Auxiliary Matrix Formalism
for Computation of Chained Integrals in Magnetic Resonance

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Introduction

Chained exponential integrals involving square matrices occur particularly often in magnetic resonance. A general form of a chained exponential integral is:

$$\int dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-2}} dt_{n-1} \left\{ e^{A_1(t-t_1)} \mathbf{B}_1 e^{A_2(t_1-t_2)} \mathbf{B}_2 \dots \mathbf{B}_{n-1} e^{A_n t_{n-1}} \right\}$$

where $\mathbf{A}_k$ and $\mathbf{B}_k$ are square matrices. Their common feature is the complexity of evaluation: expensive matrix factorisations are usually required. This makes the application of the associated theories difficult when matrix dimension exceeds 10^3, i.e. for ten spins or more.

Consider the example of spin relaxation theory. The techniques currently used for the evaluation of Redfield's integral, which involves a static Hamiltonian $\mathbf{H}$, a rotational correlation function $G(\tau)$ and an irreducible spherical component $\mathbf{Q}$ of the stochastic Hamiltonian, either involve the diagonalisation of $\mathbf{H}$ followed by the evaluation of a large number of Fourier transforms:

$$\left[\int_0^\infty G(\tau) e^{-i\mathbf{H}\tau} \mathbf{Q}^\dagger e^{i\mathbf{H}\tau} d\tau \right]_{nk} = \left[\int_0^\infty G(\tau) \left[\mathbf{V} e^{-i\mathbf{D}\tau} \mathbf{V}^\dagger \right] \mathbf{Q}^\dagger \left[\mathbf{V} e^{i\mathbf{D}\tau} \mathbf{V}^\dagger \right] d\tau \right]_{nk} =$$

$$= \left[\int_0^\infty G(\tau) \mathbf{V} e^{-i\mathbf{D}\tau} \left[\mathbf{V}^\dagger \mathbf{Q}^\dagger \mathbf{V} \right] e^{i\mathbf{D}\tau} \mathbf{V}^\dagger d\tau \right]_{nk} = \sum_{rs} \int_0^\infty G(\tau) V_{nr} e^{-iD_{rr}\tau} \left[\mathbf{V}^\dagger \mathbf{Q}^\dagger \mathbf{V} \right]_{rs} e^{iD_{ss}\tau} V_{ks}^* d\tau =$$

$$= \sum_{rs} V_{nr} \left[\mathbf{V}^\dagger \mathbf{Q}^\dagger \mathbf{V} \right]_{rs} V_{ks}^* \int_0^\infty G(\tau) e^{-i(D_{rr}-D_{ss})\tau} d\tau; \qquad \mathbf{H}=\mathbf{VDV}^\dagger$$

or a matrix-valued numerical quadrature with a large number of time steps. The latter method scales better because matrix sparsity is preserved at every stage and diagonalisation is avoided, but the evaluation is still difficult. Such situations are ubiquitous in magnetic resonance and these chained exponential integrals are the bottleneck in many important cases.

This work we proposes a solution to this problem, based on the observation that matrix exponentiation, does not require factorisations and preserves spin operator sparsity [1,2] and on the auxiliary matrix technique [3,4,5] for the evaluation of the chained exponential integrals.

Exponentiation of Auxiliary Matrices

A method for computing some of the integrals of the general type shown above was proposed by Van Loan in 1978 [3]. He noted that the integrals in question are solutions to linear block matrix differential equations and suggested that block matrix exponentials are used to compute them. In the simplest case of a single integral:

$$\exp\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{0} & \mathbf{C} \end{pmatrix} t \right] = \begin{pmatrix} e^{\mathbf{A}t} & e^{\mathbf{A}t} \int_0^t e^{-\mathbf{A}t_1} \mathbf{B} e^{\mathbf{C}t_1} dt_1 \\ \mathbf{0} & e^{\mathbf{C}t} \end{pmatrix}$$

This was later refined [5] using the block-bidiagonal auxiliary matrix:

$$\mathbf{M} = \begin{pmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{A}_{22} & \mathbf{A}_{23} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{A}_{33} & \ddots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \ddots & \mathbf{A}_{k-1,k} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{A}_{kk} \end{pmatrix}, \qquad \exp(\mathbf{M}t) = \begin{pmatrix} \mathbf{B}_{11} & \mathbf{B}_{12} & \mathbf{B}_{13} & \cdots & \mathbf{B}_{1k} \\ \mathbf{0} & \mathbf{B}_{22} & \mathbf{B}_{23} & \cdots & \mathbf{B}_{2k} \\ \mathbf{0} & \mathbf{0} & \mathbf{B}_{33} & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \ddots & \mathbf{B}_{k-1,k} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{B}_{kk} \end{pmatrix}$$

$$\mathbf{B}_{1k} = \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{k-2}} dt_{k-1} \left\{ e^{A_{11}(t-t_1)} \mathbf{A}_{12} e^{A_{22}(t_1-t_2)} \mathbf{A}_{23} \dots \mathbf{A}_{k-1,k} e^{A_{kk}t_{k-1}} \right\}$$

Spin Hamiltonians are guaranteed to be sparse in the Pauli basis [6] and their exponential propagators are also sparse when $\|\mathbf{H}\Delta t\| < 1$, if care is taken to eliminate insignificant elements after each matrix multiplication in the scaled and squared Taylor series procedure [2]:

$$e^{\mathbf{M}t} = \sum_{k=0}^\infty \frac{(\mathbf{M}t)^k}{k!}; \qquad e^{\mathbf{M}t} = \left(\left(\left(e^{\mathbf{M}/2^n} \right)^2 \right)^2 \dots \right)^2$$

Out of the multitude of "dubious ways" [7] of computing matrix exponentials, the Taylor series method with scaling and squaring is recommended here because it is compatible with dissipative dynamics, only involves matrix multiplications, uses minimal memory resources, and only requires approximate scaling.

Optimal Control Theories

Optimal control is the task of taking a system from one state to another to a specified accuracy with minimal expenditure of time and energy. Optimal solutions can be found numerically, by maximizing the overlap between the final state of the system and the desired destination state:

$$J\left[\mathbf{H}_1(t) \right] = \mathrm{Re} \left\langle \delta \middle| \exp_{(O)} \left[-i \int_0^T \left(\mathbf{H}_0 + \mathbf{H}_1(t) + i\mathbf{R} \right) dt \right] \middle| \rho_0 \right\rangle$$

where $\exp_{(O)}$ indicates a time-ordered exponential, $\mathbf{H}_0$ is the drift Hamiltonian, $\mathbf{H}_1$ is the control Hamiltonian, $\mathbf{R}$ is the relaxation operator, ρ_0 is the initial state vector and δ is the destination state. The gradient ascent pulse engineering (GRAPE) method [8,9,10] proceeds by splitting the Hamiltonian into the uncontrollable part and a number of control operators with time-dependent coefficients

$$\mathbf{H}(t) = \mathbf{H}_0 + \sum_{k=1}^K c_k(t) \mathbf{H}_k$$

$$c_k(t) \quad \rightarrow \quad \mathbf{c}_k = \begin{bmatrix} c_k(t_1) & c_k(t_2) & \cdots & c_k(t_N) \end{bmatrix}, \qquad t_1 < t_2 < \dots < t_N$$

With a piecewise-constant Hamiltonian the overlap of the final and desired states becomes

$$J(\mathbf{c}_1, \dots, \mathbf{c}_K) = \mathrm{Re} \left\langle \delta \middle| \mathbf{P}_N \dots \mathbf{P}_2 \mathbf{P}_1 \middle| \rho_0 \right\rangle, \qquad \mathbf{P}_n = \exp\left[-i\left(\mathbf{H}_0 + \sum_{k=1}^K c_{k,n} \mathbf{H}_k + i\mathbf{R} \right) \Delta t \right]$$

and the corresponding gradient and Hessian elements are

$$\frac{\partial J}{\partial c_{k,n}} = \mathrm{Re} \left\langle \delta \middle| \mathbf{P}_N \cdots \mathbf{P}_{n+1} \frac{\partial \mathbf{P}_n}{\partial c_{k,n}} \mathbf{P}_{n-1} \cdots \mathbf{P}_1 \middle| \rho_0 \right\rangle$$

$$\frac{\partial^2 J}{\partial c_{j,n} \partial c_{k,n}} = \mathrm{Re} \left\langle \delta \middle| \mathbf{P}_N \cdots \mathbf{P}_{n+1} \frac{\partial^2 \mathbf{P}_n}{\partial c_{j,n} \partial c_{k,n}} \mathbf{P}_{n-1} \cdots \mathbf{P}_1 \middle| \rho_0 \right\rangle$$

$$\frac{\partial^2 J}{\partial c_{j,n} \partial c_{k,m}} = \mathrm{Re} \left\langle \delta \middle| \mathbf{P}_N \cdots \mathbf{P}_{n+1} \frac{\partial \mathbf{P}_n}{\partial c_{j,n}} \mathbf{P}_{n-1} \cdots \mathbf{P}_{m+1} \frac{\partial \mathbf{P}_m}{\partial c_{k,m}} \mathbf{P}_{m-1} \cdots \mathbf{P}_1 \middle| \rho_0 \right\rangle$$

The first order propagator derivative can be calculated efficiently with the auxiliary matrix formalism [4,11]:

$$\begin{pmatrix} \mathbf{P}_n & \frac{\partial \mathbf{P}_n}{\partial c_{i,n}} \\ \mathbf{0} & \mathbf{P}_n \end{pmatrix} = \exp\left[-i \begin{pmatrix} \mathbf{H}(t) & \mathbf{H}_i \\ \mathbf{0} & \mathbf{H}(t) \end{pmatrix} \Delta t \right]$$

Similarly, the second order derivative can be calculated with a larger auxiliary matrix:

$$\begin{pmatrix} \mathbf{P}_n & \frac{\partial \mathbf{P}_n}{\partial c_{i,n}} & \mathbf{A}_{ij,n} \\ \mathbf{0} & \mathbf{P}_n & \frac{\partial \mathbf{P}_n}{\partial c_{j,n}} \\ \mathbf{0} & \mathbf{0} & \mathbf{P}_n \end{pmatrix} = \exp\left[-i \begin{pmatrix} \mathbf{H}(t) & \mathbf{H}_i & \mathbf{0} \\ \mathbf{0} & \mathbf{H}(t) & \mathbf{H}_j \\ \mathbf{0} & \mathbf{0} & \mathbf{H}(t) \end{pmatrix} \Delta t \right], \qquad \frac{\partial^2 \mathbf{P}_n}{\partial c_{i,n} \partial c_{j,n}} = \mathbf{A}_{ij,n} + \mathbf{A}_{ji,n}$$

Spin Relaxation Theories

Exponential integrals appear in Bloch-Redfield-Wangsness spin relaxation theory, in which the relaxation superoperator $\mathbf{R}$ arising from the stochastic rotational modulation of spin interaction anisotropies has the following general form:

$$\mathbf{R} = -\sum_{kmpq} \mathbf{Q}_{km} \int_0^\infty G_{kmpq}(\tau) e^{-i\mathbf{H}_0\tau} \mathbf{Q}_{pq}^\dagger e^{i\mathbf{H}_0\tau} d\tau, \qquad \mathbf{H}_1(t) = \sum_{km} \mathfrak{D}_{km}^{(2)}(t) \mathbf{Q}_{km}$$

where $\mathbf{H}_0$ is the time-independent part of the spin Hamiltonian commutation superoperator, $\mathbf{Q}_{km}$ are the 25 irreducible spherical components of its anisotropic part $\mathbf{H}_1(t)$.

Rotational correlation functions $G_{kmpq}(t)$ are defined as ensemble averages of products of second-rank Wigner functions of molecular orientation:

$$G_{kmpq}(t) = \left\langle \mathfrak{D}_{km}^{(2)}(t) \mathfrak{D}_{pq}^{(2)*}(0) \right\rangle$$

In systems undergoing stochastic motion these become a linear combinations of decaying exponentials, $G(t) = \sum_n a_n e^{-\lambda_n t}$, which are scalars commuting with all matrices. The individual matrix-valued integrals in $\mathbf{R}$ are now a case of an auxiliary exponential relationship:

$$\int_0^T e^{-i\mathbf{H}_0 t} \mathbf{Q} e^{i(\mathbf{H}_0 + i\lambda\mathbf{1})t} dt = \mathbf{A}^\dagger \mathbf{B}, \qquad \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{0} & \mathbf{C} \end{pmatrix} = \exp\left[\begin{pmatrix} i\mathbf{H}_0 & \mathbf{Q} \\ \mathbf{0} & i\mathbf{H}_0 - \lambda\mathbf{1} \end{pmatrix} T \right]$$

The integration limit should be set to the accuracy goal for the relaxation superoperator [1].

Wall clock time (in seconds) comparison between the matrix-valued numerical quadrature method and the auxiliary matrix method. The spin systems indicated in the figure come from the Spinach library [2] example set.

The comparison is given relative to the quadrature method - it is impossible to diagonalize an 800,000 by 800,000 matrix during a NOESY calculation for ubiquitin.

The auxiliary exponential method permits accurate quantum mechanical spin relaxation theory treatment, including all cross-correlations and non-secular pathways, for liquid state NMR systems with up to about 2000 spins [2] when it is combined with restricted state space methods.

Rotating Frame Transformations

The interaction representation transformation splits the Hamiltonian matrix into the "large, simple" part $\mathbf{H}_0$ and the "small, complicated" part $\mathbf{H}_1$. The effective rotating frame Hamiltonian over a time interval $[0,T]$, with T equal to the *period* of the propagator $\exp(-i\mathbf{H}_0 t)$ is [12]:

$$\bar{\mathbf{H}} = \frac{i}{T} \ln_{(P)} \left[e^{-i(\mathbf{H}_0 + \mathbf{H}_1)T} \right]$$

where $\ln_{(P)}$ is the principal value of the logarithm. Under the typical interaction representation assumptions, $\|\mathbf{H}_1\| < \|\mathbf{H}_0\|$, and therefore the $\mathbf{H}_1$ term under the exponential in the previous equation is a correction to the $\mathbf{H}_0$ term. The corresponding Taylor series with respect to the $\mathbf{H}_1$ direction step length parameter α is:

$$\bar{\mathbf{H}}(\alpha) = \frac{i}{T} \ln\left[e^{-i(\mathbf{H}_0 + \alpha\mathbf{H}_1)T} \right] = \frac{i}{T} \sum_{n=1}^\infty \frac{\partial^n}{\partial \alpha^n} \left(\ln\left[e^{-i(\mathbf{H}_0 + \alpha\mathbf{H}_1)T} \right] \right) \Bigg|_{\alpha=0} \frac{\alpha^n}{n!}$$

The logarithm disappears after the first differentiation and the number of matrix terms is linear with respect to the approximation order n.

$$\bar{\mathbf{H}}^{(1)} = \frac{i}{T} \mathbf{D}_0^\dagger \mathbf{D}_1, \qquad \bar{\mathbf{H}}^{(2)} = \frac{i}{2T} \left(\mathbf{D}_1^\dagger \mathbf{D}_1 + \mathbf{D}_0^\dagger \mathbf{D}_2 \right)$$

$$\bar{\mathbf{H}}^{(3)} = \frac{i}{6T} \left(\mathbf{D}_2^\dagger \mathbf{D}_1 + 2\mathbf{D}_1^\dagger \mathbf{D}_2 + \mathbf{D}_0^\dagger \mathbf{D}_3 \right) \qquad \mathbf{D}_k = \frac{\partial^k e^{-i(\mathbf{H}_0 + \alpha\mathbf{H}_1)T}}{\partial \alpha^k} \Bigg|_{\alpha=0}$$

with the general expression also obtainable using binomial coefficients:

$$\bar{\mathbf{H}} = \frac{i}{T} \sum_{n=1}^\infty \frac{1}{n} \sum_{k=1}^n \frac{\mathbf{D}_{n-k}^\dagger \mathbf{D}_k}{(k-1)!(n-k)!}$$

The simplicity of this equation stands in sharp contrast with the very large expressions produced by Magnus expansions. The derivatives, $\mathbf{D}_k$ are known [4] to have the form that matches auxiliary matrix integrals:

$$\mathbf{D}_k(T) = k e^{\mathbf{A}T} \int_0^T e^{-\mathbf{A}t} \mathbf{B} \mathbf{D}_{k-1}(t) dt, \qquad \mathbf{D}_0(t) = e^{\mathbf{A}t}, \qquad \mathbf{A} = -i\mathbf{H}_0, \qquad \mathbf{B} = -i\mathbf{H}_1$$

This makes them easy to compute by constructing and exponentiating a sparse block-bidiagonal matrix:

$$\mathbf{M} = \begin{pmatrix} \mathbf{A} & \mathbf{B} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{A} & \mathbf{B} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{A} & \ddots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \ddots & \mathbf{B} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{A} \end{pmatrix} \qquad \exp(t\mathbf{M}) = \begin{pmatrix} \mathbf{D}_0 & \mathbf{D}_1/1! & \mathbf{D}_2/2! & \cdots & \mathbf{D}_k/k! \\ \mathbf{0} & \mathbf{D}_0 & \mathbf{D}_1/1! & \cdots & \mathbf{D}_{k-1}/(k-1)! \\ \mathbf{0} & \mathbf{0} & \mathbf{D}_0 & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \ddots & \mathbf{D}_1/1! \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{D}_0 \end{pmatrix}$$

and extracting the first block row from the result. This exponential is also sparse [6] if due care is taken to eliminate inconsequentially small elements from the non-zero index after each multiplication in the Taylor series procedure [2]. The number of blocks in $\mathbf{M}$ grows linearly and the effort of exponentiating it approximately quadratically with the rotating frame correction order n.

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Spin system of methylaziridine (state space dimension 9,889 using IK-2(4) basis [13] in Liouville space), the rotating frame transformation with respect to the Zeeman Hamiltonian of the 14N nucleus is computed in seconds and the scaling of the wall clock time with respect to the approx-imation order is quadratic. Second-order transformation is sufficient in practice, but terms up to order ten were computed and timed to illustrate the fundamental improvement in automation and scalability over the commutator series approach.

Molecular geometry, chemical shielding tensors, J-couplings, and nuclear quadrupolar interaction tensors were computed using GIAO DFT M06/cc-pVDZ method in Gaussian09.