Maxima workbook for Principles of NMR Spectroscopy
Chapter 12: More quantum mechanics: Time and energy

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 workbook for Chapter 11, chapter11.wxmx

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This chapter covers the general description of the change of a wavefunction with time and the specific cases of a spin-1/2 particle in a stationary field and during a pulse.
The worksheet uses the definitions found in 1spinLib.mac

```
(%i1) load("1spinLib.mac")$
```

The list of functions defined in this macro file (and the packages it uses, can be generated with the functions command.

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

(%o2) [innerproduct (x, y) , unitvector (x) , columnvector (x) , gramschmidt $(x, [myinnerproduct])$, eigenvalues (mat) , eigenvectors (mat) , sub

2 12.2 Spin-1/2 particles in a magnetic field

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3 12.2.1 Time dependence of the wave function

Here, we express the Hamiltonian operator as a matrix. The dependence on the external field strength and gyromagnetic ratio are expressed through the Larmor frequency, nu =-gamma*B/(2*pi)

```
(%i3) H(nu);
```

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

The general form of a wavefunction, or ket, for a spin-1/2 particle is written as a column vector:

```
(%i4) k_psi;
```

(%o4) $\begin{pmatrix} ca \\ cb \end{pmatrix}$

The complex conjugate, bra, of the wavefunction is written as a row vector:

```
(%i5) b_psi;
```

(%o5) $\begin{pmatrix} \overline{ca} & \overline{cb} \end{pmatrix}$

The operation of the Hamiltonian on the wavefunction

```
(%i6) H(nu).k_psi;
```

(%o6) $\begin{pmatrix} \frac{ca \cdot h \cdot \nu}{2} \\ -\frac{cb \cdot h \cdot \nu}{2} \end{pmatrix}$

The eigenvalues and eigenvectors of the Hamiltonian

```
(%i7) uniteigenvectors(H(nu));
```

(%o7) $[[[-\frac{h \cdot \nu}{2}, \frac{h \cdot \nu}{2}], [1, 1]], [[[0, 1]], [[1, 0]]]]$

The eignenvectors of H are the same as those of Iz and the eigenvalues are -h*nu/2 and h*nu/2. For a nucleus with a positive gyromagnetic ratio, the frequency is negative and energy of the Ibeta> wavefunction (represented as a vector in Maxima list form as [0,1]) has a positive energy.

The time dependence of a wavefunction is calculated using the unitary matrix Uh, which includes terms for both the time period, t, and the Larmor frequency nu

```
(%i8) Uh(t,nu);
```

(%o8) $\begin{pmatrix} e^{-i \cdot \pi \cdot \nu \cdot t} & 0 \\ 0 & e^{i \cdot \pi \cdot \nu \cdot t} \end{pmatrix}$

The product of this matrix and the vector form of a wavefunction gives the wavefunction after time, t

```
(%i9) Uh(t,nu).k_psi;
```

(%o9) $\begin{pmatrix} ca \cdot e^{-i \cdot \pi \cdot \nu \cdot t} \\ cb \cdot e^{i \cdot \pi \cdot \nu \cdot t} \end{pmatrix}$

We use as the starting wavefunction one of the eigenfunctions of Ix

```
(%i10) k_0:ket(1/sqrt(2),1/sqrt(2));
```

(%o10) $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$

The complex conjugate of the wavefunction (i.e. the bra) is

```
(%i11) b_0:bra(k_0);
```

(%o11) $\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$

After time t, the wavefunction is

```
(%i12) Uh(t,nu).k_0;
```

(%o12) $\begin{pmatrix} \frac{e^{-i \cdot \pi \cdot \nu \cdot t}}{\sqrt{2}} \\ \frac{e^{i \cdot \pi \cdot \nu \cdot t}}{\sqrt{2}} \end{pmatrix}$

An aside on complex numbers. If we define a complex number as:

```
(%i13) declare(c,complex);
```

(%o13) *done*

```
(%i14) c:a + %i*b;
```

(%o14) $i \cdot b + a$

(%i15) c;

(%o15) $i \cdot b + a$

The exponential form of the complex number can be found using the polarform command, found as the Convert to Polar Form command in the Simplify>>Complex menu of wxMaxima

(%i16) cp:polarform(c);

(%o16) $\sqrt{b^2 + a^2} \cdot e^{i \cdot \mathrm{atan2}(b,a)}$

(%i17) cp;

(%o17) $\sqrt{b^2 + a^2} \cdot e^{i \cdot \mathrm{atan2}(b,a)}$

The term sqrt(b^2+a^2) represents the modulus, m, and atan2(b,a) is the angle theta. The function atan2 calculates the arc tangent (inverse tangent) of points defined by their x and y coordinates.

(%i18) ? atan2;

-- Function: atan2 (<y>, <x>)
- yields the value of 'atan(<y>/<x>)' in the interval '-\%pi' to
'\%pi'.

(%o18) true

Complex numbers in the exponential form can also be converted to the rectangular form (Convert to Rectangular Form in the Simplify>>Complex menu of wxMaxima).

(%i19) rectform(cp);

(%o19) $i \cdot b + a$

4 12.2.2 Time dependence of the z-magnetization

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We will call the evolving wavefunction, calculated above, k_t

(%i20) k_t:Uh(t,nu).k_0;

(%o20) $\begin{pmatrix} \frac{e^{-i \cdot \pi \cdot \nu \cdot t}}{\sqrt{2}} \\ \frac{e^{i \cdot \pi \cdot \nu \cdot t}}{\sqrt{2}} \end{pmatrix}$

The corresponding bra is b_t and can be formed using the bra function in 1spinLib.mac

(%i21) b_t:bra(k_t);

(%o21) $\begin{pmatrix} \frac{e^{i \cdot \pi \cdot \nu \cdot t}}{\sqrt{2}} & \frac{e^{-i \cdot \pi \cdot \nu \cdot t}}{\sqrt{2}} \end{pmatrix}$

The z-magnetization is calculated by multiplying the ket by the Iz operator matrix, and then multiplying the product by the bra

(%i22) Iz;

(%o22) $\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$

(%i23) b_t.Iz.k_t;

(%o23) 0

For the more general case, we can use k_psi and b_psi defined in 1spinLib.mac

```
(%i24) k_psi;
```

(%o24) $\begin{pmatrix} ca \\ cb \end{pmatrix}$

```
(%i25) b_psi;
```

(%o25) $\begin{pmatrix} \overline{ca} & \overline{cb} \end{pmatrix}$

The over scores indicate the complex conjugates of ca and cb
The initial z-magnetization is:

```
(%i26) b_psi.Iz.k_psi;
```

(%o26) $$\frac{ca \cdot \overline{ca}}{2} - \frac{cb \cdot \overline{cb}}{2}$$

The time-dependent wavefunction and its complex conjugate are then:

```
(%i27) k_psit:Uh(t,nu).k_psi;
```

(%o27) $$\begin{pmatrix} ca \cdot e^{-i \cdot \pi \cdot \nu \cdot t} \\ cb \cdot e^{i \cdot \pi \cdot \nu \cdot t} \end{pmatrix}$$

```
(%i28) b_psit:bra(k_psit);
```

(%o28) $$\begin{pmatrix} \overline{ca} \cdot e^{i \cdot \pi \cdot \nu \cdot t} & \overline{cb} \cdot e^{-i \cdot \pi \cdot \nu \cdot t} \end{pmatrix}$$

The time-dependent z-magnetization is

```
(%i29) b_psit.Iz.k_psit;
```

(%o29) $$\frac{ca \cdot \overline{ca}}{2} - \frac{cb \cdot \overline{cb}}{2}$$

Thus, the z-magnetization does not change with time, in the absence of relaxation or other perturbations.

The magnetization components can also be calculated using the meanPsi function in 1spinLib.mac.

```
(%i30) fundef(meanPsi);
```

(%o30) $$\mathrm{meanPsi}\left(op, \psi\right) := \mathrm{trigreduce}\left(\mathrm{trigsimp}\left(\mathrm{demoivre}\left(\overline{\psi}.op.\psi\right)\right)\right)$$

The functions trigreduce, trigsimp and demoivre are included in this function definition to simplify the results and express them in trigonometric form.

```
(%i31) meanPsi(Iz,k_t);
```

(%o31) 0

```
(%i32) meanPsi(Iz,k_psi);
```

(%o32) $$-\frac{cb \cdot \overline{cb} - ca \cdot \overline{ca}}{2}$$

```
(%i33) meanPsi(Iz,k_psit);
```

(%o33) $$-\frac{cb \cdot \overline{cb} - ca \cdot \overline{ca}}{2}$$

5 12.2.3 Time dependence of the x- and y-magnetization components

The Ix operator matrix is:

```
(%i34) Ix;
```

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

Using the previous definitions of k_t and b_t

```
(%i35) k_t;
```

(%o35) $\begin{pmatrix} \frac{e^{-i\cdot\pi\cdot\nu\cdot t}}{\sqrt{2}} \\ \frac{e^{i\cdot\pi\cdot\nu\cdot t}}{\sqrt{2}} \end{pmatrix}$

```
(%i36) b_t;
```

(%o36) $\begin{pmatrix} \frac{e^{i\cdot\pi\cdot\nu\cdot t}}{\sqrt{2}} & \frac{e^{-i\cdot\pi\cdot\nu\cdot t}}{\sqrt{2}} \end{pmatrix}$

The initial x-magnetization is:

```
(%i37) b_0.Ix.k_0;
```

(%o37) $\frac{1}{2}$

The time-dependent x-magnetization is:

```
(%i38) b_t.Ix.k_t;
```

(%o38) $\frac{e^{2\cdot i\cdot\pi\cdot\nu\cdot t}}{4}+\frac{e^{-2\cdot i\cdot\pi\cdot\nu\cdot t}}{4}$

This can be simplified and converted to a trigonometric form

```
(%i39) rectform(%);
```

(%o39) $\frac{\cos\left(2\cdot\pi\cdot\nu\cdot t\right)}{2}$

The conversion is done automatically by the meanPsi function

```
(%i40) meanPsi(Ix,k_t);
```

(%o40) $\frac{\cos\left(2\cdot\pi\cdot\nu\cdot t\right)}{2}$

For the y-magnetization

```
(%i41) Iy;
```

(%o41) $\begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix}$

The initial y=magnetization

```
(%i42) meanPsi(Iy,k_0);
```

(%o42) 0

The time-dependent y-magnetization

```
(%i43) b_t.Iy.k_t;
```

(%o43) $$\frac{i\cdot e^{-2\cdot i\cdot \pi\cdot \nu\cdot t}}{4}-\frac{i\cdot e^{2\cdot i\cdot \pi\cdot \nu\cdot t}}{4}$$

```
(%i44) meanPsi(Iy,k_t);
```

(%o44) $$\frac{\sin\left(2\cdot \pi\cdot \nu\cdot t\right)}{2}$$

The 1spinLib.mac library also includes a function, allMagPsi, to calculate the x, y and z magnetization components in one command

```
(%i45) allMagPsi(k_psi);
```

$$<Ix>=\frac{\overline{ca}\cdot cb+ca\cdot \overline{cb}}{2} <Iy>=\frac{i\cdot ca\cdot \overline{cb}-i\cdot \overline{ca}\cdot cb}{2} <Iz>=-\frac{cb\cdot \overline{cb}-ca\cdot \overline{ca}}{2}$$

(%o45)

```
(%i46) allMagPsi(k_0);
```

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

(%o46)

```
(%i47) allMagPsi(k_t);
```

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

(%o47)

```
(%i48) allMagPsi(k_psit);
```

$$<Ix>=-\frac{-\overline{ca}\cdot cb\cdot \cos\left(2\cdot \pi\cdot \nu\cdot t\right)-ca\cdot \overline{cb}\cdot \cos\left(2\cdot \pi\cdot \nu\cdot t\right)-i\cdot \overline{ca}\cdot cb\cdot \sin\left(2\cdot \pi\cdot \nu\cdot t\right)+i\cdot ca\cdot \overline{cb}\cdot \sin\left(2\cdot \pi\cdot \nu\cdot t\right)}{2} <Iy>= -i\cdot$$

(%o48)

The simplification rules included in the allMagPsi function don't always give the simplest results, but further manipulations can be applied to the results. For instance for the x-magnetization from k_psit

```
(%i49) meanPsi(Ix,k_psit);
```

(%o49) $$-\frac{-\overline{ca}\cdot cb\cdot \cos\left(2\cdot \pi\cdot \nu\cdot t\right)-ca\cdot \overline{cb}\cdot \cos\left(2\cdot \pi\cdot \nu\cdot t\right)-i\cdot \overline{ca}\cdot cb\cdot \sin\left(2\cdot \pi\cdot \nu\cdot t\right)+i\cdot ca\cdot \overline{cb}\cdot \sin\left(2\cdot \pi\cdot \nu\cdot t\right)}{2}$$

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

(%o50) $$-\frac{\left(-ca\cdot \overline{cb}-\overline{ca}\cdot cb\right)\cdot \cos\left(2\cdot \pi\cdot \nu\cdot t\right)+\left(i\cdot ca\cdot \overline{cb}-i\cdot \overline{ca}\cdot cb\right)\cdot \sin\left(2\cdot \pi\cdot \nu\cdot t\right)}{2}$$

This still looks pretty messy, but notice that the initial Ix and Iy components are:

```
(%i51) meanPsi(Ix,k_psi);
```

(%o51) $$\frac{\overline{ca}\cdot cb+ca\cdot \overline{cb}}{2}$$

```
(%i52) meanPsi(Iy,k_psi);
```

(%o52) $$\frac{i\cdot ca\cdot \overline{cb}-i\cdot \overline{ca}\cdot cb}{2}$$

If we call the initial values Ix0 and Iy0, we can substitute these values into the expression for the time-dependent Ix magnetization

First, let's assign the expression to a variable.

```
(%i53) IxTime:ratsimp(meanPsi(Ix,k_psit));
```

$$(\%o53)\quad -\frac{\left(-ca\cdot\overline{cb}-\overline{ca}\cdot cb\right)\cdot\cos\left(2\cdot\pi\cdot\nu\cdot t\right)+\left(i\cdot ca\cdot\overline{cb}-i\cdot\overline{ca}\cdot cb\right)\cdot\sin\left(2\cdot\pi\cdot\nu\cdot t\right)}{2}$$

Then we can use the substitution command, which is available as Simplify>>Substitute in wxMaxima. We do this in two steps.

```
(%i54) subst(2*Iy0, (%i*ca*conjugate(cb)-%i*conjugate(ca)*cb), IxTime);
```

$$(\%o54)\quad -\frac{\left(-ca\cdot\overline{cb}-\overline{ca}\cdot cb\right)\cdot\cos\left(2\cdot\pi\cdot\nu\cdot t\right)+2\cdot Iy0\cdot\sin\left(2\cdot\pi\cdot\nu\cdot t\right)}{2}$$

```
(%i55) subst(-2*Ix0, (-ca*conjugate(cb)-conjugate(ca)*cb), %);
```

$$(\%o55)\quad -\frac{2\cdot Iy0\cdot\sin\left(2\cdot\pi\cdot\nu\cdot t\right)-2\cdot Ix0\cdot\cos\left(2\cdot\pi\cdot\nu\cdot t\right)}{2}$$

Substitutions are rather tricky, and the form used in the substitution often has to match exactly the form that appears in the original expression.

6 12.3 When the Hamiltonian changes with time: The effect of radiation on the wavefunction

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6.1 An x-pulse

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The effects of pulses on the wavefunction are expressed in matrix form by rotation matrices containing the variable a, for the angle of rotation.
For an x-pulse, the rotation matrix is (from 1spinLib.mac):

```
(%i56) Rx(a);
```

$$(\%o56)\quad \begin{pmatrix}\cos\left(\frac{a}{2}\right) & -i\cdot\sin\left(\frac{a}{2}\right)\\ -i\cdot\sin\left(\frac{a}{2}\right) & \cos\left(\frac{a}{2}\right)\end{pmatrix}$$

To obtain the new wavefunction, the existing wavefunction is multiplied by the rotation matrix. (Eq 12.6, page 359)

```
(%i57) Rx(a).k_psi;
```

$$(\%o57)\quad \begin{pmatrix}\cos\left(\frac{a}{2}\right)\cdot ca-i\cdot\sin\left(\frac{a}{2}\right)\cdot cb\\ \cos\left(\frac{a}{2}\right)\cdot cb-i\cdot\sin\left(\frac{a}{2}\right)\cdot ca\end{pmatrix}$$

1spinLib.mac also contains a function to calculate this result

```
(%i58) psiPulseX(k_psi,a);
```

$$(\%o58)\quad \begin{pmatrix}\cos\left(\frac{a}{2}\right)\cdot ca-i\cdot\sin\left(\frac{a}{2}\right)\cdot cb\\ \cos\left(\frac{a}{2}\right)\cdot cb-i\cdot\sin\left(\frac{a}{2}\right)\cdot ca\end{pmatrix}$$

Additional functions are provided for the specific cases of pi and pi/2 pulses along the x-axis

```
(%i59) psiPiX(k_psi);
```

$$(\%o59)\quad \begin{pmatrix}-i\cdot cb\\ -i\cdot ca\end{pmatrix}$$

(%i60) psiPi2X(k_psi);

(%o60) $$\begin{pmatrix} \frac{ca}{\sqrt{2}} - \frac{i \cdot cb}{\sqrt{2}} \\ \frac{cb}{\sqrt{2}} - \frac{i \cdot ca}{\sqrt{2}} \end{pmatrix}$$

For the case of a (pi/2)x pulse applied to |alpha>

(%i61) psiPi2X(k_a);

(%o61) $$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} \end{pmatrix}$$

(%i62) allMagPsi(%);

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

(%o62)

6.2 y-pulses

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The y-rotation matrix is:

(%i63) Ry(a);

(%o63) $$\begin{pmatrix} \cos\left(\frac{a}{2}\right) & -\sin\left(\frac{a}{2}\right) \\ \sin\left(\frac{a}{2}\right) & \cos\left(\frac{a}{2}\right) \end{pmatrix}$$

(%i64) Ry(a).k_psi;

(%o64) $$\begin{pmatrix} \cos\left(\frac{a}{2}\right) \cdot ca - \sin\left(\frac{a}{2}\right) \cdot cb \\ \cos\left(\frac{a}{2}\right) \cdot cb + \sin\left(\frac{a}{2}\right) \cdot ca \end{pmatrix}$$

y-pulse functions

(%i65) psiPulseY(k_psi,a);

(%o65) $$\begin{pmatrix} \cos\left(\frac{a}{2}\right) \cdot ca - \sin\left(\frac{a}{2}\right) \cdot cb \\ \cos\left(\frac{a}{2}\right) \cdot cb + \sin\left(\frac{a}{2}\right) \cdot ca \end{pmatrix}$$

(%i66) psiPi2Y(k_psi);

(%o66) $$\begin{pmatrix} \frac{ca}{\sqrt{2}} - \frac{cb}{\sqrt{2}} \\ \frac{cb}{\sqrt{2}} + \frac{ca}{\sqrt{2}} \end{pmatrix}$$

(%i67) psiPiY(k_psi);

(%o67) $$\begin{pmatrix} -cb \\ ca \end{pmatrix}$$

(%i68) psiPulseX(k_a,a);

(%o68) $$\begin{pmatrix} \cos\left(\frac{a}{2}\right) \\ -i \cdot \sin\left(\frac{a}{2}\right) \end{pmatrix}$$

A (pi/2)y pulse applied to |alpha>

(%i69) psiPi2Y(k_a);

(%o69) $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$

(%i70) allMagPsi(%);

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

(%o70)

To look at the effect of an x-pulse after aligning the magnetization with the y'-axis, first define the wavefunction following a pi/2 x-pulse to |alpha>

(%i71) k_y:psiPi2X(k_a);

(%o71) $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} \end{pmatrix}$

(%i72) allMagPsi(k_y);

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

(%o72)

then apply a pi/2 y-pulse

(%i73) psiPi2Y(k_y);

(%o73) $\begin{pmatrix} \frac{i}{2} + \frac{1}{2} \\ \frac{1}{2} - \frac{i}{2} \end{pmatrix}$

(%i74) allMagPsi(%);

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

(%o74)

As expected, the second pulse has no effect.

6.3 A 2*Pi-pulse

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A 2*pi pulse applied to |alpha>

(%i75) psiPulseX(k_a,2*%pi);

(%o75) $\begin{pmatrix} -1 \\ 0 \end{pmatrix}$

The sign of the wavefunction has been reversed, but the observable magnetization components are unchanged.

(%i76) allMagPsi(%);

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

(%o76)

7 12.3.5 Transition probabilities and the absorption of energy

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The transition probability from |alpha> to |beta> is calculated as |<beta|Iminus|alpha>|^2, where Iminus is the lowering operator

```
(%i77) abs(b_b.Iminus.k_a)^2;
```

(%o77) 1

|beta> cannot be converted to |beta>

```
(%i78) abs(b_b.Iminus.k_b)^2;
```

(%o78) 0

The upward transition from an arbitrary wavefunction to |alpha>

```
(%i79) k_psi;
```

(%o79) $\begin{pmatrix} ca \\ cb \end{pmatrix}$

```
(%i80) abs(b_a.Iplus.k_psi)^2;
```

(%o80) $|cb|^2$

Because cb is a complex number, |cb| represents cb*conjugate(cb)

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