

Multiple quadrupolar pattern fitting in ssNake

24th May 2019

1 Introduction

In this tutorial, I will demonstrate how to fit multiple spectra at the same time with linked parameters. The example that we will treat here is for second order quadrupolar patterns. These patterns scale in width as a function of the magnetic field. In some cases, the occurrence of multiple atomic sites complicates a correct fitting of these line shapes. The aid with the fitting of these spectra, additional data is often recorded at different magnetic fields. Fitting these spectra simultaneously, linking their quadrupolar parameters, will then lead to a more accurate fit result.

Before continuing with this tutorial, it might be wise to check out our other tutorial about CSA fitting, to get acquainted with the fitting procedure in ssNake.

2 Data

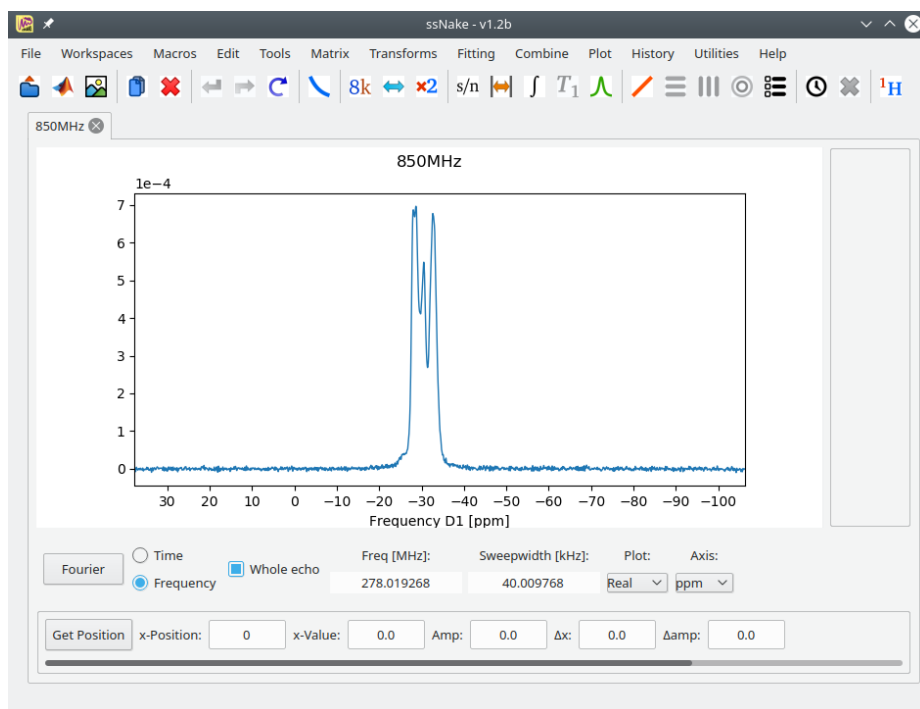
The data used in this tutorial are ^{87}Rb spectra of rubidium nitrate (RbNO_3) powder which was recorded on a Varian 300 MHz and 850 MHz spectrometer. 25 kHz MAS was used for both spectra.

3 Fitting a single quadrupole spectrum

As a start, we will load one of the spectra, and fit that one on its own.

- Load the '850MHz.mat' file that was delivered with this tutorial
- Put the x-axis on 'ppm' (via the 'Axis' dropdown in the bottomframe)

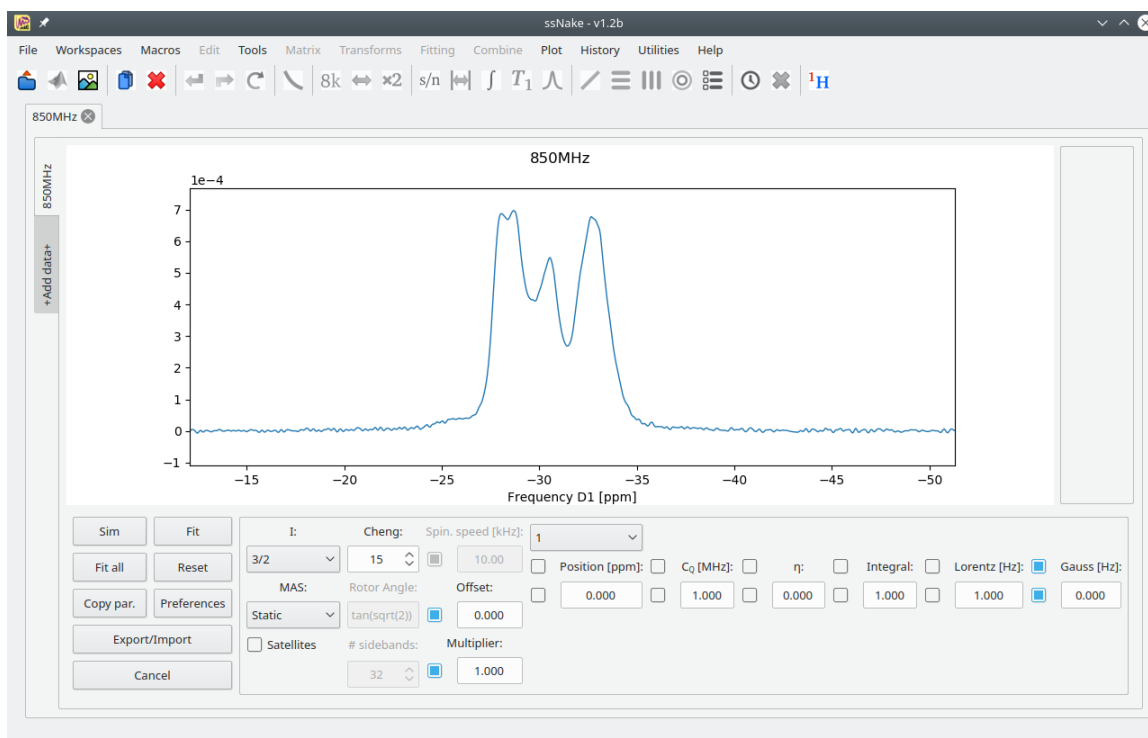
This should show:



Now we go to the fitting:

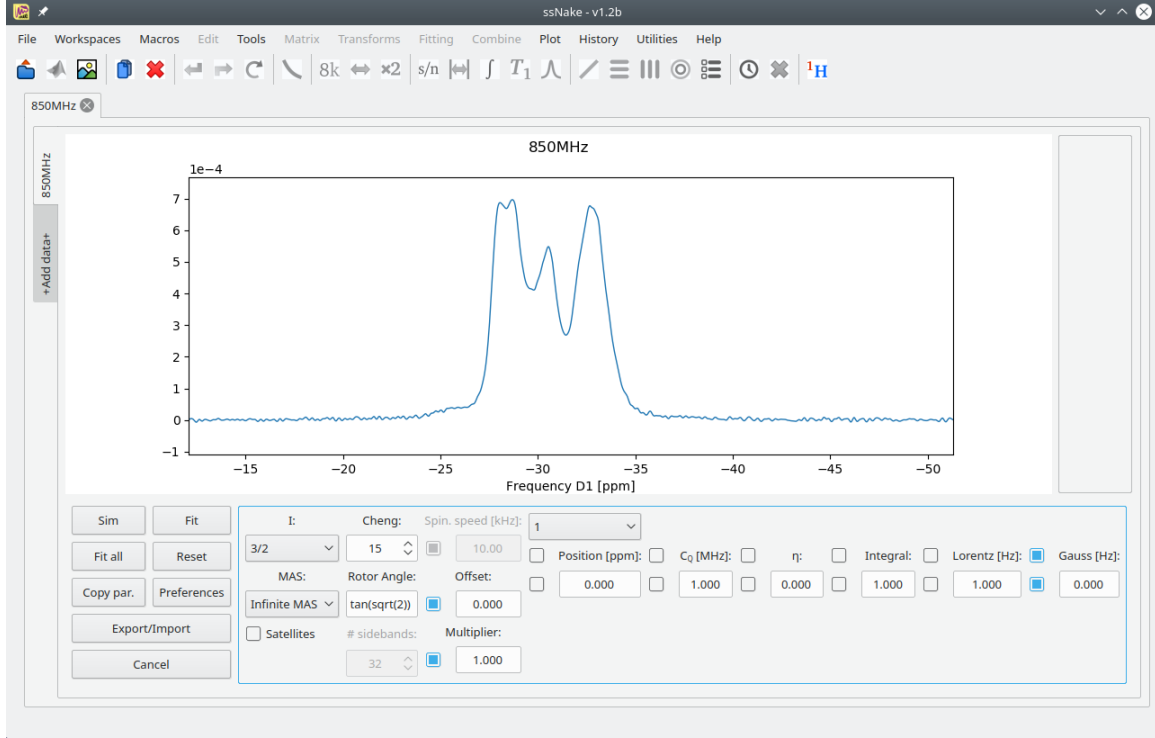
- Fitting → Quadrupole

This shows the fitting window (I zoomed the x-axis for this Figure):



Firstly, we must make sure that some general settings are correct. ^{87}Rb is a spin $3/2$ nucleus, so I should be $3/2$ (this is the default value). The MAS settings should be at 'Infinite MAS', and the satellites should be turned off¹.

This gives:

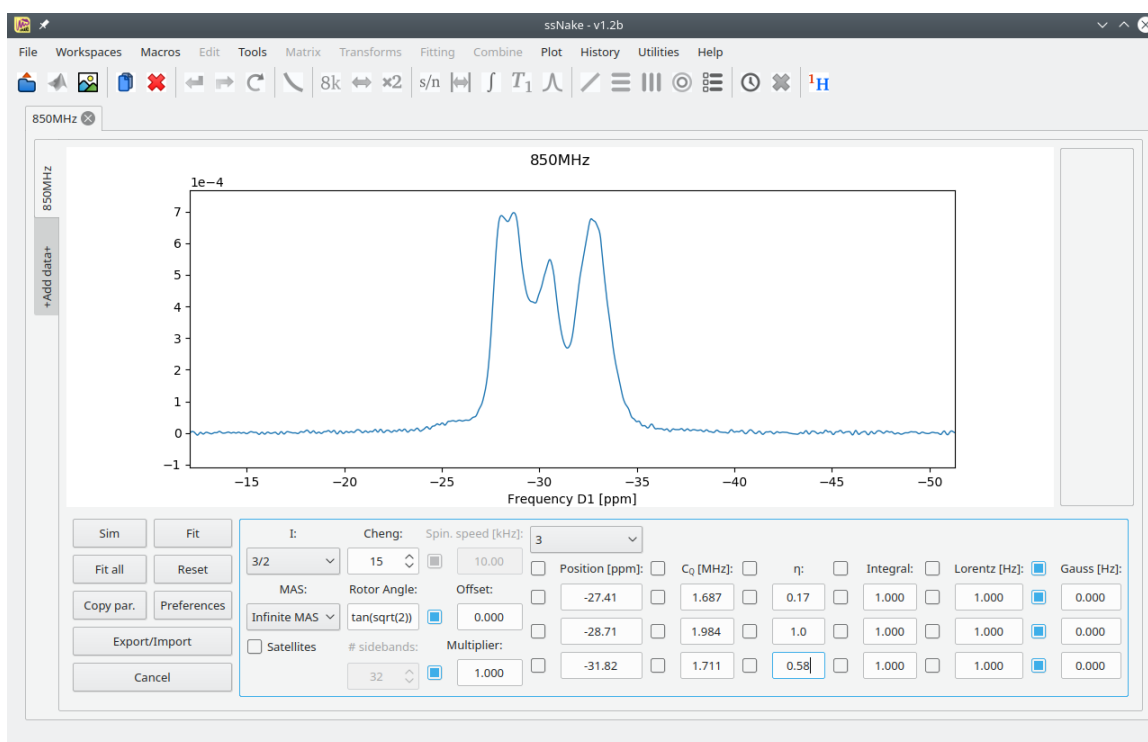


Now, we can start by filling in some starting values for the fit. These can be tricky to establish, so we will just use the literature values in this case (i.e. from the ssNake paper).

Site	Position [ppm]	C_Q [MHz]	η
1	-27.41	1.687	0.17
2	-28.71	1.984	1.0
3	-31.82	1.711	0.58

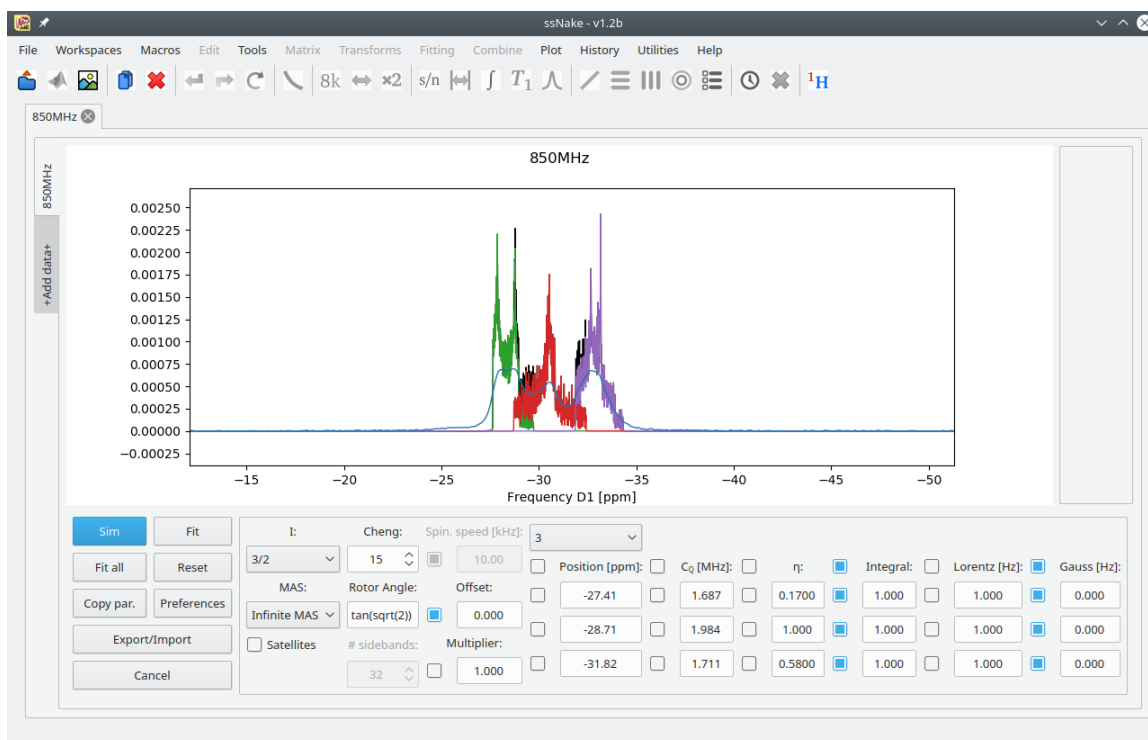
Filling this in leads to:

¹The 25 kHz MAS that was used in the experiment is fast enough for the central transition to be considered infinite. The satellite transition are ignored, as they are not properly excited in this experiment anyhow.



One thing we have to decide now, is how we are going to consider the three different sites in RbNO_3 . In principle, these should have the same integral. In this case, we will force this equality in our fit. We do this by fixing all of their integrals at 1. We then use the 'Multiplier' parameter to do the scaling to get the intensities of our simulation equal to the experiment.

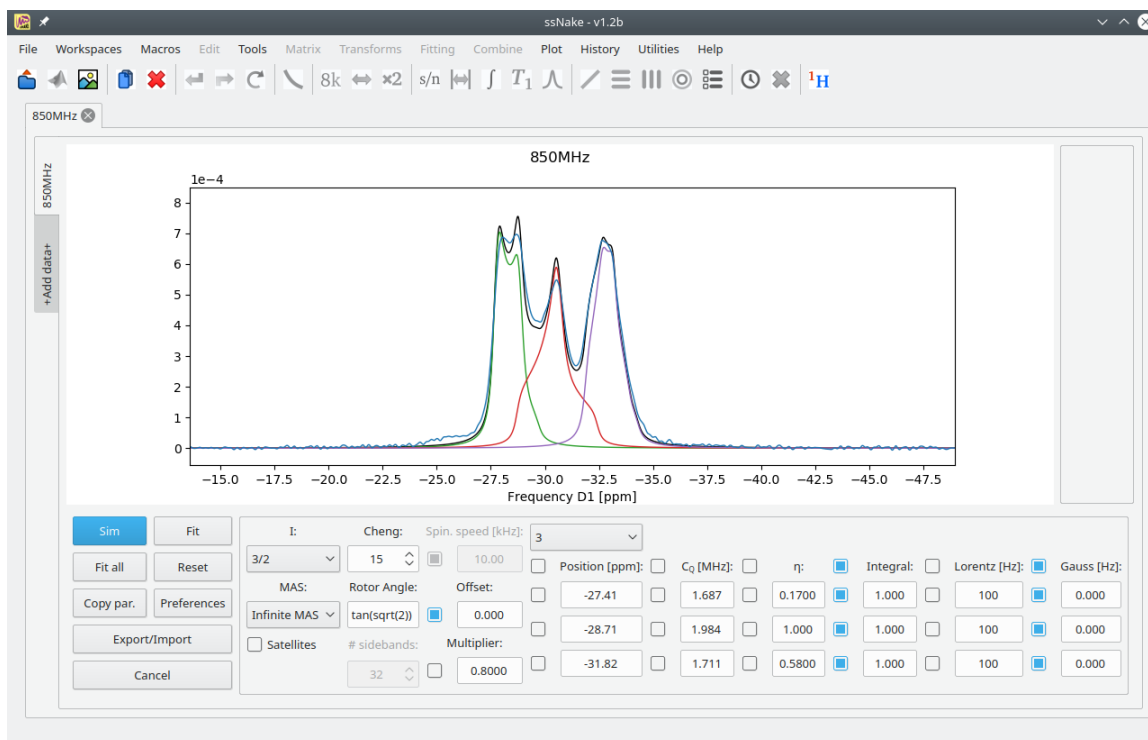
Now we can do an initial simulation, to see how that goes. Pushing 'Sim' gives:



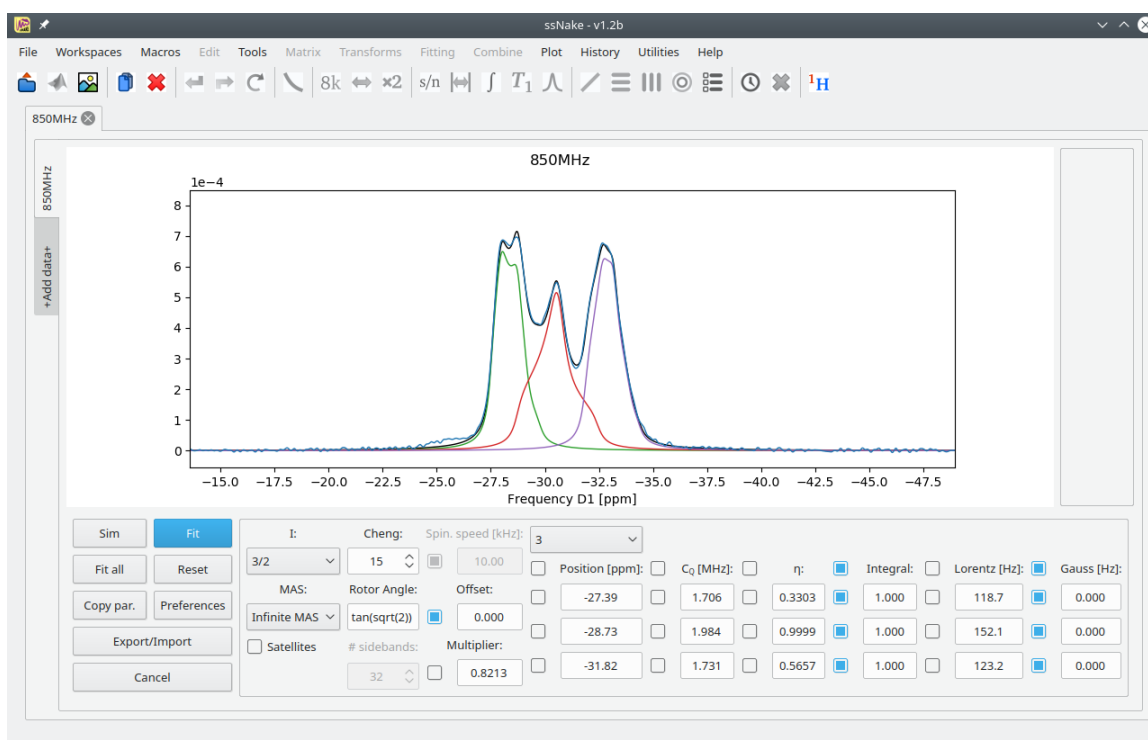
We notice multiple thing: the simulation looks very sharp, so we need some line broadening, and the intensities are a bit high.

- Put all 'Lorentz' values at 100 Hz
- Put the 'Multiplier' at 0.8

This looks much better:



Now we can fit and see where this goes. Push 'Fit' and observe (after some seconds):



This looks like a nice fit! The parameters only changed slightly, as we cheated by putting in the right values at the start. Observe that we do not describe the intensity around -25 ppm: this is the centre band of the satellites, which we do not include in the simulation (see the ssNake paper for a solution on how to include these).

Now we continue by adding extra data, to fit simultaneously.

4 Fitting multiple spectra simultaneously

- Load the '300.mat' file that was delivered with this tutorial
- Put the x-axis on 'ppm' (via the 'Axis' dropdown in the bottomframe)

Now, we are going to add this data to the fit:

- Go to the 850MHz workspace
- Click '+Add data+' in the vertical tabbar
- Select the 300MHz workspace and push 'OK'

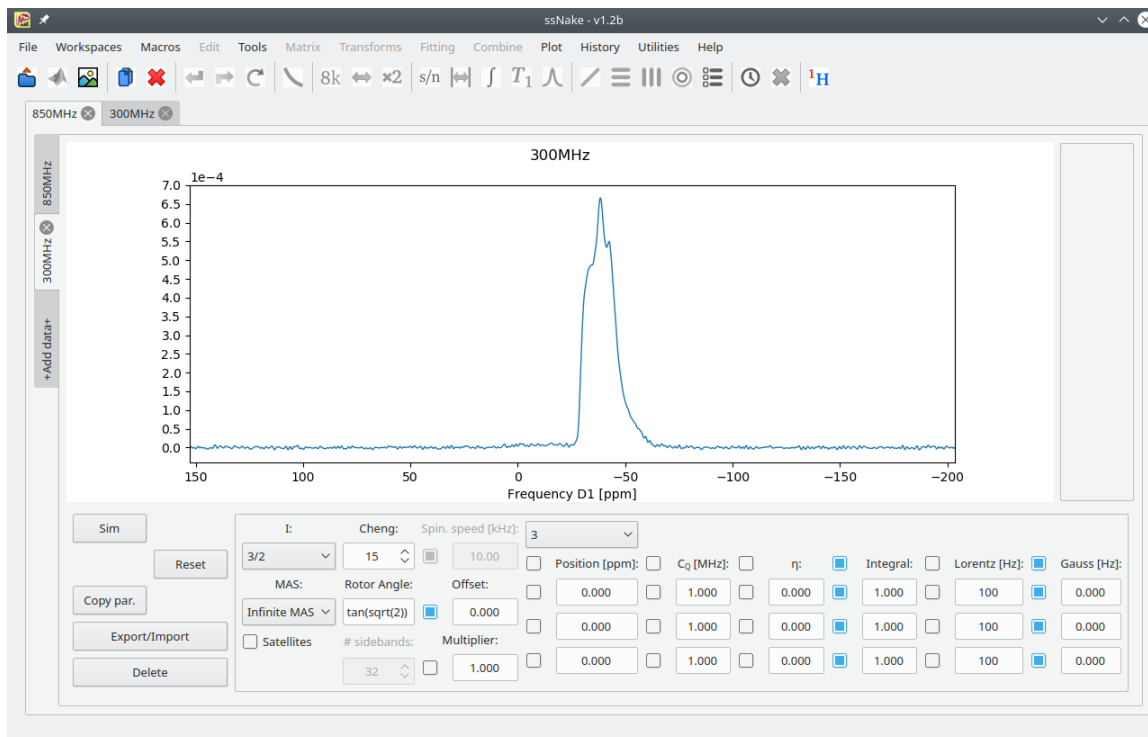
This gives us the extra data in a new fitting tab. Note that we do not have all the options present in the left hand side of the parameters. These are only available in the master fit tab (i.e. the 850MHz tab).

We start by setting some parameters right:

- Set MAS to 'Infinite MAS'

- Set the number of sites to 3 (via the dropdown menu)
- Set all Lorentz values at 100 Hz
- Fix the integrals at 1
- Unfix the 'Multiplier'

This gives:



Now for the important part: linking parameters. As we are observing the same sample in both data sets, the position, C_Q and η are identical in both spectra. We can do this by right clicking on a parameter input box, and use 'Connect parameter'. Do this for the first 'Position' entry. This gives the following input window:

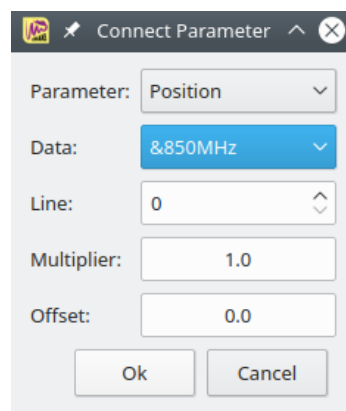
The screenshot shows the 'Connect Parameter' dialog box. It has a title bar with a small icon and the text 'Connect Parameter'. Inside the dialog, there are several input fields: 'Parameter:' (set to 'Position'), 'Data:' (set to '3&00MHz'), 'Line:' (set to '0'), 'Multiplier:' (set to '1.0'), and 'Offset:' (set to '0.0'). At the bottom, there are 'Ok' and 'Cancel' buttons.

This has the following parameters:

- Parameter: The name of the parameter that we want to link to
- Data: the name of the data tab that we want to link to
- Line: the line (i.e. sites) the we want to link to ('0' is the first, as everywhere in ssNake)
- Multiplier: multiplier the linked value by this value
- Offset: offset the linked value with this amount

In our case, we want our parameter (the first 'Position' of the 300MHz data) to be linked to the first 'Position' of the 850 MHz data. We do not need a scaling (Multiplier = 1.0) or offset.

Set properly, this gives²:



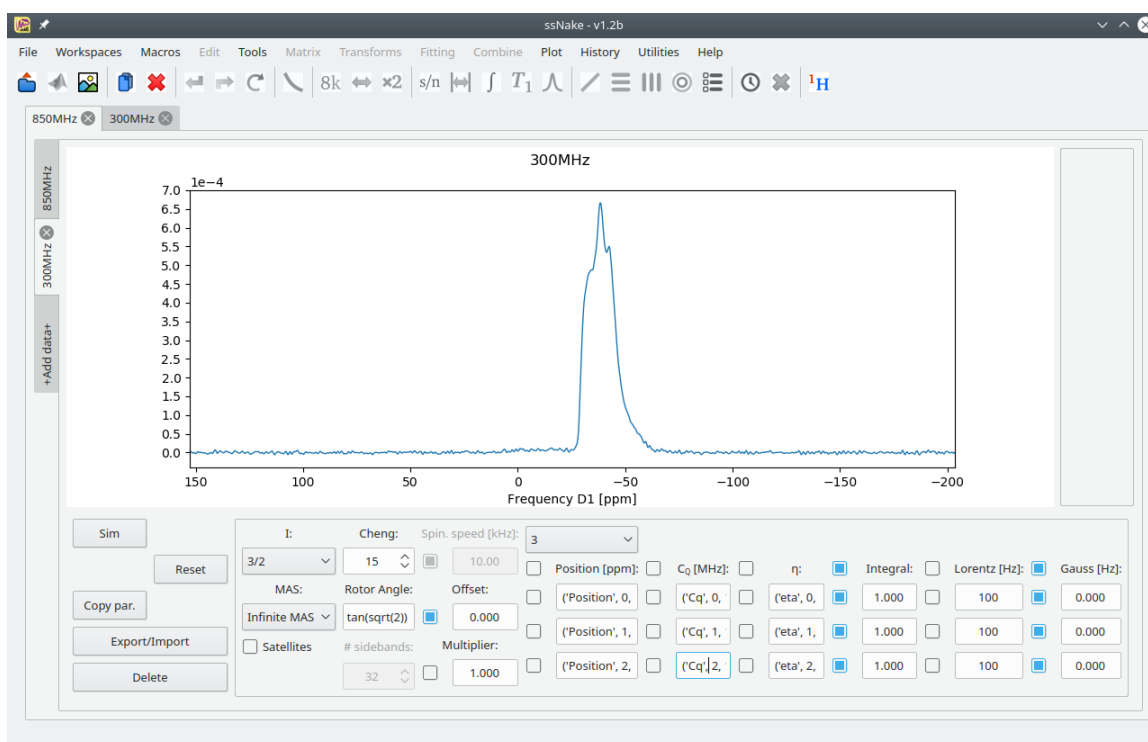
Pushing 'Ok' prints ('Position', 0, 1.0, 0.0, 0) in the box we selected with our right mouse button before. The input represents: ('Par name', Line, Multiplier, Offset, Data index). The pop-up menu we used is essentially an easy tool to create this input. Now, this value is linked, to be identical to the first Position value of the 850MHz data.

We can now do the same for the other 'Position' values, linking the to Lines 1 and 2 of the 850MHz data:

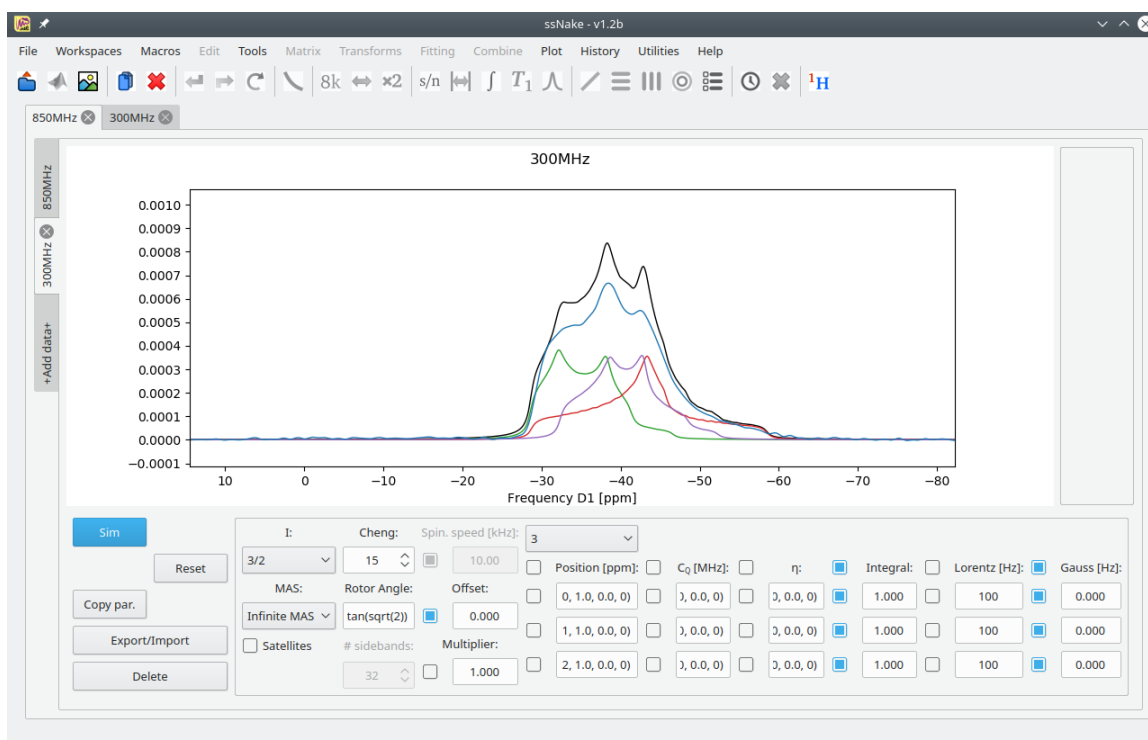
- Set the second position value to: ('Position', 1, 1.0, 0.0, 0)
- Set the third position value to: ('Position', 2, 1.0, 0.0, 0)

We can now do the same for the C_Q and η values, linking them to the 805MHz parameters. Note that the names of the parameters are not always equal to those labeled above the input boxes. η is named 'eta' for example. After linking all paramters, we should have the following:

²Ignore the & signs in the 'Data' names. This is a bug at the moment...



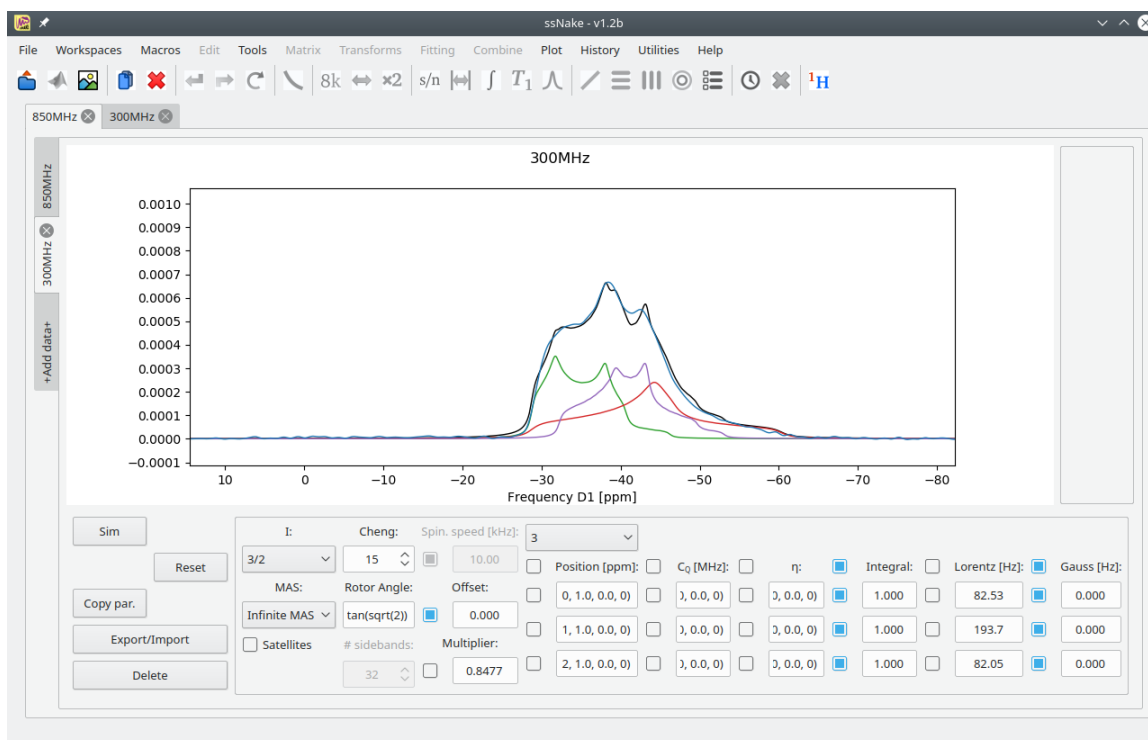
Now, we can push 'Sim' to do a simulation:



This gives a nice spectrum. Clearly the linking succeeded, otherwise we would not be able to simulate a spectrum without having any C_Q and η values.

Now, we should be ready for a fit! Go back to the '850MHz' fitting tab, and push 'Fit'. This will take some time, as we now have to calculate six powder patterns per iteration.

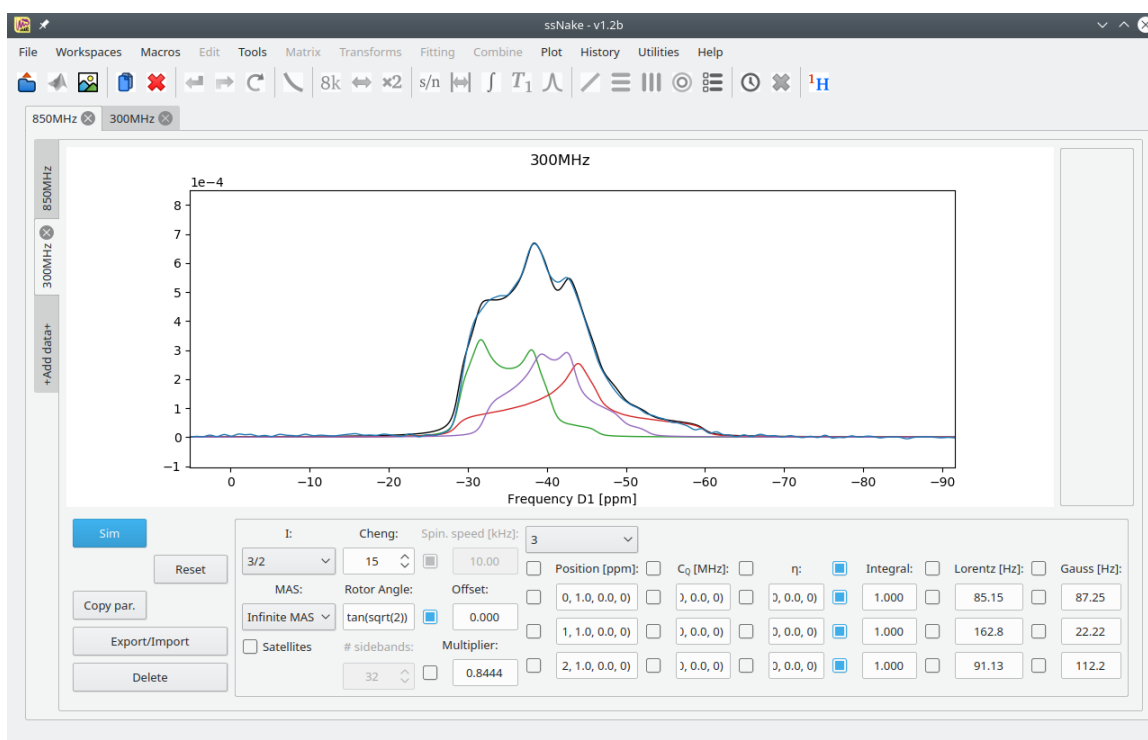
The 300MHz data for me now shows:



This is ok, but not great. Probably we need some Gaussian broadening for this line:

- Untick the Gaussian boxes and set them to 50 Hz
- Fit again

Which leads to:



which looks much better. We have therefore succeeded in doing a simultaneous fit! Fitting the data with or without the extra 300MHz data will lead to different results (you can check this yourself). Hopefully, the fit with the extra data is more accurate... Supplied with this tutorial are additional spectra recorded at 400 and 600 MHz. If you like you can replicate the 4 spectra fit that was demonstrated in the ssNake paper.

5 Do's and don'ts

When fitting multiple spectra simultaneously, we must make sure that the parameters like the quadrupolar parameters *are* indeed identical in all spectra. Be careful with temperature changes (MAS induced heating!), sample degradations, and carefully reference your ppm axis. Changes like this can actually reduce the overall quality of the fit, when including more data. Especially when fitting spectra with narrow lines, changes of 0.1 Hz in position can be of considerable influence. In some cases, we can of course chose not to link some parameters which we know to be very sensitive to temperature effects. The data in this tutorial was recorded using the same probe (a 850 MHz probe) at four different fields, using the same gas flows and the same reference compound. I might have overdone it in terms of safety, but then RbNO_3 is quite sensitive to temperature changes.

Do not chain-link parameters. This does not work. That is, do not link par2 to par1, and par3 to par2. Always refer to the original parameter (link par 2 to par1, and par3 to par1). In the future, this should hopefully give an error message...

Be very careful with the vertical scaling of the spectra. If spectrum1 has 10000x more

intensity than spectrum2, spectrum2 will be almost ignored during the fit. I always scale the spectra to have the same integral, as was also done for the data in this tutorial. This is often a safe option (scaling can be done via Matrix → Normalize). However, if one of these spectra has a lot more noise than the others, you might want to consider lowering its intensity, as to be less important during the fit. One way to do this is to scale the data to make sure the intensities of the noise band are equal. Tread carefully...