

Summer School 2004

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1 Type Faces and Other Conventions

normal

Italic is used for names of all utilities, switches, directories, and filenames and to emphasise new terms and concepts when they are first introduced. It is also used in programmes and examples to explain what is happening or what has been left out at the ... marks

Bold is used occasionally within the text to make words easy to find—just like the name of movie stars in the People section of your local newspaper

Monotype is used for sample code fragments and examples. A reference in the text to a word or item used in an example or code fragment is also shown in constant width font.

Monotype Italic is used in code fragments and examples to show variables for which a context-specific substitution should be made. (the variable *filename*, for example, would be replaced by some actual filename)

2 Structure of SIMPSON [1]

2.1 Files

simpson, simplot, simfid, simdps etc.

2.2 Important Conventions used

- use *shift conventions* not shielding
- parameters ending on a letter *p* are read as *ppm* values, to use this feature define the `proton_freq` variable in the `proc` section
- times in the `pulseq` section are assumed to be in units of 10^{-6} s

2.3 Tcl Commands and Variables in the Parameter File

The parameter file is structured in the sections: `spinsys`, `par`, `proc pulseq`, `proc main`

2.3.1 spinsys

nuclei define nuclei one is dealing with, like 1H, 13C, 15N, ...
e.g.: `nuclei 1H 15N`, or: `13C 13C ...`

channels define the RF channels in use, like 1H, 13C, 15N, ...
e.g.: `channels 1H ...`

shift define the chemical shift

form:	<code>shift</code>	Spin <i>i</i>	$\frac{\omega_{\text{iso}}^{\text{CS}_i}}{\text{[ppm]}}$	$\frac{\delta^{\text{CS}_i}}{\text{[ppm]}}$	η^{CS_i}	$\frac{\alpha_{\text{PC}}^{\text{CS}_i}}{\text{[deg]}}$	$\frac{\beta_{\text{PC}}^{\text{CS}_i}}{\text{[deg]}}$	$\frac{\gamma_{\text{PC}}^{\text{CS}_i}}{\text{[deg]}}$
e.g.	<code>shift</code>	1	5p	13p	0.25	10	20	30
	<code>shift</code>	2	3p	20p	1.0	40	90	120

dipole define direct dipole coupling between spin *i* and *j*

form:	<code>dipole</code>	Spin <i>j</i>	Spin <i>j</i>	$\frac{b_{ij}}{2\pi}$ [Hz]	$\frac{D_{ij}^{\text{D}_{ij}}}{\text{[deg]}}$	$\frac{\beta_{\text{PC}}^{\text{D}_{ij}}}{\text{[deg]}}$	$\frac{\gamma_{\text{PC}}^{\text{D}_{ij}}}{\text{[deg]}}$
e.g.	<code>dipole</code>	1	2	-5000	0	20	30
	<code>dipole</code>	1	3	2000	0	90	120

jcoupling define the J coupling between spin *i* and *j*

form:	<code>jcoupling</code>	Spin <i>j</i>	Spin <i>j</i>	$\frac{J_{\text{iso}}^{ij}}{\text{[ppm]}}$	$\frac{J_{\text{aniso}}^{ij}}{\text{[ppm]}}$	$\eta^{J_{ij}}$	$\frac{\alpha_{\text{PC}}^{J_{ij}}}{\text{[deg]}}$	$\frac{\beta_{\text{PC}}^{J_{ij}}}{\text{[deg]}}$	$\frac{\gamma_{\text{PC}}^{J_{ij}}}{\text{[deg]}}$
e.g.	<code>jcoupling</code>	1	2	5p	-10p	0	0	20	30
	<code>jcoupling</code>	1	3	3p	20p	0.2	0	90	120

quadrupole define quadrupolar coupling of spin *i*, where the order of the coupling Hamiltonian is set by the parameter `order`. `order` can take the values 1 and 2 corresponding to first or second order quadrupolar interaction

form:	<code>quadrupole</code>	Spin <i>i</i>	order	$\frac{C^{\text{Q}_{ij}}}{2\pi}$ [Hz]	$\eta^{\text{Q}_{ij}}$	$\frac{\alpha_{\text{PC}}^{\text{Q}_{ij}}}{\text{[deg]}}$	$\frac{\beta_{\text{PC}}^{\text{Q}_{ij}}}{\text{[deg]}}$	$\frac{\gamma_{\text{PC}}^{\text{Q}_{ij}}}{\text{[deg]}}$
e.g.	<code>quadrupole</code>	1	1	3.28e6	0	0	20	30
	<code>quadrupole</code>	2	2	200e6	0.2	0	90	120

2.3.2 par

spin_rate set the MAS frequency in Hz
e.g. 10000

np sampling points
e.g. 32

sw spectral width in Hz
e.g. `spin_rate/2`

crystal_file use predefined crystal orientations file describing $\frac{\alpha_{\text{CR}}^\lambda}{\text{[deg]}}$, $\frac{\beta_{\text{CR}}^\lambda}{\text{[deg]}}$ using REPULSION, ZCW or other schemes.
i.e `crystal_file rep168` or
or define own set of angles in `<filename>.cry`
i.e `crystal_file <filename>`

gamma_angles set the number of gamma angles $\frac{\gamma_{\text{CR}}^\lambda}{\text{[deg]}}$ to use

gamma_zero set the angle $\frac{\gamma_{\text{CR}}^\lambda}{[\text{deg}]}$ for a single crystal

rotor_angle set the the rotor angle (e.g. $\beta_{\text{MAS}} = \arccos \sqrt{\frac{1}{3}} \approx 54.7^\circ$)

method define numerical method to use for time evolution like direct method (**direct**), GAMMA COMPUTE (**gcompute**)

start_operator define the operator for the magnetisation to start experiment with e.g. I1x, I2y or Inx for all spins

detect_operator set the detection operator, for quadrature detection one uses to Inp, or I2p.

proton_frequency set the proton frequency that corresponds to the field strength of the \vec{B}_0 field wanted
e.g. **proton_frequency** 400e6 for a 400 MHz spectrometer

variable is a user defined parameter for later reuse in **pulseq** or **main**
e.g. **variable rf** 150000 defines a variable **rf** that would later handle the absolute RF field strength.

verbose set the verbosity of simpson on (1) or off (0) by consecutive series of 0's and 1's for the parts:
form: **verbose** SPINSYS PROGRESS PAR SIMINFO OPER POWDER
e.g. **verbose** 1 1 0 1 1 0

2.3.3 proc pulseq

global include set of parameters
e.g. **global par** to include all parameters from section **par** so they can be reused

set set typical parameters that will be reused
e.g. **set t180** [expr 0.5e6/\$par(rf)]
set duration of a 180° pulse in μs
or
i.e **set tr2** [expr 0.5e6/\$par(spin_rate)-\$t180]
the duration of half a rotor period in μs . Here the duration of the π pulse is subtracted from the half rotor period to ensure rotor synchronisation of refocusing pulses

pulse define a pulse
e.g. **pulse \$t180 0 x \$par(rf) x**
is setting up a pulse of duration **\$t180** with RF amplitude 0 and phase **x** in the first channel and RF amplitude **\$par(rf)**, as defined in section **par** as **rf** and phase **x**

pulseid use ideal pulses

delay set a delay like **\$tr2** in μs

acq obtain the current density matrix, resulting from time propagation up to this point in time. In addition, get expectation value of the `detect_operator` (e.g. a data point)

maxdt duration in μs over which the Hamiltonian can be assumed to be constant in e.g. `maxdt 1` usually a good value

store store time evolution propagator to be reused later with the `prop` command i.e `store 1` can be reused by the command `prop 1`

reset reset current time and time evolution propagator. In addition to calculate the propagator at an arbitrary time point, use this time with the `reset` command e.g. `reset [expr 7*$t360]`

prop \rightarrow store

2.3.4 proc main

XXX

2.4 Example Programme

```

spinsys {
  channels 1H
  nuclei 1H
  shift 1 10 0 0 0 0 0
}
par {
  spin_rate 0
  sw 30000
  start_operator I1x
  detect_operator I1p
  gamma_angles 1
  verbose 1101
  np 1024
  crystal_file alpha0beta0
  proton_frequency 400e6
}

proc pulseq {} {
  global par
  reset
  delay [expr 1.0e6/$par(sw)]
  store 1
  reset
  acq $par(np) 1
# Same as:

```

```
# acq
# for {set i 1} {$i < $par(np)} {incr i} {
#   prop 1
#   acq
# } }
proc main {} {
  global par
  set f [fsimpson]
  fsave $f $par(name).fid
  faddlb $f 50 0
  fzerofill $f 4096
  fft $f
  fsave $f $par(name).spe -xreim
  fsave $f $par(name).spe
  funload $f
}
```

2.5 The Powder Angles Available in Simpson's *.cry Files

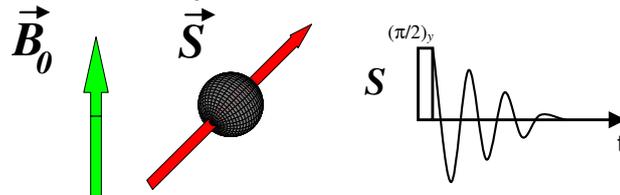
method:	BCR	REPULSION [16]	ZCW
	bcr10.cry	rep10.cry	zcw20.cry
	bcr20.cry	rep20.cry	zcw33.cry
	bcr30.cry	rep30.cry	zcw54.cry
	bcr40.cry	rep50.cry	zcw88.cry
	bcr50.cry	bcr66.cry	zcw143.cry
	bcr80.cry	rep100.cry	zcw232.cry
	bcr200.cry	rep144.cry	zcw376.cry
	bcr400.cry	rep168.cry	zcw615.cry
		rep256.cry	zcw986.cry
		rep320.cry	zcw4180.cry
		rep678.cry	
		rep2000.cry	

3 0st Exercise – Static, Single Spin \vec{S} with $S = \frac{1}{2}$

3.1 First Steps in SIMPSON

Workplace: `~/summerschool04/sim/Exercise0/intr_simp`

Situation: An isolated, single spin \vec{S} is located in a strong, homogeneous, external magnetic field \vec{B}_0 and is therefore influenced by the Zeeman interaction.



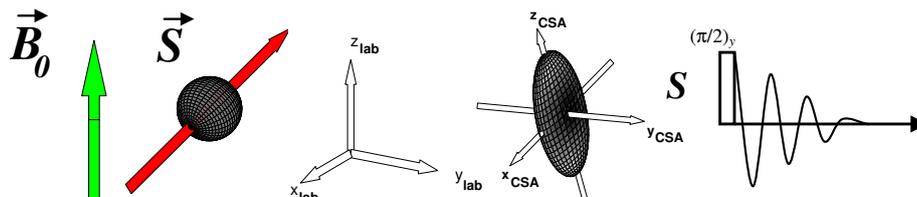
Tasks:

1. Have a look at the simpson input file `intr_simp.in` and get familiar with the structure and the variables in it.
2. Do a simulation by calling :
`$ simpson intr_simp.in`
and inspect the output with:
`$ simplot intr_simp.spe` or `$ simplot intr_simp.fid`
3. Get familiar with `simplot`
4. Check the FID corresponding to a static Hamiltonian.
What is the effect of the isotropic chemical shift on the FID.
`shift 1 100 0 0 0 0 0`
5. Detect the FID along the \hat{x} - and \hat{y} -directions by adjusting:
`detect_operator I1x`
and/or
`start_operator I1p`
in the input file `intr_simp.in` .

3.2 NMR on a Single Crystal

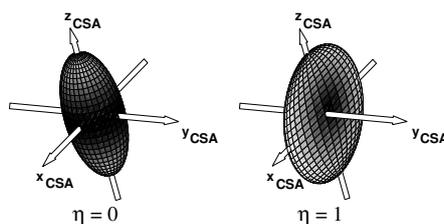
Workplace: `~/summerschool04/sim/Exercise0/static/csa-single`

Situation: An isolated single spin \vec{S} in a strong, homogeneous, external magnetic field \vec{B}_0 , located in a single crystal and, therefore, influenced by the Zeeman and the Chemical Shift interaction.



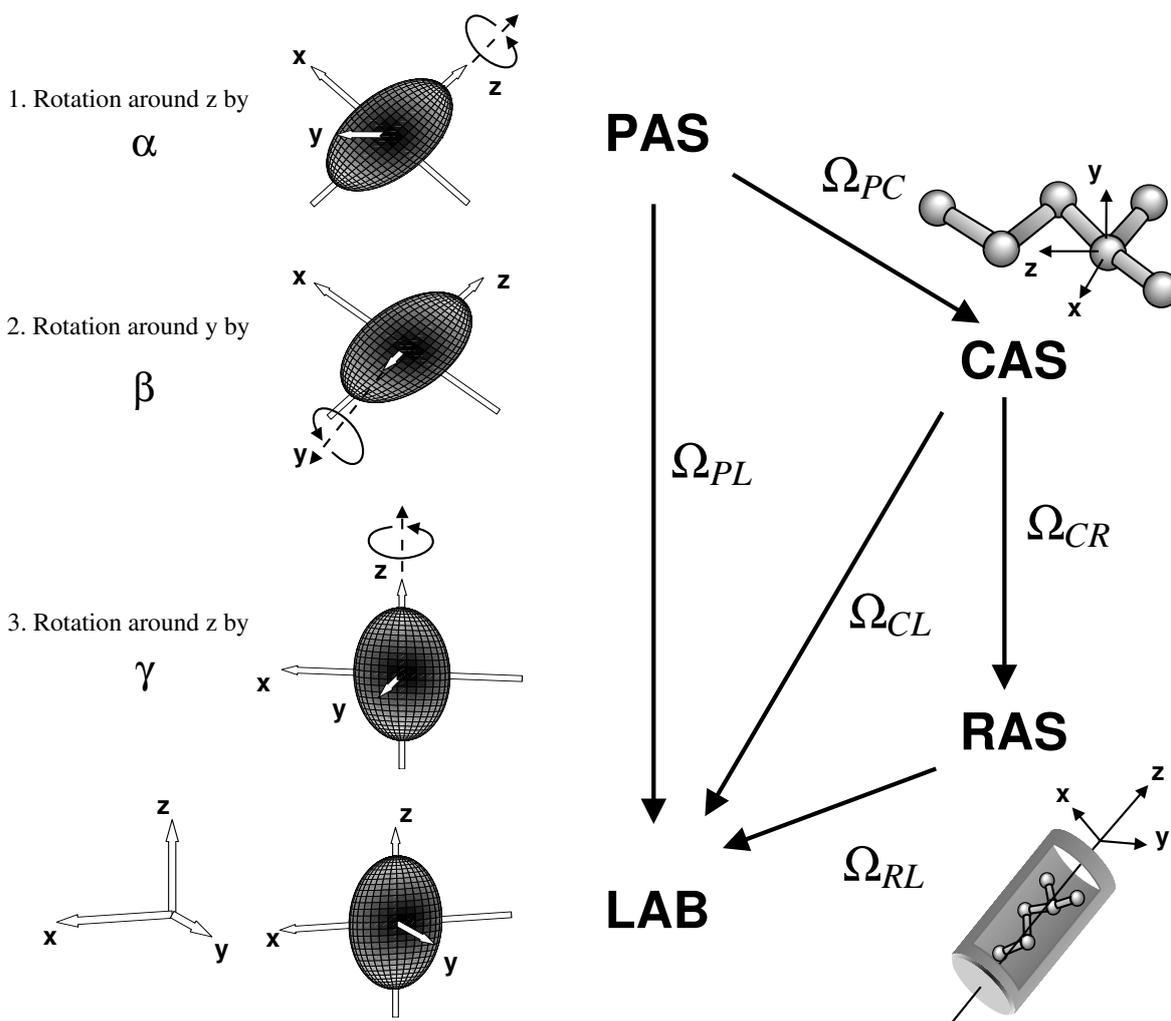
Tasks:

1. Get familiar with the crystal file *my_alphabet.cry* and the `gamma_zero` parameter in *csa.in*
2. The Euler angles $\{\alpha_{CL}, \beta_{CL}, \gamma_{CL}\}$ are used to transform the coordinate system of the single crystal frame to the laboratory frame (detector). Check which Euler angle has an influence on the NMR signal using the file *csa.in* and modifying the line:
`gamma_zero 0`
 therein and the file *my_alphabet.cry*
3. Extract the eigenvalues of the CSA tensor for the cases where the asymmetry parameter is $\eta = 0$ and $\eta = 1$ from single crystal simulations by orienting the single crystal in the appropriate way with respect to the \vec{B}_0 field. Use the files *csaeta0_alpha0beta0.in*, *csaeta0_alpha0beta90.in*, *csaeta0_alpha90beta90.in*
4. Since there is no need to distinguish between the coordinate system of the single crystal and the principal axes system of the CSA tensor here, one can choose both to be coincident. (this is **not** generally the case when multiple, orientation dependent interactions are present!).



3.3 The Axes Systems of NMR

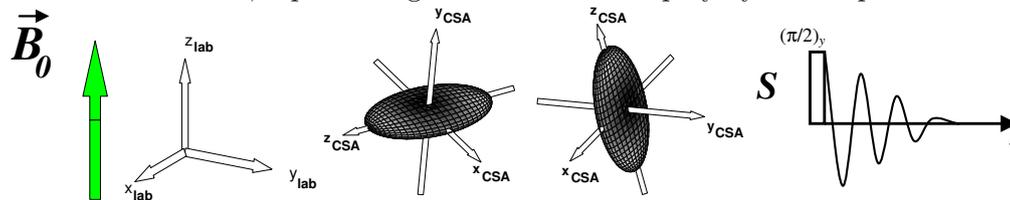
Euler Angles $\Omega = \{\alpha; \beta; \gamma\}$



3.4 Powder Averaging

Workplace: `~/summerschool04/sim/Exercise0/static/csa-powder`

Situation: Same case as before but now we take into account a multitude of single crystals with different orientations, representing the situation in a polycrystalline powder.



Tasks:

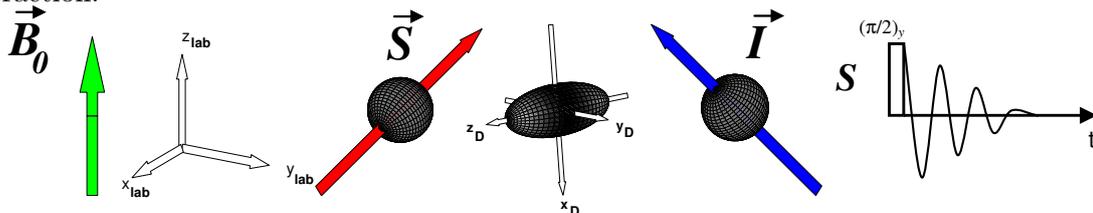
1. Use the available crystal files in Section 2.5 to gradually increase the number of orientations in the simulations (use the files `csaeta0.in`, `csaeta1.in`) until there is no change in lineshape anymore and a complete powder average is simulated (eventually use `zcw28656.cry` and `zcw832039.cry` provided in the workplace folder)
2. Compare the simulated CSA powder-patterns to the resonances of the CSA eigenvalues simulated in `~/summerschool04/sim/Exercise0/static/csa-single/`
3. Simulate CSA powder patterns for arbitrary values of $\omega_{\text{iso}}^{\text{CS}}$, δ^{CS} , η^{CS} (including negative values of δ^{CS}).

4 1st Exercise – Spin Interactions and MAS

4.1 Direct Dipolar Coupling

Workplace: `~/summerschool04/sim/Exercise1/dipole`

Situation: Two spins \vec{S} , \vec{I} , with $S, I = \frac{1}{2}$, in a strong, homogeneous, external magnetic field \vec{B}_0 , in spatial proximity to each other and, therefore, influenced by mutual dipolar coupling interaction.



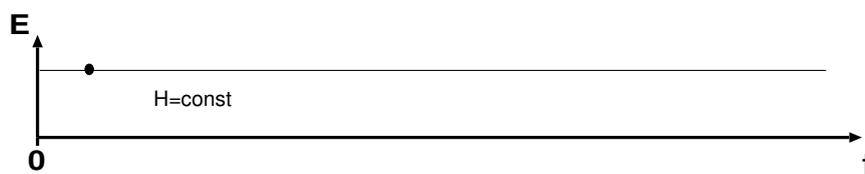
Tasks:

1. Simulate the spectrum for a heteronuclear dipolar coupled spin pair using `pakehetero.in`. Compare the result to the simulation of a single spin subjected only to the CSA interaction using `csaet0.in` (change the sign of δ^{CS}).
2. Repeat the simulation, but this time for a powder by using an appropriate crystal angle file from the table in Section 2.5.
3. Simulate the spectrum of a homonuclear dipolar coupled spin pair using `pakehomo.in` and compare it to the spectrum of the heteronuclear spin pair in Section 5.1.

4.2 Gamma-COMPUTE and Efficient Simulation of NMR Spectra

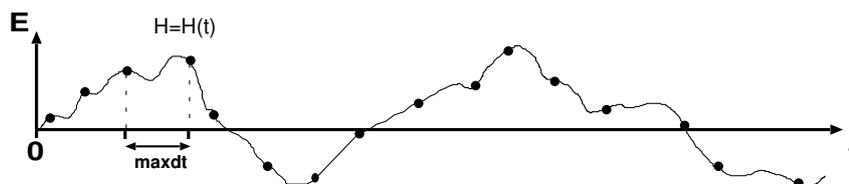
Time Evolution

static



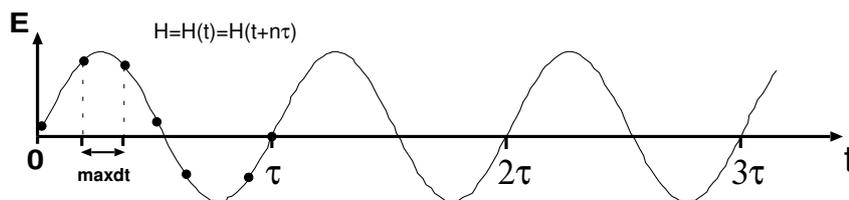
time dependent

direct method



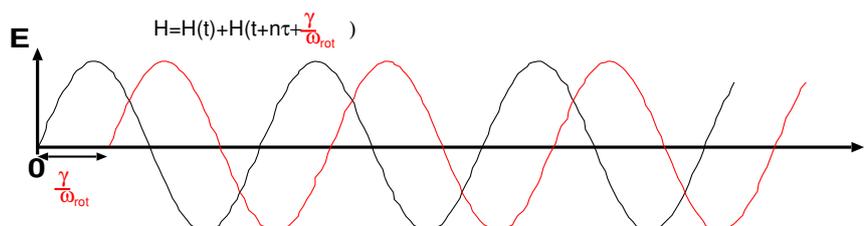
time dependent periodic

COMPUTE method



powder

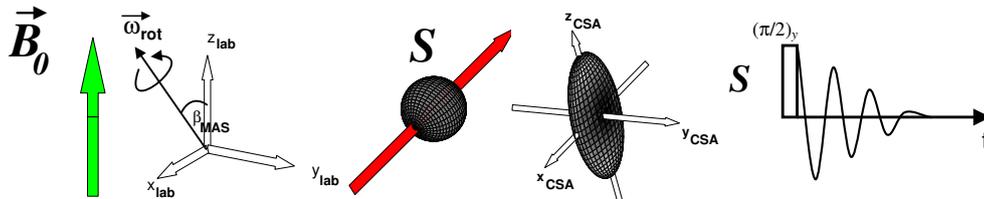
γ -COMPUTE method



4.3 The Magic Angle Spinning (MAS) Experiment [2]

Workplace: `~/summerschool04/sim/Exercise1/csa-mas/direct/`

Situation: The same situation as in Section 3.4 but now the crystallites are rotated with the spinning speed ω_{rot} , continuously around an axis inclined at an angle β_{MAS} with respect to \vec{B}_0 .



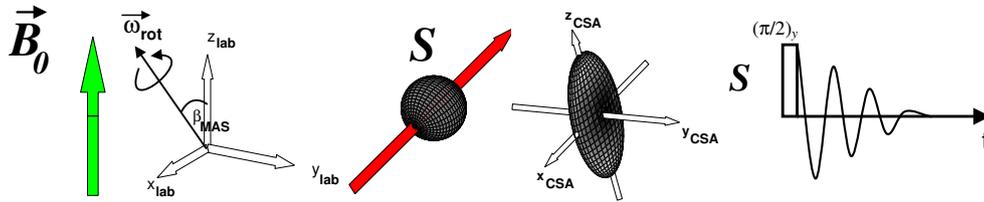
Tasks:

1. Simulate MAS spectra with different spinning speeds using the files: `csa-static.in`, `csad-slow.in`, `csadfast.in`
2. Use `csadfastsingle.in` to check which powder angles $\{\alpha_{\text{CL}}, \beta_{\text{CL}}, \gamma_{\text{CL}}\}$ are now encoded in the spectrum.
3. Simulate the MAS spectra of task 1. again, now using the Gamma-COMPUTE method, where:
`method direct`
is changed to
`method gcompute`
in the input file `csaslow.in`, `csafast.in`

4.4 The Off Magic Angle Spinning (OMAS) Experiment

Workplace: `~/summerschool04/sim/Exercise1/csa-omas`

Situation: same as in Section 4.3 but now the angle β_{MAS} is no longer fixed to the magic angle.



Tasks:

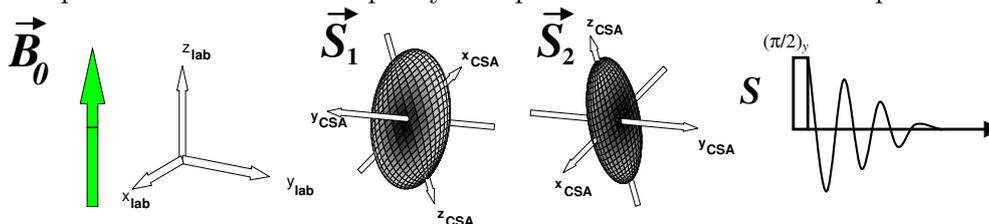
1. Simulate OMAS spectra by varying the spinning speed in `csafast.in`. What is the line-shape as compared to MAS simulations?
2. Simulate spectra, varying the rotor angle in line:
`rotor_angle 54.7`
in the input file `csafast.in` (use angles larger and smaller than the magic angle ($\beta_{\text{MAS}} \approx 54.7^\circ$)).
3. Compare the simulation of the OMAS experiment with the corresponding static CSA powder pattern of this spin system by using `csa-static.in`

4.5 Fit CSA in a MAS Spectrum

Workplace: `~/summerschool04/sim/Exercise1/csa-mas/gamma/csafit`

Situation: Given the MAS spectrum of a powdered sample where the spin system consists of three uncoupled spins \vec{S}_1 , \vec{S}_2 both experiencing CSA.

How is it possible to extract the spin-system parameters encoded in the spectrum.



Tasks:

1. Which parameters can be extracted from the spectrum?
2. Try to extract the CSA parameters from the given experimental spectrum *expl.spe* by running *csafit1S.in* and compare to *csafit1S.spe*. If the fit result does not agree to the solution in *expl.in*, insert the obtained “best-fit parameters” into the proc main section of *csafit1S.in* as new start parameters:

```
mnpar scl1 10 100  
mnpar iso1 -10.5 1  
mnpar csa1 90 100  
mnpar eta1 0.5 0.1 0.0 1.0  
mnpar lb 30 10
```

repeat till fit is not improving anymore. (remember to reduce uncertainty of fit parameters)
3. Try to extract the remaining two CSA parameter sets (given iso1 is 0, 10 respectively). Remember to adjust the frequency intervals in

```
set rms [frms $f $g -re [list [list 16500 17100] ...
```

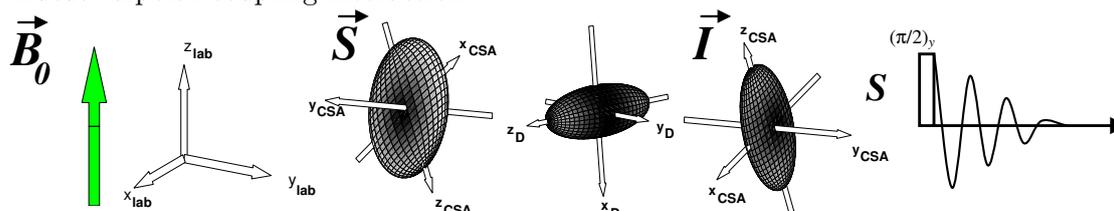
to match the respective MAS sideband pattern.

5 2nd Exercise – Heteronuclear De- and Recoupling

5.1 Heteronuclear Spin Pair under MAS

Workplace: `~/summerschool04/sim/Exercise2/hetero-mas`

Situation: Two heteronuclear spins \vec{S} , \vec{I} with $S, I = \frac{1}{2}$, in a powder, in a strong, homogeneous, external magnetic field \vec{B}_0 , in spatial proximity to each other and, therefore, influenced by mutual dipolar coupling interaction.



Tasks:

1. Simulate the MAS spectrum of \vec{S} by running `all_hetero.in`.
2. Modify the Euler angles $\{\alpha_{PC}^{CS}, \beta_{PC}^{CS}, \gamma_{PC}^{CS}\}$ for \vec{S} and \vec{I} and check which are encoded in the spectrum.
3. The spin system in the powder now consists of three spins \vec{S} , \vec{I}_1 , \vec{I}_2 . Both \vec{I}_1 and \vec{I}_2 are dipolar coupled to \vec{S} . In addition the two homonuclear spins \vec{I}_1 , \vec{I}_2 are dipolar coupled to each other. All spins \vec{S} , \vec{I}_1 , \vec{I}_2 experience CSA. We observe the spectrum of \vec{S} . Simulate the spectrum of \vec{S} under MAS, once including the \vec{I}_1 - \vec{I}_2 homonuclear dipolar coupling, once assuming absence of this \vec{I}_1 - \vec{I}_2 homonuclear dipolar coupling by changing the line:

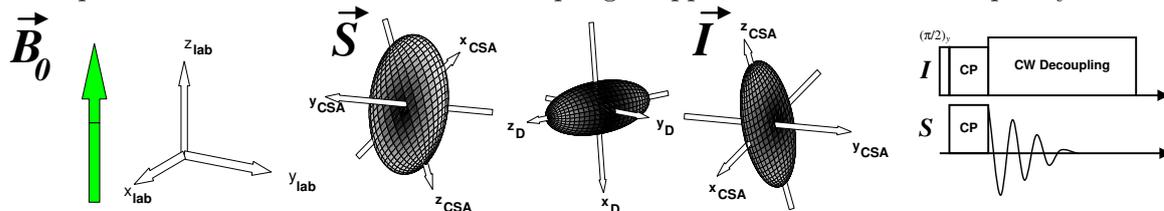
```
dipole 2 3 -7183 0 80 0
to
# dipole 2 3 -7183 0 80 0
in SiF2.in
```

5.2 Continuous Wave (CW) [3] Decoupling

Workplace: `~/summerschool04/sim/Exercise2/heterodec/cwdec`

Situation: Two dipolar coupled heteronuclear spins \vec{S} , \vec{I} in a powder, in a strong, homogeneous, external magnetic field \vec{B}_0 , in spatial proximity to each other and, therefore, influenced by mutual dipolar coupling interaction.

The spectrum of \vec{S} is observed. CW decoupling is applied at the Larmor frequency of \vec{I} .



Tasks:

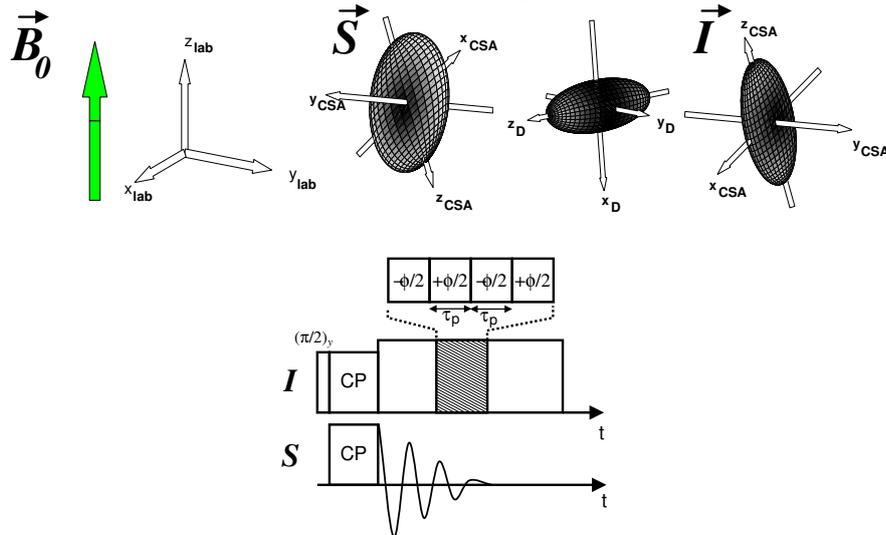
1. Run the simulation in `cwdec.in`
2. Modify the offset of the CW r.f. irradiation in the I -channel by setting `offset 0 0` to nonzero values in `cwdec.in`. Inspect the decoupling performance.
3. Adjust the r.f. amplitude in `cwdec.in` by modifying the line `pulse 1e6 0 0 100000 x` to get optimum decoupling. Compare the optimum decoupling result with a simulation where the spin pair \vec{S} , \vec{I} is assumed to have **no** \vec{S} - \vec{I} dipolar coupling using `cwdec_nodip.in`

5.3 Two Pulse Phase Modulation (TPPM) [4] Decoupling

Workplace: `~/summerschool04/sim/Exercise2/heterodec/tppmdec`

Situation: A dipolar coupled heteronuclear spin pair \vec{S} , \vec{I} in a powder, under MAS, in a strong, homogeneous, external magnetic field \vec{B}_0 , with \vec{S} and \vec{I} in spatial proximity to each other and, therefore, influenced by mutual dipolar coupling interaction. Both \vec{S} and \vec{I} experiencing CSA.

Spectrum of \vec{S} is taken with TPPM decoupling applied at the \vec{I} -spin Larmor frequency.



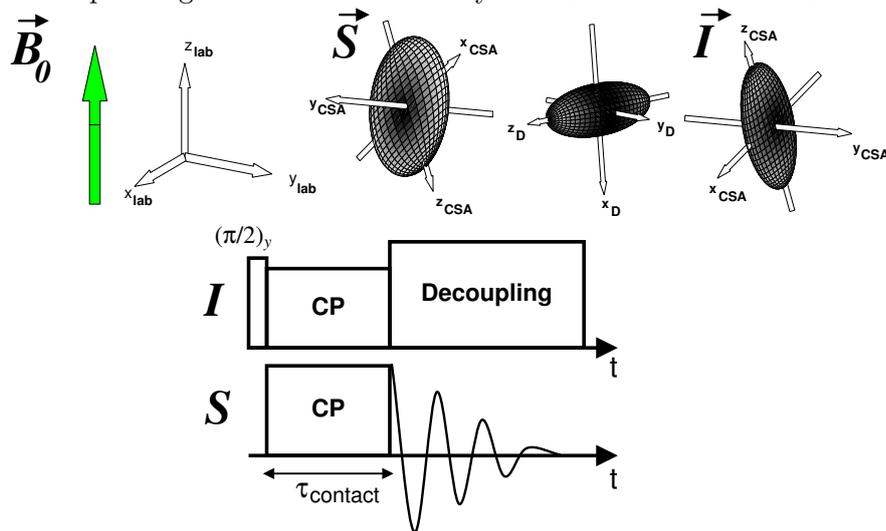
Tasks:

1. Simulate the effect of TPPM decoupling on the \vec{S} -spin spectrum by running the file `hetdec.in`
Compare the result to the CW decoupling situation (is done automatically by `hetdec.in`).
2. Increase the amount of decoupling power by adjusting the line:
`variable rf 80000`
to higher values (e.g. 160000)
3. Remove the CSA of the \vec{I} -spins and rerun `hetdec.in`.
Compare the effect of TPPM and CW decoupling on the \vec{S} -spin spectrum.

5.4 The Cross Polarization (CP) [5, 6] Experiment

Workplace: `~/summerschool04/sim/Exercise2/heterorec/cp/`

Situation: A dipolar coupled heteronuclear spin pair \vec{S} , \vec{I} in a powder, under MAS, both \vec{S} , \vec{I} experiencing CSA. The \vec{S} -spin spectrum is observed under conditions of \vec{I} -spin decoupling. The observable \vec{S} -spin magnetisation is created by $\vec{I} \rightarrow \vec{S}$ Hartman-Hahn CP.



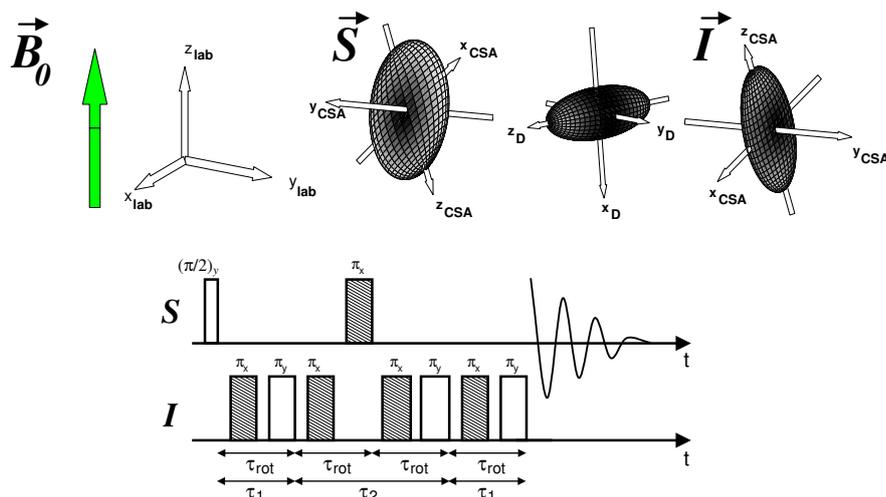
Tasks:

- Run `cp.in` in order to observe \vec{I} -spin and \vec{S} -spin spectra (`cp-1H.spe` and `cp-13C.spe`) depicting the magnetisation residing on the ^1H and ^{13}C spins. How do the spectral intensities change when the \vec{I} -spin r.f. channel amplitude:
 - variable `rf2 34000`
 - or CP duration $\tau_{contact}$:
 - variable `cpmix 100`
 - is modified.
- Run `cp-hhahn.in` in order to get a scan of the amplitude of the \vec{S} -spin resonance (^{13}C) as a function of the amplitude of the r.f. irradiation at the \vec{I} -spin Larmor frequency (`rf2`) in `cp-hhahn.fid`. Explain the relationship with the spin rate ω_{rot} .
- Take an optimum setting of the I - and S -channel r.f. amplitudes (`rf2, rf`) for CP. Run `cp-scan_tauexc.in` to calculate series of simulations where the the contact time $\tau_{contact}$ (`cpmix`) is varied. The resulting files `cp-scan_tauexc-1H.fid` and `cp-scan_tauexc-13C.fid` display integrated spectral intensities of the respective nucleus.
- Check the influence of different dipolar coupling strengths on the oscillation curves produced by `cp-scan_tauexc.in`

5.5 The REDOR Experiment [7]

Workplace: `~/summerschool04/sim/Exercise2/heterorec/redor/sim`

Situation: A Heteronuclear spin pair \vec{S} , \vec{I} in a powder under MAS, both \vec{S} , \vec{I} experiencing CSA. Spectrum of \vec{S} spins is taken with series of S -channel and I -channel pulses applied as indicated.

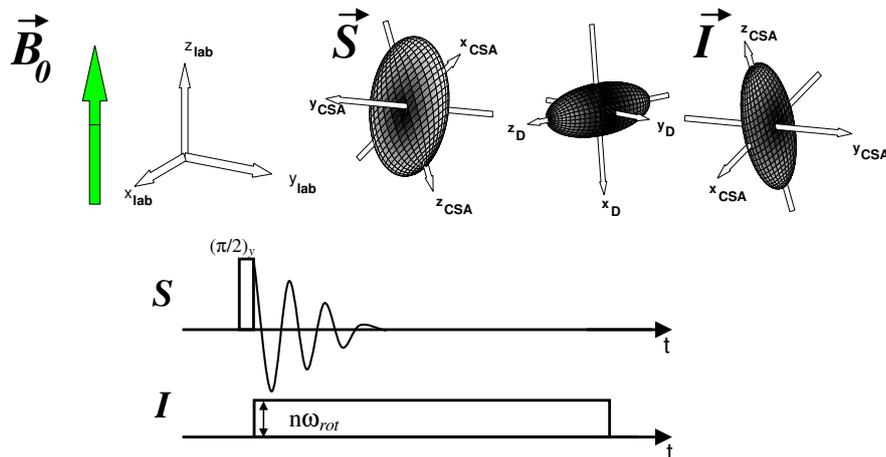


1. Run `redor.in` to obtain a so-called REDOR curve in `redor.fid`
2. Examine the dependence of the REDOR curve on the magnitude of the dipolar coupling and the CSA eigenvalues of \vec{S} and \vec{I} .
3. Set the number of acquisition points in `redor.in` :
`np 32`
to
`np 4`
and run:
`$ simdps redor.in`
to get a sketch of the pulseprogramme in `redor.ps` (if you can not display postscript use AcrobatReader to look at `redor.pdf` :-)
4. Going to `~/summerschool04/sim/Exercise2/heterorec/redor/fit` . Obtain a fit of an experimental REDOR curve `redorex.fid` in order to extract the magnitude of the dipolar coupling constant by running `redorfit.in` and compare the result to `redorex.in`. Use a fitting procedure similar to the one used for fitting CSA in Section 4.5.

5.6 The Rotary Resonance Recoupling (R^3) [8] Experiment

Workplace: `~/summerschool04/sim/Exercise2//heterorec/r3`

Situation: A heteronuclear spin pair \vec{S} , \vec{I} in a powder, under MAS, both \vec{S} , \vec{I} experiencing CSA. Spectrum of the \vec{S} -spin is taken with CW irradiation applied at the \vec{I} -spin Larmor frequency as indicated.



Tasks:

1. run `r3.in` and afterwards examine which of the \vec{S} and \vec{I} CSA parameters are sensitively encoded in the \vec{S} -spin spectrum.
2. Modify the amplitude of the r.f irradiation at the \vec{I} spin Larmor frequency. Simulate \vec{S} -spin spectra for:

- a) $\omega_{r.f} = n\omega_{rot}$; $n \in \mathbb{N}^+$
- b) $\omega_{r.f} \ll n\omega_{rot}$;
- c) $\omega_{r.f} \gg n\omega_{rot}$;

by changing the line:

```
set rf 3000
```

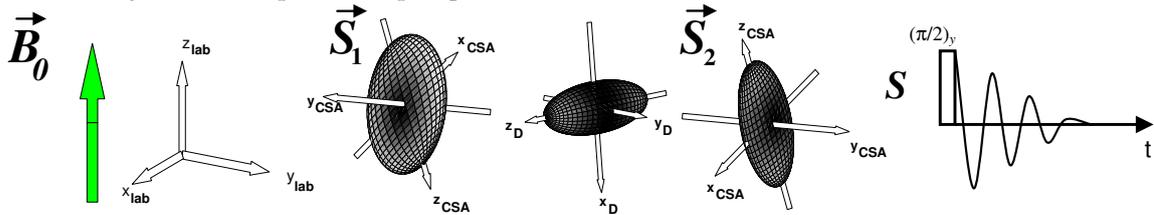
3. Compare the results to a \vec{S} -spin spectrum of the \vec{S} -, \vec{I} -spin pair obtained without r.f. irradiation at the \vec{I} -spin Larmor frequency (Section: 5.1)

6 3rd Exercise – Homonuclear Spin Pairs

6.1 Homonuclear Spin Pairs under MAS

Workplace: `~/summerschool04/sim/Exercise3/homo-mas`

Situation: Two homonuclear spins \vec{S}_1, \vec{S}_2 , with $S_1, S_2 = \frac{1}{2}$, in a powder, in a strong, homogeneous, external magnetic field \vec{B}_0 , in spatial proximity to each other and, therefore, influenced by mutual dipolar coupling interaction.



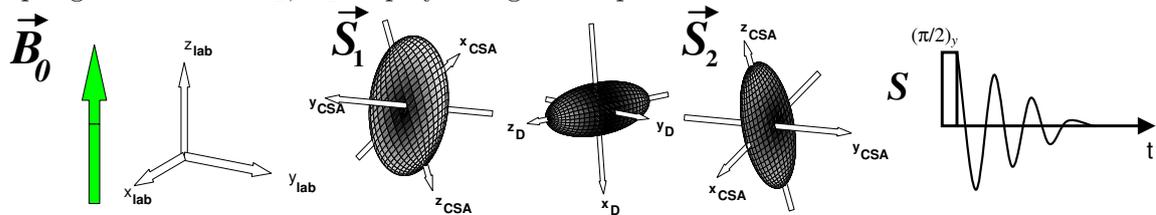
Tasks:

1. Simulate a MAS spectrum of the \vec{S}_1, \vec{S}_2 spin pair by running `all_homo.in`.
2. Modify the Euler angles $\{\alpha_{\text{PC}}^{\text{CS}}, \beta_{\text{PC}}^{\text{CS}}, \gamma_{\text{PC}}^{\text{CS}}\}$ for \vec{S}_1 and \vec{S}_2 and check which are encoded in the spectrum.
Compare the findings with the results for Section: 5.1

6.2 The Rotational Resonance (R^2) [9, 10, 11, 12] Experiment

Workplace: `~/summerschool04/sim/Exercise3/homorec/r2`

Situation: A homonuclear spin pair \vec{S}_1, \vec{S}_2 in a powder under MAS, both \vec{S}_1, \vec{S}_2 experiencing CSA, in spatial proximity to each other and, therefore, influenced by mutual dipolar coupling interaction. \vec{S}_1, \vec{S}_2 display a large isotropic chemical shift difference.



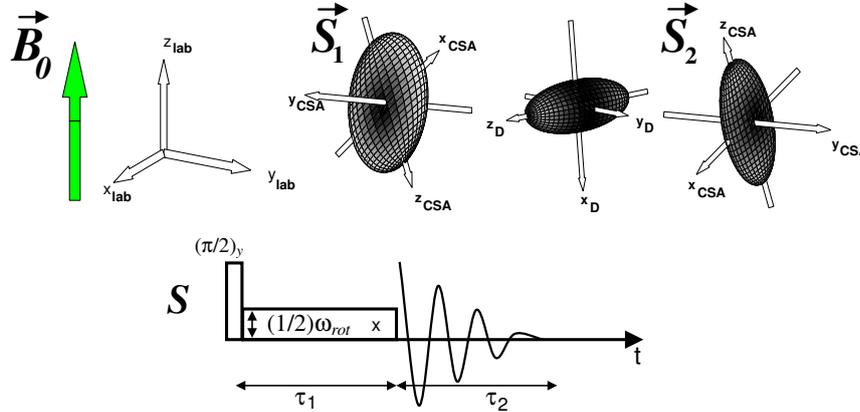
Tasks:

1. Run `r2_single.in` and modify the spinning speed ω_{rot} by changing:
`spin_rate 5000`
 Focus on the Rotational Resonance condition $\Delta\omega_{\text{iso}}^{\text{CS}} = n\omega_{\text{rot}}$.
2. Use `r2_single.in` to examine the width of the $n = 1$ Rotational Resonance condition.

6.3 The Homonuclear Rotary Resonance (HORROR) [8, 13] Experiment

Workplace: `~/summerschool04/sim/Exercise3/homorec/horror`

Situation: A homonuclear spin pair \vec{S}_1, \vec{S}_2 in a powder under MAS.



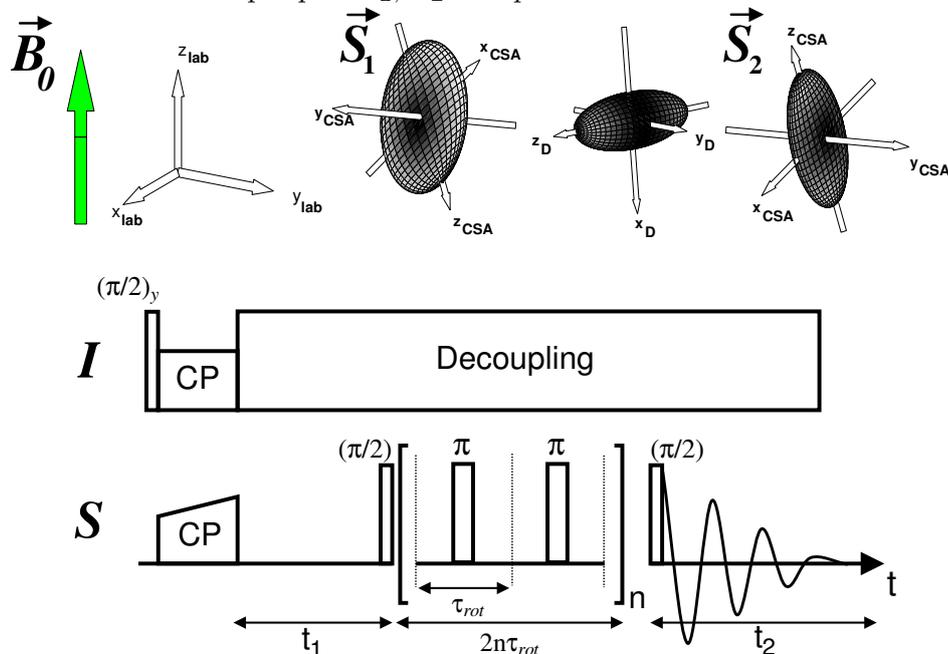
Tasks:

1. Run `horror.in` where the r.f field amplitude $\omega_{r.f.}$ is set to fulfill the horror condition $\omega_{rot} = 2\omega_{r.f.}$
2. Compare the simulated spectrum to an analogous conventional MAS experiment by setting the r.f. amplitude in the input file to zero by modifying:
`variable rf 0.5*spin_rate`
in `horror.in` to
`variable rf 0`

6.4 The Radio Frequency-Driven Dipolar Recoupling (RFDR) [14] Experiment

Workplace: `~/summerschool04/sim/Exercise3/homorec/rfdr`

Situation: A homonuclear spin pair \vec{S}_1, \vec{S}_2 in a powder under MAS.



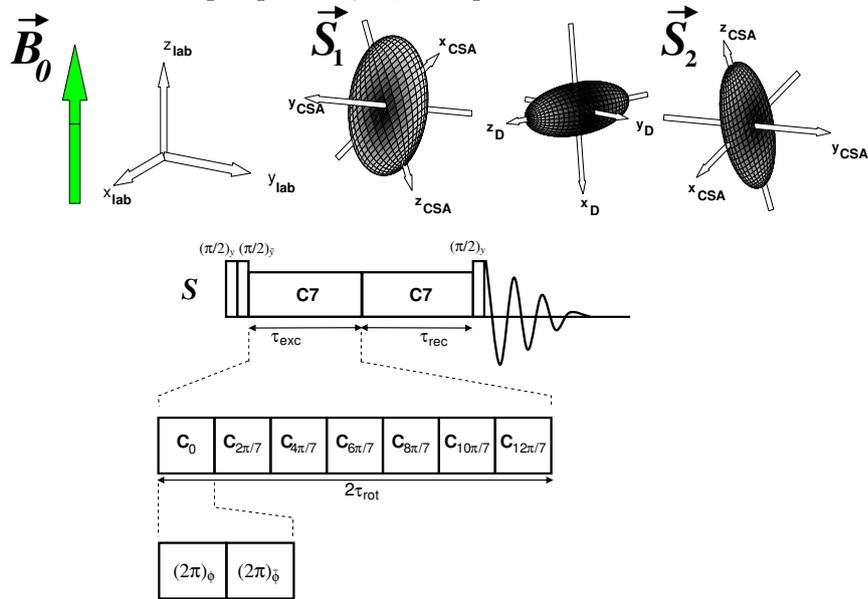
Tasks:

1. Run `rfdrsim.in` to simulate a RFDR experiment with initial magnetisation only at the \vec{S}_1 -spin site (`start_operator I1z`). How do the spectral intensities of the \vec{S}_1 - and \vec{S}_2 -spin resonances change when modifying the RFDR mixing time $2n\tau_{rot}$ by varying: variable `n 64`
2. Examine the influence of non-ideal pulses (finite amplitude, finite duration) on a RFDR spectrum by running `rfdrsimreal.in`. To do so change the r.f. amplitude of the RFDR π -pulses: variable `rf 250000` in order to get agreement with the ideal-pulse case.
3. Run `rfdrscan.in` to get a scan of the \vec{S}_1 - or \vec{S}_2 -spin integrated spectral intensities as a function of the RFDR mixing time $2n\tau_{rot}$ in `rfdrscan-first.fid` and `rfdrscan-second.fid` respectively.
4. Modify variable `rf 250000` in `rfdrscanreal.in` to examine the effect of real pulses on the RFDR curves obtained before.
5. What is the effect of different dipolar coupling constants (dipole 1 2 `-2250 0 0 0`) on the RFDR curves created by `rfdrscan.in`.

6.5 The $C7$ [15] Experiment

Workplace: `~/summerschool04/sim/Exercise3/homorec/c7`

Situation: A homonuclear spin pair \vec{S}_1, \vec{S}_2 in a powder under MAS.



Tasks:

1. Run the `c7_21.in` file to simulate a so-called $C7$ curve, where the integrated \vec{S} -spin signal intensities are plotted as a function of the number n of $C7$ cycles applied during τ_{exc} and τ_{rec} .
2. Vary the magnitude of the dipolar coupling constant and the CSA eigenvalues of \vec{S}_1 and \vec{S}_2 in order to examine which parameters are encoded in the so-called $C7$ curve.

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