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NUMERICAL APPROXIMATION OF THE TIME-ORDERED EXPONENTIAL FOR SPIN DYNAMIC SIMULATION

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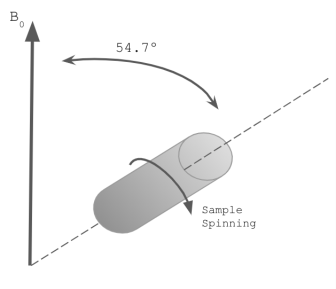
INTRODUCTION

Aim: First comparison between $\star$-product approach and well established numerical methods for the solution of non-autonomous ODEs.

Case Study: Solid-state Nuclear magnetic resonance (NMR) spectroscopy with magic-angle spinning (MAS).



Schrödinger equation

$$\begin{cases} \frac{\mathrm{d}}{\mathrm{d}t}\psi(t) = -i\mathcal{H}(t)\psi(t), \quad t \geqslant 0 \\ \psi(0) = \psi_0 \end{cases}$$

where $\mathcal{H}$ is the time-dependent Hamiltonian operator.

General Problem

$$\begin{cases} \frac{\mathrm{d}}{\mathrm{d}t} u(t) = A(t) u(t), & t \in (t_0, T) \\ u(t_0) = u_0 \end{cases}$$

with time-dependent coefficients $A(t)$.

Difficulty: Analytic expression not always available

→ Role of numerical approaches is crucial

$\star$-PRODUCT APPROACH

[Pozza, Van Buggenhout, 2023]

Problem

$$\frac{d}{dt}\tilde{u}(t) = \tilde{f}(t)\tilde{u}(t), \quad \tilde{u}(-1) = 1, \quad t \in [-1,1]$$

- Heaviside step function: $\Theta(t-s) = \begin{cases} 0, & \text{if } t < s \\ 1, & \text{otherwise} \end{cases}$
- $\mathcal{A}_\Theta$ = set of all scalar distribution of the kind $f(t,s) = \tilde{f}(t,s)\Theta(t-s)$, with $\tilde{f}$ analytic function
- $\star$-product:

$$f(t,s) \star g(t,s) := \int_{-1}^{1} g(t,\tau) f(\tau,s) d\tau, \quad f,g \in \mathcal{A}_\Theta, \quad t,s \in [-1,1]$$

- $\star$-identity: Dirac delta distribution $\delta(t-s)$
- $\star$-expression of the solution:

$$\frac{d}{dt}u(t,s) = f(t,s)u(t,s), \quad u(s,s) = 1, \quad t,s \in [-1,1]$$

$$u(t,s) = \Theta(t-s) \star R_\star(f)(t,s), \quad R_\star(f)(t,s) = \delta(t-s) + \sum_{k\geq 1} f^{\star k}(t,s)$$

$$\tilde{u}(t) = u(t,-1)$$

Expansion in Legendre polynomials:

- For a function $\tilde{f}$: $\tilde{f}(t) = \sum_{d=0}^{\infty} \alpha_d p_d(t)$, with $\alpha_d = \int_{-1}^{1} \tilde{f}(t) p_d(t) dt$
  $\rightarrow$ For $\tilde{f}$ analytic, $|\alpha_d| \leq C\rho^{-d-1}$, $\rho > 1$
- For a distribution $f \in \mathcal{A}_\Theta$:

$$f(t,s) = \sum_{k=0}^{\infty} \sum_{\ell=0}^{\infty} f_{k,\ell} p_k(t) p_\ell(s), \quad \text{for every } t \neq s, \quad t,s \in [-1,1]$$

with $f_{k,\ell} = \int_{-1}^{1} \int_{-1}^{1} f(\tau,\rho) p_k(\tau) p_\ell(\rho) d\rho d\tau$

$$\implies F := \left[f_{k,\ell}\right]_{k,\ell=0}^{\infty} = \begin{bmatrix} f_{0,0} & f_{0,1} & f_{0,2} & \cdots \\ f_{1,0} & f_{1,1} & f_{1,2} & \cdots \\ f_{2,0} & f_{2,1} & f_{2,2} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

We can express the coefficients $\{c_k\}_{k\geq 0}$ of the Legendre expansion of the **solution in terms of the coefficient matrix** F:

$$\begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \end{bmatrix} = T(\mathbb{I} - F)^{-1} \begin{bmatrix} p_0(-1) \\ p_1(-1) \\ p_2(-1) \\ \vdots \end{bmatrix}$$

with T the coefficient matrix of the Heaviside function.

Truncated Matrix Problem

1. Construct $F_M = [f_{k,l}]_{k,\ell=0}^{M-1}$, i.e., construct the matrix of Fourier coefficients;
2. Solve $(\mathbb{I} - F_M)x = \phi(-1)$, i.e., solve a linear system;
3. Compute $T_M x = \begin{bmatrix} c_0 & c_1 & c_2 & \cdots & c_{M-1} \end{bmatrix}^T$, i.e., compute a matrix-vector product.

Problem

$$\frac{\mathrm{d}}{\mathrm{d}t}u(t) = \tilde{A}(t)\Theta(t-s)u(t), \quad u(-1) = u_0, \quad t \in [-1,1]$$

where $\tilde{A}(t)$ is an analytic matrix-valued function over $[-1,1]$.

$$\rightarrow u(t) \approx (\mathbb{I}_N \otimes \phi_M(t)^T T_M)(\mathbb{I}_{MN} - \mathcal{A}_M)^{-1}(u_0 \otimes \phi_M(-1))$$

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If $\tilde{A}(t) = \sum_{k=1}^{d} A_k \tilde{f}_k(t)$, then $\mathcal{A}_M = \sum_{k=1}^{d} A_k \otimes F_M^{(k)}$

$$X - \sum_{k=1}^{d} F_M^{(k)} X A_k^T = \phi_M(-1) u_0^T, \quad x = vec(X)$$

$$X_{n+1} = \sum_{k=1}^{d} F_M^{(k)} X_n A_k^T + \phi_M(-1) u_0^T$$

- Use **low-rank approximations**, i.e., $X_n \approx V_n W_n^H, \quad V_n, W_n \in \mathbb{C}^{N \times r}, r << M$

[Pozza, Van Buggenhout, 2023]

GEOMETRIC NUMERICAL INTEGRATORS

The Magnus Expansion provides the **solution** of

$$\begin{cases} \frac{\mathrm{d}}{\mathrm{d}t} u(t) = A(t)u(t), \quad t \in (0, T) \\ u(0) = u_0 \end{cases}$$

as the **exponential of an infinite series**

$$u(t) = e^{\Omega(t)} u_0, \qquad \Omega(t) = \sum_{m=1}^{\infty} \Omega_m(t)$$

where $\Omega_m(t)$ is the m-th nested integral containing $m-1$ nested commutator of $A(t)$.

$$\Omega_1(t) = \int_0^t dt_1 A(t_1),$$
$$\Omega_2(t) = \frac{1}{2} \int_0^t dt_1 \int_0^{t_1} dt_2 [A(t_1).A(t_2)],$$
$$\Omega_3(t) = \frac{1}{6} \int_{t_0}^t dt \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 \, [A(t_1), [A(t_2), A(t_3)]] + [[A(t_1), A(t_2)], A(t_3)]$$

[Alvermann, Fehske, 2011]

Idea

- **Truncate** the infinite series
- Use **quadrature formula** to estimate integrals in the Magnus Expansion

$\rightarrow \tilde{u}^{(N)} = exp\left[\sum_{m=1}^{N} \Omega_m(t)\right]$

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Nested integrals → Expand $A(t)$ in a series of (Shifted) Legendre Polynomials. For a fix τ:

$$A(t) = \frac{1}{\tau}\sum_{n=1}^{N} A_n P_{n-1}\left(\frac{t}{\tau}\right) + \mathcal{O}(\tau^{N+1}), \quad A_n = (2n-1)\int_0^{\tau} A(t) P_{n-1}\left(\frac{t}{\tau}\right) dt, \quad t \in [0,\tau].$$

→ **Reduce** the nested integrals **to single** integrals by symmetry and orthogonality

[Alvermann, Fehske, Blanes, Casas]

Generalization of the Splitting Methods, but with significantly less exponentials.

Aim

Avoid commutators to decrease the computational effort

$$\tilde{u}_{CF}^{(N)}(\tau) = e^{\Omega_1} e^{\Omega_2} \dots e^{\Omega_s}$$

$$\Omega_i = \sum_{n=1}^{N} f_{i,n} A_n, \quad \forall\, i = 1, \dots, s$$

- Completely determined by the choice of the coefficient $f_{i,n}$
- For a prescribed order, $f_{i,n}$ can be found through **order conditions**

[Alvermann, Fehske, Blanes, Casas]

Gauss - Legendre quadrature

$$\int_0^1 f(x)dx \approx \sum_{m=1}^{M} w_m f(x_m)$$

M nodes $x_1, \ldots, x_M$ which are the zeros of the (shifted) Legendre polynomial $P_M(x)$ and weights $w_1, \ldots, w_M$

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$\Rightarrow$ We can approximate the Legendre coefficients $A_n(t)$

$$A_n \approx (2n-1)\tau \sum_{m=1}^{N/2+1} w_m P_{n-1}(x_m) A(x_m \tau)$$

We **obtain** Ω_i as a linear combination of $A(t)$ at different time $x_m\tau$ with new coefficients

$$g_{i,m} = w_m \sum_{n=1}^{N/2+1} (2n-1) P_{n-1}(x_m) f_{i,n}.$$

We have **reduced** the problem of finding a solution to the non-autonomous ODE **to a computation of** one or multiple **exponentials of a matrix**.

Approximation of the matrix exponential e^M

- **Padé Approximation** $R_{pq}(M) = [D_{pq}(M)]^{-1} N_{pq}(M)$
- **Scaling and Squaring** $e^M = \left(e^{\frac{M}{n}}\right)^n$

[Moler, Van Loan, 2003]

Approximation of the action of the matrix exponential on a vector $e^M \xi$

- **Scaling/Squaring - like strategy** $Z_{i+1} = r_m(s^{-1}M)Z_i, \quad Z_0 = \xi$
- **Krylov subsbace methods** $e^M \xi \approx \|\xi\|_2 V_m e^{H_m} e_1$
- **Chebyshev technique** $e^{-i\tau M} \approx \sum_{n=0}^m c_n Q_n(\tau M)$

[Al-Mohy, Higham, Saad]

NUMERICAL COMPARISON

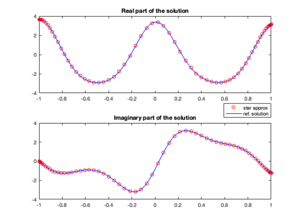
$$\frac{\mathrm{d}}{\mathrm{d}t}u(t) = -i\mathcal{H}_{BS}(t)u(t), \quad u(0) = u_0, \quad t \in [0, 2\pi/\omega_r]$$

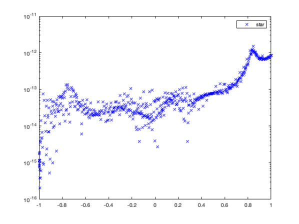
$$\mathcal{H}_{BS} = \begin{bmatrix} \omega_0/2 & 2\beta\cos(\omega_r t) \\ 2\beta\cos(\omega_r t) & -\omega_0/2 \end{bmatrix}$$

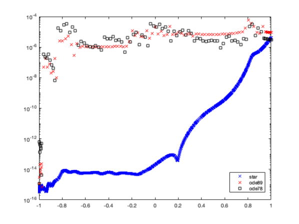
- Resonant: $\omega_0 = \omega_r$
- Strong-coupling $\beta/\omega_r > 1$
- $\omega_r = 20000$ and $\beta = 1.2\omega_r$
- u_0 = random vector (`randn`)

[Giscard, Bonhomme, 2020]

Taking the Runge-Kutta $(8,9)$ method with tolerance 10^{-12} (ode89) as reference, we see that the $\star$-solution computed with tolerance 10^{-12} is reliable







$\leftarrow$

- Reference: $\star$-solution with $tol = 10^{-12}$
- $\star$-process with $tol = 10^{-4}$
- Runge-Kutta $(8,9)$ with $tol = 10^{-3}$
- Runge-Kutta $(7,8)$ with $tol = 10^{-3}$

$$\mathcal{H}(t) = \mathcal{H}_{ICS} + \mathcal{H}_{DD}(t), \quad t \in [0, \tfrac{1}{10\omega_r}]$$

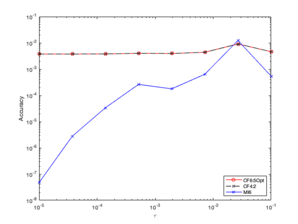
$$\mathcal{H}_{ICS} = \sum_{k=1}^{N_s} \Omega_k I_{k_z}$$

$$\mathcal{H}_{DD} = \delta \sum_{k=1}^{N_s-1} \sum_{q=k+1}^{N_s} \left(\sum_{n=-2}^{2} e^{in(\gamma+\omega_r t)} C_n(\beta) \right) \cdot \frac{1}{r_{kq}^3} \left[2 I_{k_z} I_{q_z} - (I_{k_x} I_{q_x} + I_{k_y} I_{q_y}) \right]$$

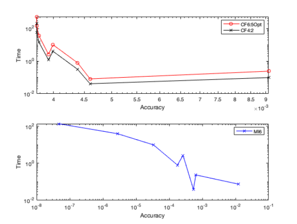
- N_s = number of spins
- $C_1(\beta) = C_{-1}(\beta) = -\frac{1}{2\sqrt{2}} \sin(2\beta)$
  $C_2(\beta) = C_{-2}(\beta) = \frac{1}{4} \sin^2(\beta)$
- δ = fixed constant
- u_0 randomly generated
- Ω_k = chemical shift differences (→ randomly generated)
- r_{kq} = interspin distance between spins k and q (→ cationic tin oxo-cluster)
- $\omega_r = 20000$, $\beta = \pi/4$ and $\gamma = \pi$

$$I_{k_x} := \mathbb{I}_{2^{k-1}} \otimes \sigma_x \otimes \mathbb{I}_{2^{N_s-k}}, \quad \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

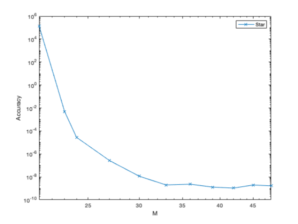
[Malaer, et al., 2019] [Bak, et al., 2000]



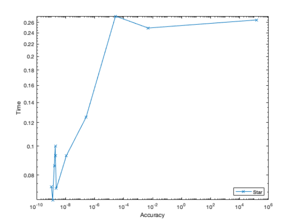
Accuracy vs τ



GNI: Accuracy vs Time



Accuracy vs M



$\star$-process: Accuracy vs Time

- $N_s = 6$

The accuracy is governed by the parameter τ, M

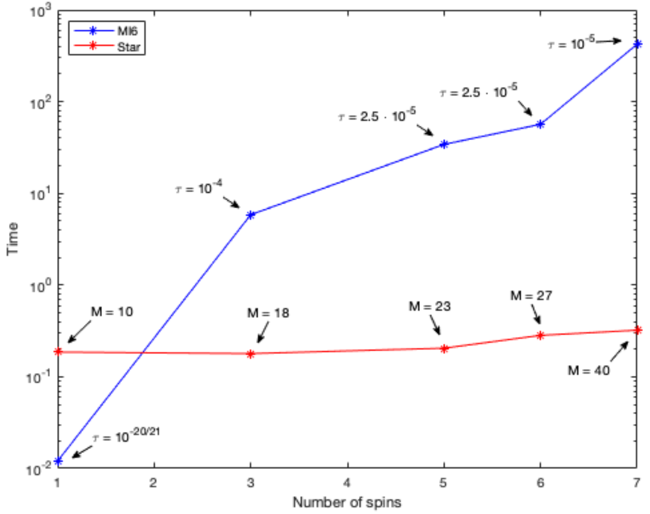
- Reference: $\star$-process, $tol = 10^{-13}$
- $\star$-process, $tol = 10^{-4}$
- 6-th order CFEI with 5 exponentials
- 4-th order CFEI with 2 exponentials
- 6-th order Magnus Integrator

DIPOLAR INTERACTIONS IN ROTOR FRAME: RESULTS

- $N_s = 6$

Accuracy	Method	Parameter	Total computational time
10^{-3}	$\star$ -process	$M = 23$	$0.1969s$
	MI6	$\tau = 10^{-\frac{20}{21}}$	$0.0463s$
	CF6:5Opt	$\tau = 10^{-1}$	$0.1324s$
	CF4:2	$\tau = 10^{-1}$	$0.0701s$
10^{-5}	$\star$ -process	$M = 24$	$0.1370s$
	MI6	$\tau = 1.4 \cdot 10^{-4}$	$10.3845s$
	CF6:5Opt	$\tau < 10^{-5}$	$> 540s$
	CF4:2	$\tau < 10^{-5}$	$> 220s$
10^{-8}	$\star$ -process	$M = 30$	$0.0766s$
	MI6	$\tau = 10^{-5}$	$149.9658s$

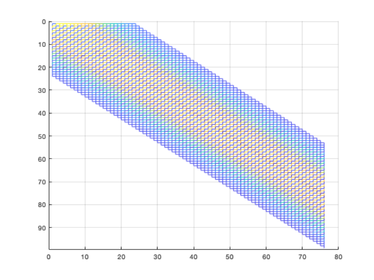
MI6 and $\star$-process: Time vs Number of spins



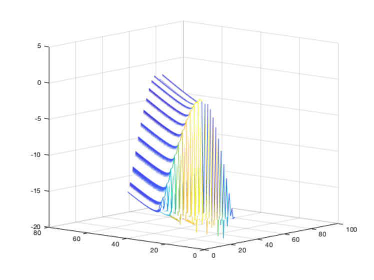
POSSIBLE DEVELOPMENTS

- Use more efficient **implementations** of Geometric Numerical **Integrators**
- Consider **other methods** for comparison
- Consider **more complicated** NMR **problems**
- Comparison with commonly-used **software** in quantum chemistry, e.g. SIMPSON
- Consider experiment **data** totally linked to **real-world problems**

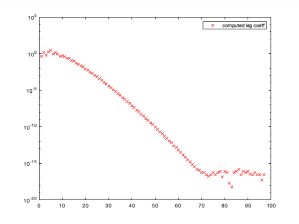
Thank you!



Banded Property



Decay phenomenon



Decay of the Legendre coefficients

- Tolerance: 10^{-12}
- $M = 100$
- $N = 24$