

# Efficient geometric integrators for nonadiabatic quantum dynamics. II. The diabatic representation

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The first- and second-order split-operator algorithms are widely used integrators for solving the time-dependent Schrödinger equation. These two integrators preserve some important geometric properties of the exact evolution operator: both are unitary and symplectic while only the second-order split-operator algorithm is time-reversible [1]. Higher-order split-operator based integrators are not commonly used because they are thought to be inefficient due to the large number of Fourier transforms they require. The aim of this study [2] is to show that higher-order integrators based on the split-operator algorithm can be much more efficient (by orders of magnitude) if higher accuracy is desired.

For this, the first- and second-order split-operator algorithms were implemented. In addition, we also implemented several higher-order integrators by composing the second-order split-operator algorithm with different composition schemes [3-6]. To test the different integrators, we performed a convergence analysis by computing the photodissociation of NaI on a two-state one-dimensional [7]. The effect of dimensionality on the efficiency and accuracy of the integrators was also explored using a three-state three-dimensional model of pyrazine [8].

From the results, we observe that the higher-order integrators converge faster, in the time step, and are also more efficient than the first- and second-order integrators in both one- and multi-dimensional systems. We also confirm that, as long they are obtained using symmetric composition methods, the higher-order integrators preserve all the geometric properties of the second-order split-operator algorithm.

## References

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