

A Group Preserving Time Integration Scheme for Chemistry

L. Angelilli*, V. Raman*

Email: langelil@umich.edu

* Department of Aerospace Engineering, University of Michigan, Ann Arbor, MI 48105, USA

Abstract

The integration of the chemical system always presents considerable challenges due to the wide variety of time scales embedded within. Stiff integrators, necessary for the stability properties they offer, allow the system to evolve over significant time steps. However, backward integration generally becomes computationally expensive as the size of the chemical kinetics mechanism increases. Since a nonlinear ODE can always be recast as a Lie group action, we can constrain the integration onto the manifold with a Group Preserving Scheme (GPS). This property allows for the definition of high-order, explicit, unconditionally stable time integration schemes that are also Jacobian free. The performance of the GPS, compared in terms of computational time and accuracy with the canonical integrator CVODE, reveals a tenfold speed-up while preserving the same accuracy for large mechanisms.

Introduction

The field of computational chemistry frequently encounters the challenge of solving ordinary differential equations (ODEs) that arise in the modeling of chemical kinetics. These equations often exhibit stiff behavior due to the vastly different reaction time scales present within the system. Traditional numerical methods based on backward time integration, while broadly effective, can sometimes fail to maintain the inherent geometric properties of the underlying physical processes, leading to potential inaccuracies and inefficiencies.

Another approach to deal with stiffness is to adaptively filter the fast time scales according to the Computational Singular Perturbation (CSP) principles. This approach, encapsulated by the CSP solver [1], leverages a local low-dimensional manifold derived from the CSP fast/slow decomposition. It adaptively mitigates stiffness by selectively eliminating rapid scales from the vector of chemical source terms, leading to a simplified set of non-stiff equations. These equations can be integrated with explicit schemes using larger time-steps. However, the CSP solver depends on generating a costly on-the-fly basis known as the CSP projector, derived from the eigensystem of the Jacobian matrix associated with the local chemical source terms.

A second strategy introduces a data-based reduced-order model (ROM) designed to mitigate the stiffness derived from various chemical time scales [2]. The goal is to create a ROM that serves as a fluid surrogate for tracking the time evolution of the

thermochemical state vector (comprising temperature and species mass fractions) throughout a complex, stiff, and nonlinear ignition sequence. The approach utilizes an encode-forecast-decode strategy, incorporating a nonlinear autoencoder (AE) for reducing dimensionality (through encoding and decoding) combined with a neural ordinary differential equation (NODE) to model the system dynamics within the latent space provided by the AE.

The main issue of employing these techniques is that they are computationally expensive when the size of the mechanism becomes large and Lie group integrators present a promising solution to these challenges. For over a hundred years, Lie groups have been crucial in shaping our understanding of the geometry inherent in differential equations. It is widely thought that the concept of Lie groups, as part of the broader framework of differential geometry, is extremely useful in developing advanced numerical methods for discretizing ODEs while preserving their invariant properties. By maintaining the geometric structure and invariance of the original ODEs, these new methods are more precise, more stable, and more efficient than traditional numerical approaches [3].

This approach is particularly advantageous in the context of chemical kinetics, where the preservation of certain invariants—like total mass or energy—can be crucial for achieving physically realistic and stable simulations.

In this paper, we explore the application of Lie group integrators to the domain of chemistry, focusing on their potential to enhance the accuracy and stability of simulations compared to conventional numerical methods.

Numerical Methods

This section summarizes the numerical approach adopted to formulate the time integration schemes.

The chemistry evolution is described through a stiff ODE

$$\frac{d\mathbf{y}}{dt} = \mathbf{f}(\mathbf{y})$$

Where \mathbf{y} represents the state vector of the N_s species mass fractions and the RHS $\mathbf{f}(\mathbf{y})$ the chemical source term modeled by the Arrhenius law. From a mathematical perspective, the $\mathbf{y}(t)$ is a curve in R^N parametrized by the time t that goes from the initial condition to the equilibrium point. Recalling a fundamental theorem of differential geometry, since the curve is uniquely determined, we can define an *atlas* and finite number of *maps* to represent the curve, the \mathbf{y} is a manifold. Additionally, the tangent to $\mathbf{y}(t)$ is given by $\mathbf{f}(\mathbf{y})$, which is always defined. Since the tangent bundle is defined everywhere, the manifold is differentiable.

The main goal of this manuscript is to formulate a numerical scheme that constrains the integration to the manifold itself following Liu's idea of Group Preserving Scheme [3-4]. This is possible if and only if the tangent bundle can be expressed as a left Lie group action on the manifold, which means that there exists an operator H such that

$$\frac{d\mathbf{y}}{dt} = \mathbf{f}(\mathbf{y}) = \mathbf{H}(\mathbf{y})\mathbf{y}$$

And this operator must be differentiable, invertible and the inverse must be differentiable as well. To define a suitable operator \mathbf{H} , consider the augmented system $\mathbf{x} = [\mathbf{y} \ ||\mathbf{y}||]^T$. The time evolution of \mathbf{x} is then

$$\frac{d}{dt} \begin{pmatrix} \mathbf{y} \\ ||\mathbf{y}|| \end{pmatrix} = \begin{pmatrix} \mathbf{0}_{N_s \times N_s} & \frac{\mathbf{f}}{||\mathbf{y}||} \\ \frac{\mathbf{f}^T}{||\mathbf{y}||} & 0 \end{pmatrix} \begin{pmatrix} \mathbf{y} \\ ||\mathbf{y}|| \end{pmatrix} = \mathbf{H} \begin{pmatrix} \mathbf{y} \\ ||\mathbf{y}|| \end{pmatrix}$$

The operator \mathbf{H} is a *Special Orthogonal* Lie group ($SO(N_s)$), then we can integrate on manifold. The milestone of the integration on manifold is that we can define a linear operator linear \mathbf{A} (Lie algebra) such that

$$\begin{pmatrix} \mathbf{y} \\ ||\mathbf{y}|| \end{pmatrix}_{n+1} = \mathbf{A} \begin{pmatrix} \mathbf{y} \\ ||\mathbf{y}|| \end{pmatrix}_n$$

And is function of the Lie group. The Lie theorem guarantees that for each Lie group there exists a Lie algebra. A canonical way to define \mathbf{A} is by the exponential mapping, i.e. we consider the direct resolution of Eq. then

$$\mathbf{A} = \exp(\mathbf{H}\Delta t)$$

Although the exponential mapping is generally the best way of proceeding, it does not perform well when \mathbf{f} tends to 0, i.e. in the neighborhood of the initial condition and equilibrium point, with a subsequent stiffer integration. For this reason, the Cayley transform is more suitable to describe the corresponding Lie algebra

$$\begin{aligned} \mathbf{A}_n &= \text{Cay}(\Delta t \mathbf{H}_n) \\ &= \begin{pmatrix} \mathbf{I}_{N_s} + \frac{4\Delta t^2}{4||\mathbf{y}_n||^2 - \Delta t^2 ||\mathbf{f}_n||^2} \mathbf{f}_n \mathbf{f}_n^T & \frac{4\Delta t ||\mathbf{y}_n||}{4||\mathbf{y}_n||^2 - \Delta t^2 ||\mathbf{f}_n||^2} \mathbf{f}_n \\ \frac{4\Delta t ||\mathbf{y}_n||}{4||\mathbf{y}_n||^2 - \Delta t^2 ||\mathbf{f}_n||^2} \mathbf{f}_n^T & \frac{4||\mathbf{y}_n||^2 + \Delta t^2 ||\mathbf{f}_n||^2}{4||\mathbf{y}_n||^2 - \Delta t^2 ||\mathbf{f}_n||^2} \end{pmatrix} \end{aligned}$$

Taking only the first line of the RHS of Eq. we obtain a first order Group Preserving Scheme

$$\mathbf{y}_{n+1} = \mathbf{y}_n + \frac{4||\mathbf{y}_n||^2 + 2\Delta t \mathbf{f}_n \cdot \mathbf{y}_n}{4||\mathbf{y}_n||^2 - \Delta t^2 ||\mathbf{f}_n||^2} \Delta t \mathbf{f}_n = \mathbf{y}_n + \eta_n \mathbf{f}_n$$

Note that if $\mathbf{f}_n = \mathbf{0}$, $\eta_n = 1$ then the scheme can handle equilibrium points. However, to have a proper integration scheme $\eta_n > 0$, then it is necessary to impose another condition on the time step. In particular,

$$||\mathbf{f}_n|| \leq L ||\mathbf{y}_n||$$

Where L is the Lipschitz constant defined as the maximum absolute value of the eigenvalues of the Jacobian of the system. Since we want to build a Jacobian-free scheme, we will impose L arbitrarily large and function of the time step as

$$L = C \frac{\|f_n\|}{\|y_n\|} \text{ where } C = 10^{11} \Delta t_{global}$$

Where Δt_{global} is the prescribed time step of the simulation. To guarantee stability we need to integrate with smaller substeps defined as

$$\Delta t_{local} = \frac{1 - e^{-L\Delta t_{global}}}{L}$$

This ensures that the integration scheme is unconditionally stable.

Furthermore, to better reconstruct the trajectory, we want to use higher order integration schemes. Following the Butcher tableau to determine the weights of the 4th order Runge-Kutta scheme, we can write

$$\begin{aligned} \mathbf{k}_1 &= \mathbf{f}(\mathbf{y}_n) & \eta_1^c &= \frac{4\|\mathbf{y}_n\|^2 + 2(\Delta t/2)\mathbf{f}_n \cdot \mathbf{y}_n}{4\|\mathbf{y}_n\|^2 - (\Delta t/2)^2\|\mathbf{f}_n\|^2} (\Delta t/2) \\ \mathbf{y}_2 &= \mathbf{y}_n + \eta_1^c \mathbf{k}_1 & \mathbf{k}_2 &= \mathbf{f}(\mathbf{y}_2) & \eta_2^c &= \frac{4\|\mathbf{y}_n\|\|\mathbf{y}_2\| + 2(\Delta t/2)\mathbf{f}_n \cdot \mathbf{y}_n}{4\|\mathbf{y}_n\|^2 - (\Delta t/2)^2\|\mathbf{f}_n\|^2} (\Delta t/2) \\ \mathbf{y}_3 &= \mathbf{y}_n + \eta_2^c \mathbf{k}_2 & \mathbf{k}_3 &= \mathbf{f}(\mathbf{y}_3) & \eta_3^c &= \frac{4\|\mathbf{y}_n\|\|\mathbf{y}_3\| + 2(\Delta t/2)\mathbf{f}_n \cdot \mathbf{y}_n}{4\|\mathbf{y}_n\|^2 - (\Delta t/2)^2\|\mathbf{f}_n\|^2} (\Delta t/2) \\ \mathbf{y}_4 &= \mathbf{y}_n + \eta_3^c \mathbf{k}_3 & \mathbf{k}_4 &= \mathbf{f}(\mathbf{y}_4) \\ \mathbf{F}_n &= \frac{1}{6}(\mathbf{k}_1 + 2\mathbf{k}_2 + 2\mathbf{k}_3 + \mathbf{k}_4) & \eta_n &= \frac{4\|\mathbf{y}_n\|\|\mathbf{y}_3\| + 2\Delta t\mathbf{f}_n \cdot \mathbf{y}_n}{4\|\mathbf{y}_n\|^2 - \Delta t^2\|\mathbf{f}_n\|^2} \Delta t \\ \mathbf{y}_{n+1} &= \mathbf{y}_n + \eta_n \mathbf{F}_n \end{aligned}$$

To have a 4th order group preserving scheme.

Results

This section shows the performances of the Lie Group Preserving Scheme. To assess the performances of the integrator, we consider a constant volume and energy reactor of a n-dodecane oxygen mixture at the pressure of 10 bar and we compare the performances against the stiff integrator CVODE.

Figure 1 shows the execution time of a time step (t_{wall}) in function of the physical time of the simulation. The Group Preserving Scheme is 10~12 times faster than CVODE before achieving the equilibrium solution, while the evaluation at the equilibrium point is about 100 times faster.

Figure 2 shows a comparison of the temperature and key species profiles to analyze the accuracy of the proposed solver. In particular, the Lie integrator has been tested with three different time steps (10^{-9} , 10^{-8} and 10^{-7}) and the reference profiles are computed with Cantera. The Group Preserving Scheme accurately reconstructs the Cantera solution for any species independently from the choice of the time step. The only small discrepancy is observed for $\Delta t = 10^{-7}$ s for HO_2 implying that the scheme is robust.

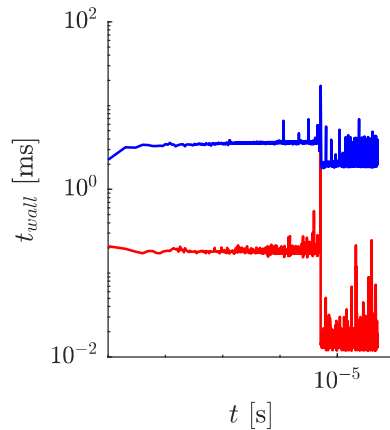


Figure 1 Execution time for the evaluation of each time step of a batch reactor.

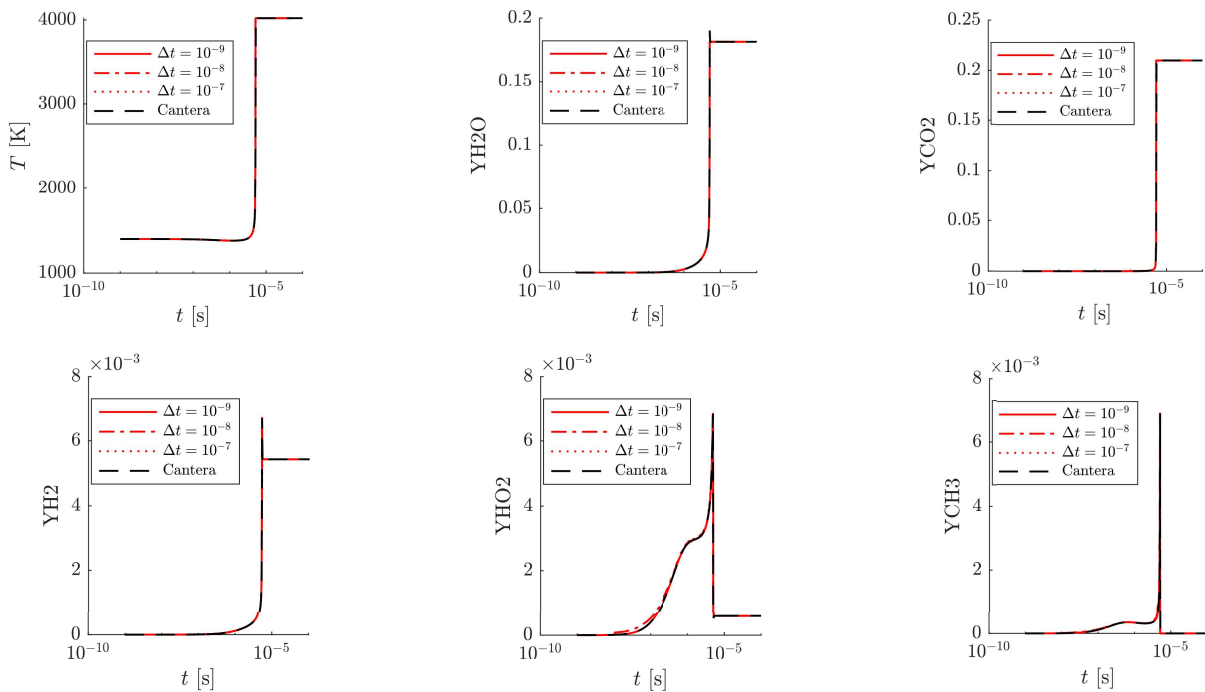


Figure 2 Comparison of the batch reactor with the Lie integrator with different time steps and the Cantera solution.

Conclusion

A Group Preserving Scheme based on the Lie group theory has been presented and its performances in terms of accuracy and speed are compared against the canonical solvers CVODE and Cantera. The new integrator achieves a speedup of 10 times during the actual evolution of the system and 100 times for the evaluation of the equilibrium point preserving the same accuracy as Cantera. The robustness of a manifold-constrained time integration scheme has been proved and this opens to a possible coupling with a full CFD solver.

References

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