Jellyfish manual

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1 Introduction

Jellyfish is a program for the simulation of 1D NMR spectra for liquid state samples specialised in complicate J-coupling patterns. It features a graphical user interface for intuitive simulations, and a python library for advanced use. Jellyfish is written in the Python programming language, and is cross-platform and open-source (GPL3 licence).

The Jellyfish graphical interface is aimed for teaching purposes, especially when it comes to demonstrating the influence of strong coupling effects on NMR spectra in the liquid state. The engine itself is quite fast, as several more advanced techniques for simulating J-coupling patterns are implemented. These are discussed in the technical mart of this manual. Note that Jellyfish calculations are exact: no approximations are made to reduce the calculation time.

2 Running Jellyfish

2.1 Python and library versions

Jellyfish has been programmed to run on both the python 2.x and 3.x. Jellyfish should run on python versions starting from 2.7 and 3.4. For the library version, the following are needed:

- `numpy` >= 1.11.0
- `matplotlib` >= 1.4.2
- `scipy` >= 0.14.1

Jellyfish also needs the `PyQt` (version 4 or 5) library.

2.2 Installing

2.2.1 Linux

On Linux, Jellyfish can be most efficiently run using the python libraries that are in the repositories. For Ubuntu, these can be installed by running:

```
sudo apt install python python-numpy python-matplotlib python-scipy
python-pyqt5
```

Navigating to the `Jellyfish` directory in a terminal, Jellyfish can then be run by executing `python Jellyfish.py`.

2.2.2 Windows

On Windows, the relevant python libraries can be installed by installing `anaconda`: https://www.anaconda.com/download/. If you do not have another python version installed already, make sure to add anaconda to the `path` during the install. In this case, Jellyfish can be run by executing the `WindowsRun.bat` file in the `Jellyfish` directory. Destktop and start menu shortcuts to this file can be created by executing the `WindowsInstall.vbs` file.

If you already have other version of python installed, adding anaconda to the `path` might create issues. Do not do this in this case. When not added to the path, the `WindowsRun.bat` should be edited in such a way that `pythonw` is replaced with the path to your `pythonw.exe` executable in the anaconda install directory.

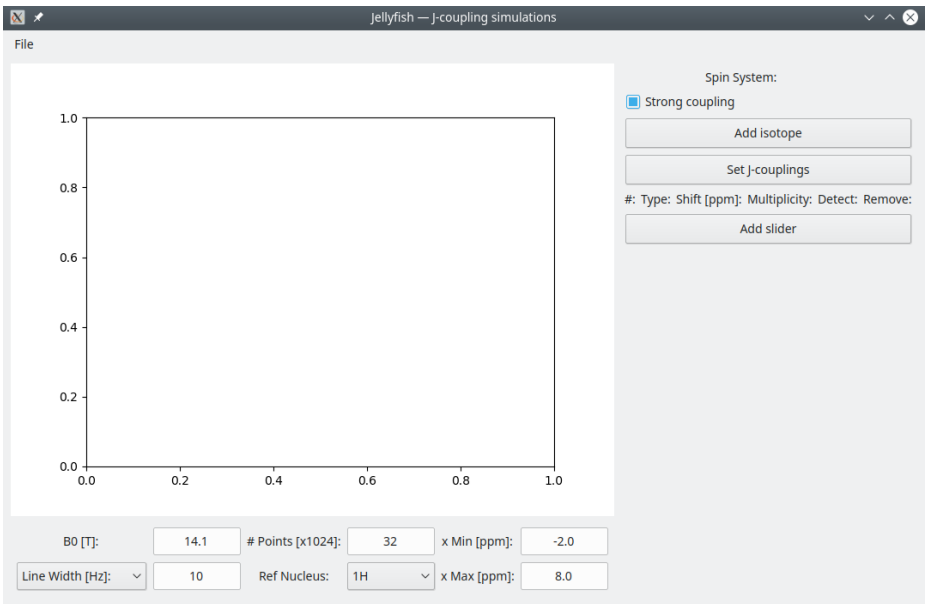
2.2.3 OS X

On OS X, the relevant python libraries can be installed by installing `anaconda`: https://www.anaconda.com/download/. Navigating to the `Jellyfish` directory in a terminal, Jellyfish can then be run by `anacondapython Jellyfish.py`, with `anacondapython` replaced by the path to your anaconda python executable.

3 The graphical user interface

Jellyfish can be run either as a standalone program, via its graphical user interface (GUI), or as a library by loading it in a Python script. Firstly, I will describe how to use the GUI.

Opening the program shows the main menu:



The window has two regions of settings: the spin system on the right, and the spectrum settings in the bottom. Also, there is a plot region.

3.1 Plot region

There are several ways to control the display of the spectrum using the mouse. Below, a list of these is given:

- Dragging a box while holding the left mouse button creates a zoombox, and will zoom to that region.
- Dragging while holding the right mouse button drags (i.e. pans) the spectrum. Doing this while holding the Control button pans only the x-axis, holding Shift pans only the y-axis.
- Double clicking with the right mouse button resets the view to fit the whole plot (both x and y).
- Scrolling with the mouse wheel zooms the y-axis. Doing this while also holding the right mouse button zooms the x-axis. By holding Control the zooming will use a larger step size.

3.2 The bottom frame

In the bottom frame, several parameters can be changed:

- B0 [T]: the magnetic field strength in Tesla. This value can also be changed from a slider (see below)
- Line Width [Hz/ppm]: the line broadening added to the spectrum simulation. Input either in Hertz or ppm (can be changed via the dropdown menu). The ppm setting is most useful when changing the magnetic field: the effective line width remains constant then.
- # Points [x1014]: The number of points in the spectrum.
- Ref Nucleus: Defines the reference frequency (i.e. nucleus) of the spectrum.
- x Min [ppm]: The minimum x-value in ppm
- x Max [ppm]: The maximum x-value in ppm

3.3 The spin system frame

On the right-hand side of the window, the spin system can be defined. Jellyfish support spin systems of any size (but your computer will not be able to handle very large systems, of course). There are several buttons always available:

- Strong coupling: toggle that determines if strong coupling is present. This determines if the J_{xy} part of the Hamiltonian is added. In realty, this is always on. The toggle is provide here to be able to show the effect of this strong coupling.
- Add isotope: Adds an isotope to the spin system. The gives a pup-up window were the type of nucleus can be selected, the chemical shift can be given, and the multiplicity defined. Pushing OK adds this spin to the system. This adds a row of input boxes to the interface, were the shift and multiplicity can be changed.
- Set J-couplings: Opens a window to set the J-coupling parameters. By default, all are 0. The amount of entries depends on the spin-system that has been defined at the moment.
- Add slider: Adds a slider to the interface. This can be used to change a specific parameter while watching the resulting spectrum. Ideal for teaching purposes on the effect of strong coupling, field strengths, etc. Pushing this button opens an input window, where the type (B0, Shift, or J-coupling) needs to be defined, as well as the minimum and maximum value of the slider. For the 'Shift' or 'J-coupling' type, one or two spin numbers also need to be given.

When a spin is defined, an extra line is added to the interface with the following options:

- Shift [ppm]: the chemical shift in ppm
- Multiplicity: the multiplicity of the nucleus (i.e. the ^{1}H multiplicity of a CH_3 group is '3')
- Detect: whether or not this nucleus is detected (i.e. added to the spectrum)

- X: remove this nucleus from the spin system. This also clears all relevant J-couplings, and removes and slider that has a relation to this spin.

When a slider is defined, it adds a row to the slider space. Here, there now is a slider which can be used to change the specified parameter. There is also a 'X' button to remove the slider. When using a slider, the respective value is also changed in the rest of the interface (e.g. chemical shift are also updated in the spin system rows).

3.4 Menu

Jellyfish also has a menu on the top of the interface. It has the following options:

- File:
  - Export Figure: export the current plot as an .png image.
  - Export Data (ASCII): save the current spectrum as a text file (x and y data).
  - Export as ssNake .mat: save spectrum as a Matlab file as used by the ssNake software (see https://www.ru.nl/science/magneticresonance/software/ssnake/).
  - Export as Simpson: save as a text file as supported by the Simpson simulation software (see http://inano.au.dk/about/research-centers/nmr/software/simpson/).
  - Quit: closes the program

4 Running as a script

Apart from running Jellyfish as a program via the user interface, it can also be used as a library from within python. This requires that you have the source code of Jellyfish (and not a compiled version). The 'Examples' directory holds some examples on how to do simulations from a script. Below an easy example is given. Here, it is assumed that the Jellyfish main directory (which holds `engine.py`) is one directory higher than this file.

```
import numpy as np
import sys
sys.path.append("..")
import engine as en

#--------Spectrum settings----------
Base = 42.577469e6
RefFreq = 600e6 #zero frequency
```

```
B0 = RefFreq/Base #B0 is proton freq divided by the base scale
StrongCoupling = True #Strong coupling on
Lb = 0.2 #Linewidth in Hz
NumPoints = 1024*128 #Number of points
Limits = np.array([-1,3]) #Limits of the plot in ppm

#-------Spin system-----------
# add spin as ['Type', shift, multiplicity, Detect]
SpinList = [['1H',0,1,True]]
SpinList.append(['1H',2,1,True])

Jmatrix = np.array([[0, 10],
                    [ 0, 0]])


#-------Make spectrum----------
# Prepare spinsys:
spinSysList = en.expandSpinsys(SpinList,Jmatrix)
# Get frequencies and intensities
Freq, Int = en.getFreqInt(spinSysList, B0, StrongCoupling)
# Make spectrum
Spectrum, Axis, RefFreq = en.MakeSpectrum(Int, Freq,
                                          Limits, RefFreq,Lb,NumPoints)
#Save as ssNake Matlab file
en.saveMatlabFile(Spectrum,Limits,RefFreq,Axis,'easy.mat')
```

5 Technical background

In the following, I will discussed the algorithms that are implemented in Jellyfish for the simulation of strong coupling patterns. This part is both a documentation, as well as a tutorial on how to approach these calculations. Any suggestions to improve the algorithm are appreciated.

5.1 Basics

In order to simulate a spectrum, we need to know which frequencies are present, and the amplitude of these frequencies. based on that, we can draw a spectrum directly (as a histogram), or simulate the FID (as a series of complex exponentials). Calculating the spectrum directly is much faster, and this is used in Jellyfish. This is accurate if the number of points is high enough.

In order to calculate the energies, we need the Hamiltonian of the system. The total Hamiltonian is the Hamiltonian of all spins, including the Zeeman interaction (with the chemical shift)

and the scalar coupling (J-coupling) interaction between all pairs of spins:

$$\mathscr{H} = \sum_i \mathscr{H}_i^{\text{zee}} + \sum_i \sum_{s>i} \mathscr{H}_{i,s}^{\text{J}} \tag{1}$$

Here, the double sum is only needed for a part of all pairs ([i,s] and [s,i] are equal, and [i,i] = 0).

To get the energies of the transitions, we need to transform the Hamiltonian to a diagonal frame (i.e. gets its eigenvalues)[1]:

$$\mathscr{H}^{\text{int}} = T^{-1} \bullet \mathscr{H} \bullet T \tag{2}$$

where the 'int' superscript indicates we have gone to the interaction frame. Here T represents the eigenfunction matrix, we we can use to transform the Hamiltonian to a new frame. T^{-1} is the inverse of this matrix. In this representation, the energy of transition $i \rightarrow j$ is equal to $\mathscr{H}^{\text{int}}[i,i] - \mathscr{H}^{\text{int}}[j,j]$.

Apart from the energy, we also need the transition probability, i.e. the intensity of the transient. This depends on two things: the start operator, and the detection operator. We use the following definitions:

$$\rho_0 = I_x \tag{3}$$

as a starting operator. And

$$\text{Detect} = I_+ \tag{4}$$

To get the probability of a transition, we multiply these values in a point-wise fashion: $\rho_0 \cdot \text{Detect} = I_x \cdot I_+$. However, we want this result to be defined in the interaction frame:

$$P = (T^{-1} \bullet I_x \bullet T) \cdot (T^{-1} \bullet I_+ \bullet T) \tag{5}$$

Having calculated this, we can get the intensity of transition $i \rightarrow j$ as $P[i,j]$.

5.2 Strong coupling

Strong coupling is an effect which is relevant when the chemical shift difference between two spins is not much larger than the strength of the J-coupling. Spectra that are influenced by strong coupling effects are called 'higher order' spectra. Within the J-coupling Hamiltonian, the strong coupling effects are contained in the x and y parts. The full Hamiltonian is:

$$\mathscr{H}^{\text{J}} = \sum_i \sum_{s>i} \mathscr{H}_{i,s}^{\text{J}} = \sum_i \sum_{s>i} J_{i,s}(I_x S_x + I_y S_y + I_z S_z) \tag{6}$$

If we take only the $I_z S_z$ part into account, we can calculate a spectrum without strong coupling effects. A better representation is therefore:

$$\mathscr{H}^{\text{J}} = \mathscr{H}_{\text{weak}}^{\text{J}} + \mathscr{H}_{\text{strong}}^{\text{J}} \tag{7}$$

[1] Note that I use the • symbol to represent a matrix multiplication, and a · for a point-wise multiplication.

with:

$$\mathscr{H}^{\mathrm{J}}_{\mathrm{weak}} = \sum_i \sum_{s>i} J_{i,s}(I_z S_z) \tag{8}$$

and

$$\mathscr{H}^{\mathrm{J}}_{\mathrm{strong}} = \sum_i \sum_{s>i} J_{i,s}(I_x S_x + I_y S_y) \quad . \tag{9}$$

In Jellyfish, setting `strong coupling = False` makes sure only $\mathscr{H}^{\mathrm{J}}_{\mathrm{weak}}$ is calculated and used. For later use, the alternative representation:

$$\mathscr{H}^{\mathrm{J}}_{\mathrm{strong}} = \sum_i \sum_{s>i} J_{i,s}(I_x S_x + I_y S_y) = \sum_i \sum_{s>i} J_{i,s}(I_+ S_- + I_- S_+)/2 \tag{10}$$

is more convenient.

6 Contact

To contact the `Jellyfish` team write to `ssnake@science.ru.nl`.

Bibliography