Numerical simulations of spin dynamics

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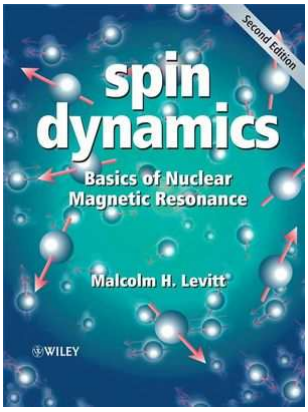
Spin dynamics



behavior of spins

nuclear spin

magnetic moment

in magnetic field

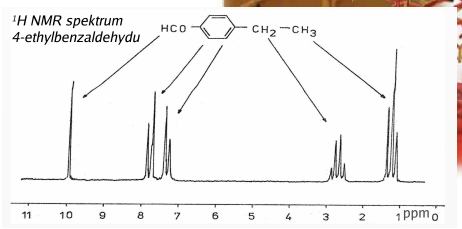
quantum mechanical problem

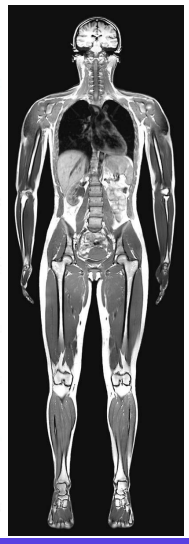
$$\frac{d}{dt}\rho = -i[H, \rho]$$

density matrix ***Hamiltonian***

Nuclear magnetic resonance

- local microscopic method with atomic resolution
- structure, chemical analysis, dynamics
- in solution as well as solid materials
- noninvasive imaging of living objects
- and much more...

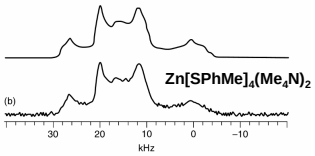




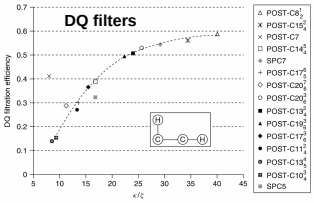
Numerical simulations

... when analytical tools fail or become too complicated

- Extracting structural and dynamical properties from spectra fitting

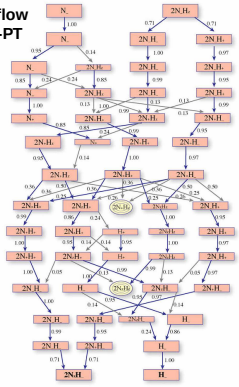


- Performance tests of new pulse sequences



- Insight into the underlying spin dynamics

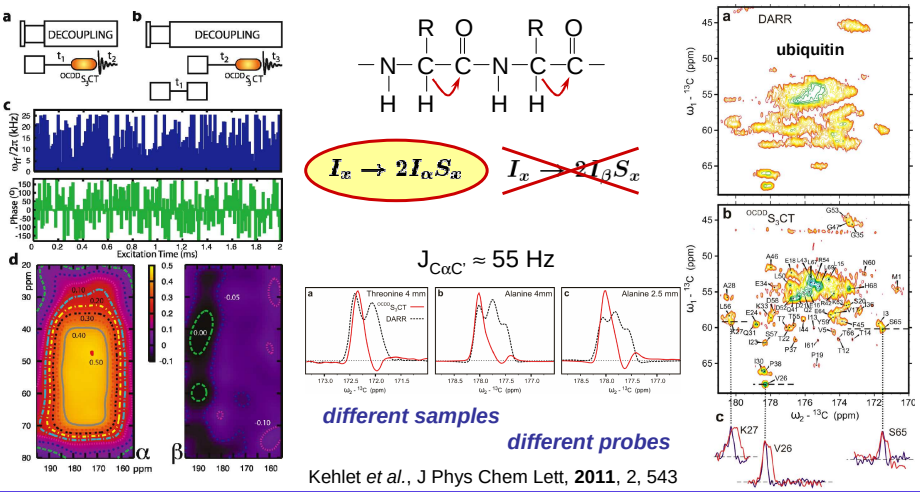
magnetization flow in TROSY-ST2-PT



- Design of new pulse sequences

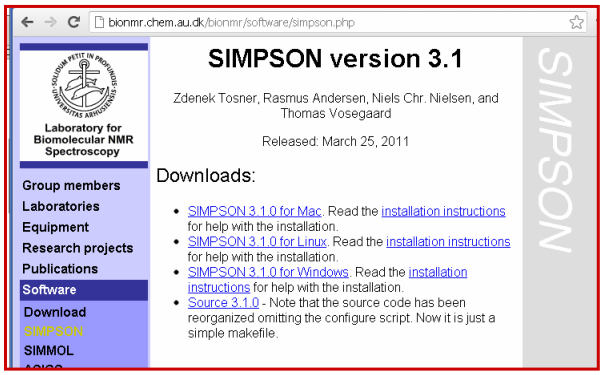
Optimal Control

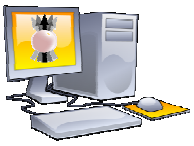
Spin-state-selective coherence transfer driven by dipolar interactions



Kehlet *et al.*, J Phys Chem Lett, **2011**, 2, 543

SIMPSON – virtual NMR spectrometer





original paper:
close to 750 citations

SIMPSON:

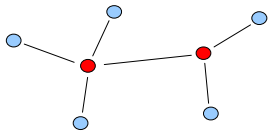
• Bak, Rasmussen, Nielsen, *J. Magn. Reson.* **147**, 296 (2000).

SIMPSON with Optimal Control:

• Tosner, Vosegaard, Kehlet, Khaneja, Glaser, Nielsen, *J. Magn. Reson.* **197**, 120 (2009).

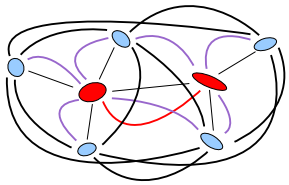
NMR interactions and Hamiltonian

molecule in solution



chemical shift J-coupling

in solid phase



anizotropic chemical shift J-coupling

anizotropic dipole-dipole interactions

Hamiltonian usualy very sparse	Hamiltonian still quite sparse
simple NMR experiments	complicated NMR experiments
long periods of constant **H**	always time-dependent **H**

Basic approaches

Hilbert space

$$\frac{d}{dt}\rho = -i[H,\rho] = -i\mathcal{L}\rho$$

Liouville space

$$\rho(t) = U(t)\rho(0)U^{\dagger}(t)$$

$$U(t) = \prod_{j=0}^{n-1} \exp\{-iH(j\Delta t)\Delta t\}$$

$$\rho(t) = P(t)\rho(0)$$

$$P(t) = \prod_{j=0}^{n-1} \exp\{-i\mathcal{L}(j\Delta t)\Delta t\}$$

$U \rightarrow 2^N \times 2^N$ $\rho \rightarrow 2^N \times 2^N$ $P \rightarrow 4^N \times 4^N$

Memory: ***density matrix for 15 spins 1/2*** $2\times8\times2^{15}\times2^{15}$ = 16 GB

CPU time:
- matrix exponential
- matrix – matrix or matrix – vector operations
- algorithms:
  - ***reuse of propagators***
  - ***γ- COMPUTE***
  - ***block-diagonalization***
- parallelization:
  - ***powder averages***
  - ***mathematical operations***

Propagators

Matrix exponential

$$U_j = \exp\{-iH_j\Delta t\}$$

H is real symmetric

diagonalization by eigen-decomposition

golden standard, works always...

Padé approximation

requires scaling & squaring

time consuming matrix division

Taylor expansion

requires scaling & squaring

only matrix multiplications, can be efficient when discarding "small" elements

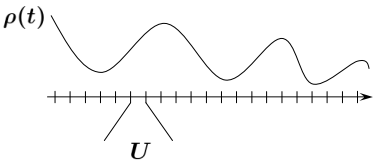
Chebyshev expansion

requires scaling and shifting (eigenvalues between -1 and +1)

only matrix multiplications (possibly sparse x dense)

...?... Lanczos?

Constant Hamiltonian



Liouville space

$$P = \exp\{-i\mathcal{L}\Delta t\} \qquad P \to 4^N \times 4^N$$

Hilbert space

$$\rho(t_n) = U^n \rho_0 \left(U^\dagger\right)^n$$

(similarity transform)

$$\rho(t_n) = P^n \rho_0$$

evaluate in propagator eigenbasis

➡ Krylov propagation $e^{-i\mathcal{L}t}\rho$

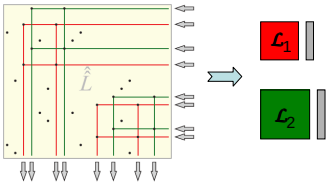
calculate propagator action without evaluating matrix exponential

Constant Hamiltonian

Liouville space

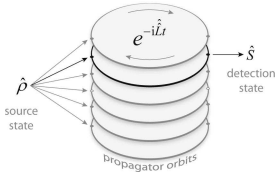
more tricks

- decomposition into non-interacting subspaces



smaller matrices

- identify relevant subspaces for simulation



skip empty/non-observable subspaces

Time dependent Hamiltonian

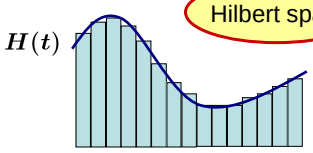
$$\frac{d}{dt}\rho = -i\,[H, \rho]$$

$$\rho(t) = U(0,t)\rho(0)U^{\dagger}(0,t)$$

$$U(0,t) = U(t_N, t_{N-1}) \ldots U(t_2, t_1)U(t_1, 0)$$

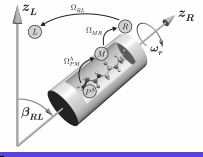
$$U(t_2, t_1) = \exp\{-iH(t_1)(t_2 - t_1)\}$$

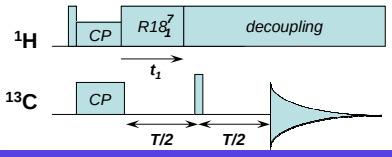
Hilbert space

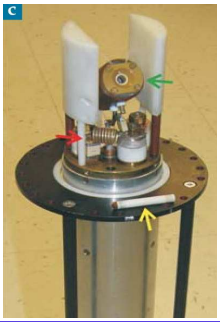


piece-wise constant approximation

Magic angle spinning & complicated rf irradiation

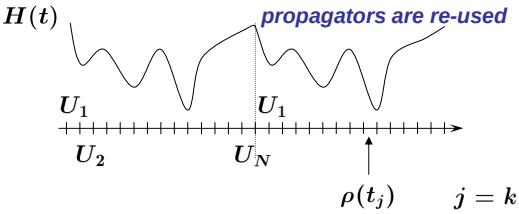






Hamiltonian periodicity

No periodicity – no way around re-evaluation of propagators



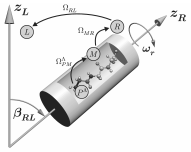
propagator of period

$$\boldsymbol{U}(0,\boldsymbol{T}) = \boldsymbol{U}_N \cdots \boldsymbol{U_2 U_1}$$

$$\rho(t_j) = \boldsymbol{U}_l \cdots \boldsymbol{U}_1 \boldsymbol{U}^k(0,\boldsymbol{T}) \rho_0 \left(\boldsymbol{U}^\dagger(0,\boldsymbol{T})\right)^k \boldsymbol{U}_1^\dagger \cdots \boldsymbol{U}_l^\dagger$$

efficiently evaluated at eigenbasis of period propagator

Hamiltonian and MAS



single interaction

$$H^\lambda = R_{2,0}^{\lambda,\mathrm{LAB}}(t) X_{2,0}^\lambda = \sum_{n=-2}^{+2} \underbrace{\mathscr{D}_{n,0}^{(2)}\left(\Omega_{\mathrm{MOL}}^{\mathrm{LAB}}(t)\right)}_{w_n(t)} R_{2,n}^{\lambda,\mathrm{MOL}} X_{2,0}^\lambda$$

Wigner coefficients

total interaction Hamiltonian

$$H_{\mathrm{TOT}} = \sum_\lambda H^\lambda = w_0(t) Q_0 + 2\mathrm{Re}\left\{w_1(t) Q_1 + w_2(t) Q_2\right\}$$

can this structure be used?

eigenvalues estimation
evolution of eigenvectors
interpolation

combination with rf irradiation

$$\boldsymbol{H}(t) = \boldsymbol{H_{TOT}}(t) + \boldsymbol{H}_{rf}(t)$$

Summary

Most time consuming operation is calculation of propagators

how to do it best?

Propagators are most efficiently re-used in their eigenbasis

eigendecomposition is necessary (or?)

Calculations in Liouville space can be faster due to matrix-vector operations,

possible subspace decomposition and exploiting high sparsity

not used due to necessity of eigendecomposition