Maxima workbook for Principles of NMR Spectroscopy Chapter 13:Quantum description of a scalar-coupled spin pair

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 Chapter 11 and 12, chapter11.wxmx and chapter12.wxmx, respectively.

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This chapter covers the general description of a scalar-coupled pair of spin-1/2 nuclei
The worksheet uses the definitions found in 2spinLib.mac

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

2spinLib.mac, and the packages it loads, defines the following functions.

```
(%i2) functions;
```

(%o2) $[\mathrm{innerproduct}(x, y), \mathrm{unitvector}(x), \mathrm{columnvector}(x), \mathrm{gramschmidt}(x, [\mathit{myinnerproduct}]), \mathrm{eigenvalues}(\mathit{mat}), \mathrm{eigenvectors}(\mathit{mat}), \mathrm{sub}$

2 13.1 Interacting spins in the absence of an external field

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2.1 13.1.1 Magnetization operators

The kets and bras representing the eigenfunctions for the z-magnetization operator

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

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

```
(%i4) b_aa;
```

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

```
(%i5) k_ab;
```

(%o5) $\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$

(%i6) b_ab;

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

(%i7) k_ba;

(%o7) $\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$

(%i8) b_ba;

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

(%i9) k_bb;

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

(%i10) b_bb;

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

The eigenfunctions of Iz are orthonormal

(%i11) b_aa.k_aa;

(%o11) 1

(%i12) b_ab.k_ab;

(%o12) 1

(%i13) b_ba.k_ba;

(%o13) 1

(%i14) b_bb.k_bb;

(%o14) 1

(%i15) b_aa.k_ab;

(%o15) 0

(%i16) b_aa.k_ba;

(%o16) 0

(%i17) b_aa.k_bb;

(%o17) 0

and so on.

The general form of the wavefunction expressed as a superposition of the eigenfunctions of the Iz-operator

(%i18) k_psi;

$$\begin{pmatrix} caa \\ cab \\ cba \\ cbb \end{pmatrix} \quad (\%o18)$$

(%i19) b_psi;

$$\begin{pmatrix} \overline{caa} & \overline{cab} & \overline{cba} & \overline{cbb} \end{pmatrix} \quad (\%o19)$$

The matrix representation of the Ix operator

(%i20) Ix;

$$\begin{pmatrix} 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \end{pmatrix} \quad (\%o20)$$

The Ix operator applied to an arbitrary wavefunction

(%i21) Ix.k_psi;

$$\begin{pmatrix} \frac{cba}{2} \\ \frac{cbb}{2} \\ \frac{caa}{2} \\ \frac{cab}{2} \end{pmatrix} \quad (\%o21)$$

The average Ix-magnetization for an arbitrary wavefunction.

(%i22) b_psi.Ix.k_psi;

$$\frac{cab \cdot \overline{cbb}}{2} + \frac{\overline{cab} \cdot cbb}{2} + \frac{caa \cdot \overline{cba}}{2} + \frac{\overline{caa} \cdot cba}{2} \quad (\%o22)$$

2spinLib.mac defines a function to calculate the average value for a measurement represented by an operator for a wavefunction.

(%i23) fundef(meanPsi);

$$\mathrm{meanPsi}\,(op, \psi) := \mathrm{ratsimp}\left(\mathrm{trigreduce}\left(\mathrm{trigsimp}\left(\mathrm{demoivre}\left(\overline{\psi}.op.\psi\right)\right)\right)\right) \quad (\%o23)$$

(%i24) meanPsi(Ix,k_psi);

$$\frac{\overline{caa} \cdot cba + caa \cdot \overline{cba} + \overline{cab} \cdot cbb + cab \cdot \overline{cbb}}{2} \quad (\%o24)$$

The Sx operator

(%i25) Sx;

$$\begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \end{pmatrix} \quad (\%o25)$$

(%i26) Sx.k_psi;

(%o26) $$\begin{pmatrix} \frac{cab}{2} \\ \frac{caa}{2} \\ \frac{cbb}{2} \\ \frac{cba}{2} \end{pmatrix}$$

The average value of Sx

```
(%i27) b_psi.Sx.k_psi;
```

(%o27) $$\frac{cba \cdot \overline{cbb}}{2} + \frac{\overline{cba} \cdot cbb}{2} + \frac{caa \cdot \overline{cab}}{2} + \frac{\overline{caa} \cdot cab}{2}$$

```
(%i28) meanPsi(Sx,k_psi);
```

(%o28) $$\frac{\overline{caa} \cdot cab + caa \cdot \overline{cab} + \overline{cba} \cdot cbb + cba \cdot \overline{cbb}}{2}$$

The full set of magnetization operators is: Ix, Sx, Iy, Sy, Sz, Sz All of these are defined in 2spinLib.mac
The library also contains a function to calculate all six of the average magnetization components from a wavefunction

```
(%i29) allMagPsi(k_psi);
```

$$< Ix >= \frac{\overline{caa} \cdot cba + caa \cdot \overline{cba} + \overline{cab} \cdot cbb + cab \cdot \overline{cbb}}{2}$$

$$< Iy >= \frac{-i \cdot \overline{caa} \cdot cba + i \cdot caa \cdot \overline{cba} - i \cdot \overline{cab} \cdot cbb + i \cdot cab \cdot \overline{cbb}}{2}$$

$$< Iz >= -\frac{-caa \cdot \overline{caa} - cab \cdot \overline{cab} + cba \cdot \overline{cba} + cbb \cdot \overline{cbb}}{2}$$

$$< Sx >= \frac{\overline{caa} \cdot cab + caa \cdot \overline{cab} + \overline{cba} \cdot cbb + cba \cdot \overline{cbb}}{2}$$

$$< Sy >= \frac{-i \cdot \overline{caa} \cdot cab + i \cdot caa \cdot \overline{cab} - i \cdot \overline{cba} \cdot cbb + i \cdot cba \cdot \overline{cbb}}{2}$$

$$< Sz >= -\frac{-caa \cdot \overline{caa} + cab \cdot \overline{cab} - cba \cdot \overline{cba} + cbb \cdot \overline{cbb}}{2}$$

(%o29)

2.2 13.1.2 Shift operators

The shift operators are:

```
(%i30) Iplus;
```

(%o30) $$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

```
(%i31) Ix + %i*Iy;
```

(%o31) $$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

```
(%i32) Iminus;
```

(%o32) $$\begin{pmatrix}0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{pmatrix}$$

```
(%i33) Ix-%i*Iy;
```

(%o33) $$\begin{pmatrix}0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{pmatrix}$$

```
(%i34) Splus;
```

(%o34) $$\begin{pmatrix}0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0\end{pmatrix}$$

```
(%i35) Sx+%i*Sy;
```

(%o35) $$\begin{pmatrix}0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0\end{pmatrix}$$

```
(%i36) Sminus;
```

(%o36) $$\begin{pmatrix}0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0\end{pmatrix}$$

```
(%i37) Sx-%i*Sy;
```

(%o37) $$\begin{pmatrix}0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0\end{pmatrix}$$

The effects of the shift operators on an arbitrary wavefunction

```
(%i38) Iplus.k_psi;
```

(%o38) $$\begin{pmatrix}cba\\ cbb\\ 0\\ 0\end{pmatrix}$$

```
(%i39) Iminus.k_psi;
```

(%o39) $$\begin{pmatrix}0\\ 0\\ caa\\ cab\end{pmatrix}$$

```
(%i40) Splus.k_psi;
```

(%o40) $\begin{pmatrix} cab \\ 0 \\ cbb \\ 0 \end{pmatrix}$

```
(%i41) Sminus.k_psi;
```

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

Transition probabilities
The relative probability of an upward transition of the I-spin from |beta alpha> to |alpha alpha>

```
(%i42) abs(b_aa.Iplus.k_ba)^2;
```

(%o42) 1

The relative probability of an upward transition of the I-spin from |alpha beta> to |alpha alpha>

```
(%i43) abs(b_aa.Iplus.k_ab)^2;
```

(%o43) 0

This transition has zero probability because the I-spin is already in the alpha state in |alpha beta>

The relative probability of a downward transition of the S-spin from |beta alpha> to |beta beta>

```
(%i44) abs(b_bb.Sminus.k_ba);
```

(%o44) 1

The total upward and downward shift operators

```
(%i45) Iplus+Splus;
```

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

```
(%i46) Fplus;
```

(%o46) $\begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}$

```
(%i47) Iminus+Sminus;
```

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

```
(%i48) Fminus;
```

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

```
(%i49) Fplus.k_psi;
```

(%o49) $$\begin{pmatrix} cba + cab \\ cbb \\ cbb \\ 0 \end{pmatrix}$$

```
(%i50) Fminus.k_psi;
```

(%o50) $$\begin{pmatrix} 0 \\ caa \\ caa \\ cba + cab \end{pmatrix}$$

The probability of an upward transition from lbeta beta> to lbeta alpha>

```
(%i51) abs(b_ba.Fplus.k_bb);
```

(%o51) 1

The probability of an upward transition from lbeta beta> to lalpha beta>

```
(%i52) abs(b_ab.Fplus.k_bb);
```

(%o52) 1

The probability of a downward transition from lalpha alpha> to lbeta beta>

```
(%i53) abs(b_bb.Fminus.k_aa);
```

(%o53) 0

The probability of an upward transition from lalpha beta> to lbeta alpha>

```
(%i54) abs(b_ba.Fminus.k_ab);
```

(%o54) 0

Both of the above transitions are forbidden.

2.3 13.1.3 The Hamiltonian operator

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An aside on vector multiplication (information that is already necessary for using these workbooks!)

```
(%i55) A:matrix([Ax,Ay,Az]);
```

(%o55) $\begin{pmatrix} Ax & Ay & Az \end{pmatrix}$

```
(%i56) B:matrix([Bx,By,Bz]);
```

(%o56) $\begin{pmatrix} Bx & By & Bz \end{pmatrix}$

The dot product

```
(%i57) A.B;
```

(%o57) $Az \cdot Bz + Ay \cdot By + Ax \cdot Bx$

The length of a vector

(%i58) `sqrt(A.A);`

(%o58) $\sqrt{Az^2 + Ay^2 + Ax^2}$

The product formed from Iz and Sz

(%i59) `Iz.Sz;`

(%o59) $\begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 \\ 0 & 0 & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$

(%i60) `Iz.Sz.k_psi;`

(%o60) $\begin{pmatrix} \frac{caa}{4} \\ -\frac{cab}{4} \\ -\frac{cba}{4} \\ \frac{cbb}{4} \end{pmatrix}$

(%i61) `Iz.Sz.k_aa;`

(%o61) $\begin{pmatrix} \frac{1}{4} \\ 0 \\ 0 \\ 0 \end{pmatrix}$

(%i62) `Iz.Sz.k_ab;`

(%o62) $\begin{pmatrix} 0 \\ -\frac{1}{4} \\ 0 \\ 0 \end{pmatrix}$

(%i63) `Iz.Sz.k_ba;`

(%o63) $\begin{pmatrix} 0 \\ 0 \\ -\frac{1}{4} \\ 0 \end{pmatrix}$

(%i64) `Iz.Sz.k_bb;`

(%o64) $\begin{pmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{4} \end{pmatrix}$

k_aa, k_ab, k_ba and k_bb are all eigen functions of Iz.Sz

The Hamiltonian operator for coupled spins in the absence of an external field.
(Here we use the symbol Hsc0, rather than Hsc, as used in the text, to avoid conflict with Hsc defined in 2spinLib.mac, for the Hamiltonian in an external field, under the weak-coupling limit.)

(%i65) Hsc0:h*J*(Ix.Sx + Iy.Sy + Iz.Sz);

(%o65) $$\begin{pmatrix} \frac{h\cdot J}{4} & 0 & 0 & 0 \\ 0 & -\frac{h\cdot J}{4} & \frac{h\cdot J}{2} & 0 \\ 0 & \frac{h\cdot J}{2} & -\frac{h\cdot J}{4} & 0 \\ 0 & 0 & 0 & \frac{h\cdot J}{4} \end{pmatrix}$$

(%i66) Hsc0.k_psi;

(%o66) $$\begin{pmatrix} \frac{caa\cdot h\cdot J}{4} \\ \frac{cba\cdot h\cdot J}{2} - \frac{cab\cdot h\cdot J}{4} \\ \frac{cab\cdot h\cdot J}{2} - \frac{cba\cdot h\cdot J}{4} \\ \frac{cbb\cdot h\cdot J}{4} \end{pmatrix}$$

k_aa and k_bb are eigenfunctions of the Hamiltonian.

(%i67) Hsc0.k_aa;

(%o67) $$\begin{pmatrix} \frac{h\cdot J}{4} \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

(%i68) Hsc0.k_bb;

(%o68) $$\begin{pmatrix} 0 \\ 0 \\ 0 \\ \frac{h\cdot J}{4} \end{pmatrix}$$

But, k_ab and k_ba are not eigenfunctions of the Hamiltonian.

(%i69) Hsc0.k_ab;

(%o69) $$\begin{pmatrix} 0 \\ -\frac{h\cdot J}{4} \\ \frac{h\cdot J}{2} \\ 0 \end{pmatrix}$$

(%i70) Hsc0.k_ba;

(%o70) $$\begin{pmatrix} 0 \\ \frac{h\cdot J}{2} \\ -\frac{h\cdot J}{4} \\ 0 \end{pmatrix}$$

Maxima can find the eigenvectors for the Hsc0 operator matrix

(%i71) uniteigenvectors(Hsc0);

(%o71) $$[[[-\frac{3\cdot h\cdot J}{4}, \frac{h\cdot J}{4}], [1,3]], [[[0, \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0]], [[1,0,0,0], [0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0], [0,0,0,1]]]]$$

There are two eigenvalues: -(3*h*J)/4 and (h*J)/4
The first eigenvalue is associated with one eigenvector: [0,1/sqrt(2),-1/sqrt(2),0]] We call this eigenvector k_psi0
The second eigenvalue is associated with three eigenvectors: [1,0,0,0] [0,1/sqrt(2),1/sqrt(2),0] [0,0,0,1] The first and third are k_aa and k_bb, respectively The second one, we call k_psi1

```
(%i72) k_psi0:matrix([0],[1/sqrt(2)],[-1/sqrt(2)],[0]);
```

$$(\%o72)\quad \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}$$

```
(%i73) Hsc0.k_psi0;
```

$$(\%o73)\quad \begin{pmatrix} 0 \\ -\frac{h\cdot J}{2^{\frac{3}{2}}}-\frac{h\cdot J}{2^{\frac{5}{2}}} \\ \frac{h\cdot J}{2^{\frac{3}{2}}}+\frac{h\cdot J}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

```
(%i74) factor(%);
```

$$(\%o74)\quad \begin{pmatrix} 0 \\ -\frac{3\cdot h\cdot J}{2^{\frac{5}{2}}} \\ \frac{3\cdot h\cdot J}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

```
(%i75) k_psi1: matrix([0],[1/sqrt(2)],[1/sqrt(2)],[0]);
```

$$(\%o75)\quad \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}$$

```
(%i76) Hsc0.k_psi1;
```

$$(\%o76)\quad \begin{pmatrix} 0 \\ \frac{h\cdot J}{2^{\frac{3}{2}}}-\frac{h\cdot J}{2^{\frac{5}{2}}} \\ \frac{h\cdot J}{2^{\frac{3}{2}}}-\frac{h\cdot J}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

```
(%i77) factor(%);
```

$$(\%o77)\quad \begin{pmatrix} 0 \\ \frac{h\cdot J}{2^{\frac{5}{2}}} \\ \frac{h\cdot J}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

2.4 13.1.4 Spin correlations and the product operators

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Calculating the average magnetization components of k_psi0 and k_psi1, using the allMagPsi function in 2spinLib.mac

```
(%i78) allMagPsi(k_psi0);
```

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

(%o78)

```
(%i79) allMagPsi(k_psi1);
```

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

(%o79)

No magnetization in any direction!

Applying product operators to k_psi0 and k_psi1 The product operators can be obtained by matrix multiplication, but they are pre-defined in 2spinLib.mac

```
(%i80) Ix.Sx;
```

(%o80) $$\begin{pmatrix} 0 & 0 & 0 & \frac{1}{4} \\ 0 & 0 & \frac{1}{4} & 0 \\ 0 & \frac{1}{4} & 0 & 0 \\ \frac{1}{4} & 0 & 0 & 0 \end{pmatrix}$$

```
(%i81) IxSx;
```

(%o81) $$\begin{pmatrix} 0 & 0 & 0 & \frac{1}{4} \\ 0 & 0 & \frac{1}{4} & 0 \\ 0 & \frac{1}{4} & 0 & 0 \\ \frac{1}{4} & 0 & 0 & 0 \end{pmatrix}$$

```
(%i82) IxSx.k_psi0;
```

(%o82) $$\begin{pmatrix} 0 \\ -\frac{1}{2^{\frac{5}{2}}} \\ \frac{1}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

```
(%i83) IySy.k_psi0;
```

(%o83) $$\begin{pmatrix} 0 \\ -\frac{1}{2^{\frac{5}{2}}} \\ \frac{1}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

```
(%i84) IzSz.k_psi0;
```

(%o84) $$\begin{pmatrix} 0 \\ -\frac{1}{2^{\frac{5}{2}}} \\ \frac{1}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

Applying these product operators to k_psi1

```
(%i85) IxSx.k_psi1;
```

(%o85) $$\begin{pmatrix} 0 \\ \frac{1}{2^{\frac{5}{2}}} \\ \frac{1}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

```
(%i86) IySy.k_psi1;
```

(%o86) $$\begin{pmatrix} 0 \\ \frac{1}{2^{\frac{5}{2}}} \\ \frac{1}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

```
(%i87) IzSz.k_psi1;
```

(%o87) $$\begin{pmatrix} 0 \\ -\frac{1}{2^{\frac{5}{2}}} \\ -\frac{1}{2^{\frac{5}{2}}} \\ 0 \end{pmatrix}$$

The average value of the product of the measurements of an I- and an S-magnetization component can can be calculated in the usual way. For, instance the average value of the product of the Iz and Sz magnetization for the Ialpha alpha> wavefunction

```
(%i88) b_aa.IzSz.k_aa;
```

(%o88) $\frac{1}{4}$

For the other Iz- Sz- eigenfunctions

```
(%i89) b_ab.IzSz.k_ab;
```

(%o89) $-\frac{1}{4}$

```
(%i90) b_ba.IzSz.k_ba;
```

(%o90) $-\frac{1}{4}$

```
(%i91) b_bb.IzSz.k_bb;
```

(%o91) $\frac{1}{4}$

The full set of average products can be calculated with the allCorrPsi function in 2spinLib.mac

```
(%i92) allCorrPsi(k_aa);
```

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

(%o92)

For the k_psi0 and k_psi1 correlations, the averages are:

```
(%i93) allCorrPsi(k_psi0);
```

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

(%o93)

```
(%i94) allCorrPsi(k_psi1);
```

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

(%o94)

Other operator products
Sz and Ix are commutative

```
(%i95) Sz.Ix;
```

(%o95) $$\begin{pmatrix} 0 & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & -\frac{1}{4} \\ \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 \end{pmatrix}$$

```
(%i96) Ix.Sz;
```

$$(\%o96)\quad \begin{pmatrix} 0 & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & -\frac{1}{4} \\ \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 \end{pmatrix}$$

But, Iz and Ix are not

```
(%i97) Iz.Ix;
```

$$(\%o97)\quad \begin{pmatrix} 0 & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \\ -\frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 \end{pmatrix}$$

```
(%i98) Ix.Iz;
```

$$(\%o98)\quad \begin{pmatrix} 0 & 0 & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & -\frac{1}{4} \\ \frac{1}{4} & 0 & 0 & 0 \\ 0 & \frac{1}{4} & 0 & 0 \end{pmatrix}$$

```
(%i99) (Iz.Ix).k_psi;
```

$$(\%o99)\quad \begin{pmatrix} \frac{cba}{4} \\ \frac{cbb}{4} \\ -\frac{caa}{4} \\ -\frac{cab}{4} \end{pmatrix}$$

```
(%i100) (Ix.Iz).k_psi;
```

$$(\%o100)\quad \begin{pmatrix} -\frac{cba}{4} \\ -\frac{cbb}{4} \\ \frac{caa}{4} \\ \frac{cab}{4} \end{pmatrix}$$

3 13.3 Scalar coupled spins in the presence of an external field

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The total Hamiltonian for a scalar-coupled spin pair in an external field, expressed in terms of the I and S Larmor frequencies, nuI and nuS, and the scalar-coupling constant, J

```
(%i101) Ht:h*nuI*Iz+h*nuS*Sz+h*J*(Ix.Sx + Iy.Sy + Iz.Sz);
```

$$(\%o101)\quad \begin{pmatrix} \frac{h\cdot nuS}{2}+\frac{h\cdot nuI}{2}+\frac{h\cdot J}{4} & 0 & 0 & 0 \\ 0 & -\frac{h\cdot nuS}{2}+\frac{h\cdot nuI}{2}-\frac{h\cdot J}{4} & \frac{h\cdot J}{2} & 0 \\ 0 & \frac{h\cdot J}{2} & \frac{h\cdot nuS}{2}-\frac{h\cdot nuI}{2}-\frac{h\cdot J}{4} & 0 \\ 0 & 0 & 0 & -\frac{h\cdot nuS}{2}-\frac{h\cdot nuI}{2}+\frac{h\cdot J}{4} \end{pmatrix}$$

```
(%i102) Ht.k_psi;
```

$$(\%o102)\quad \begin{pmatrix} caa\cdot\left(\frac{h\cdot nuS}{2}+\frac{h\cdot nuI}{2}+\frac{h\cdot J}{4}\right) \\ cab\cdot\left(-\frac{h\cdot J}{4}+\frac{h\cdot nuI}{2}-\frac{h\cdot nuS}{2}\right)+\frac{cba\cdot h\cdot J}{2} \\ cba\cdot\left(-\frac{h\cdot J}{4}-\frac{h\cdot nuI}{2}+\frac{h\cdot nuS}{2}\right)+\frac{cab\cdot h\cdot J}{2} \\ cbb\cdot\left(-\frac{h\cdot nuS}{2}-\frac{h\cdot nuI}{2}+\frac{h\cdot J}{4}\right) \end{pmatrix}$$

k_aa and k_bb are eigenvectors of the Hamiltonian

```
(%i103) Ht.k_aa;
```

$$(\%o103)\quad \begin{pmatrix} \frac{h\cdot nuS}{2}+\frac{h\cdot nuI}{2}+\frac{h\cdot J}{4} \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

```
(%i104) Ht.k_bb;
```

$$(\%o104)\quad \begin{pmatrix} 0 \\ 0 \\ 0 \\ -\frac{h\cdot nuS}{2}-\frac{h\cdot nuI}{2}+\frac{h\cdot J}{4} \end{pmatrix}$$

k_ab and k_ba are not eigenvectors of the Hamiltonian

```
(%i105) Ht.k_ab;
```

$$(\%o105)\quad \begin{pmatrix} 0 \\ -\frac{h\cdot nuS}{2}+\frac{h\cdot nuI}{2}-\frac{h\cdot J}{4} \\ \frac{h\cdot J}{2} \\ 0 \end{pmatrix}$$

```
(%i106) Ht.k_ba;
```

$$(\%o106)\quad \begin{pmatrix} 0 \\ \frac{h\cdot J}{2} \\ \frac{h\cdot nuS}{2}-\frac{h\cdot nuI}{2}-\frac{h\cdot J}{4} \\ 0 \end{pmatrix}$$

The eigenvalues and (unnormalized) eigenvectors of Ht are given by

```
(%i107) eigenvectors(Ht);
```

$$(\%o107)\quad [[[-\frac{h\cdot J+2\cdot h\cdot\sqrt{nuS^2-2\cdot nuI\cdot nuS+nuI^2+J^2}}{4},\frac{2\cdot h\cdot\sqrt{nuS^2-2\cdot nuI\cdot nuS+nuI^2+J^2}-h\cdot J}{4},-\frac{-h\cdot J+2\cdot h\cdot nuI+}{4}$$

The eigenvalues are: -(2*h*sqrt(nuS^2-2*nuI*nuS+nuI^2+J^2)+h*J)/4 (2*h*sqrt(nuS^2-2*nuI*nuS+nuI^2+J^2)-h*J)/4 -(2*h*nuS+2*h*nuI-h*J)/4 (2*h*nuS+2*h*nuI+h*J)/4
The first two eigenvalues correspond to the two eigenvectors that are linear combinations of k_ab and k_ba. Showing that the eigenvectors given above, when normalized, correspond to the ones given in the text is not so easy, but it can be done using the definitions of D and theta given in the text, along with some trigonometric identities. We will proceed assuming that the eigenfunctions in the text are valid.
The last two eigenvalues correspond to the eigenvectors k_bb and k_aa, respectively.

```
(%i108) k_A:-sin(theta)*k_ab+cos(theta)*k_ba;
```

$$(\%o108)\quad \begin{pmatrix} 0 \\ -\sin(\theta) \\ \cos(\theta) \\ 0 \end{pmatrix}$$

```
(%i109) k_B:cos(theta)*k_ab+sin(theta)*k_ba;
```

(%o109) $$\begin{pmatrix} 0 \\ \cos(\theta) \\ \sin(\theta) \\ 0 \end{pmatrix}$$

```
(%i110) b_A:bra(k_A);
```

(%o110) $$\begin{pmatrix} 0 & -\sin(\theta) & \cos(\theta) & 0 \end{pmatrix}$$

```
(%i111) b_B:bra(k_B);
```

(%o111) $$\begin{pmatrix} 0 & \cos(\theta) & \sin(\theta) & 0 \end{pmatrix}$$

Eigenvalues correspond to the energies of the eigenfunctions

```
(%i112) Eaa:h*(nuI+nuS)/2 +h*J/4;
```

(%o112) $$\frac{h\cdot(nuI+nuS)}{2}+\frac{h\cdot J}{4}$$

```
(%i113) EA:-h*sqrt(J^2+(nuI-nuS)^2)/2-h*J/4;
```

(%o113) $$-\frac{h\cdot\sqrt{(nuI-nuS)^2+J^2}}{2}-\frac{h\cdot J}{4}$$

```
(%i114) EB:h*sqrt(J^2+(nuI-nuS)^2)/2-h*J/4;
```

(%o114) $$\frac{h\cdot\sqrt{(nuI-nuS)^2+J^2}}{2}-\frac{h\cdot J}{4}$$

```
(%i115) Ebb:-h*(nuI+nuS)/2 +h*J/4;
```

(%o115) $$\frac{h\cdot J}{4}-\frac{h\cdot(nuI+nuS)}{2}$$

Transition probabilities and frequencies All of the possible transitions between k_A and k_B

```
(%i116) abs(b_A.Fplus.k_B)^2;
```

(%o116) 0

```
(%i117) abs(b_B.Fplus.k_A)^2;
```

(%o117) 0

```
(%i118) abs(b_A.Fminus.k_B)^2;
```

(%o118) 0

```
(%i119) abs(b_B.Fminus.k_A)^2;
```

(%o119) 0

The downward transition from k_aa to k_A Probability

```
(%i120) abs(b_A.Fminus.k_aa)^2;
```

(%o120) $$(\sin(\theta)-\cos(\theta))^2$$

```
(%i121) trigrat(%);
```

(%o121) $$1-\sin(2\cdot\theta)$$

Frequency

(%i122) (Eaa-EA)/h;

$$\text{(\%o122)} \quad \frac{\frac{h\cdot J}{2}+\frac{h\cdot\sqrt{(nuI-nuS)^2+J^2}}{2}+\frac{h\cdot(nuI+nuS)}{2}}{h}$$

(%i123) factor(%);

$$\text{(\%o123)} \quad \frac{J+nuI+nuS+\sqrt{nuS^2-2\cdot nuI\cdot nuS+nuI^2+J^2}}{2}$$

The downward transition from k_aa to k_B Probability

(%i124) abs(b_B.Fminus.k_aa)^2;

$$\text{(\%o124)} \quad (\cos(\theta)+\sin(\theta))^2$$

(%i125) trigrat(%);

$$\text{(\%o125)} \quad \sin(2\cdot\theta)+1$$

Frequency

(%i126) (Eaa-EB)/h;

$$\text{(\%o126)} \quad \frac{\frac{h\cdot J}{2}-\frac{h\cdot\sqrt{(nuI-nuS)^2+J^2}}{2}+\frac{h\cdot(nuI+nuS)}{2}}{h}$$

(%i127) factor(%);

$$\text{(\%o127)} \quad -\frac{-J-nuI-nuS+\sqrt{nuS^2-2\cdot nuI\cdot nuS+nuI^2+J^2}}{2}$$

The downward transition from k_A to k_bb Probability

(%i128) abs(k_bb.Fminus.k_A)^2;

$$\text{(\%o128)} \quad (\sin(\theta)-\cos(\theta))^2$$

(%i129) trigrat(%);

$$\text{(\%o129)} \quad 1-\sin(2\cdot\theta)$$

Frequency

(%i130) (EA-Ebb)/h;

$$\text{(\%o130)} \quad \frac{-\frac{h\cdot J}{2}-\frac{h\cdot\sqrt{(nuI-nuS)^2+J^2}}{2}+\frac{h\cdot(nuI+nuS)}{2}}{h}$$

(%i131) factor(%);

$$\text{(\%o131)} \quad -\frac{J-nuI-nuS+\sqrt{nuS^2-2\cdot nuI\cdot nuS+nuI^2+J^2}}{2}$$

The downward transition from K_B to k_bb Probability

(%i132) abs(k_bb.Fminus.k_B)^2;

$$\text{(\%o132)} \quad (\cos(\theta)+\sin(\theta))^2$$

(%i133) trigrat(%);

$$\text{(\%o133)} \quad \sin(2\cdot\theta)+1$$

Energy

```
(%i134) (EB-Ebb)/h;
```

$$(\%o134)\quad \frac{-\frac{h\cdot J}{2}+\frac{h\cdot\sqrt{(nuI-nuS)^2+J^2}}{2}+\frac{h\cdot(nuI+nuS)}{2}}{h}$$

```
(%i135) factor(%);
```

$$(\%o135)\quad \frac{-J+nuI+nuS+\sqrt{nuS^2-2\cdot nuI\cdot nuS+nuI^2+J^2}}{2}$$

For all three cases below, we assume that J>0 and nuI>nuS

```
(%i136) assume(J>0);
```

$$(\%o136)\quad [J>0]$$

```
(%i137) assume(nuI>nuS);
```

$$(\%o137)\quad [nuI>nuS]$$

Case 1: J=0, which is satisfied when theta = 0 k_A = k_ba, and k_B=k_ab

```
(%i138) subst(theta=0, k_A);
```

$$(\%o138)\quad \begin{pmatrix}0\\0\\1\\0\end{pmatrix}$$

```
(%i139) subst(theta=0, k_B);
```

$$(\%o139)\quad \begin{pmatrix}0\\1\\0\\0\end{pmatrix}$$

Case 2: J^2 >> (nuI-nuS)^2 theta = pi/4

```
(%i140) subst(theta=%pi/4, k_A);
```

$$(\%o140)\quad \begin{pmatrix}0\\-\frac{1}{\sqrt{2}}\\\frac{1}{\sqrt{2}}\\0\end{pmatrix}$$

```
(%i141) subst(theta=%pi/4,k_B);
```

$$(\%o141)\quad \begin{pmatrix}0\\\frac{1}{\sqrt{2}}\\\frac{1}{\sqrt{2}}\\0\end{pmatrix}$$

Energy differences

```
(%i142) EA-Eaa;
```

(%o142) $$-\frac{h\cdot (nuI+nuS)}{2}-\frac{h\cdot \sqrt{(nuI-nuS)^2+J^2}}{2}-\frac{h\cdot J}{2}$$

```
(%i143) subst(nuI-nuS=0,%);
```

(%o143) $$-\frac{h\cdot (nuI+nuS)}{2}-h\cdot J$$

```
(%i144) EB-Eaa;
```

(%o144) $$-\frac{h\cdot (nuI+nuS)}{2}+\frac{h\cdot \sqrt{(nuI-nuS)^2+J^2}}{2}-\frac{h\cdot J}{2}$$

```
(%i145) subst(nuI-nuS=0,%);
```

(%o145) $$-\frac{h\cdot (nuI+nuS)}{2}$$

```
(%i146) Ebb-EB;
```

(%o146) $$-\frac{h\cdot (nuI+nuS)}{2}-\frac{h\cdot \sqrt{(nuI-nuS)^2+J^2}}{2}+\frac{h\cdot J}{2}$$

```
(%i147) subst(nuI-nuS=0,%);
```

(%o147) $$-\frac{h\cdot (nuI+nuS)}{2}$$

```
(%i148) Ebb-EA;
```

(%o148) $$-\frac{h\cdot (nuI+nuS)}{2}+\frac{h\cdot \sqrt{(nuI-nuS)^2+J^2}}{2}+\frac{h\cdot J}{2}$$

```
(%i149) subst(nuI-nuS=0,%);
```

(%o149) $$h\cdot J-\frac{h\cdot (nuI+nuS)}{2}$$

Transition probabilities k_aa to k_A

```
(%i150) abs(b_A.Fminus.k_aa)^2;
```

(%o150) $$(\sin(\theta)-\cos(\theta))^2$$

```
(%i151) subst(theta=%pi/4,%);
```

(%o151) $$0$$

```
(%i152) abs(b_B.Fminus.k_aa)^2;
```

(%o152) $$(\cos(\theta)+\sin(\theta))^2$$

```
(%i153) subst(theta=%pi/4,%);
```

(%o153) $$2$$

```
(%i154) abs(b_bb.Fminus.k_A)^2;
```

(%o154) $$(\sin(\theta)-\cos(\theta))^2$$

```
(%i155) subst(theta=%pi/4,%);
```

(%o155) $$0$$

```
(%i156) abs(b_bb.Fminus.k_B)^2;
```

(%o156) $$(\cos(\theta)+\sin(\theta))^2$$

```
(%i157) subst(theta=%pi/4,%);
```

(%o157) 2

It may seem odd that the calculated probabilities for the two transitions involving k_B are greater than 1, But, these are really only relative probabilities. The important point is that only the transitions with frequencies (nuI+nu2)/2 are allowed.

Case 3: Case 3: J^2 << (nuI-nuS)^2
theta approximately = 0

```
(%i158) subst(theta=0,k_A);
```

(%o158) $$\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

```
(%i159) subst(theta=0,k_B);
```

(%o159) $$\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

k_A → k_ba k_B → k_ab
The energy differences are

```
(%i160) EA-Eaa;
```

(%o160) $$-\frac{h\cdot (nuI+nuS)}{2}-\frac{h\cdot \sqrt{(nuI-nuS)^2+J^2}}{2}-\frac{h\cdot J}{2}$$

Eliminating J from the middle term, since J^2 << (nuI-nuS)^2

```
(%i161) -(h*(nuS+nuI))/2-(h*sqrt((nuI-nuS)^2))/2-(h*J)/2;
```

(%o161) $$-\frac{h\cdot (nuI+nuS)}{2}-\frac{h\cdot (nuI-nuS)}{2}-\frac{h\cdot J}{2}$$

```
(%i162) ratsimp(%);
```

(%o162) $$-\frac{h\cdot J+2\cdot h\cdot nuI}{2}$$

```
(%i163) EB-Eaa;
```

(%o163) $$-\frac{h\cdot (nuI+nuS)}{2}+\frac{h\cdot \sqrt{(nuI-nuS)^2+J^2}}{2}-\frac{h\cdot J}{2}$$

Eliminating J from the middle term, since J^2 << (nuI-nuS)^2

```
(%i164) -(h*(nuS+nuI))/2+(h*sqrt((nuI-nuS)^2))/2-(h*J)/2;
```

(%o164) $$-\frac{h\cdot (nuI+nuS)}{2}+\frac{h\cdot (nuI-nuS)}{2}-\frac{h\cdot J}{2}$$

```
(%i165) ratsimp(%);
```

(%o165) $$-\frac{h\cdot J+2\cdot h\cdot nuS}{2}$$

```
(%i166) Ebb-EA;
```

(%o166) $$-\frac{h\cdot (nuI+nuS)}{2}+\frac{h\cdot \sqrt{(nuI-nuS)^2+J^2}}{2}+\frac{h\cdot J}{2}$$

Eliminating J from the middle term, since J^2 << (nuI-nuS)^2

```
(%i167) -(h*(nuS+nuI))/2+(h*sqrt((nuI-nuS)^2))/2+(h*J)/2;
```

(%o167) $$-\frac{h\cdot(nuI+nuS)}{2}+\frac{h\cdot(nuI-nuS)}{2}+\frac{h\cdot J}{2}$$

```
(%i168) ratsimp(%);
```

(%o168) $$-\frac{2\cdot h\cdot nuS-h\cdot J}{2}$$

```
(%i169) Ebb-EB;
```

(%o169) $$-\frac{h\cdot(nuI+nuS)}{2}-\frac{h\cdot\sqrt{(nuI-nuS)^2+J^2}}{2}+\frac{h\cdot J}{2}$$

Eliminating J from the middle term, since J^2 << (nuI-nuS)^2

```
(%i170) -(h*(nuS+nuI))/2-(h*sqrt((nuI-nuS)^2))/2+(h*J)/2;
```

(%o170) $$-\frac{h\cdot(nuI+nuS)}{2}-\frac{h\cdot(nuI-nuS)}{2}+\frac{h\cdot J}{2}$$

```
(%i171) ratsimp(%);
```

(%o171) $$-\frac{2\cdot h\cdot nuI-h\cdot J}{2}$$

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