Efficient geometric integrators for nonadiabatic quantum dynamics in the adiabatic representation

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Geometric integrators [1] of the Schrödinger equation conserve exactly many invariants of the exact solution. Among these integrators, the split-operator algorithm is explicit and easy to implement but, unfortunately, is restricted to systems whose Hamiltonian is separable into kinetic and potential terms. We present several implicit geometric integrators applicable to both separable and nonseparable Hamiltonians and, in particular, to the nonadiabatic molecular Hamiltonian in the adiabatic representation [2]. These integrators combine the dynamic Fourier method with recursive symmetric composition [3,4] of the trapezoidal rule or implicit midpoint method, which results in an arbitrary order of accuracy in the time step. Moreover, these integrators are exactly unitary, symplectic, symmetric, time-reversible, and stable and, in contrast to the split-operator algorithm, conserve energy exactly, regardless of the accuracy of the solution. The order of convergence and conservation of geometric properties are proven analytically and demonstrated numerically on a two-surface NaI model in the adiabatic representation. Although each step of the higher order integrators is more costly, these algorithms become the most efficient ones if higher accuracy is desired; a thousand-fold speedup compared to the second-order trapezoidal rule (the Crank-Nicolson method) was observed for a wavefunction convergence error of 10^{-10}. In a companion paper [5], we discuss analogous, arbitrary-order compositions of the split-operator algorithm and apply both types of geometric integrators to a higher-dimensional system in the diabatic representation.

References

1. E. Hairer, C. Lubich, and G. Wanner, *Geometric Numerical Integration: Structure-Preserving Algorithms for Ordinary Differential Equations* (Springer Berlin Heidelberg New York, 2006).
2. S. Choi and J. Vaníček, *J. Chem. Phys.* **150**, 204112 (2019).
3. M. Suzuki, *Phys. Lett. A* **146**, 319 (1990).
4. H. Yoshida, *Phys. Lett. A* **150**, 262 (1990)
5. J. Roulet, S. Choi, and J. Vaníček, *J. Chem. Phys.* **150**, 204113 (2019).