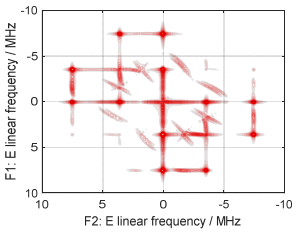
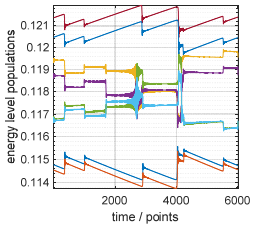


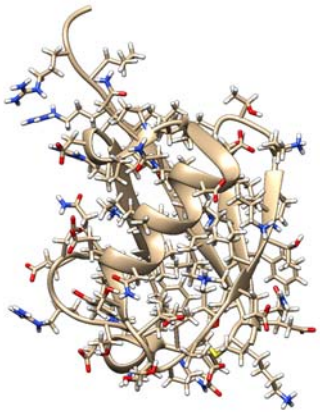


What is Spinach and what does it do?

Ilya Kuprov
University of Southampton

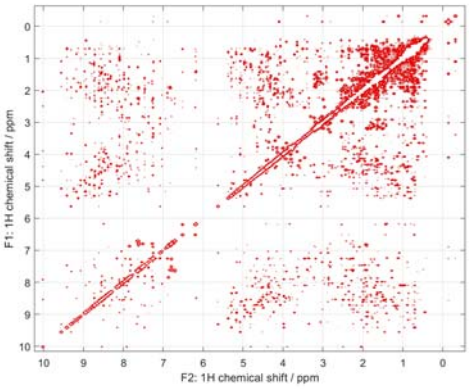
Spinach package

- Magnetic resonance theory library for **large-scale** time-domain simulation work



***Ubiquitin**: 76 amino acids, 1060 magnetic nuclei, about 60,000 spin-spin couplings*

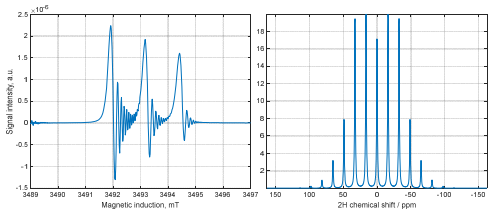
***NOESY**: needs full Redfield super-operator, including cross-correlations*

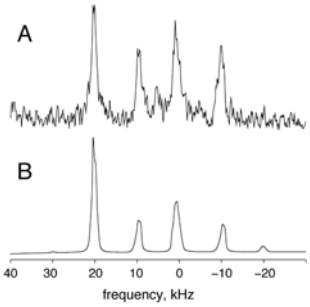


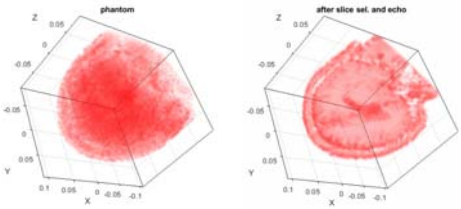
Downloads, documentation, tutorials, lectures - http://spindynamics.org

Spinach package

- Magnetic resonance theory library for **large-scale** time-domain simulation work
- All types of magnetic resonance (NMR, EPR, MRI, DNP, PHIP, SQUID, *etc.*)







+ kinetics, diffusion, hydrodynamics, spatial encoding, off-resonance soft pulses, etc.

Downloads, documentation, tutorials, lectures - http://spindynamics.org

Spinach package

- Magnetic resonance theory library for **large-scale** time-domain simulation work
- All types of magnetic resonance (NMR, EPR, MRI, DNP, PHIP, SQUID, *etc.*)
- Over 600 pages of docs and tutorials, over 100 real-life simulation examples

+PhD level spin dynamics lecture course (50 hours of video, 200 pages of handouts)

Downloads, documentation, tutorials, lectures - http://spindynamics.org

Spinach package

- Magnetic resonance theory library for **large-scale** time-domain simulation work
- All types of magnetic resonance (NMR, EPR, MRI, DNP, PHIP, SQUID, *etc.*)
- Over 600 pages of docs and tutorials, over 100 real-life simulation examples
- Well-annotated open-source code, clear variable names, informative error messages

Code quality and readability enforcement is militant – the validation block in most functions is longer than the science block.

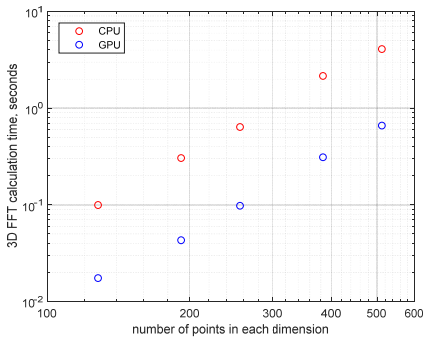
```
function fid=hyscore(spin_system,parameters,H,R,K)

% Check consistency
grumble(spin_system,parameters,H,R,K);

% Compose Liouvillian
L=H+1i*R+1i*K;

% Get the pulse operators
Lp=operator(spin_system,'L+','E');
Lm=operator(spin_system,'L-','E');
Lx=(Lp+Lm)/2;

% Calculate timestep and number of steps for tau evolution
[tau_dt,tau_np]=stepsize(L,parameters.tau);

% Apply the first pulse
rho=step(spin_system,Lx,parameters.rho0,pi/2);

% Run the tau evolution
rho=evolution(spin_system,L,[],rho,tau_dt,tau_np,'final');

% Apply the second pulse
rho=step(spin_system,Lx,rho,pi/2);

% Apply coherence filter
rho=coherence(spin_system,rho,{{'E',0}});

% Run the indirect dimension evolution
rho_stack=evolution(spin_system,L,[],rho,1/parameters.sweep,...
                    parameters.nsteps(1)-1,'trajectory');
```

Downloads, documentation, tutorials, lectures - http://spindynamics.org

Spinach package

- Magnetic resonance theory library for **large-scale** time-domain simulation work
- All types of magnetic resonance (NMR, EPR, MRI, DNP, PHIP, SQUID, *etc.*)
- Over 600 pages of docs and tutorials, over 100 real-life simulation examples
- Well-annotated open-source code, clear variable names, informative error messages
- Parallel processing, GPU support, tensor structured object support.

We do not actually need to open any of the Kronecker products in spin physics.



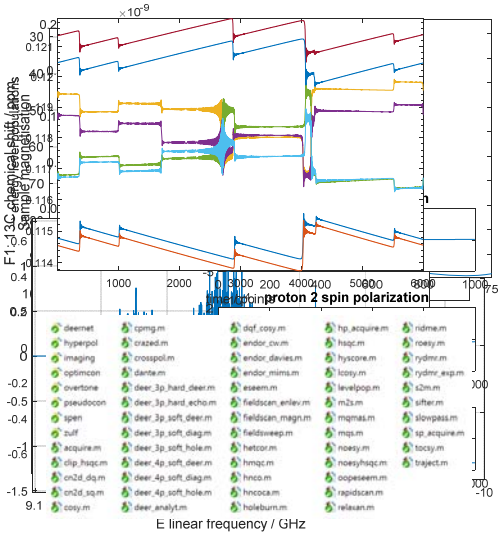
$$[\mathbf{A}\otimes\mathbf{B}]\mathbf{v}=\mathrm{vec}\left(\mathbf{B}\mathbf{V}\mathbf{A}^{\mathrm{T}}\right)$$

$$\exp(\mathbf{A})\mathbf{v}=\sum_{n=0}^{\infty}\frac{1}{n!}\left(\mathbf{A}\left(\mathbf{A}\ldots\left(\mathbf{A}\mathbf{v}\right)\right)\right)$$

Downloads, documentation, tutorials, lectures - http://spindynamics.org

Spinach package

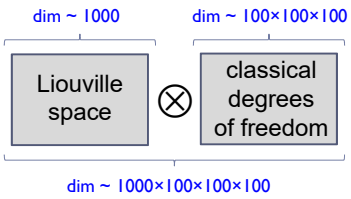
- Magnetic resonance theory library for **large-scale** time-domain simulation work
- All types of magnetic resonance (NMR, EPR, MRI, DNP, PHIP, SQUID, *etc.*)
- Over 600 pages of docs and tutorials, over 100 real-life simulation examples
- Well-annotated open-source code, clear variable names, informative error messages
- Parallel processing, GPU support, tensor structured object support
- Over 50 developers and contributors, 12 years of full-time programming



Downloads, documentation, tutorials, lectures - http://spindynamics.org

Last 6 months: classical degrees of freedom

The evolution happens in the direct product of spin and lab spaces:



…we had (kind of) solved the Liouville space dimension problem, but this looks hopeless!

However… all terms in the evolution generator have a kron structure:

$$[\text{space dynamics}]\otimes[\text{reaction kinetics}]\otimes[\text{spin dynamics}]$$

…and the components are krons themselves, *e.g.*

$$D\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)=D\left(\left[\frac{\partial^2}{\partial x^2}\right]\otimes\mathbf{1}_Y\otimes\mathbf{1}_Z+\mathbf{1}_X\otimes\left[\frac{\partial^2}{\partial y^2}\right]\otimes\mathbf{1}_Z+\mathbf{1}_X\otimes\mathbf{1}_Y\otimes\left[\frac{\partial^2}{\partial z^2}\right]\right)$$

It is only *when you multiply the krons out* that you run out of memory.

Last 6 months: classical degrees of freedom

Chemical degrees of freedom are another kron:

$$\frac{d}{dt}\begin{bmatrix}\boldsymbol{\rho}_A\\ \boldsymbol{\rho}_B\end{bmatrix}=\left[-i\begin{pmatrix}\mathbf{H}_A & \mathbf{0}\\ \mathbf{0} & \mathbf{H}_B\end{pmatrix}+\begin{pmatrix}\mathbf{R}_A & \mathbf{0}\\ \mathbf{0} & \mathbf{R}_B\end{pmatrix}+\begin{pmatrix}-k_+\mathbf{1} & +k_-\mathbf{1}\\ +k_+\mathbf{1} & -k_-\mathbf{1}\end{pmatrix}\right]\begin{bmatrix}\boldsymbol{\rho}_A\\ \boldsymbol{\rho}_B\end{bmatrix}$$

The result is a sum of krons repeatedly acting on a vector:

best not open this

$$\boldsymbol{\rho}(t+dt)=\exp\{-i[\text{a sum of krons}]dt\}\boldsymbol{\rho}(t)$$

$$\exp[\mathbf{A}]\mathbf{v}=\sum_{n=0}^{\infty}\frac{1}{n!}\mathbf{A}(\ldots(\mathbf{A}(\mathbf{A}\mathbf{v})))$$

only matrix-vector multiplications

A *short* sum of krons of *small* matrices! Need a product with a vector…

dim[**A**] = 1000
dim[**B**] = 1000
dim[**A**(x)**B**] = 10^6
numel(**v**) = 10^6

$$[\mathbf{A}\otimes\mathbf{B}]\mathbf{v}=\mathrm{vec}[\mathbf{B}\mathbf{V}\mathbf{A}^{\mathrm{T}}]$$

~10^{12} FLOP ~10^9 FLOP

dim[**A**] = 1000
dim[**B**] = 1000
dim[**V**] = 1000

We do not actually need to open *any* Kronecker products in spin dynamics…

Last 6 months: classical degrees of freedom

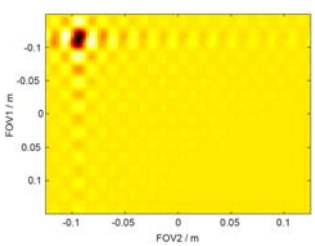
Synthetic benchmark (random matrices with typical NMR density):

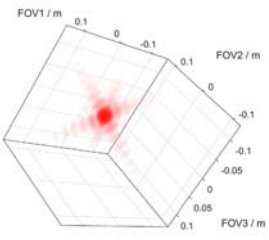
Matrix-vector multiplication task	Wall clock time, polyadic rep	Wall clock time, explicit rep
$[\mathbf{A}\otimes\mathbf{B}]\mathbf{v}$ with $\dim(\mathbf{A},\mathbf{B})\le 64$, full	0.37 ± 0.01 ms	0.88 ± 0.12 ms
$[\mathbf{A}\otimes\mathbf{B}\otimes\mathbf{C}]\mathbf{v}$ with $\dim(\mathbf{A}\text{-}\mathbf{C})\le 64$, full	1.8 ± 0.3 ms	Out of RAM
$[\mathbf{A}\otimes\mathbf{B}\otimes\mathbf{C}\otimes\mathbf{D}]\mathbf{v}$ with $\dim(\mathbf{A}\text{-}\mathbf{D})\le 64$, full	97 ± 14 ms	Out of RAM
$[\mathbf{A}\otimes\mathbf{B}]\mathbf{v}$ with $\dim(\mathbf{A},\mathbf{B})\le 64$, sparse	0.21 ± 0.01 ms	0.05 ± 0.01 ms
$[\mathbf{A}\otimes\mathbf{B}\otimes\mathbf{C}]\mathbf{v}$ with $\dim(\mathbf{A}\text{-}\mathbf{C})\le 64$, sparse	2.1 ± 0.3 ms	11.4 ± 1.6 ms
$[\mathbf{A}\otimes\mathbf{B}\otimes\mathbf{C}\otimes\mathbf{D}]\mathbf{v}$ with $\dim(\mathbf{A}\text{-}\mathbf{D})\le 64$, sparse	105 ± 16 ms	Out of RAM

Computer:

32 Xeon cores
256 GB of RAM

Not faster for small systems, but scales much better.



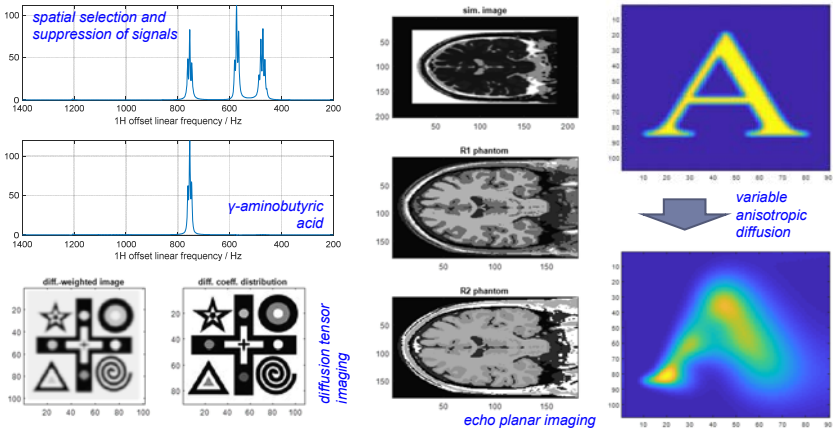


2D and 3D localised NMR excitation with an explicit shaped pulse under a field gradient, a typical metabolite (6 spins).

with Ahmed Allami and Maria Grazia Concilio

Last 6 months: classical degrees of freedom

Result: arbitrary spatial dynamics with quantum description of spin.



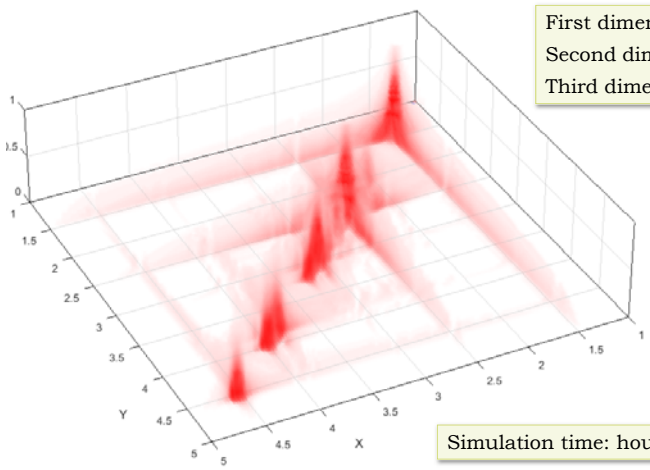
All other packages (MRI, DOSY, *etc.*) use Bloch equations in the spin subspace.

with Ahmed Allami and Pavan Lally

Last 6 months: classical degrees of freedom

Rotenone (22 spins), three-dimensional diffusion, complicated chirps, *etc.*

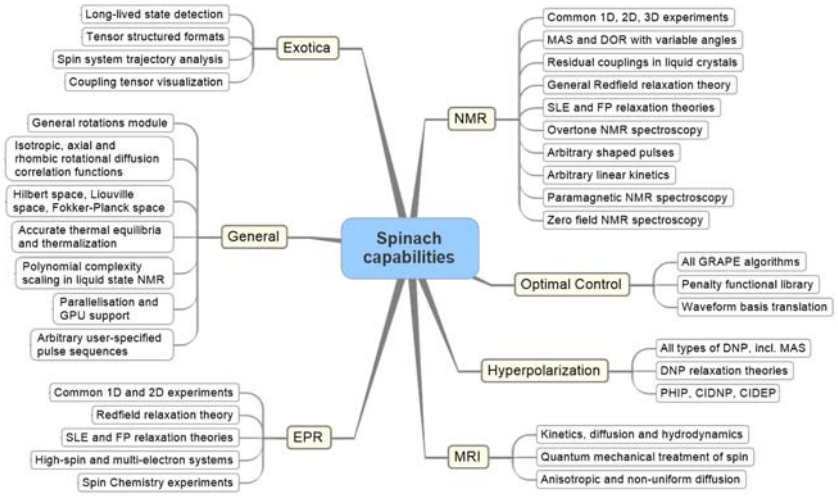
First dimension: UF SPEN
Second dimension: DOSY
Third dimension: crushers



Simulation time: hours – we are done!

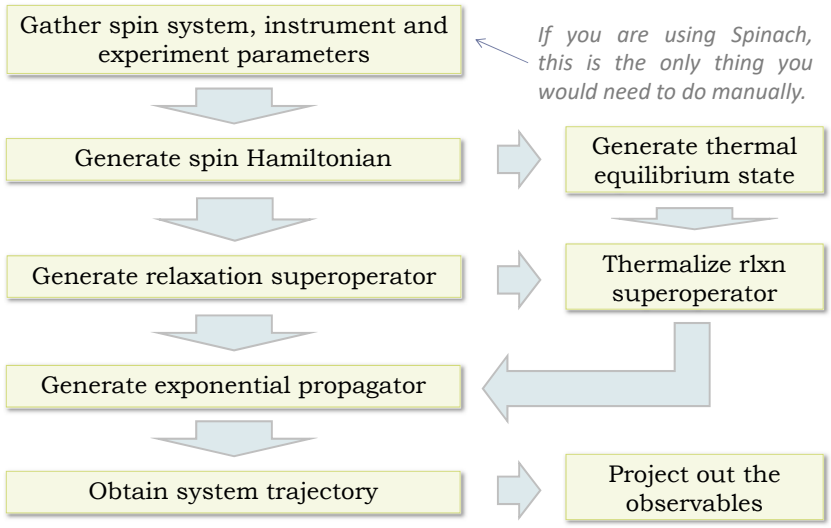
with Jean-Nicolas Dumez and Ludmilla Guduff

Spinach package



- Latest version of Matlab is strongly recommended.

Time domain simulation flowchart



- *Spinach* is not a black box – it is an open-source *Matlab* library of infrastructure functions.

What you need to provide

Zeeman interactions — electron-nuclear interactions — microwave and radiofrequency terms

$$\hat{H} = \hat{H}_{\mathrm{Z}} + \hat{H}_{\mathrm{NN}} + \hat{H}_{\mathrm{EN}} + \hat{H}_{\mathrm{EE}} + \hat{H}_{\mathrm{MW}}$$

inter-nuclear and quadrupolar interactions — inter-electron interactions and zero-field splitting

Zeeman interactions: chemical shielding tensors for nuclei and *g*-tensors for electrons.

Where to get: from the literature or from quantum chemistry packages (Gaussian, CASTEP, ORCA, *etc.*).

$$\hat{H}_{\mathrm{Z}} = \sum_k \vec{B}_0 \cdot \mathbf{A}_{\mathrm{E}}^{(k)} \cdot \hat{\vec{E}}^{(k)} + \sum_k \vec{B}_0 \cdot \mathbf{A}_{\mathrm{N}}^{(k)} \cdot \hat{\vec{N}}^{(k)}$$

GIAO DFT B3LYP/cc-pVTZ or similar is generally accurate for small CHNO molecules.

N.B.: DFT calculations for heavy metals and large aromatic systems require considerable skill.

What you need to provide

Zeeman interactions — electron-nuclear interactions — microwave and radiofrequency terms

$$\hat{H} = \hat{H}_{\mathrm{Z}} + \hat{H}_{\mathrm{NN}} + \hat{H}_{\mathrm{EN}} + \hat{H}_{\mathrm{EE}} + \hat{H}_{\mathrm{MW}}$$

inter-nuclear and quadrupolar interactions — inter-electron interactions and zero-field splitting

Inter-nuclear interactions: *J*-couplings, nuclear quadrupolar interactions, inter-nuclear dipolar interactions.

Where to get: literature or DFT for *J*-coupling and NQI. Dipolar couplings are most conveniently extracted from Cartesian coordinates of the spins.

$$\hat{H}_{\mathrm{NN}} = 2\pi \sum_{j<k} J_{\mathrm{NN}}^{(j,k)} \left(\hat{\vec{N}}_j \cdot \hat{\vec{N}}_k \right) + \sum_k \hat{\vec{N}}_k \cdot \mathbf{A}_{\mathrm{Q}}^{(k)} \cdot \hat{\vec{N}}_k -$$

$$- \frac{\mu_0}{4\pi} \sum_{j<k} \frac{\gamma_{\mathrm{N}}^{(j)} \gamma_{\mathrm{N}}^{(k)} \hbar}{r_{jk}^5} \left(3(\hat{\vec{N}}_j \cdot \vec{r}_{jk})(\vec{r}_{jk} \cdot \hat{\vec{N}}_k) - r_{jk}^2 (\hat{\vec{N}}_j \cdot \hat{\vec{N}}_k) \right)$$

N.B.: despite the common “scalar coupling” moniker, *J*-coupling is actually a tensor too.

What you need to provide

Zeeman interactions — electron-nuclear interactions — microwave and radiofrequency terms

$$\hat{H} = \hat{H}_{\mathrm{Z}} + \hat{H}_{\mathrm{NN}} + \hat{H}_{\mathrm{EN}} + \hat{H}_{\mathrm{EE}} + \hat{H}_{\mathrm{MW}}$$

inter-nuclear and quadrupolar interactions — inter-electron interactions and zero-field splitting

Electron-nuclear interactions: isotropic (*aka* Fermi contact) and anisotropic hyperfine couplings.

Where to get: literature or DFT (requires specialized basis sets). For remote electron-nuclear pairs (10 Angstroms or more), Cartesian coordinates.

$$\hat{H}_{\mathrm{EN}} = \sum_{j,k} \hat{\vec{E}}_j \cdot \mathbf{A}_{\mathrm{EN}}^{(j,k)} \cdot \hat{\vec{N}}_k$$

Note the strong directionality of some HFC tensors.

N.B.: "anisotropic hyperfine" and "electron-nuclear dipolar" interactions are the same thing.

What you need to provide

Zeeman interactions — electron-nuclear interactions — microwave and radiofrequency terms

$$\hat{H} = \hat{H}_{\mathrm{Z}} + \hat{H}_{\mathrm{NN}} + \hat{H}_{\mathrm{EN}} + \hat{H}_{\mathrm{EE}} + \hat{H}_{\mathrm{MW}}$$

inter-nuclear and quadrupolar interactions — inter-electron interactions and zero-field splitting

Inter-electron interactions: exchange interaction, zero field splitting, inter-electron dipolar interactions.

Where to get: literature or DFT for exchange coupling and ZFS. Dipolar couplings are most conveniently extracted from Cartesian coordinates of the spins.

$$\hat{H}_{\mathrm{EE}} = 2\pi \sum_{j<k} J_{\mathrm{EE}}^{(j,k)} \left(\hat{\vec{E}}_j \cdot \hat{\vec{E}}_k \right) + \sum_k \hat{\vec{E}}_k \cdot \mathbf{A}_{\mathrm{ZFS}}^{(k)} \cdot \hat{\vec{E}}_k -$$

$$- \frac{\mu_0}{4\pi} \sum_{j<k} \frac{\gamma_{\mathrm{E}}^{(j)} \gamma_{\mathrm{E}}^{(k)} \hbar}{r_{jk}^5} \left(3(\hat{\vec{E}}_j \cdot \vec{r}_{jk})(\vec{r}_{jk} \cdot \hat{\vec{E}}_k) - r_{jk}^2 (\hat{\vec{E}}_j \cdot \hat{\vec{E}}_k) \right)$$

N.B.: the practical accuracy of DFT for exchange coupling and particularly ZFS is very low.

What you need to provide

Zeeman interactions

electron-nuclear interactions

microwave and radiofrequency terms

$$\hat{H} = \hat{H}_{\mathrm{Z}} + \hat{H}_{\mathrm{NN}} + \hat{H}_{\mathrm{EN}} + \hat{H}_{\mathrm{EE}} + \hat{H}_{\mathrm{MW}}$$

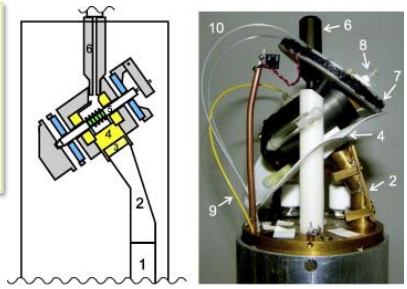
inter-nuclear and quadrupolar interactions

inter-electron interactions and zero-field splitting

Microwave and radiofrequency terms: amplitude coefficients in front of the L_{X} and L_{Y} terms in the Hamiltonian.

Where to get: from the pulse calibration curves of the instrument. The RF/MW power (in Hz) is equal to the reciprocal width of the 360-degree pulse.

$$\hat{H}_{\mathrm{MW}} = \cos\left(\omega_{\mathrm{MW}} t\right) \sum_{k} a_{\mathrm{MW}}^{(k)} \hat{E}_{\mathrm{X}}^{(k)}$$



(K.R. Thurber, A. Potapov, W.-M. Yau, R. Tycko)

N.B.: the direction of the B_1 field in most MAS experiments is parallel to the spinning axis.

Time domain simulation mathematics

$$\hat{H}(t) = \hat{H}_0 + \sum_k a_k(t) \hat{H}_k$$

$$\hat{\hat{L}}(t) = \hat{\hat{H}}(t) + i\hat{\hat{R}} + i\hat{\hat{K}}$$

$$\hat{\rho}_{\mathrm{eq}} = \frac{\exp\left(-\hat{H}_0/kT\right)}{\mathrm{Tr}\left[\exp\left(-\hat{H}_0/kT\right)\right]}$$

Spinach kernel provides all operators and states

$$\hat{\rho}(t+dt) = \exp\left[-i\hat{\hat{L}}(t)dt\right]\hat{\rho}(t)$$

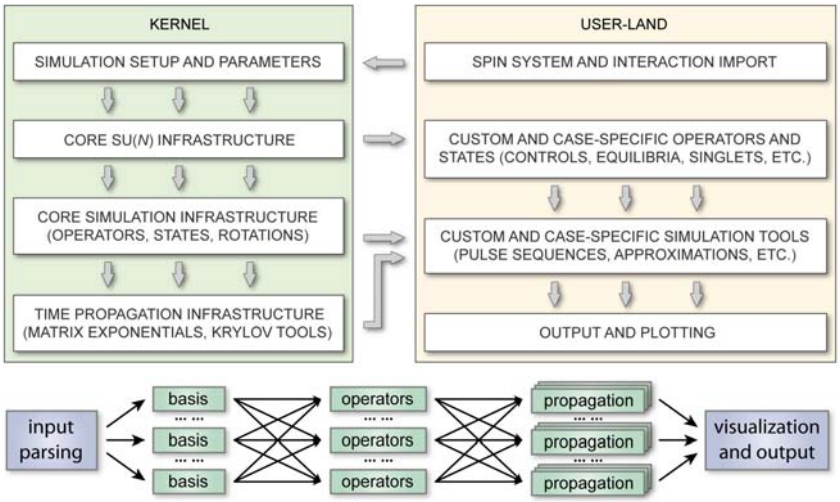
The mathematics is quite simple: apply this equation with some small step dt until you are done!

$$f(t) = \left\langle \hat{f} \middle| \hat{\rho}(t) \right\rangle \qquad \bar{f} = \frac{1}{\|\Omega\|} \int_{\Omega} f(\alpha, \beta, \gamma)\, d\Omega$$

Powder averages are slow, but not hard.

This mathematics is hidden from casual users, but the code is open source.

Spinach architecture

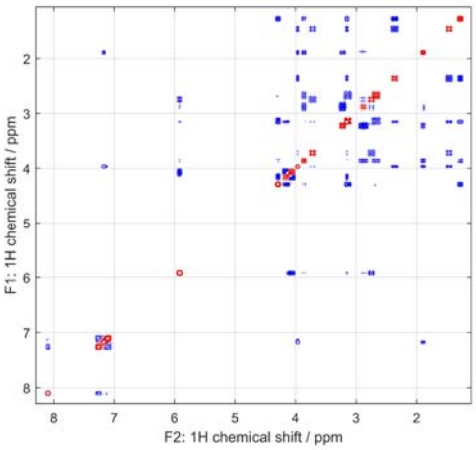


- *N.B.*: most functions are parallelized and would take advantage of a multi-core computer.

Simple NMR simulations in *Spinach*

```
% Spin system
sys.magnet=3.4;
sys.isotopes={'1H','1H'};

% Zeeman interactions
inter.zeeman.scalar={1.5 2.4};

% J-couplings
inter.coupling.scalar={0.0 7.4
                       0.0 0.0};

% Coordinates
inter.coordinates={[0.0 0.0 0.0]
                   [0.0 2.0 0.0]};

% Simulation formalism
bas.formalism='sphten-liouv';
bas.approximation='none';

% Relaxation theory
inter.relaxation='redfield';
inter.equilibrium='levitt';
inter.rlx_keep='secular';
inter.temperature=298;
inter.tau_c=10e-12;
```

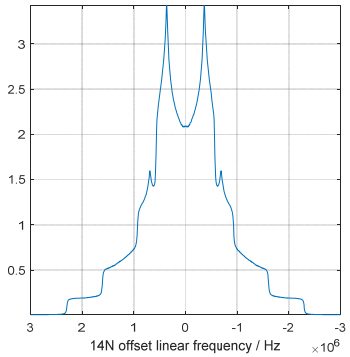
NOESY of strychnine



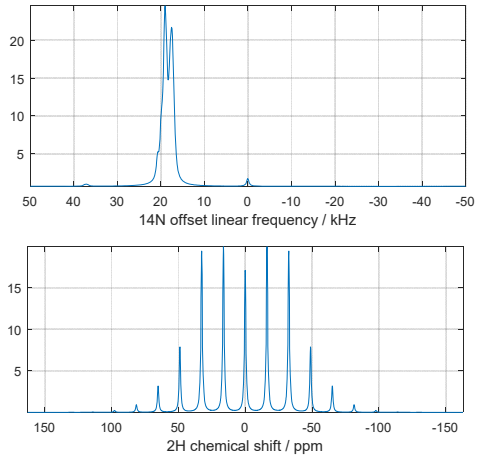
- *Spinach* has a very detailed input checker – if something is amiss, it would tell you.

Simple NMR simulations in *Spinach*

```
% System specification
sys.magnet=9.4;
sys.isotopes={'14N'};
inter.coupling.eigs={[-1e6 -2e6 3e6]};
inter.coupling.euler={[0.0 0.0 0.0]};
```

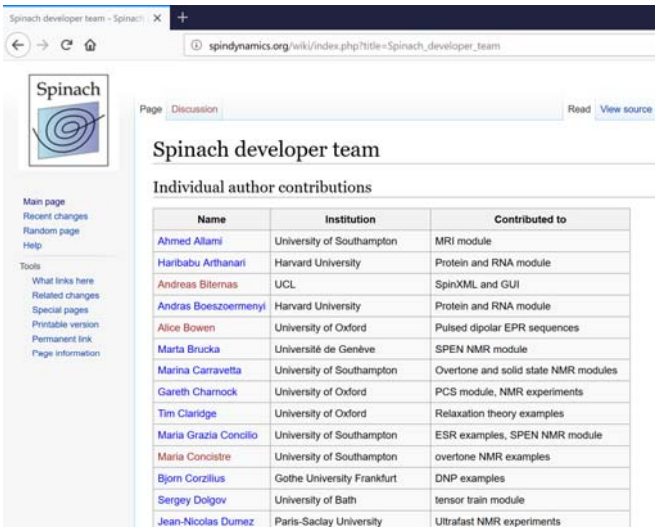


DOR and MAS quadrupolar NMR



- Powder averaging is an expensive operation, but it runs in parallel.

Spinach developer team



Name	Institution	Contributed to
Ahmed Allami	University of Southampton	MRI module
Haribabu Arthanari	Harvard University	Protein and RNA module
Andreas Biternas	UCL	SpinXML and GUI
Andras Boeszoermenyi	Harvard University	Protein and RNA module
Alice Bowen	University of Oxford	Pulsed dipolar EPR sequences
Marta Brucka	Université de Genève	SPEN NMR module
Marina Carravetta	University of Southampton	Overtone and solid state NMR modules
Gareth Charnock	University of Oxford	PCS module, NMR experiments
Tim Claridge	University of Oxford	Relaxation theory examples
Maria Grazia Concilio	University of Southampton	ESR examples, SPEN NMR module
Maria Concistre	University of Southampton	overtone NMR examples
Bjorn Corzilius	Gothe University Frankfurt	DNP examples
Sergey Dolgov	University of Bath	tensor train module
Jean-Nicolas Dumez	Paris-Saclay University	Ultrafast NMR experiments

- SPEN module: Ahmed Allami, Maria Grazia Concilio