

## Modelling NMR spectra of Quadrupolar Nuclei using SIMPSON<sup>1</sup>

<http://inano.au.dk/about/research-centers/nmr/software/simpson/>

[thibault.charpentier@cea.fr](mailto:thibault.charpentier@cea.fr) , [frank.fayon@cnrs-orleans.fr](mailto:frank.fayon@cnrs-orleans.fr), [jeannicolas.dumez@cnrs.fr](mailto:jeannicolas.dumez@cnrs.fr)

The aims of this tutorial is to give the tools for simulating NMR spectra from the output of DFT NMR calculations (typically using the GIPAW method) in order to allow you to compare by eye the quality of your calculation. This tutorial also offers the opportunity to review some basics of NMR of quadrupolar nuclei as well as NMR ssimulation under static and MAS (magic angle spinning) conditions. The input files will serve you later during the week if you want to make your own simulations.

### Exercise 0. Introduction (**00\_printing**)

*Simpson* offers some capabilities that can be useful to get information before performing a calculation. The script given below illustrates some of them (often not documented in tutorials we found on the web), for example to extract information about the nucleus of interest, or to convert some data such as principals values of the chemical shift tensor (  $\delta_{ii}$  ordered such that  $\delta_{11} > \delta_{22} > \delta_{33}$  ) into the parameters used by *simpson* (  $\delta_{iso}$   $\delta_{aniso}$   $\eta$  ). This example does not perform any simulation.

```
spinsys {  
  channels 17O  
  nuclei 17O  
  quadrupole 1 2 0.5e6 0.5 0 0 0  
}
```

```
par {
```

```
  proton_frequency 500.13e6  
  crystal_file zcw986  
  method direct  
  gamma_angles 1  
  spin_rate 0  
  start_operator I1z  
  detect_operator I1p  
  np 2048  
  sw 2e6  
  verbose 1101  
  variable tsw 2e6/sw  
}
```

```
proc pulseseq {} {  
  global par  
  acq_block {  
    delay $par(tsw)  
  }  
}
```

**The spinsys section describes the spin system.**

NMR isotope(s)

Number of nuclei

Quadrupolar (EFG) interaction for nuc. (here 17O) #n

n k  $C_Q$   $\eta_Q$   $\alpha_Q$   $\beta_Q$   $\gamma_Q$

k=1,2: first and second order quadrupolar interaction

$\alpha_Q, \beta_Q, \gamma_Q$  : orientation of the EFG PAS.

Standard value for 11.75 T (500 MHz)

(see next exercices for more details)

**NMR Simulation block**

<sup>1</sup> The code is maintained by Thomas Vosegaard [tv@chem.au.dk](mailto:tv@chem.au.dk)

```

proc main {} {
  global par
  puts " ~~~~~~ "      Printing in Tcl
  puts " Welcome to simpson 4.1 "
  puts " ~~~~~~ "
  puts " crystal_file is $par(crystal_file) "      Printing some input parameters
  puts " start operator is $par(start_operator) "
  puts " detect operator is $par(detect_operator) "
  puts " Proton frequency is $par(proton_frequency) Hz "
  set nu [ expr $par(proton_frequency)*1e-6 ]      assignment from a numerical calculation
  puts " Proton frequency is $nu MHz "
  puts " ~~~~~~ "
  # ~~~~~~      a comment
  # Example for 17O [site A] in beta-glycine
  # K. Yamada et al. Chem. Lett. 37, 2008, 472-473
  # delta_11 = 470 ppm
  # delta_22 = 318 ppm
  # delta_33 = 67 ppm
  # ~~~~~~
  set PAS {470 318 67}      a list
  puts " Principal values \"$PAS\" (ppm) "
  set l [length $PAS]      size of a list
  puts " length = $l "
  foreach i {0 1 2} {      a simple loop
    puts " delta_${i} = [lindex $PAS $i] ppm "      access to a list element
  }
  set CSA [csapar 470 318 67]      simpson built-in function csapar :
  puts " CSA is $CSA "      it returns the CSA parameters
  puts " diso = [lindex $CSA 0] ppm "      from the PAS values
  puts " aniso = [lindex $CSA 1] ppm "
  puts " eta = [lindex $CSA 2] "
  puts " ~~~~~~ "
  set pi [expr {atan(1) * 4}]       $\pi$ !
  set gam_17O [gamma 17O]      gamma returns the gyromagnetic ratio
  set gam_1H [gamma 1H]
  puts " gyromagnetic ratio for 1H is $gam_1H rad/T "
  puts " gyromagnetic ratio for 17O is $gam_17O rad/T "
  set Bo [expr 0.2*$pi*$nu/$gam_1H ]      magnetic field
  puts " The magnetic field is $Bo T "
  puts " 1H frequency is $nu MHz "
  puts " 17O frequency is $nu_17O MHz "      get the Larmor frequency of the nucleus of interest
  set nu_17O [ expr {10.*$gam_17O*$Bo/2./$pi } ]
  puts " 1 ppm = $nu_17O Hz "      some useful numbers
  set kHz [ expr 1000./$nu_17O ]
  puts " 1 kHz = $kHz ppm "
  puts " ~~~~~~ "
}

```

Modify this example using the *simpson* function `csaprinc`  $\delta_{iso}$   $\delta_{aniso}$   $\eta$  (return a list of the PAS parameters) and check its self-consistency. Look at the official documentation<sup>2</sup> for other useful built-in functions, notably :

$r_{12}$	dip2dist N1 N2	$b_{12}/2\pi$	Distance Å from dipolar coupling constant Hz
----------	----------------	---------------	--

<sup>2</sup> <http://inano.au.dk/about/research-centers/nmr/software/simpson/>

$$b_{12}/2\pi \quad \text{dist2dip N1 N2} \quad r_{12}$$

dipolar coupling constant (Hz) from distance Å

**Exercise 1. Static spectra of quadrupolar nuclei (01\_quadrupolar\_static)**

Let's start with real NMR now. We consider here the case of a quadrupolar nucleus with a large quadrupole interaction ( $C_Q \sim \text{MHz}$ ), typically the case of oxygen-17. We want to simulate the spectrum of all transitions (see below) under static conditions (i.e. for a non-spinning sample). Run the script :

```

spinsys {
  channels 17O
  nuclei 17O
  shift 1 100p 0 0 0 0
  quadrupole 1 1 1e6 0.0 0 0 0
}

par {
  proton_frequency 500.13e6
  method direct
  gamma_angles 1
  spin_rate 0
  crystal_file zcw986
  start_operator I1x
  detect_operator I1p
  np 2048
  sw 1e6
  verbose 1101
  variable tsw 1e6/sw
}

proc pulseseq {} {
  global par
  acq_block {
    delay $par(tsw)
  }
}

proc main {} {
  global par
  set f [fsimpson]
  fadddb $f 1000 0
  fsave $f $par(name).fid
  fzerofill $f 4096
  fft $f
  fsave $f $par(name).spe
}

```

*shift* : chemical shift for nucleus #n  
 format : n  $\delta_{\text{iso}}$   $\delta_{\text{csa}}$   $\eta_{\text{csa}}$   $\alpha_{\text{csa}}$   $\beta_{\text{csa}}$   $\gamma_{\text{csa}}$   
*quadrupole* : quadrupolar interaction for nucleus #n  
 format: n k  $C_Q$   $\eta_Q$   $\alpha_Q$   $\beta_Q$   $\gamma_Q$

**Experimental and numerical parameters**  
 proton frequency in MHz (defines the magnetic field, here 11.75T)  
 simulation algorithm  
 1 for static experiments  
 spin rate, 0 for static experiments  
 orientations for the powder averaging  
 Initial density matrix  $\rho(0)=I_x$   
 detection operator  $Q=I_+$   
 number of points (fid and spe)  
 spectra width (Hz)  
 verbosity  
 A user-defined parameter (keyword *variable*) :  
 dwell time for the *direct time* simulation method

**Definition of the pulse sequence**  
*global* give access to the *par* parameters  
 Time-propagation with dwell time *tsw*  
*This is the standard block for most of spectrum simulation*  
**pulseseq{}** is the function called in the NMR simulation.

**The main procedure**  
*call of the simulation engine fsimpson : here simulation of the FID*  
 Apodize the FID (to get a smooth spectrum)  
 write the fid (name=input file name)  
 add 0's to the fid (*interpolation in the frequency space*)  
 FFT of the FID to obtain the spectrum  
 write the spectrum

Each interaction is defined by a set of parameters : isotropic part, anisotropic part and Euler angles. The latter define the orientation of interactions in a common frame, i.e., the one with (0,0,0) is the reference frame.

Run the simulation as follows :

```
simpson quadrupolar_static_0.in
```

The program generates two files : `simpson.fid` (the NMR signal or Free Induction Decay) and `simpson.spe` (the NMR spectrum). Those files can be visualized with *simpson* tools : **simplot**<sup>3</sup> or through a drag-and-drop onto an empty page of jsnmr<sup>4</sup> (<http://www.jsnmr.net/empty.html>). To facilitate the visualization with standard tools (like `xmgrace`)<sup>5</sup>, we provide the program `read_simpson`<sup>6</sup> which converts `simpson` file to an `ascii` file.<sup>7</sup>

```
read_simpson -i simpson.spe -o output
```

The output file is in `ascii` format (  $v_i \text{re}_i \text{im}_i$  (unit Hz) for a `xxx.spe` file or  $t_i \text{re}_i \text{im}_i$  (unit s) for `xxx.fid` file).

If you start with the *crystal\_file* like `zwcw143` (143 optimized orientations), you will obtain a poor (noisy) spectrum. Increase the number of crystal orientations to `zwcw4180`. You can also compare with different algorithm such as REPULSION (*rep2000*).<sup>8</sup>

Change the  $\eta$  value (for example 0.5). What happens ? Why the data looks like so noisy ? (remember that for  $\eta=0$  the frequency depends on a single angle -  $\beta$ ). A file with much more orientations is provided : `zwcw28656.cry`. Try it. Now you should observe a satisfactory lineshape (increasing *lb* can smooth the residual numerical noise but your lose then the sharp singularities which are indeed seen in a nicely crystallized sample). You can also run a single orientation simulation with *crystal\_file* set to `alpha0beta0` to clearly see the number of transitions.

We now switch to a faster simulation using *method direct frequency*. Use the input file `quadrupolar_static_1.in`. As the simulation is performed in the frequency domain, the `main()` block needs to be modified so as to account for the fact the spectrum is calculated first (not the trick for making properly the inverse Fourier Transform)

<pre>[...] proc main {} {   global par   set f [fsimpson]   fsave \$f \$par(name).spe   fft \$f -inv   fsave \$f \$par(name).fid   fadddb \$f 1000 0   set z [findx \$f 1]   fsetindex \$f 1 [expr [lindex \$z 0]*0.5] [expr [lindex \$z 1]*0.5]   fzerofill \$f 4096</pre>	<p><b>SIMPSON simulation</b></p> <p>Save the spectrum</p> <p>Inverse FFT</p> <p>Save the FID</p> <p>apodisation</p> <p>* :</p> <p>* : trick for proper inverse FFT<sup>9</sup></p> <p>interpolation</p>
---	---

- 3 Just enter the command `simplot&` to open it.
- 4 <http://inano.au.dk/about/research-centers/nmr/software/jsnmr/>
- 5 We WARMLY recommend this option for the present tutorial.
- 6 This program is free (written by [thibault.charpentier@cea.fr](mailto:thibault.charpentier@cea.fr)). `read_simpson -h` for usage.
- 7 `Ascii` format «  $t_i \text{re}_i \text{im}_i$  ». Use the option « `NPXY` » to open the file with `xmgrace` in a mode reading both the real and imaginary part. Otherwise, the standard mode will give the real part, which is enough for all exercises.
- 8 To get the full list of available orientation files, just enter a wrong keyword such as « `zwcwxxx` »
- 9 You can try to comment those two lines to see the effect on the baseline in the smoothed spectrum.

```
fft $f
fsave $f $par(name)_smooth.spe
}
```

FFT  
save the smoothed spectrum

If the simulation is faster, the spectrum is the same. For timing the calculation use can use the command *time* (like *time simpson simpson.in*) to get the CPU time.

In conclusion, we need to use an interpolation method in the frequency domain that will make the calculation both much faster and better in the lineshape with *method direct frequency ASGinterpolation*. The input file only changes in the *par* section (*quadrupolar\_static\_2.in*):

```
par {
[...]
crystal_file Alderman/alderman36
method direct frequency ASGinterpolation
[...]
}
```

Orientation and triangles are read from two files :  
*alderman36.cry* and *alderman36.tri*

Now run the program. You should get a nice lineshape with sharp singularities (*we found a bug : only half of the spectrum is calculated*)<sup>10</sup>.

We now propose to explicitly calculate the spectrum of each transition, but for <sup>23</sup>Na (I=3/2) which has two satellite transitions (ST)  $3/2 \Leftrightarrow 1/2$  and  $-1/2 \Leftrightarrow -3/2$  ; the central transition (CT) is  $1/2 \Leftrightarrow -1/2$  . Run first the file *quadrupolar\_static\_3.in*, you should see the two ST transitions. In order to select each transition, we have introduced in the input file their own detection operator (*quadrupolar\_static\_4.in*) :

```
[...]
proc pulseseq {} {
  global par
  matrix set detect list $par(detect)
  acq_block {delay $par(tsw)}
}

proc main {} {
  global par
  set ST1 {{0 1 0 0}} {{0 0 0 0}} {{0 0 0 0}} {{0 0 0 0}}
  set ST2 {{0 0 0 0}} {{0 0 0 0}} {{0 0 0 1}} {{0 0 0 0}}
  foreach i {ST1 ST2} {
    set par(detect) [set $i]
    set f [fsimpson]
    fsave $f $par(name)_${i}.spe
    funload $f
  }
}
```

**SELECT the current« detect » operator**

**[\*] detect first ST  $I_+^{12}$**   
**[\*] detect second ST  $I_+^{34}$**   
**Tcl loop**  
**\$par(detect) = ST1, ST2**  
**perform the simulation**  
**save the spectrum**  
**clean the memory**  
**end of the loop**

Which value should be used in [\*] to have the same spectrum (in height) obtained with *quadrupolar\_static\_2.in* ? (remember the matrix representation  $I_x$  of for I=3/2).

Add the CT in the simulation. Why do you get an empty spectrum ?. Now try to include the second order quadrupolar broadening : *quadrupole 1 2 0.5e6 0.0 0 0 0*. Do you see a difference on

<sup>10</sup> Only simulating ST transitions with *detect\_operator I1p-I1c* solve the bug. This instruction remove the central detection operator of the central transition.

the ST transitions ? Look at the central transition lineshape (increase np to 32768 to resolve the lineshape), we will focus on this transition in the next exercise. Compare the height of the sub-spectra. If you are not familiar with quadrupolar nuclei, you now realize how difficult it is to get nice static spectra on ST and why NMR spectroscopists mostly focus on the CT transition.

As an extra, modify the program for  $I=5/2$  ( $^{17}\text{O}$  or  $^{27}\text{Al}$ ),  $7/2$  ( $^{93}\text{Nb}$ ).

## Exercise 2. The Central transition under static and MAS conditions (02\_quadrupolar\_CT)

Start with the `quadrupolar_CT_0.in` input file to get the CT static lineshape. Note the definition of the detection operator `detect_operator I1c` to detect the central transition only. You can vary  $\eta$  from 0 to 1 if you are not familiar with quadrupolar nuclei in solids. You can also try different magnetic field (`proton_frequency` 300 MHz, 500 MHz and 850 MHz for example). You should see a decrease of the spectrum width : remember that the second order quadrupolar broadening scales as  $1/B_0$  in Hz.

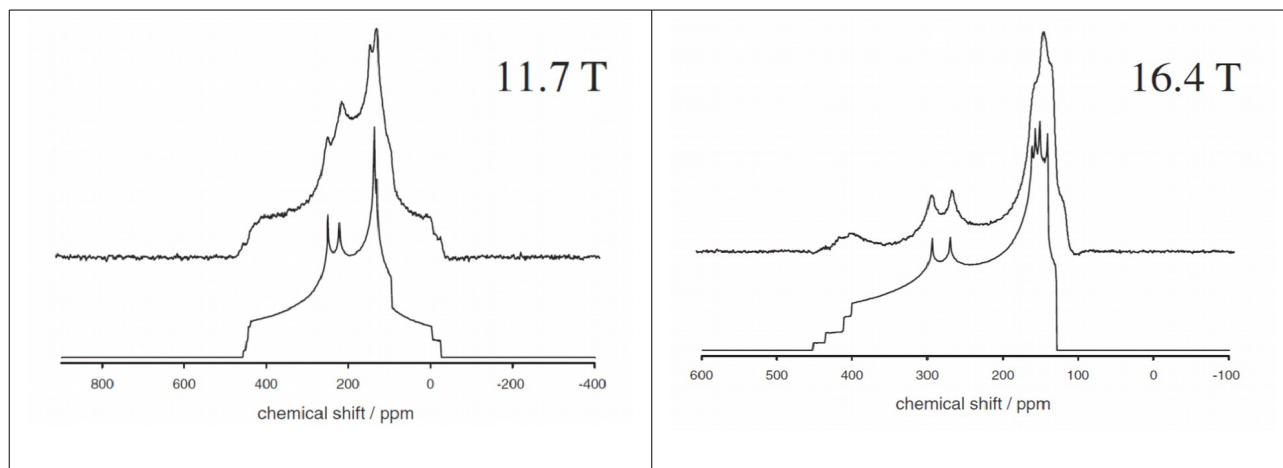
Try to reproduce  $^{17}\text{O}$  NMR data of  $\beta$ -glycine (K. Yamada *et al.* *Chemical Letters* 37 (2008) 472-473), summarized in the table below :

	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	$\delta_{iso}$	$C_Q$	$\eta_Q$	$\alpha$	$\beta$	$\gamma$
$\beta$ -glycine									
Site-A	470(8)	318(8)	67(8)	285(2)	7.48(8)	0.48(4)	0(4)	90(4)	154(4)
Site-B	468(8)	318(8)	54(8)	280(2)	7.10(8)	0.50(4)	0(4)	90(4)	147(4)

Experimental  $^{17}\text{O}$  CSA, EFG tensors and Euler angles from K. Yamada *et al.* *Chemical Letters* 37 (2008) 472-473. In parentheses are given the estimated errors.

First simulate the Site-A only (solution in `quadrupolar_CT_1.in`). You can use the exercise 0 to retrieve  $\delta_{iso}$   $\delta_{aniso}$   $\eta$  from the experimental  $\delta_{ii}$  values. First set the angle to (0,0,0). Now add a second site using `nuclei 17O 17O` in the `spinsys` block and adding a second set of quadrupole/shift parameters for this second site ( $n=2$ ) (`quadrupolar_CT_2.in`). Note that in order to have both nuclei detected; we first use the global start operator (tensorial product)  $I_x = I_x^1 \otimes I_x^2$  denoted `start_operator Inx` in `simpson`. Similarly for the detection : `detect_operator Inc`. If you compare now with the simulations shown in the original paper, we are getting closer the displayed data in the figure below. Now the tricky part is to adjust the Euler angles that defines the relative orientation of the EFG and CSA tensor. Indeed, they are multiple definition (passive and active, zxz or zyz rotation). So you have to try the different possibilities (our solution in `quadrupolar_CT_3.in`) ... *good luck!*<sup>11</sup>. You can also improve the crystal file by using `crystal_file ROSELEBh/ROSELEBh6145` instead of `crystal_file Alderman/alderman36`. Now, modify the program to plot the spectrum or each site (solution in `quadrupolar_CT_4.in`).

11 If you feel comfortable with Tcl now, you can insert a loop in the program to make simulations on a grid to find the solution.



Experimental and simulated  $^{17}\text{O}$  static NMR spectra (data adapted from K. Yamada et al. Chemical Letters 37 (2008) 472-473).

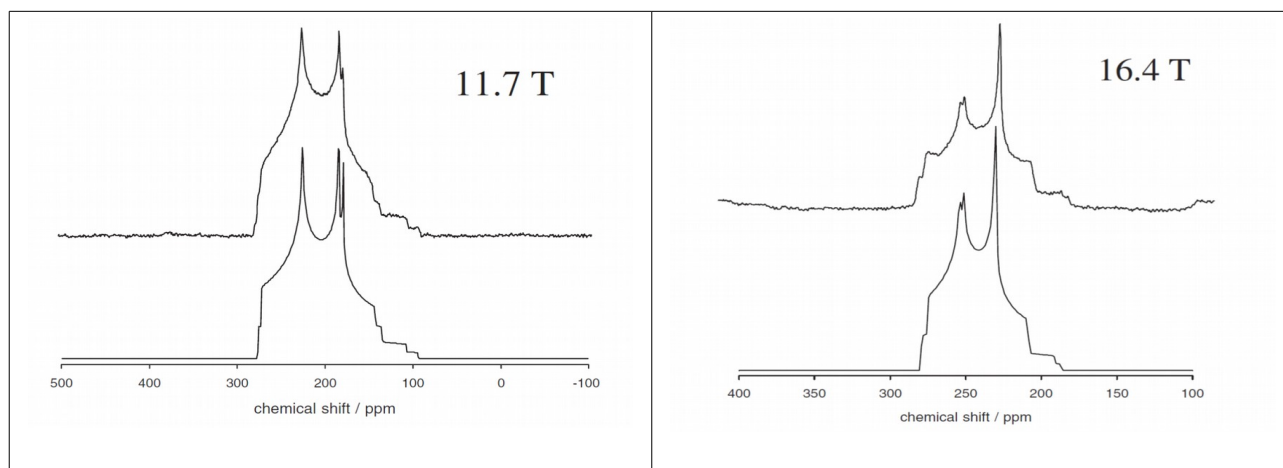
Let's us now turn to the MAS NMR lineshape and start with the file [quadrupolar\\_CT\\_10.in](#). If you are not familiar with quadrupolar nuclei under MAS, you can vary different parameters, especially the spin rate and the magnetic field (for sake of simplicity you can comment the CSA first). Note the new input parameters

```
[...]
par {
  proton_frequency 500.13e6
  method gcompute frequency
  ASGinterpolation
  crystal_file Alderman/alderman36
  gamma_angles 16
  spin_rate 12500
  start_operator I1x
  detect_operator I1c
  np 8192
  sw gamma_angles*spin_rate
  verbose 1101
  variable tsw 1e6/sw
}
[...]
```

**gcompute** is the reference method for MAS (analytical averaging on the third Euler angle  $\gamma$  for the powder averaging)

**Number of spinning sidebands**  
spin rate in Hz

sw must be commensurate with the sample spinning for gcompute to be effective and the rotation period must match exactly  $N \cdot tsw$ .



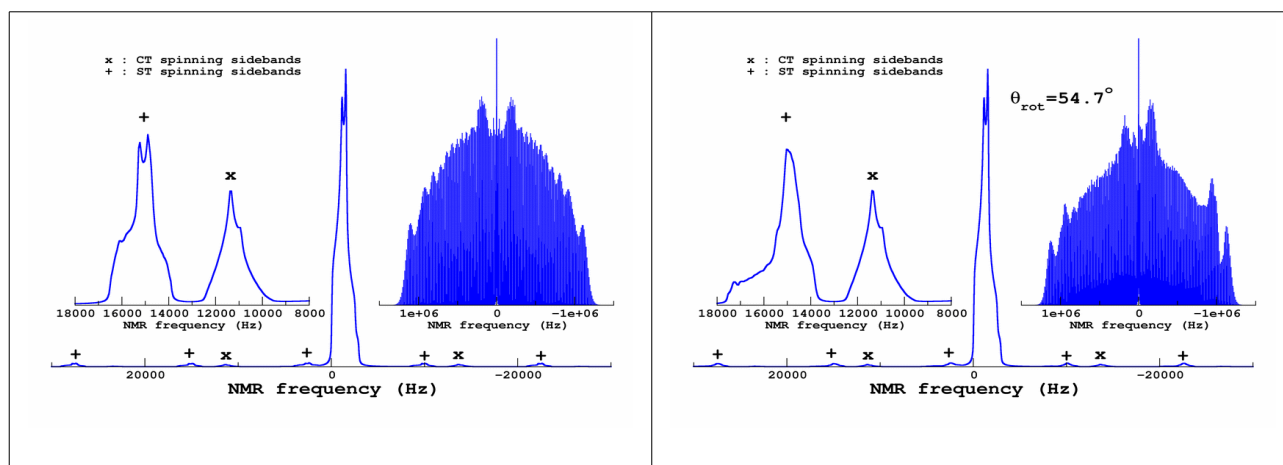


Experimental and simulated  $^{17}\text{O}$  MAS NMR spectra (data adapted from K. Yamada et al. Chemical Letters 37 (2008) 472-473).

Try to play with the Euler angles of the CSA ( $\gamma_{\text{CSA}}$ ) to see the huge influence they have on the spinning sidebands pattern intensity; find the angle that minimize it. Next you can proceed with the full system ([quadrupolar\\_CT\\_11.in](#)), and compare with the experimental data.

You have now all the necessary knowledge to simulate MAS/static spectra from the NMR parameters. As an extra, you can see how the rotation angle affect the MAS lineshape ([quadrupolar\\_CT\\_12.in](#)). Note the **rotor\_angle** parameter.<sup>12</sup> Is the magic angle the best angle for have a narrow line ?

**Extra 1:** run now the simulation for all transitions ([quadrupolar\\_CT\\_20.in](#)). Observe the spinning sidebands pattern of the ST transition. Increase gamma\_angles so as to have all spinning sidebands. What reminds you the spinning sidebands manifold pattern (exercice 1) ? Now just change the magic angle by something like  $0.01^\circ$ . See the effect. See some results below. You can repeat the exercice for  $I=5/2$ ,  $7/2$  and even  $I=9/2$  and determine with ST is most resolved under MAS.



Variation of the MAS NMR spectrum (CT and ST) with respect to the angle of the rotor axis.

### Exercise 3. Nutation of quadrupolar nuclei. ([03\\_quadrupolar\\_nutation](#))

In this exercise, we analyse the effect of finite pulse. In previous simulations by considering [start\\_operator 11x](#), we were implicitly working under ideal conditions : all transitions are excited with the same efficiency. We show here that this is only true under certain conditions we will determine. Let's start with the file [quadrupolar\\_nutation\\_0.in](#) (static conditions first).

```
spinsys {
  channels 11B
  nuclei 11B
  quadrupole 1 1 2.5e6 0.2 0 0 0
}
par {
```

**11B  $I=3/2$**

**Cq=2.5 MHz, typical value in oxides for BO3**

<sup>12</sup> The magic angle is given by  $3\cos^2\theta_m - 1 = 0$  :  $\theta_m \approx 54.7356^\circ$



```

method          direct
gamma_angles    1
spin_rate       0
crystal_file    zcw615
start_operator  I1z
detect_operator I1p
np              128
sw              5e6
variable tsw    1e6/sw
verbose         1101
variable rf      50000
}

proc pulseseq {} {
  global par
  acq_block {
    pulse $par(tsw) $par(rf) y
  }
}

proc main {} {
  global par
  set f [fsimpson]
  fsave $f $par(name).fid
  puts " ~~~~~~ "
  puts " dt = $par(tsw) us "
  puts " rf = $par(rf) Hz "
  puts " ~~~~~~ "
}

```

**Time propagation static conditions**

**powder averaging**  
**Thermal Equilibrium  $I_z$**   
**Detection of all transitions**  
**nutaton on 128 points**  
**Just to control dt (tsw)**  
**dt (here 0.2us)**

**rf field in Hz**

**pulse with phase y (ideal):**  
 $I_z(t_w) = I_z \cos(2\pi t_w) + I_x \sin(2\pi t_w)$  [\*]

**save nutation curve**

We expect to see a pure sinusoidal oscillation [\*] if  $\nu_{rf} \gg C_Q$ . Is it the case? Try to increase and decrease the RF (or  $C_Q$ ). The comparison of the curve can be made easier if you convert the pulse duration into the nutation angle defined as  $\theta = 2\pi \nu_{rf} \tau_w$ . See input file [quadrupolar\\_nutation\\_1.in](#). To facilitate the extraction of the theta curve, you can redirect the output in file as follows

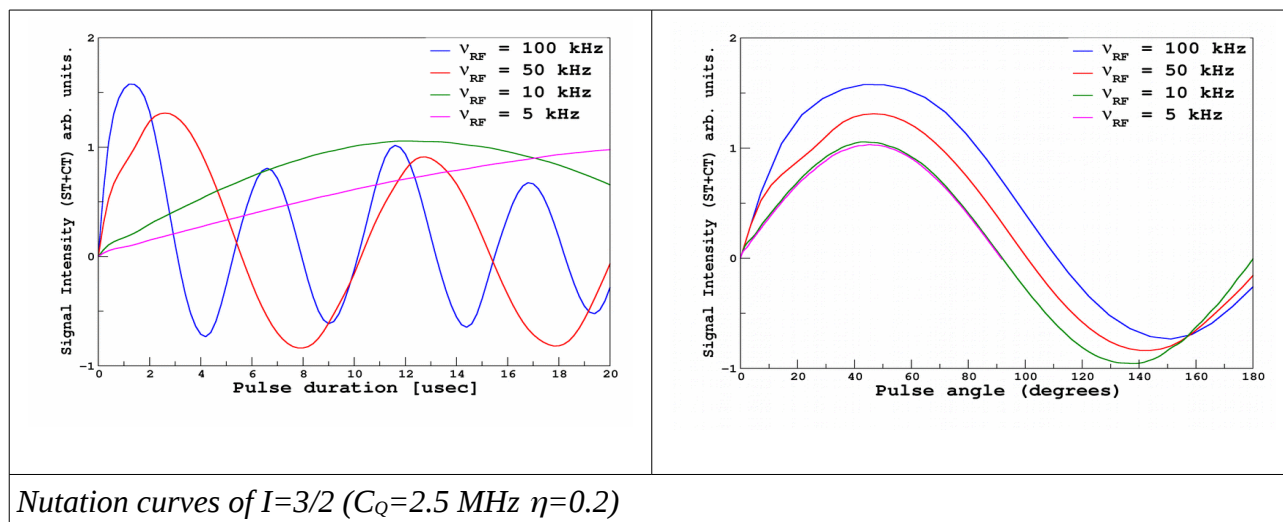
```
simpson xxx.in > foo
```

And then edit the foo to copy/paste data in a file xxx.dat that can be visualized with xmgrace. Below are exemples of the nutation curves you should obtain.

What do you observe for low RF field? Repeat the same calculation but now looking only the central transition (for correction see inputs/[quadrupolar\\_nutation\\_2.in](#)) Determine the maximum value for the pulse angle in order to be quantitative.<sup>13</sup> For weak RF field (say ~ 10 kHz), what is the optimal pulse length for the excitation of the central transition?<sup>14</sup> Repeat for  $I=5/2$ . Using the previous exercises you can also look at the nutation of the satellite transitions.

<sup>13</sup> You should find a angle close to  $\pi / \{4(I+1/2)\}$

<sup>14</sup> In the weak RF field regime, the effective RF acting the central transition (selective regime) is  $\nu_{RF}^S = (I+1/2)\nu_{RF}$



#### Exercise 4. Acquisition with an spin echo pulse sequence (04\_spin\_echo)

In this exercise, we want to simulate the effect of the spin echo pulse sequence on the static and MAS lineshape. The pulse sequence is :  $90_{\phi_1} - \tau_E - 180_{\phi_2} - \tau_E - ACQ$  . Experimentally, the pulse phases are cycled so that only the coherence pathway  $I_z \rightarrow I_+ \rightarrow I_-^{CT}$  is selected. All what we need is to change the initial state `start_operator` so as to account for the pulse effects. This can be accomplished easily by introducing initial pulse sequence in the `pulseseq{}` block. Make the simulation using the input file `spin_echo_0.in` :

```
spinsys {
  channels 23Na
  nuclei 23Na
  quadrupole 1 2 2.5e6 0.7 0 0 0
}
```

```
par {
  proton_frequency 500.13e6
  method direct frequency ASGinterpolation
# crystal_file Alderman/alderman36
crystal_file ROSELEBh/ROSELEBh6145
gamma_angles 1
spin_rate 0
start_operator I1z
detect_operator I1c
np 4096
sw 2e5
verbose 1101
variable tsw 1e6/sw
variable rf 50000
variable tp 0.25e6/rf
}
```

**Start from Equilibrium Magnetization  
central transition detection**

**RF field  
90° in usec**

```
proc pulseseq {} {
  global par
  set tp180 [ expr 2*$par(tp) ]
  pulseid $par(tp) $par(rf) y
```

**calculate 180° pulse  
90° pulse**

```

pulseid $tp180 $par(rf) y
acq_block {delay $par(tsw)}
}

proc main {} {
  global par
  set f [fsimpson]
  fsave $f $par(name).spe
  fft $f -inv
  fadddb $f 150 0.5
  set z [findx $f 1]
  fsetindex $f 1 [expr [lindex $z 0]*0.5] [expr [lindex $z 1]*0.5]
  fft $f
  fsave $f $par(name)_smooth.spe
  puts " ~~~~~~ "
  puts " 90 = $par(tp) us "
  puts " rf = $par(rf) Hz "
  puts " ~~~~~~ "
}

```

**180° pulse Acquisition**

**Spectrum**

Start with ideal pulse (*pulseid*). Select the correct phase of the 180° pulse so as to have the spectrum positive in the real channel. After switch to real pulse (finite width) (*pulse*). What should be the 90° pulse length to observe the CT (exercise 3) ?

```
variable tp      0.25e6/rf
```

You can observe that the spectrum is not in-phase. Adjust the phase to have a pure absorption spectrum (*spin\_echo\_1.in*).

```

[...]
puts " ~~~~~~ "
set ph 20.0
puts " phase correction $ph "
puts " ~~~~~~ "
fphase $f -rp $ph
fsave $f $par(name)_smooth_phase.spe
[...]

```

**Phase correction in degrees**

**phase correction (see doc)**  
**save the phased spectrum**

Now reduce the rf field and adjust the pulse length to the (central transition) selective 90° pulse. For example for 90°=12.5 us @ RF=10 kHz.

Now we insert a coherence purification between the 90° and 180° (*spin\_echo\_2.in*). Repeat the calculation. Try by using a ST coherence instead, what do you observe ? What is the most excited coherence by the pulse sequence.

```

[...]

proc pulseq {} {
  global par
  matrix set 1 list $par(CT)
  set tp180 [ expr 2*$par(tp) ]
  pulse $par(tp) $par(rf) y
  filter 1
  pulse $tp180 $par(rf) x
  acq_block {delay $par(tsw)}
}

```

Read the filter matrix

90°  
Coherence selection

180°  
ACQ

```

}

proc main {} {
  global par
  # ~~~~~
  # CT +1 coherence
  # ~~~~~
  set CT {{0 0 0 0} {0 0 1 0} {0 0 0 0} {0 0 0 0}}      CT  $I_+^{CT}$ 
  set par(CT) [ set CT ]
  # ~~~~~
[...]
```

Rigorously, to match the experiment we should use instead ([spin\\_echo\\_3.in](#))

```

[...]
```

matrix set 1 coherence {+1}	Evolution of +1 during the echo delay.
-----------------------------	--

```

[...]
```

because the phase cycling used in real experience cannot separate the ST +1 from the CT +1 coherence (whereas we have some selectivity with the rf field strength for large  $C_Q$  nuclei). You can now try to increase the quadrupolar coupling constant (say 5 MHz). Compare the efficiency on the lineshape of a spin echo performed with short pulses (increase the rf field to a typical large value of 100 kHz) with a  $\theta - \tau_E - \theta - \tau_E - ACQ$  sequence.

Now, you can write your own script to perform the same simulation under MAS conditions.