Advanced MQMAS processing in ssNake

18th January 2024

1 Introduction

This tutorial will make a review of MQMAS experiment principles and will present several ways to process and fit Multiple Quantum Magic Angle spinning (MQMAS) NMR data using ssNake. The tutorial delivered with the ssNake program is considered as prior knowledge and having done MQMAS tutorial is advized. If you have not yet studied this, please do so before continuing with these examples.

This tutorial is assuming ssNake version 1.5 to be used. There is a change on sign of shearing and scaling with respect to previous versions depending on spin I and MQ level. ssNake v1.5 calculations for shearing and scale assume an evolution on $-pQ$ (p =3, 5, 7 or 9 for MQMAS and $p = 1 or 2$ for STMAS and DQ-STMAS. While previous versions assume a coherence pathway such that quadrupolar echo is shifting towards positive t_2 time.

2 MQMAS principles

MQMAS is a 2D experiment for half-integer quadrupolar nuclei which is used to obtain isotropic information from nuclei broadened by the second order quadrupole interaction. This allows the separation of multiple overlapping quadrupolar sites on the basis of their 'isotropic' value (which is a combination of the isotropic chemical shift, and the isotropic quadrupolar shift, which is also called the quadrupolar induced shift).

The experiment can be quite difficult to process. Not because of the complication of the steps involved, but due to the large number of different MQMAS experiments and the various ways to process these. This advanced tutorial will give several examples of MQMAS processing in various cases and give hints on parameters that must be considered to run processing in the proper way. Moreover, it will explain how to simulate different kind of processing.

The principle of MQMAS is to correlate $-pQ$ coherence ($p = 3$, 5, 7 or 9) during t_1 evolution with the observable $-1Q$ coherence. The total signal phase evolution during t_1 and t_2 is

$$\omega_Q(-pQ) \cdot t_1 + \omega_Q(-1Q) \cdot t_2$$

for quadrupolar interaction and

$$\omega_{CS}(-pQ) \cdot t_1 + \omega_{CS}(-pQ) \cdot t_2$$

for chemical shift interaction.

The dephasing can cancel at a point in t_2 evolution when $t_2 = -\frac{\omega(-pQ)}{\omega(-pQ)} t_1$. The ratio of dephasing occuring during $-pQ$ and $-1Q$ is

$$R = \frac{\omega_Q(-pQ)}{\omega_Q(-1Q)}$$

for the second order quadrupolar interaction and

$$\frac{\omega_{CS}(-pQ)}{\omega_{CS}(-1Q)} = p$$

for the chemical shift interaction.

The reason for MQMAS to be working is that ratios R and p are independant of C_Q/η_Q and chemical shift amplitudes respectively, and these ratio are different ($R \neq p$) which allows to separate their contributions along different axes. Depending on p and spin S, the ratio R of quadrupolar dephasing can be positive or negative. For chemical shift the ratio is $+p$. A negative ratio means that dephasing in t_1 and t_2 are canceling leading to the formation of an echo at positive time ($t_2 = -R \cdot t_1$). A positive ratio means that dephasings are cumulative in t_1 (evolution on $-pQ$) and t_2 (evolution on $-1Q$). The echo is shifting to negative t_2. Note that a positive R will result in a spectrum correlation with slope $F_1 = R \cdot F_2$, but a quadrupolar echo that shifts with $t_2 = -R \cdot t_1$.

Depending on the dominating interaction one can observe the formation of an echo at position $t_2 = -R \cdot t_1$ if the quadrupolar interaction is strong or at $t_2 = -3 \cdot t_1$ if chemical shift distribution is dominating.

Z-Filter MQMAS is acquired in hyper-complex mode (for example State): echo and anti-echo are recorded simultaneously so a signal is always observed at positive t_2. The way quadrature is implemented (within the pulse sequence and hardware) will select the $\pm pQ$ pathway (more often the expected $-pQ$). A full echo MQMAS only selects one pathway. It can be $\pm pQ$ depending on the pulse sequence implementation and on the requirement to have signal in positive acquisition time (t_2). Indeed very often the pulse sequence will select the pathway for which an echo shifts towards increasing t_2 times ($R < 0$). If $+pQ$ is selected by the pulse sequence, then one will need to perform a Complex conjugate operation on D1 time domain, or a flip Left/Right operation on D1 frequency domain to flip the spectrum (indeed $\omega(pQ) = -\omega(-pQ)$).

Therefore, apodization should be done along $-R$ axis (or ±R axes for Z-Filter MQMAS when echo and anti-echo are selected). In some experiments the dominating interaction is chemical shift distribution. In that case, the echo is mostly appearing at $t_2 = -p \cdot t_1$. Then the slope for shifting should be ±p. Eventualy one should look at the FID to determine the best apodization and slope.

Shearing process aligns the correlation peaks horizontally instead of along the R slope by rolling each column (in D1 dimension). Shearing should always be done relative to the carrier frequency to get proper scale (the column at the carrier in D2 remains unchanged). In time domain shearing is equivalent to make the quadrupolar echo be positioned at $t_2 = 0$ (time when second order quadrupolar dephasings are canceled).

Once shearing is done, a universal scale can be designed that will make the peaks appear at the same position (in ppm) whatever p is used (3QMAS, 5QMAS, or even STMAS). There are two way to achieve such scale:

- Scale the spectral window (SW).
- Scale the carrier and reference frequencies used to calculate ppm scale).

When using SW scaling, the spinning sidebands will appear at scaled spinning speed in kHz. When using carrier and reference scaling, the spinning sideband separation remains at the spinning speed in kHz, however the Chemical Shift axis slope is scaled (due to shearing operation) and is 1 only when both axis are in ppm unit.

2.1 Split-t1 experiments

Split-t1 MQMAS experiments are designed to refocus the second order quadrupolar anisotropy at a fix time in D2. This corresponds to applying a shearing processing operation. It is usually done by defining a delay τ, on $\pm 1Q$ quantum level, which duration depends on t1 (pQ coherence evolution) such that $\tau = R \cdot t_1$ before the acquisition during t_2.

Therefore, one just need to deal with such experiment just the same as a pQMAS experiment. The experiment does not need be sheared, and should be scaled as pQMAS experiment with t_1 evolution defined as evolution time on pQ.

3 ssNake tools for MQMAS processing

Note that current ssNake tools assume that the quadrupolar echo is shifting towards positive t_2 time. For example, for spin 5/2 3QMAS, it will use a ratio $R = 19/12$ corresponding to $R = \frac{\omega_Q(+3Q)}{\omega_Q(-1Q)}$ that is evolution on $+3Q$ during t_1. It will apply the corresponding ratio for shearing. Since in that case the spectrum in D1 is reversed, the Scale SW tool will propose to use a negative factor (-12/17) that will reverse the D1 axis (instead of the data as when using Flip L/R tool or using complex conjugate in time domain before FT).

Fitting of MQMAS will also The simulation procedure calculate the frequency of $-pQ$ and $-1Q$ for each crystallite. The 'Auto' button calculates the the shear and Scale SW parameters adequately.

4 Data

In this tutorial we will use several datasets:

- a Z-filter 3QMAS of 5/2 spin nucleus (^{27}Al).
- an unconventional split-t1 full echo 3QMAS of 3/2 spin nucleus (^{35}Cl).
- a Z-filter STMAS recorded with NUS of 3/2 spin nucleus (^{87}Rb).

5 Z-Filter MQMAS processing

First, we will look into the processing of MQMAS data recorded using a Z-Filter experiment (also called three pulse MQMAS). Note that data recorded with a regular two pulse MQMAS (the standard MQMAS experiment) can be processed in the same way.

Open the '3QMAS-Z' dataset. This is a ^{27}Al 3QMAS experiment of AlPO VPI-5 mesoporous sample. It has been recorded in States-TPPI mode on a 18.8 T spectrometer at 20 kHz MAS rate.

Be careful that some information in the dataset may be wrong or unexpected. Especially the carrier and reference frequencies in dimension D1 may be already scaled (if xfshear has been applied under Topspin) or even correspond to a wrong nucleus. In the worst case, the SW could be wrong. This could happen if actual t_1 evolution increment (on Bruker this would often be parameter IN0) does not correspond to declared spectral window (parameter SW_h in Bruker).

Processing of the data is performed in the following steps:

- Remove digital filter.
- Set the view to D1 (sideframe, radiobutton).
- Convert the hypercomplex data via Transforms ⟶ Hypercomplex ⟶ selecting 'States-TPPI'.
- Set the view back to D2 (sideframe, radiobutton).
- Apodize in D2 using a gaussian apodization (50 Hz), with shifting (select 'Spin 5/2 3QMAS' which enter a Value or 19/12).

Note the shifting option. We chose to shift apodization along the quadrupolar echo slope. But in some spectra, chemical shift distribution could be dominant and a slope of 3 would be better. One can also choose a compromise that is a slope in between the two.

The FID should now look like this:

- Zero-fill (Matrix ⟶ Sizing) 2048 points. (actual FID will be truncated).
- Fourier Transform D2, and phase the first slice.
- Set the view to D1 (sideframe, radiobutton).
- Processing of the indirect dimension D1 (zerofill, Fourier, apodize, phase).

At that point we have several options for processing:

- whether to shear the spectrum.
- whether to scale the spectral width or the carrier and reference frequencies in the indirect dimension.

5.1 3Q-1Q representation

First we can choose to represent the spectrum in 3Q-1Q scale. To do that we need to adjust the reference frequency to $3 \cdot Ref - 2 \cdot Car$ where Ref is D2 dimension reference frequency and Car is the carrier frequency in D2 (and D1). Indeed this will ensure that the center of the spectrum will correspond to ppm coordinates $(F1, F2) = (p, 3p)$. First we need to ensure that D1 Carrier and Reference frequencies in D1 correspond to D2. This may not be necessary but as said before they may not be correct. Go to menu 'Tools' $\longrightarrow$ 'Reference' $\longrightarrow$ 'Set Reference'. Give name 'D2' and validate. Copy (crtl-C) the carrier frequency shown in D2 dimension. Select dimension D1 Paste the Carrier Frequency from D2. Go to menu 'Tools' $\longrightarrow$ 'Reference' $\longrightarrow$ 'Apply'. Select 'D2'. Go to menu 'Tools' $\longrightarrow$ 'Reference' $\longrightarrow$ 'Set Reference', then apply the operation $3Ref - 2Car$ for the reference frequency (There you can also 'Paste' the Carrier frequency that was copied above to write the equation).

This results in the following spectrum:

One can fit such spectrum with MQMAS model. There are 3 sites with main parameters summarized in table 5.1.

Site	δ_{iso} [ppm]	C_{Q} [MHz]	η_{Q}
1	-10.10	3.448	0.8992
2	41.74	1.274	0.4267
3	43.69	2.292	0.8697

Now, we should process the indirect dimension (D1):

- Switch to D1 (sideframe, radiobutton), and select data point 614 in D2.
- Perform a complex conjugate (Tools $\longrightarrow$ Complex Conjugate)[1]

This result in:

Now we should apply some zerofilling etc.:

- Set the size to 1024 points (Matrix $\longrightarrow$ Sizing)
- Fourier Transform

This reesults in this spectrum along D1 for this trace:

[1]The Varian data we loaded has a different complex definition, so a conjugate in the indirect dimension is required (this depends on how the pulse sequence was programmed).

The phase looks good, so we do not need to apply any phasing.

We have now processed both dimensions, so we can view the data as a contour plot:

- Switch to D2 (sideframe, radiobutton)
- Change the view to a contour plot: Plot ⟶ Contour

We now have:

And zoomed:

Note that the right projection was changed to 'Max' instead of the standard 'Sum'. This results in a skyline projection, which is affected less by the noise regions of the data.

As can be seen, the different powder patterns are all tilted. This is expected for a Z-Filter MQMAS, and can be corrected by shearing the spectrum.

- Shear via Matrix ⟶ Shearing, using the 'Spin 3/2, -3Q' setting, and direction '1' and axis '2'

This results in (zoomed):

Which is a nice spectrum! This is the final figure, we now only need to fix the axes.

By processing the spectrum in this way, we have removed the second order quadrupolar broadening from the indirect dimension. This dimension is therefore referred to as the isotropic dimension. The position along this axis is determined by the scaled isotropic chemical shift, and the scaled quadrupole induced shift. However, it is more convenient to have a frequency axis which shows the unscaled isotropic chemical shift. To accomplishing this, we must scale the spectral width by a specific value (which depends on the spin quantum number and the MQ transition of the experiment).

- Switch to D1 (sideframe, click on the upper left radiobutton)
- Use Tools ⟶ Scale SW, and select 'Spin 3/2, -3Q' and apply

Now, we have scaled the axis. As a last step, we should apply the chemical shift reference. This was determined using a rubidium nitrate solution. Based on this the 0 ppm frequency is at: 196.3182865 MHz.

- Set the reference via Tools ⟶ Reference ⟶ Set Reference, and put '196.3182865' in the Frequency box
- Switch to D2 (sideframe, click on the lower left radiobutton)

- Set the reference in the same way

The final spectrum should now look like this (zoomed):

This spectrum is also delivered with this tutorial, and named 'Rb87_3Q_Zf_(final_spectrum).mat'. Note that I extracted the relevant region before saving (to reduce size of the file).

Now, we can fit this spectrum. Either by fitting a specific trace with a regular second order quadrupolar line, or by fitting the entire MQMAS spectrum. Another alternative is to only determine the isotropic shift and the quadupolar product $P_Q = C_Q\sqrt{1+\eta^2/3}$. For this, we must determine the Centre of Mass for each site, in both D1 and D2. This can be done by going to the relevant trace, and using Fitting ⟶ Centre of Mass. Note that in D1, the peaks are symmetric, so the highest point is the centre in this case.

Site	δ_1 [ppm]	δ_2 [ppm]	δ_{iso} [ppm]	P_Q [MHz]
1	−30.5	−34.17	−31.86	1.89
2	−26.8	−31.96	−28.71	2.24
3	−26.3	−29.76	−27.58	1.83

The last two columns have been calculated using the MQMAS Extraction utility (see the Utilities menu).

6 Split T_1 processing

In a split T_1 experiment, the additional shift of the echo is taken into account within the pulse sequence. This leads to regular echo data, were the position of the echo in the time domain is always the same. Due to this, the shearing is no longer required. Also, the data is recorded in such a way that no hypercomplex processing is necessary. The following assumes that you have read the information above (about the Z-Filter processing).

- Open the Varian file Rb87_3Q_splitt1.fid using File ⟶ Open

Now, we must process this data as a whole echo acquisition (see the tutorial on this).

- Swap the echo at position 375 (Tools ⟶ Swap Echo)
- Set the size to 4096 points (Matrix ⟶ Sizing)
- Apply apodization if required (not used in this case)
- Fourier Transform
- Phase the imaginary part to zero (168.9 degrees, via Tools ⟶ Phasing)

This should result in (zoomed):

Now we can process D1:

- Switch to D1 (sideframe, radiobutton)
- View position 2081 along D2
- Tools ⟶ Complex Conjugate
- Set size to 512
- Fourier Transform

This results in:

Now, me must scale the spectral width of this dimension, as described above. However, with this experiment something strange is going on. According to the Varian pulse sequence used to record this data, the SW that you supply is 9/16 times the desired spectral width. For the processing, this means that this scaling should first be undone.

- Multiply the spectral width by 16.0/9.0 (either via Tools ⟶ Scale SW, or by typing at the SW box in the bottom frame).
- Multiply the SW by the MQMAS scaling value: Tools ⟶ Scale SW, and select 'Spin 3/2, -3Q'

Now, we should reference the ppm axis in both dimension. As before:

- Set the reference via Tools ⟶ Reference ⟶ Set Reference, and fill in '196.3182865' in the Frequency box
- Switch to D2 (sideframe, click on the lower left radiobutton)
- Set the reference in the same way

Switching to a contour plot results in (zoomed):

This is equivalent to the spectrum obtained before, for the Z-Filter data. This spectrum is also supplied together with this tutorial, and named 'Rb87_3Q_splitt1_(final_spectrum).mat'. Note that the relevant region was extracted (to reduce the size of the file).

7 Equations

The following Section will show some equations for the relevant shearing and scaling constants used for MQMAS processing.[2]

These are all included in ssNake in such a way that there is no need to remember these values. However, for the sake of completeness, they are provided here.

The following table summarises the values:

I	pQ	k	$1/a$	z
3/2	$-3Q$	7/9	9/34	680/27
5/2	$3Q$	19/12	−12/17	8500/81
	$-5Q$	25/12	12/85	8500/81
7/2	$3Q$	101/45	−45/34	6664/27
	$5Q$	11/9	−9/34	6664/27
	$-7Q$	161/45	45/476	6664/27
9/2	$3Q$	91/36	−36/17	1360/3
	$5Q$	95/36	−36/85	1360/3
	$7Q$	7/18	−18/117	1360/3
	$-9Q$	31/6	6/85	1360/3

Here, k is the shearing factor, $1/a$ the scaling of the spectral width, and z is a value required to determine the quadrupolar product P_Q from an MQMAS spectrum (see later). The equations are:

$$k = p\frac{36I(I+1)-17p^2-10}{36I(I+1)-27} \tag{1}$$

$$1/a = 1/(k-p) \tag{2}$$

$$z = \frac{1}{\frac{b}{a}-r} \tag{3}$$

With:

$$b = r(k+\lambda) \tag{4}$$

and

$$r = -\frac{3}{10}\frac{I(I+1)-3/4}{[2I(2I-1)]^2} \tag{5}$$

$$\lambda = p\frac{I(I+1)-3/4\cdot p^2}{-I(I+1)+3/4} \tag{6}$$

[2]This sections is based on: P. P. Man, *Phys. Rev. B*, **5**, 2764 (1998) and T. Anupõld, A. Reinhold, P. Sarv, A. Samoson, *Solid State Nucl. Magn. Reson.*, **13**, 87 (1998).

7.1 Further background

Here, we will quickly derive the relevant equations shown above.

The centre of mass of a line in the MQMAS spectrum is located in D2 at:

$$\delta_{\mathrm{D2}} = \delta_{\mathrm{iso}} + \delta_{\mathrm{QIS}} = \delta_{\mathrm{iso}} + r\frac{P_{\mathrm{Q}}^2}{\nu_0^2} \cdot 10^6 \tag{7}$$

with

$$r = -\frac{3}{10}\frac{I(I+1)-3/4}{[2I(2I-1)]^2} \tag{8}$$

In D1 the centre of mass, before shearing is located at:

$$\delta_{\mathrm{D1}} = -p\delta_{\mathrm{iso}} + \delta_{\mathrm{QIS}} = -p\delta_{\mathrm{iso}} + \lambda r\frac{P_{\mathrm{Q}}^2}{\nu_0^2} \cdot 10^6 \tag{9}$$

with:

$$\lambda = p\frac{I(I+1)-3/4 \cdot p^2}{-I(I+1)+3/4} \tag{10}$$

After shearing, the centre of mass gets shifted to:

$$\delta_{\mathrm{D1'}} = \delta_{\mathrm{D1}} + k\delta_{\mathrm{D2}} = (k-p)\delta_{\mathrm{iso}} + r(k+\lambda)\frac{P_{\mathrm{Q}}^2}{\nu_0^2} \cdot 10^6 \tag{11}$$

$$= a\delta_{\mathrm{iso}} + b\frac{P_{\mathrm{Q}}^2}{\nu_0^2} \cdot 10^6 \tag{12}$$

with constants:

$$a = k(I,p) - p \tag{13}$$

$$b = r(I)(k(I,p) + \lambda(I,p)) \tag{14}$$

A good way to processes this data, is to scale the spectral width of F1 by $1/a$. This means in the resulting spectrum, changes in chemical shift will be along the diagonal of the spectrum. This leads to:

$$\delta_{\mathrm{D1''}} = \delta_{\mathrm{iso}} + \frac{b}{a}\frac{P_{\mathrm{Q}}^2}{\nu_0^2} \cdot 10^6 \tag{15}$$

When this processing is performed, nuclei which have a quadrupolar coupling are always located in the lower right part of the spectrum, beneath the diagonal that is. When a lineshape is located on the diagonal, and stretched along it, this is caused by a distribution in chemical shift.

Based on the centre of mass in D1" and D2, the NMR parameters δ_{iso} and P_{Q} can be determined:

$$\delta_{\mathrm{iso}} = \delta_{\mathrm{D1''}} - \frac{b}{a \cdot r}\delta_{\mathrm{D2}} = \delta_{\mathrm{D1''}} - \frac{k+\lambda}{a}\delta_{\mathrm{D2}} \tag{16}$$

$$= \frac{17\delta_{\mathrm{D1''}} + 10\delta_{\mathrm{D2}}}{27} \tag{17}$$

This value is independent of I and p.

For P_Q the calculation is a bit more difficult:

$$\delta_{D1''} - \delta_{D2} = \left(\frac{b}{a} - r\right) \frac{P_Q^2}{\nu_0^2} \cdot 10^6 \tag{18}$$

$$P_Q = \sqrt{\frac{1}{\frac{b}{a} - r} \cdot 10^{-6} \nu_0^2 (\delta_{F1''} - \delta_{F2})} \tag{19}$$

$$= \sqrt{z \cdot 10^{-6} \nu_0^2 (\delta_{F1''} - \delta_{F2})} \tag{20}$$

With a scaling factor of:

$$z = \frac{1}{\frac{b}{a} - r} \tag{21}$$

These depend only on I and are tabulated above. These equation can be used to calculate the isotropic shift and quadrupolar product (P_Q) of a line based on the centre of mass of the line in both dimension. These equations have been included in ssNake in the form of a utility, which can by found in the Utilities menu.