Simulation of NMR Experiments with SPINEVOLUTION

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Exact Simulations in NMR

- Extraction of structural parameters
- Design of new experiments
- Theoretical insights

Before you do anything – simulate it !

SPINEVOLUTION

- General NMR simulation program
- Highly efficient
  - New methodology for NMR computations
  - Advanced numerical techniques
  - Computer Science: optimized code, data flow, etc.
- Easy to use

SPINEVOLUTION vs. SIMPSON

CPU time, seconds

1.2 GHz ATHLON CPU

Problem:

TPPM - decoupled ^{13}C line shape

Spin system	SPINEVOLUTION	SIMPSON
CH_1	0.13	8.8
CH_2	0.33	19.1
CH_3	1.27	73.4
CH_4	6.16	638
CH_5	35.0	13300
CH_6	246	822000
CH_7	1600	-
CH_8	9460	-
CH_9	60500	-

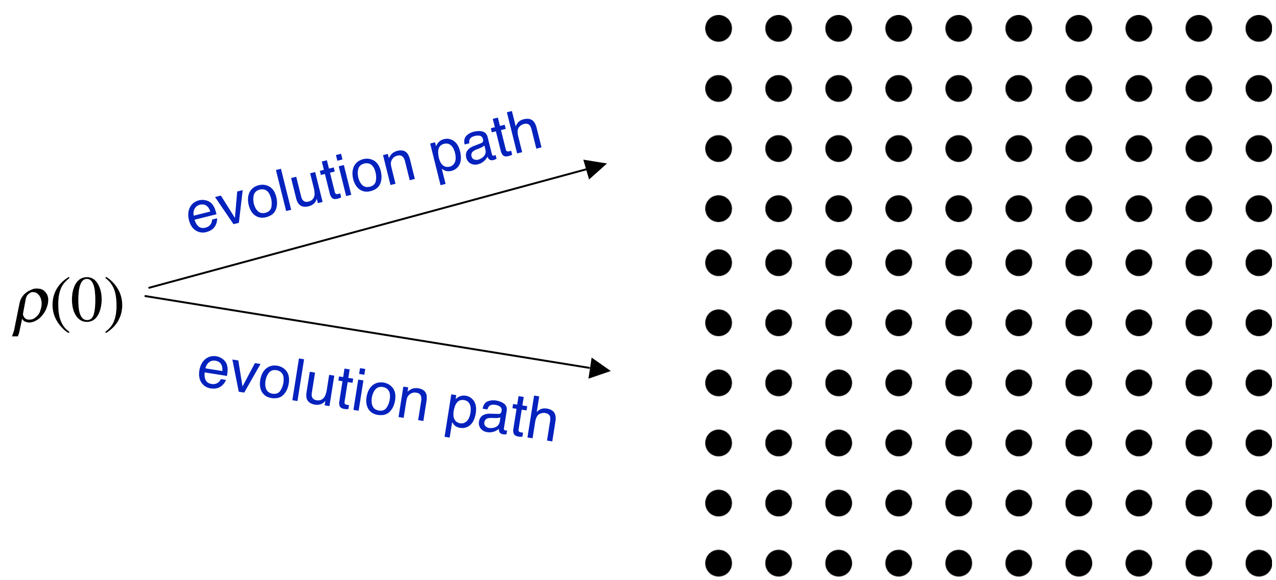
How to Learn

- Try examples
- Do the problems/exercises
- Read the JMR paper
- Read the Reference
- Visit or subscribe to the spinev-discuss forum
- Use it in your work and study

Simulation of NMR Experiment

$$\rho(0) \quad \rightarrow \quad \frac{d\rho}{dt} = -i\left[H(t), \rho\right] \quad \rightarrow \quad Tr(\rho(t) I^{+})$$

Data Points:



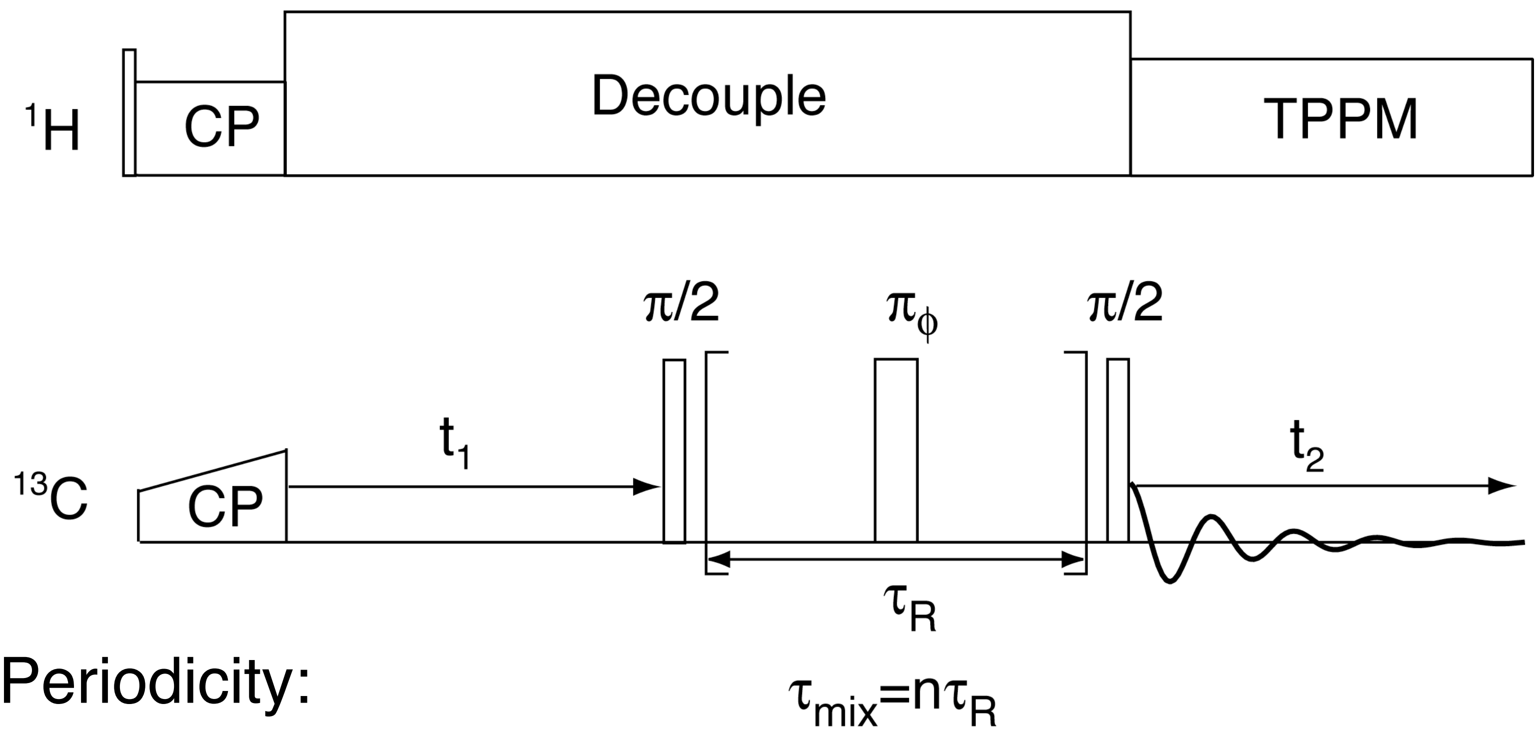
Strategy of the Simulation

- Local integration

$$\frac{d}{dt}U(t) = -iH(t)U(t) \qquad U(t_2, t_1) = e^{-iH_N \Delta t} \ldots e^{-iH_2 \Delta t} e^{-iH_1 \Delta t}$$

- Construction of the long-term evolution
  – Time domain
  – Frequency domain
- Powder averaging
  – Weighted sum
  – Interpolative integration

Experiment Pulse Sequence



Periodicity:

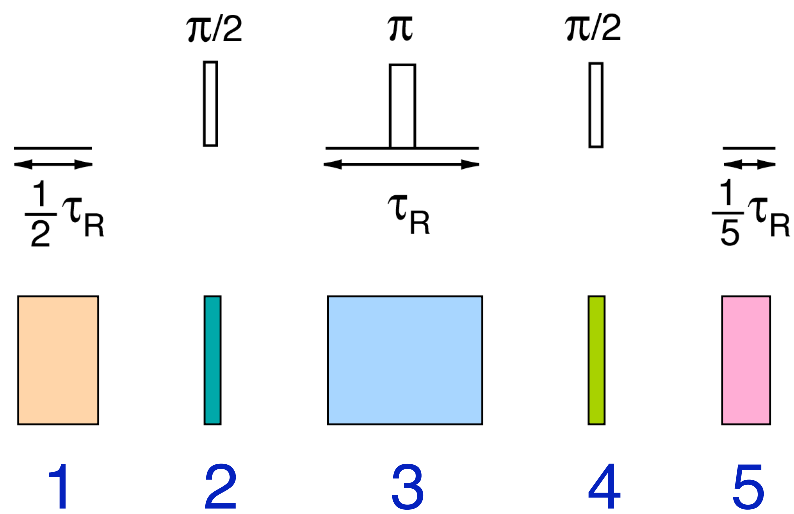
- Pulse sequence: RF cycles
- Pulse sequence: Sampling
- Spinning: Rotor cycles

Elementary Pulse Sequence

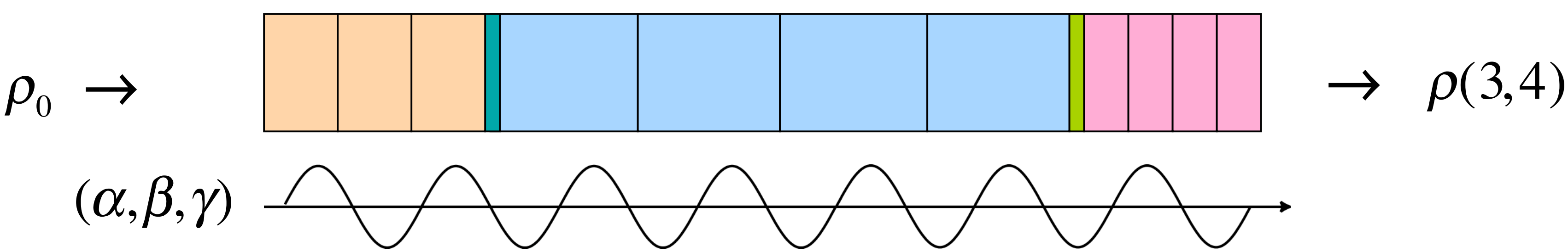
- Fixed group of pulses: RF cycle
  - Delays are treated as pulses of zero power
  - Duration t_{seq}
- Characterized by sampling pattern:
  - Dimension
  - Sampling direction
  - Sampling rate
- Rotor-synchronized: $n \cdot t_{seq} = m \cdot \tau_R$

Canonical Representation of NMR Experiments

Pulse Sequences:



Evolution Path:



Data Dimensions

- Pulse Sequence dimensions
- Parameter scan dimensions
- Trajectory
- Initial density matrices & observables

Pulse Sequence: Examples

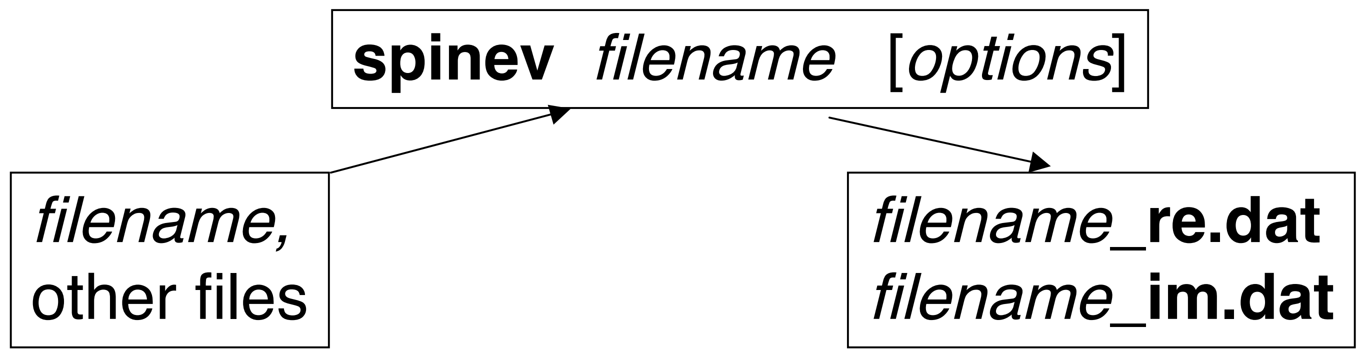
$\pi/2$ - pulse followed by acquisition:

timing(usec)	5	(20)1024
power(kHz)	50	0
phase(deg)	0	0
freq_offs(kHz)	0	0

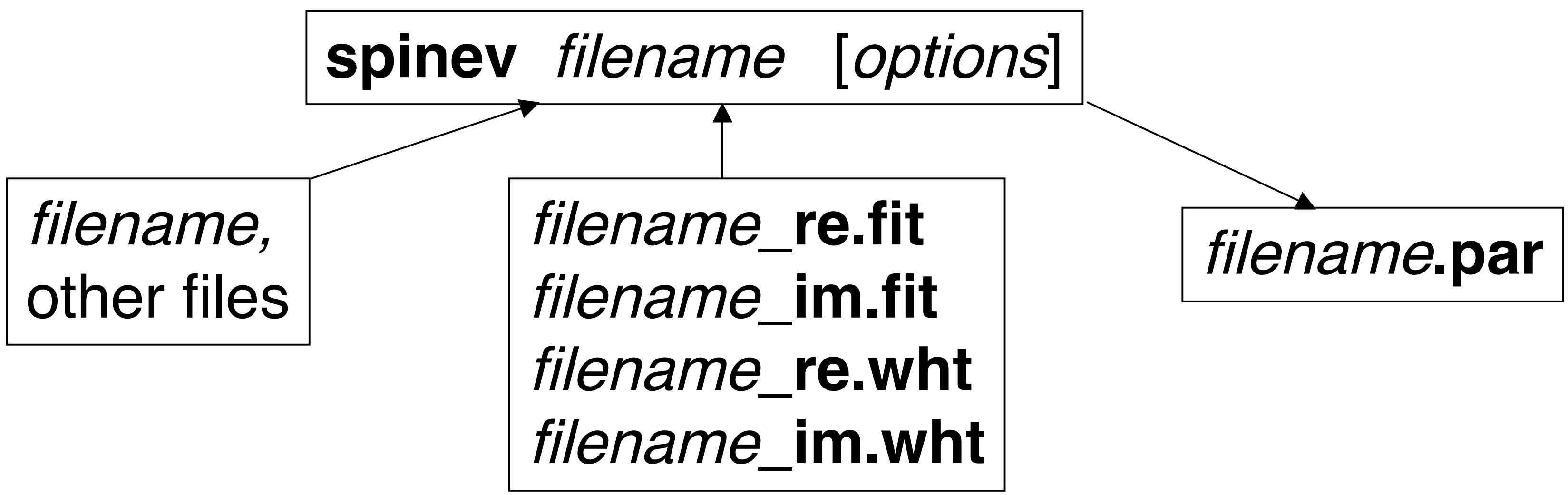
2D experiment:

timing(usec)	(50)256D1	5	(rfdr.pp)x2	5	(20)1024D2
power(kHz)	0	50	*	50	0
phase(deg)	0	0	*	0	0
freq_offs(kHz)	0	0	*	0	0

Running a Simulation



Data Fitting / Optimization



Main Input File

- System
- Pulse Sequence
- Variables
- Options

```
****** The System *******
spectrometer(MHz)    400
spinning_freq(kHz)   8.0
channels             C13
nuclei               C13 C13 C13 C13 C13 C13
atomic_coords        leu.cor
cs_isotropic         leu.cs
csa_parameters       *
j_coupling           leu.j
quadrupole           *
dip_switchboard      *
csa_switchboard      *
exchange_nuclei      *
bond_len_nuclei      *
bond_ang_nuclei      *
tors_ang_nuclei      *
groups_nuclei        *
******* Pulse Sequence ************************************
CHN 1
timing(usec)         (0)2048D1 0.5 (rfdr8.pp)x2 0.5 (0)1024D2
power(kHz)            0        500   *          500  0
phase(deg)            0        270   *          90   0
freq_offs(kHz)        0        0     *          0    0
******* Variables ******************************************
variable             spinning_freq=8
variable             taur=1000/spinning_freq
variable             pulse_1_1_1=taur/6
variable             pulse_1_5_1=taur/3
******* Options ************************************
rho0                 F1x
observables          F1p
EulerAngles          rep100.dat
n_gamma              12
line_broaden(Hz)     0 0 60 60
zerofill             *
FFT_dimensions       1c 2
options              -re
```

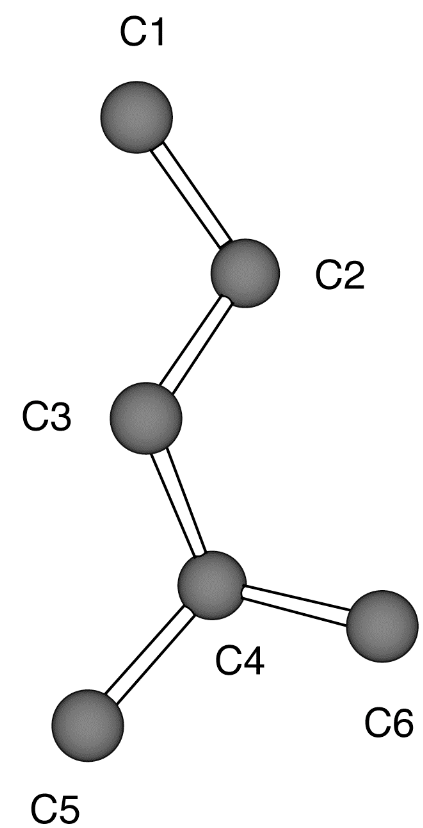
The System

```
****** The System *******
spectrometer(MHz)   400
spinning_freq(kHz)  8.0
channels            C13
nuclei              C13 C13 C13 C13 C13 C13
atomic_coords       leu.cor
cs_isotropic        leu.cs
csa_parameters      *
j_coupling          leu.j
quadrupole          *
dip_switchboard     *
csa_switchboard     *
exchange_nuclei     *
bond_len_nuclei     *
bond_ang_nuclei     *
tors_ang_nuclei     *
groups_nuclei       *
```

Supplementary Files

leu.cor

```
% Leu from N-Ac-VL crystal structure
3.734   6.733   2.822    C32/C'
3.522   7.597   1.589    C17/CA
4.043   6.870   0.351    C14/CB
4.541   7.765  -0.791    C12/CG
3.423   8.516  -1.497    C28/CD1
5.340   6.943  -1.789    C8 /CD2
```



Supplementary Files

lue.j

```
1    2    40
2    3    40
3    4    40
4    5    40
4    6    40
```

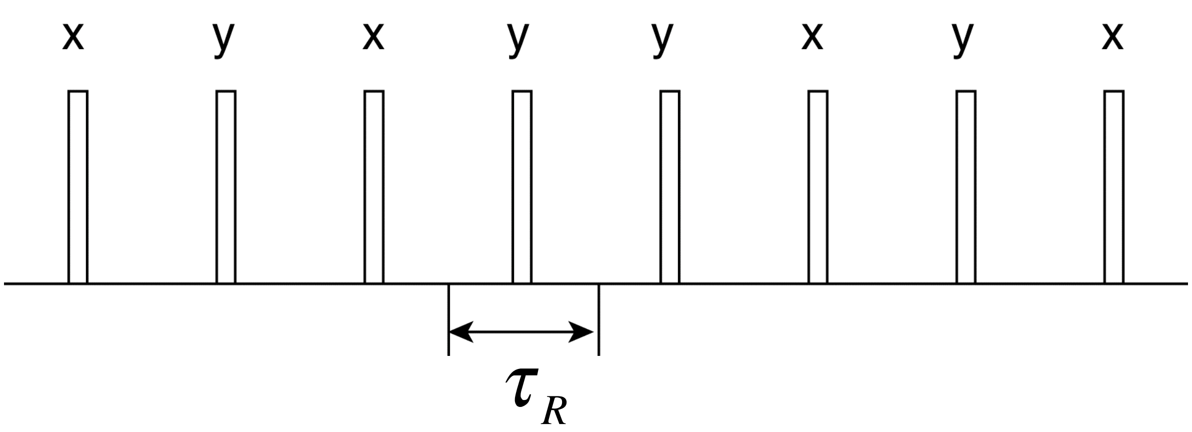
lue.cs

```
% Chemical Shifts at 400MHz
4.232       C'
-7.699      CA
-9.654      CB
-10.329     CG
-11.043     CD1
-11.137     CD2
```

Pulse Sequence

```
******* Pulse Sequence ******************************
CHN 1
timing(usec)  (0)2048D1 0.5 (rfdr8.pp)x2 0.5 (0)1024D2
power(kHz)     0        500   *          500  0
phase(deg)     0        270   *          90   0
freq_offs(kHz) 0        0     *          0    0
```

RFDR Pulse Sequence



rfdr8.pp

30	0	0	0
4	125	0	0
60	0	0	0
4	125	90	0
60	0	0	0
4	125	0	0
60	0	0	0
4	125	90	0
60	0	0	0
4	125	90	0
60	0	0	0
4	125	0	0
60	0	0	0
4	125	90	0
60	0	0	0
4	125	0	0
30	0	0	0

Variables

```
******* Variables *********************
spinning_freq=8
taur=1000/spinning_freq
pulse_1_1_1=taur/6
pulse_1_5_1=taur/3
```

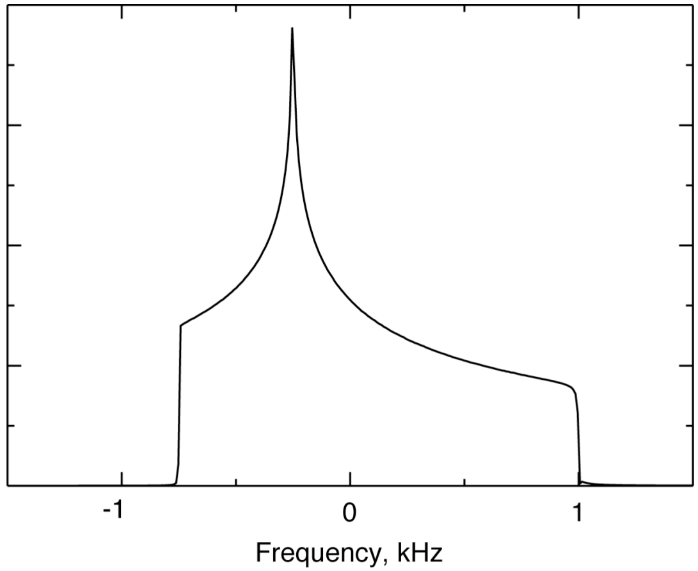
- User-defined or Internal
- Active or passive
- Special type
  - Signal
  - Pre-processing
  - Post-processing
- Matrices, scalars, or strings

Options

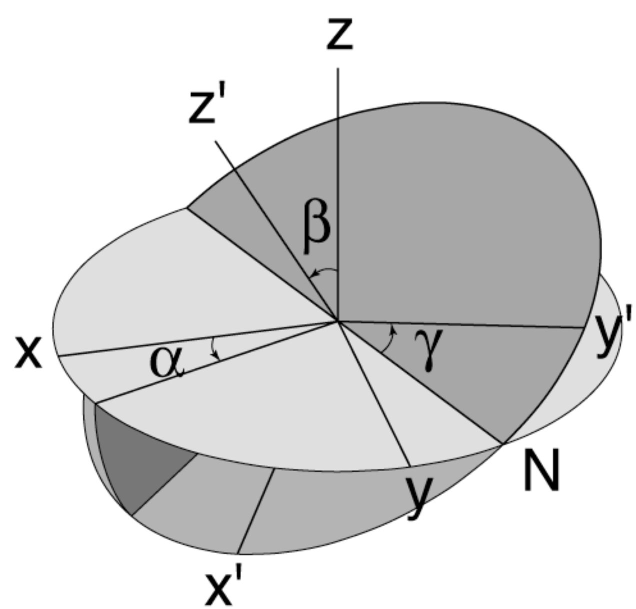
```
**** Options etc **************
rho0                    F1x
observables             F1p
EulerAngles             rep100
n_gamma                 12
line_broaden(Hz)        0 0 60 60
zerofill                *
FFT_dimensions          1c 2
options                 -re
```

Static CSA Powder Pattern

```
****** The System *******
spectrometer(MHz)   500
channels            C13
nuclei              C13
csa_parameters      1 1 0.5 0 0 0
******* Pulse Sequence *********
CHN 1
timing(usec)       (200)512
power(kHz)          0
phase(deg)          0
freq_offs(kHz)      0
******* Variables **************
******* Options ****************
rho0                I1x
observables         I1p
EulerAngles         asgind100o
n_gamma             *
FFT_dimensions      1
options             -re
```



Specifying Crystallite Orientations



- 2 reference frames + Euler angles
- Static solids: CL
- Rotating solids: CR

Powder Averaging Set Types

$$\overline{s}(t) = \frac{1}{8\pi^2} \int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin(\beta) \int_0^{2\pi} d\gamma \; s(\alpha, \beta, \gamma; t)$$

- Three-angle sets: $(\alpha, \beta, \gamma, w)$
- Two-angle sets: (α, β, w)
- β-angle only: (β, w)

Orientational Symmetry

Static Powders

- Reference frames: CL
- No dependence on γ_{CL} in high-field approx.

$$A_{20}^{L} = \sum_{M=-2}^{2} A_{2M}^{C} D_{M0}^{(2)}\left(\alpha_{CL}\beta_{CL}\gamma_{CL}\right)$$

$$D_{MK}^{(2)}\left(\alpha_{CL}\beta_{CL}\gamma_{CL}\right) = e^{-iM\alpha} d_{MK}^{(2)}\left(\beta\right) e^{-iK\gamma}$$

- C_i (hemisphere)
- D_{2h} (octant)
- $D_{\infty h}$ ($0 \leq \beta \leq \pi/2$)

Orientational Symmetry

Rotating Powders

- Reference frames: CR
- Special dependence on γ_{CR}

$$A_{2,q}(t) = \sum_{k=-2}^{2} A_{2,q}^{(k)} e^{ik\omega_R t}$$

$$A_{2,q}^{(k)} = \frac{3}{\sqrt{6}} A_{aniso} \left\{ D_{0k}^{(2)}(\Omega_{\mathrm{PR}}) - \frac{\eta_A}{\sqrt{6}} \left[D_{2k}^{(2)}(\Omega_{\mathrm{PR}}) + D_{-2k}^{(2)}(\Omega_{\mathrm{PR}}) \right] \right\} d_{kq}(\beta_{RL})$$

- C_i ((α,β)-hemisphere + γ)
- D_{2h} ((α,β)-octant + γ)
- $D_{\infty h}$ ($0 \leq \beta \leq \pi/2$ + γ)

Sets Available in SPINEVOLUTION

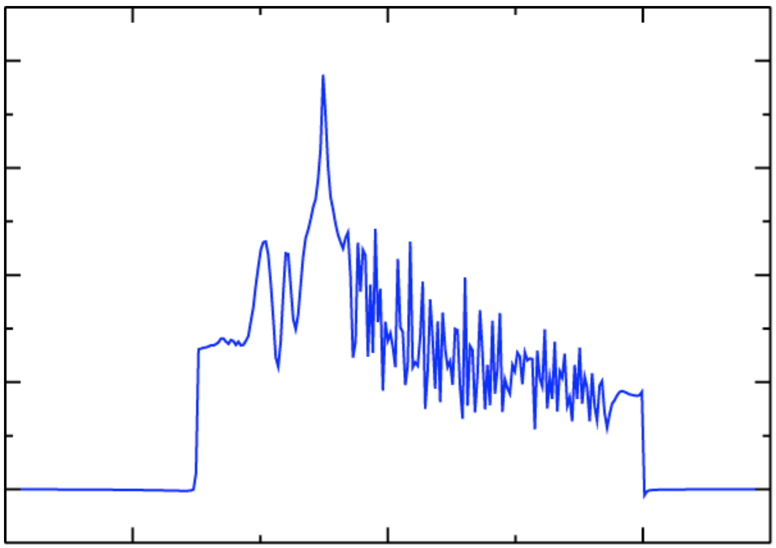
EulerAngles	b500o		
EulerAngles	a200b500h		
EulerAngles	rep168		
EulerAngles	asg5151o	~	asgind100o
EulerAngles	sophe5151	~	sopheind100
EulerAngles	leb5810	~	lebind65
EulerAngles	*filename*		

DEMO

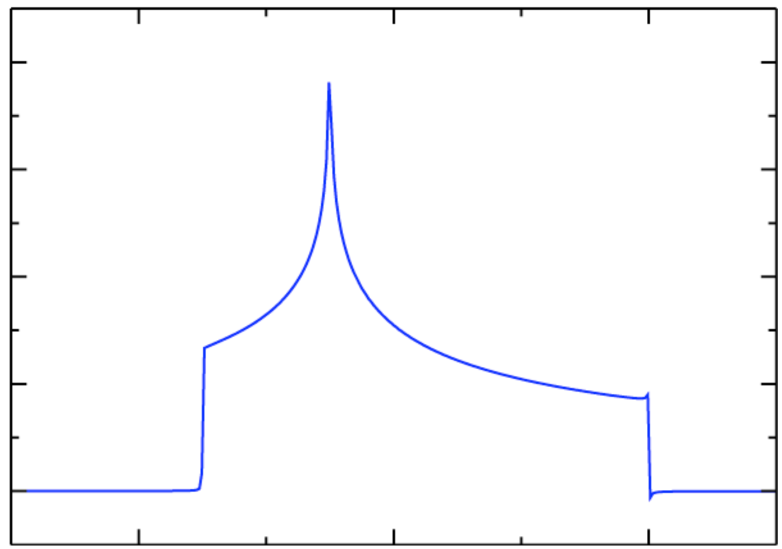
- What different sets look like

Weighted Sum vs. Interp. Integration

`spinev csa -ws`

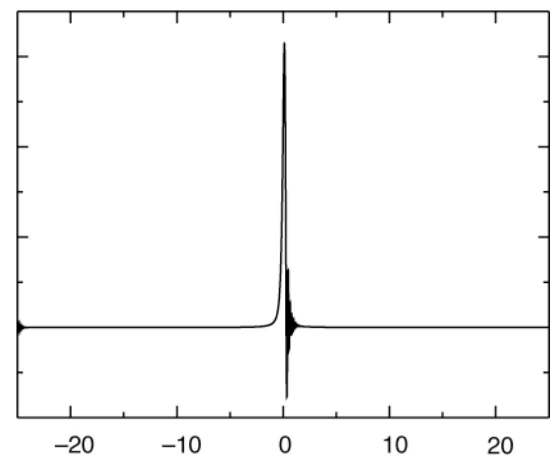


`spinev csa`

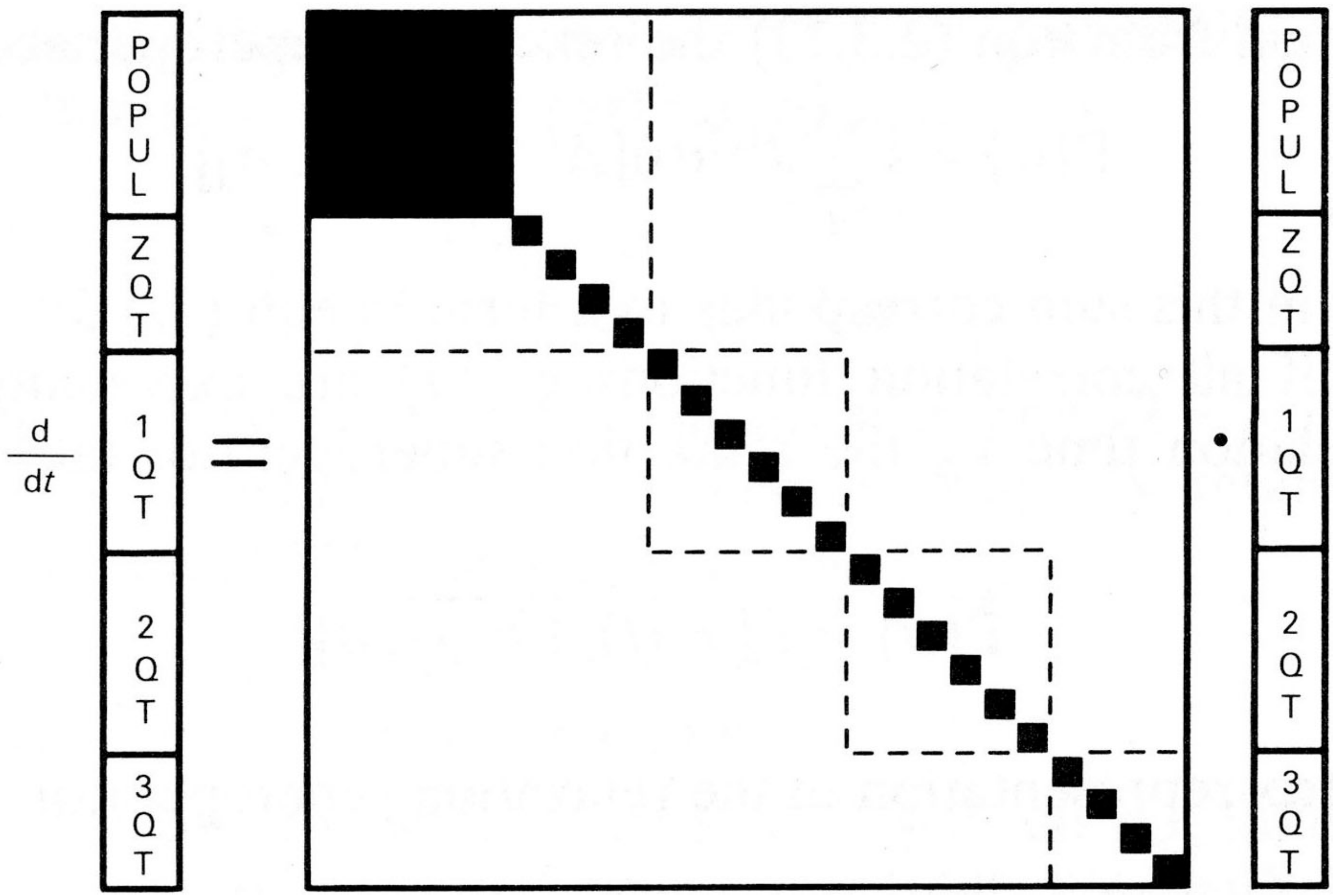


CW NMR

```
******* Pulse Sequence *************
CHN 1
timing(usec)         500100000
power(kHz)           0.0001
phase(deg)           90
freq_offs(kHz)       0
CHN G
timing(usec)         [100000]5001
gradient(Gs/cm)      [0]5001
******* Variables ******************
T1SQ_1_1=2000
T2SQ_1_1=2000
grad_offs=1
freq=colmatrix("-0.025:1e-5:0.025")
grad_1=freq/1.0708
******* Options ********************
rho0                 0.25*I1z
observables          I1p
options              -oes -dt10000
```

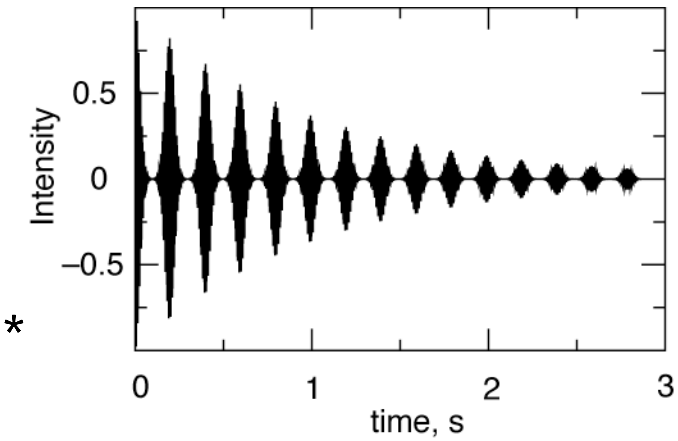


Relaxation Matrix



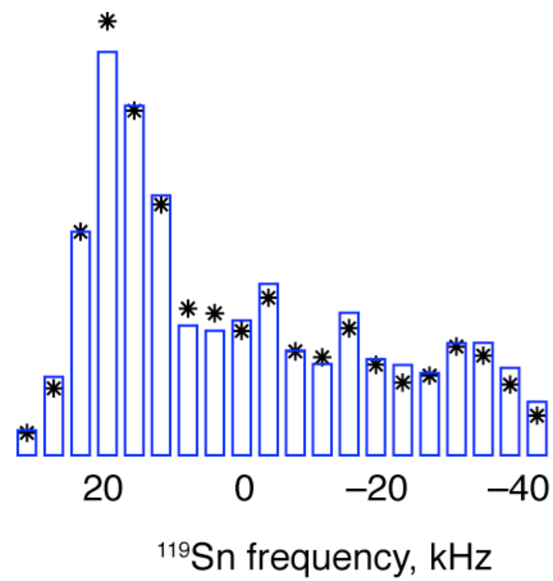
Carr-Purecell Echo Train

```
******* Pulse Sequence ***************
CHN 1
timing(usec)          0.5 [1000]2900
power(kHz)            500 [0]2900
phase(deg)             90 [0]2900
freq_offs(kHz)          0 [0]2900
******* Variables *****************
T2SQ_1_1=1000
sigma=0.006
pulse_1_1_[100:200:2900]=1.0
power_1_1_[100:200:2900]=500
ave_par x/-0.02:0.0025:0.02/
cs_iso_1=0.1+x
ave_wht=0.0025*exp(-0.5*(x/sigma)^2)/sqrt(2*pi)/sigma
******* Options **************************
rho0                  I1z
observables           I1p
options               -oes -re
```



CSA Sidebands Fitting

```
****** The System *******
spectrometer(MHz)  500
spinning_freq(kHz) 3.8
channels           Sn(74.56 -1/2)
nuclei             Sn
csa_parameters     1 -600 0.1 0 0 0 ppm
******* Pulse Sequence *****************
CHN 1
timing(usec)      (0)32
power(kHz)         0
phase(deg)         0
freq_offs(kHz)     0
******* Variables *********************************
pulse_1_1_1=1000/spinning_freq/32
signal_sf=40
fit_par  cs_ani_1 cs_asy_1 signal_sf
******* Options ************************************
rho0               I1x
observables        I1p
EulerAngles        lebind29o
n_gamma            10
FFT_dimensions     1
options            -re -fft1 -sz5 -ws -confint
```



SnC2O4_re.fit	SnC2O4_re.wht
0.0000000e+00	0
0.0000000e+00	0
0.0000000e+00	0
0.0000000e+00	0
1.8500000e+01	0
3.3000000e+01	0
4.6500000e+01	0
5.0750000e+01	1
3.7250000e+01	1
3.4000000e+01	1
4.2250000e+01	1
5.9250000e+01	1
4.5750000e+01	1
4.8500000e+01	1
7.3500000e+01	1
5.8000000e+01	1
6.6250000e+01	1
6.8500000e+01	1
1.1700000e+02	1
1.6075000e+02	1
2.0250000e+02	1
1.0425000e+02	1
3.1250000e+01	1
1.0500000e+01	1
0.0000000e+00	1
0.0000000e+00	1
0.0000000e+00	1
0.0000000e+00	0
0.0000000e+00	0
0.0000000e+00	0
0.0000000e+00	0
0.0000000e+00	0

SnC2O4.par

```
cs_ani_1=-45.7632
cs_asy_1=0.144041
signal_sf=43.0485
*** RSS=594.756
```

SnC2O4.cls

```
cs_ani_1=-4.57632e+01 +/-  6.014e-01
cs_asy_1= 1.44041e-01 +/-  3.654e-02
signal_sf= 4.30485e+01 +/-  1.661e+00
```

Frequency Domain Calculation

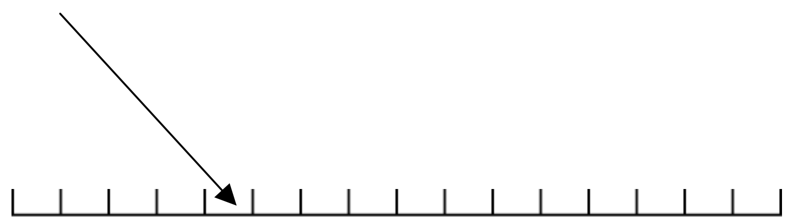
For each coherence:

$$s_\Omega(t) = A_\Omega e^{i\omega_\Omega t} \qquad \overline{s}(t) = \frac{1}{4\pi}\oint A_\Omega e^{i2\pi\nu_\Omega t}\, d\Omega$$

Binning:

$$\left(A_\Omega, \omega_\Omega\right) \qquad \Omega \in \left\{\Omega_k, w_k\right\}_{k=1}^{M}$$

Frequency bins:



REDOR via "Analytic" Calculations

```
******* Pulse Sequence ****************************************
CHN 1
timing(usec)        (100)100
power(kHz)           0
phase(deg)           0
freq_offs(kHz)       0
CHN 2
timing(usec)      (redor1.pp)
power(kHz)           *
phase(deg)           *
freq_offs(kHz)       *
******* Variables ************************************************
tauR=1/spinning_freq
k=1/sqrt(6)
w=k*(ID20_1_2(0,tauR/2)-ID20_1_2(tauR/2,tauR))/tauR
signal_re=cos(w*t_1)
******* Options **************************************************
rho0                 I1x
observables          I1p
EulerAngles          ^asgind30h
options              -re -am
```

$$H(t) = D_{20}(t)\frac{2}{\sqrt{6}} I_z S_z$$

$$\bar{H} = \frac{2I_z S_z}{\tau_R\sqrt{6}}\left\{\int_0^{\tau_R/2} D_{20}(t)\,dt - \int_{\tau_R/2}^{\tau_R} D_{20}(t)\,dt\right\}$$

Demos

- NOESY
- quad1_full
- batch-fit
- tppm-fit
- struct
- -calc mode