The Constant Hamiltonian Toggling Frame Approach in Comparison with Different Spin Dynamics Simulation Algorithms for Single- and Two-Spin Systems

Bayerisches NMR Zentrum

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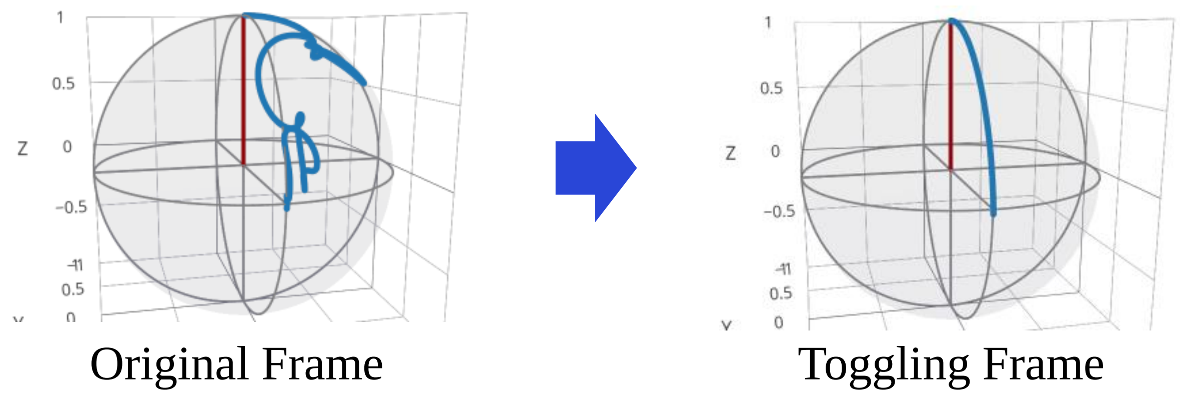
Introduction

- Motivation: Open problem in spin dynamics simulations is computational cost
- Constant Hamiltonian toggling frame: faster by skirting repeated matrix exponentiation [1]



Converting the Hamiltonian to a new frame:

$$\hat{H}_{Tog}(t) = V(t)\,\hat{H}_{Rot}(t)V^*(t) + i\,\dot{V}(t)V(t)$$

Chose $V(t)$ to remove the oscillating part of an axis, e.g. x:

$$V(t) = e^{iP(t)I_x} \qquad P(t) = \int_0^T h_x^{osc}(t)\,dt \qquad h_x(t) = h_x^{osc}(t) - \overline{h_x}$$

After rotation around the x-axis:

$$\hat{H}_{Tog:x}(t) = \overline{h_x}I_x + \left[h_y\cos(P(t)) + h_z\sin(P(t))\right]I_y + \left[h_z\cos(P(t)) - h_y\sin(P(t))\right]I_z$$

Repeat with each axis until convergence

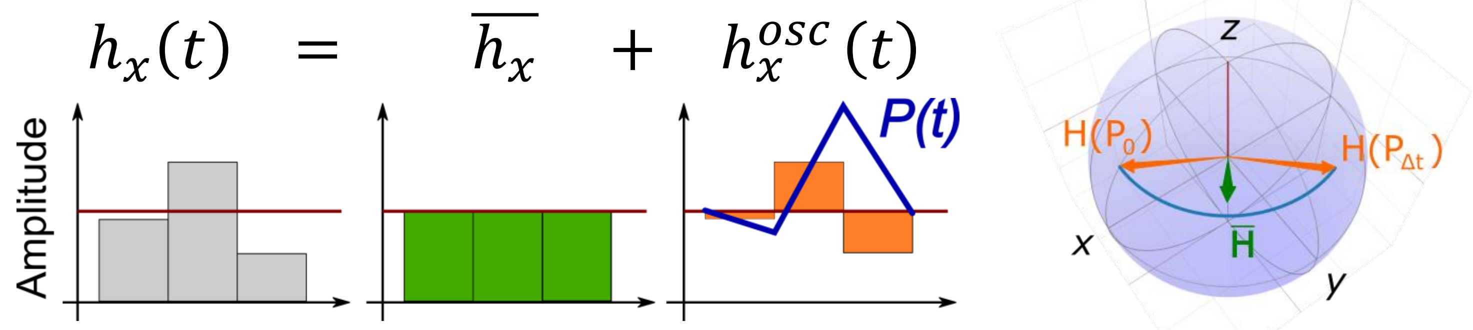
Rotation of the density matrix at the nth rotation:

$$V_{tot}(t) = V_n(t)\ldots V_2(t)V_1(t)$$

$$\rho_{Ori}(t) = V_{tot}^*(t)\,\rho_{Tog}(0)\,V_{tot}(t)$$

Accuracy Enhancement

$$h_x(t) = \overline{h_x} + h_x^{osc}(t)$$

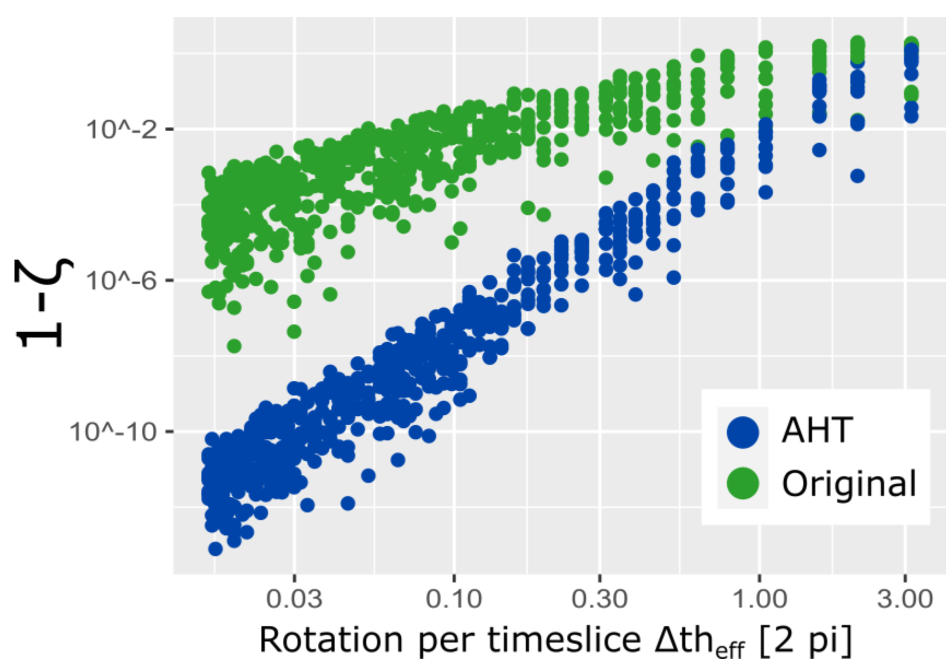


- Problem: The existing method is inaccurate because $P(t)$ is not constant during time steps.
- Correction: rotation via an average Hamiltonian: $\overline{H} = \int_0^T H(t)\,\frac{dt}{T}$

$$\overline{H}_{Tog:x}(t) = \overline{h_x}I_x + \frac{2\sin\left(\frac{P_{\Delta t}-P_0}{2}\right)}{P_{\Delta t}-P_0}\left[h_y\cos\left(\frac{P_{\Delta t}+P_0}{2}\right) + h_z\sin\left(\frac{P_{\Delta t}+P_0}{2}\right)\right]I_y + \frac{2\sin\left(\frac{P_{\Delta t}-P_0}{2}\right)}{P_{\Delta t}-P_0}\left[h_z\cos\left(\frac{P_{\Delta t}+P_0}{2}\right) - h_y\sin\left(\frac{P_{\Delta t}+P_0}{2}\right)\right]I_z$$

Accuracy of this method can be described by :

$$\zeta(t) = \langle\rho_{Ori}(t)|V_{tot}^*(t)\,\rho_{Tog}(t)\,V_{tot}(t)\rangle$$



➢ Accuracy greatly increased

Single-Spin System Computational Time

Compare to:

- Propagator calculation using matrix exponentiation (**ME**)
- Propagator calculation using the fast exponential solution (**FES**)[2]:

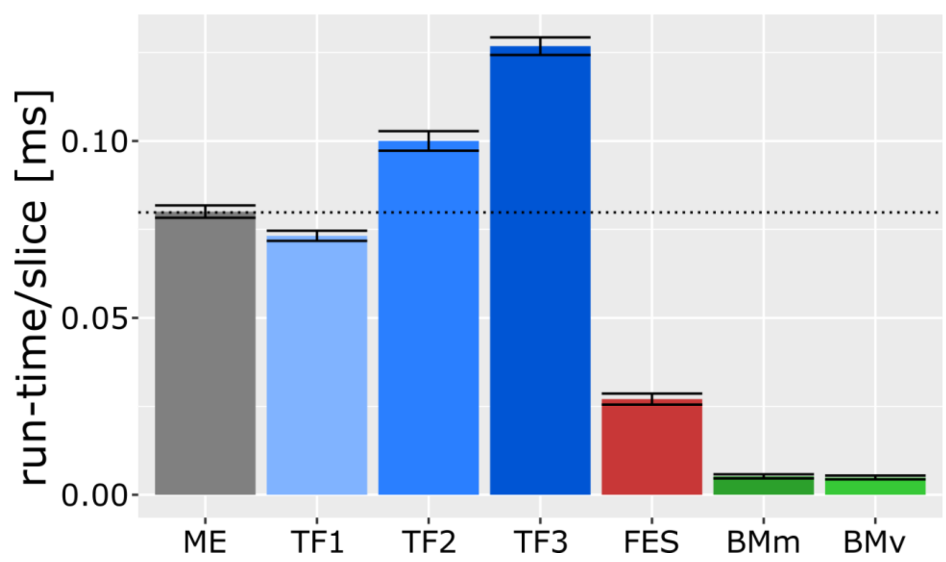
$$U = \cos\left(\frac{\phi}{2}\right)1 - 2i\sin\left(\frac{\phi}{2}\right)\left[n_xI_x + n_yI_y + n_zI_z\right]$$

$$\phi = \Delta t\sqrt{h_x^2 + h_y^2 + h_z^2} \qquad n_{x,y,z} = \Delta t\frac{2\pi h_{x,y,z}}{\phi}$$

- Direct calculations using Bloch magnetisation vectors (**BM**)
  - With rotation matrices (**BMm**) or vector products (**BMv**)

$$\vec{M}(t) = \vec{M}(0) + \sin\beta\,\vec{V} + 2\sin\frac{\beta}{2}\vec{n}\times\vec{V}$$

$$\beta = \Delta t\sqrt{h_x^2 + h_y^2 + h_z^2} \qquad \vec{n} = \frac{\Delta t}{\beta}\left[h_x, h_y, h_z\right]^T \qquad \vec{V} = \vec{n}\times\vec{M}(0)$$



C++ data (Eigen library)

➢ Time depends on the # of iterations to reach the constant H
➢ Analytical solution and magnetisation vector calculations faster

Generalisation to Multi-Spin Systems

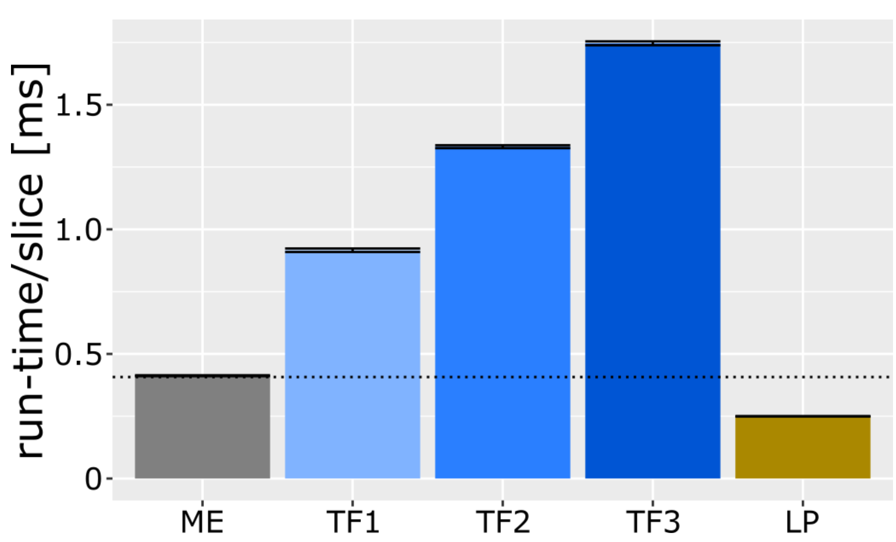
$$\overline{H}_{Tog:n} = \sum_{m=1}^{axes}\begin{cases} a\left[h_m\cos(b) + h_{[h_n,h_m]}\sin(b)\right]I_m & \text{for } [h_n,h_m] \neq 0 \\ h_mI_m & \text{for } [h_n,h_m] = 0\end{cases}$$

$$a = \frac{2\sin\left(\frac{P_{\Delta t}-P_0}{2}\right)}{P_{\Delta t}-P_0} \qquad b = \frac{P_{\Delta t}+P_0}{2}$$

Introduction to Loewdin Projections (spectral projections)[3]:

$$exp(\pm i\Delta tH) = \sum_i exp(\pm i\Delta t\lambda_i)P_{\lambda_i} \qquad P_{\lambda_i} = \prod_{j\neq i}\frac{H-\lambda_j}{\lambda_i-\lambda_j}$$

Two spins:



C++ data (Eigen library)

➢ Broad comparison of spin dynamics simulation methods
➢ Constant Hamiltonian toggling frame is slower than the benchmark for a two-spin system
➢ Loewdin projectors are a good alternative to ME

[1] Coote, P. *et al.*, Rapid convergence of optimal control in NMR using numerically-constructed toggling frames. Journal of Magnetic Resonance, 2017
[2] Kobzar, K. *et al.*, Exploring the limits of broadband 90 and 180 universal rotation pulses .Journal of Magnetic Resonance, 2012
[3] Chandrakumar, N. Application of Löwdin projectors to evaluate density matrix evolutions. Journal of Magnetic Resonance (1969), 1990