In[302]:= **opBasisRep[rhoTime[IxSy, t] /. {nuI → 0, nuS → 0}]**

$\text{IxSy}$