B12

SIMPSON Exercises

Thomas Vosegaard

SIMPSON may be downloaded from http://www.bionmr.chem.au.dk/download/b12.

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Everything typed in `Courier` refers to commands to be typed on the keyboard in a command line (Start -> Run, type `cmd`). SIMPSON is a command-line program – meaning that it should be executed from the command line. `Courier italic` refers to file names and content of files. The input files will store spectra or FID's named after the input file. For example, the input file 1_Static.in will produce output files named *1_Static,1.fid*, *1_Static,2.fid*, *1_Static,1.spe*, etc. The number after the comma is an index controlled by the line *variable index 1* in the *par* section of the input files. Increasing this number after each change in the input file will let you store all the simulations rather than overwriting when performing new simulations.

Exercise 1: Introduction to SIMPSON and simulations
File: *1_Static.in*

> We look at a single spin (^{1}H) located in an external magnetic field and with a certain chemical shift anisotropy. Single crystal.
> - Use this exercise to get familiar with SIMPSON. Open a command line and run the file by typing `simpson 1_Static.in`. Look at the output from the file by typing `simplot 1_Static,1.fid` or `simplot 1_Static,1.spe`.
> - Open the input file in wordpad. Change the angles in the line *shift 1 0 100 0 0 0 0*. The angles are the three last entries, all set to zero initially. Look at the resulting spectrum.
> - Change the line *crystal_file alpha0beta0* to *crystal_file rep678*. This changes the number of crystallites from a single crystal to a powder consisting of 678 independent crystal orientations. You may need to try other crystal files to get a nice spectrum.
> - Change the size of the CSA and asymmetry parameter and observe the effect in the simulated spectrum.

Exercise 2: Magic-angle spinning
Files: *2_MAS.in* and *2_MASg.in*

> This exercise is similar to Exercise 1 but now the sample is spinning. The spin rate is controlled by the *spin_rate* in the *par* section of the input file. Start working with the file *2_MAS.in*.
> - Change the crystal file from *alpha0beta0* to *repXX* and observe the resulting spectra.
> - Change the CSA and asymmetry parameter and observe the spectrum. Eventually compare with the spectra simulated in Exercise 1.
> - Change the spin rate and observe the result.
> - The file *2_MASg.in* performs the same simulation as 2_MAS.in but uses a special simulation technique called γ-compute. Try it, appreciate it, and be aware that the pulse sequence looks different in this case. Can only be used for rotor-synchronous pulse sequences.

Exercise 3: Cross polarization
File: *3_CP.in*

This exercise investigates the coherence transfer from ^{1}H to ^{13}C using cross polarization. We will not look at the real spectrum, but only investigate the build-up of signal on ^{13}C.
- Look at the input file, beware that the *par* section contains two lines reading: *start_operator I2x* and *detect_operator I1p*. Run the simulation and observe the build-up in the file *3_CP,1.fid*.
- Change the rf field strength on the ^{13}C channel. This is controlled by the line *variable rfC 50000* in the *par* section of the input file. By changing this value you move away from Hartmann-Hahn match.
- Change back *rfC* and modify the dipolar coupling. Look at the oscillations of the build up curve.
- All simulations so far have been performed on a single crystal. Change the crystal file to *rep68* and observe the resulting fid.

Exercise 4: Heteronuclear decoupling
File: *4_Dec.in*

We will use this exercise to investigate different decoupling techniques like CW, TPPM and XiX decoupling.
- Run the simulation and look at the three output files *4_Dec_cw,1.spe*, *4_Dec_tppm,1.spe*, and *4_Dec_xix,1.spe*.
- Vary the dipole coupling strengths and observe the changes in the spectra.

Exercise 5: Heteronuclear recoupling
Files: *5_REDOR.in* and *5_REDORp.in*

This example deals with heteronuclear recoupling under magic-angle spinning using the REDOR pulse sequence.
- The input files *5_REDOR.in* and *5_REDORp.in* perform the same action. Try both of them. The output files are called *5_REDOR,1.fid* and *5_REDORp,1.fid*. These files show the dephasing as a function of the REDOR time. The file *5_REDORp.in* is faster because it takes advantage of the repeated properties of REDOR.
- Vary the dipole coupling strength and examine the dephasing curve.
- Change the number of points to 4 by editing the line *np 32* in the *par* section of the input file. Run the command *simdps 5_REDORp.in* to get a visualization of the pulse sequence.

Exercise 6: Rotational resonance
File: *6_RR.in*

We will investigate the possibility to transfer magnetization from one ^{13}C nucleus to another using rotational resonance.
- Try to run the simulation with different spinning frequencies around the rotational resonance condition ($\Delta\omega_{iso} = \omega_r$).
- What is the width of the rotational resonance condition?

Exercise 7: Fit an experimental spectrum
Files: *7_Exp.in* and *7_Fit.in*

> We will cheat a bit and create our own "experimental" spectrum by adding noise to a simulated spectrum.
> - Open the file *7_exp.in* and run the simulation. You may play around with the amount of noise by changing the line *variable noise XX* in the par section of the input file.
> - Open the file 7_fit.in and inspect the lines containing the instructions *simplex::newpar*, *simplex::run*, and *simplex::scan*. The input file loads the spectrum *7_exp,1.spe* and optimizes the chemical shielding anisotropy magnitude and asymmetry parameter. Run the simulation and compare the spectra *7_Exp,1.spe* and *7_Fit,1.spe*.
> - You may try to run the simulation for experimental spectra with different noise levels.

Exercise 8: Static spectra of all transitions for quadrupolar nuclei
File: *8_Static.in*

> Open the file *8_Static.in*. Execute the input file and verify the resulting fid and spectrum.
> - How many lines do you observe in the spectrum? and how many did you expect?
> - What is the intensity-ratio between the lines? Ideally the ratio should follow the equation I(I+1)-m(m-1). Is this true?
> - Try the same simulation with ^{93}Nb instead of ^{27}Al.
> - What happens if you use *I1c* or *I1p-I1c* as detect operator?
> - Change the crystal file to *rep678* or even higher to get a nice powder pattern.
> - Are the singularities located where you expected them to be?
> - Try similar simulations with different values for the asymmetry parameter.

Exercise 9: Finite pulse effects
File: *9_Pulse.in*

> Back to aluminum-27, we want to investigate the effect of pulsing on a quadrupolar nucleus. First, we want to simulate the intensity buildup during a pulse. The start operator should be *I1z* and the detect operator *I1c*, so we only observe the central transition. The pulseq procedure should now acquire np points inbetween pulses of length 1/sw. An rf power of 50 kHz (controlled by the line *variable rf 50000* in the *par* section) is applied. Execute the input file and verify the resulting fid and spectrum.
> - So, you expect to see a sinusoidal oscillation, but what about the period?
> - Try to lower the power to 10 kHz while increasing the number of points to 1024. What happens?
> - Now try with an rf power of 500 kHz (don't try that at home on your spectrometer) and increase the spectral width to 50 MHz. What happens?
> - Back to an rf power of 50 kHz and a spectral width of 5 MHz. Change the detect operator to detect all transitions. What happens with the nutation curve?

Exercise 10: Second-order quadrupolar lineshape in static and MAS spectra
Files: *10_Second_Stat.in* and *10_Second_MAS.in*

When the quadrupole coupling becomes larger (some MHz) we will start to observe the second-order quadrupolar broadening of the central transition. This exercise will exploit this. The file *10_Second_Stat.in* is setup to perform a static simulation of a [23]Na nucleus with quadrupole coupling parameters of C_Q = 2.6 MHz, η_Q = 0.2. Execute the input file and verify the resulting spectrum.
- Are you happy with the simulation? Too noisy? What to do about that? Eventually try with more crystallites (zcw4180). Did that improve the spectrum?
- What is – approximately – the centre of gravity for the line? How does that match with the isotropic chemical shift of 0 ppm?
- Run the input file *10_Second_MAS.in* and compare this MAS spectrum with the static spectrum just simulated. What is the ratio between the linewidths? How are the intensities of the two spectra?
- Try the two input files with different values for the asymmetry parameter.

Exercise 11: 3Q excitation profile
File: *11_3Qexc.in*

To simulate the triple-quantum buildup during a pulse we do not need to simulate a whole spectrum. We will just acquire the triple-quantum coherence using simpson. In the pulseq procedure of the file *11_3Qexc.in*, you will find the command *matrix set detect coherence {3}*. This is used to specify that the detect operator should be of coherence 3. The pulse sequence is otherwise quite similar to the one in Exercise 3, but here we are spinning. Execute the input file and verify the resulting fid.
- At what pulse length is the maximum intensity?
- Try the simulation but comment out the *matrix set …* command (commenting out is performed by a hash '#'). What operator do you detect here?
- Now acquire the triple-quantum coherence again – and vary the quadrupole coupling constant in the range 2-10 MHz. What do you observe?
- Use a quadrupole coupling constant of 2.6 MHz, try to vary the rf field strength from 50 to 500 kHz. What do you observe?
- Set the spinning frequency up to 30 kHz and the rf power down to 37 kHz and compare the simulation with the first 100 kHz simulation. Which one has the better sensitivity? You may need to phase the latter spectrum!

Exercise 12: 3Q → 1Q mixing profile with single-pulse and fast amplitude modulation
File: *12_Mixing.in*

The mixing is just as critical as the 3Q excitation. We will investigate two of the typical ways of performing the mixing: single-pulse and fast-amplitude modulated pulses. We will investigate the transfer from 3Q to +1Q, I_z, and -1Q coherence, corresponding to echo, z-filter, and antiecho pathways. The file *12_Mixing.in* is set up to run three simulations corresponding to these target operators. Execute the input file and verify the resulting fid.
- Which mixing curve has the first maximum (maximum at shortest pulse length)?
- Change the number of points to 16, the spectral width to 1, and use the FAM mixing sequence (pulse-delay-pulse-delay) corresponding to the sequence commented out in the input file. Compare the simulations with the previous ones. Which sequence gives the best sensitivity?

Exercise 13: The second-order lineshape in MQMAS experiments
File: 13_3Qshape.in

The different sequences for 3Q excitation and subsequent mixing are not equally efficient for all crystallites. Hence they will distort the second-order lineshape. The input file *13_3Qshape.in* exploits this fact. The file is very similar to the one used in Exercise 10, but here the acquisition is preceeded by a 3Q excitation pulse and a 3Q-1Q mixing pulse. Execute the input file and observe the resulting spectrum.

- How does the intensity compare with the one obtained in Exercise 10.
- How is the lineshape?
- Try to vary the excitation and mixing pulse lengths.
- Make the mixing pulse a quarter and a half of a rotor period long – this corresponds to the RIACT mixing. What happens to the intensity and lineshape?