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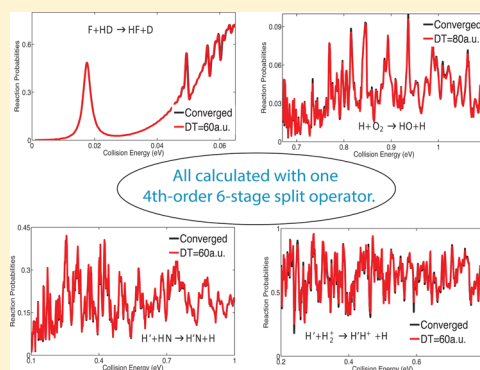
Efficient Fourth-Order Split Operator for Solving the Triatomic Reactive Schrödinger Equation in the Time-Dependent Wavepacket Approach

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ABSTRACT: An efficient fourth-order split operator (named 4A6a in the main text), which was presented in the work by Blanes and Moan and was a partitioned Runge–Kutta method (*J. Comput. Appl. Math.* **2002**, *142*, 313), is recommended for general usage in a reactive scattering calculation by the time-dependent quantum wavepacket method. This 4A6a propagator is constructed in a TVT form, that is, splitting in kinetic–potential–kinetic form, which is an optimal one among a series of higher-order split operators in examining with several typical triatomic reactive scattering processes, $\text{H} + \text{H}_2$, $\text{H} + \text{H}_2^+$, $\text{H} + \text{NH}$, $\text{H} + \text{O}_2$, and $\text{F} + \text{HD}$ reactions. A detailed comparison between the performances of higher-order split operators in the VTV form, that is, splitting in a potential–kinetic–potential, which was reported by Sun et al. (*Phys. Chem. Chem. Phys.* **2012**, *14*, 1827), and in the TVT form reported in the current work suggests that the recommended 4A6a operator in the TVT form always has good numerical efficiency. This fact may suggest that this fourth propagator in the TVT form can be safely chosen without any further examination, at least among all of the higher-order split operators tested in this work, to apply in an efficient time-dependent wavepacket numerical calculation for describing a triatomic reactive scattering process.



1. INTRODUCTION

The time-dependent quantum wavepacket (TDWP) method has become a popular theoretical computational tool for studying atom–diatom and polyatomic reaction scattering problems.^{1–3} This is mainly due to the fact that the TDWP method has computational advantage and physical intuition when compare to the time-independent close-coupling method. For a complicated reaction, such as on a potential energy surface (PES) with a deep well, it is still challenging for the modern TDWP method. At the same time, it is of great interest to extend the ability of a quantum dynamics study. Therefore, numerical development on improving the efficiency of the TDWP method is always important. On the other hand, it needs to be noted that some recent numerical developments for solving the eigenvalues and eigenvectors, such as the guided spectral transform method⁴ and Chebyshev real wavepacket method,⁵ have broken the numerical scaling law of the time-independent close-coupling method and obscured the difference between the time-independent and the time-dependent methods.

When we carry out quantum dynamics study by the TDWP method, an initial wavepacket needs to first be defined. Then, a suitable grid representation and an efficient time propagator need to be chosen. Finally, we are able to extract the scattering attributes from the evolving wavepacket. Thus, we roughly have

two choices to improve the numerical efficiency. One is to improve the numerical efficiency of the grid points, but the other one is to improve the numerical efficiency of the time propagator.

In the past decades, there has been much effort on developing an efficient grid representation method. Since the generalized discrete variable representation⁶ and fast Fourier transformation (FFT)⁷ were introduced into the chemical dynamics field in the 1980s, many kinds of discrete variable representation methods based upon classical polynomials have been proposed for further improving the numerical efficiency.^{8–20} With these advances, now accurate rovibrational eigenvalues and eigenfunctions of a 12D molecular PES without any approximation can be found,²¹ and molecular reactive scattering dynamics can be simulated including nine degrees of freedom.²²

In the time propagation of an initial wave function, the exponential evolution operator ($e^{-i\hat{H}t/\hbar}$, where \hat{H} is the Hamiltonian) must be approximated. The efficient wavepacket evolution method raised much interest in the past decades. The time propagation can be realized by expanding the exponential

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operator in terms of orthogonal polynomials such as Chebyshev polynomials⁸ or Faber polynomials,^{9,10} and so forth.^{11–14} Using orthogonal polynomials to propagate the wavepacket, usually the results can be obtained with high accuracy. However, the required iteration numbers have a direct ratio with the complication of the studied system, and we have little room to adjust. An alternative and popular propagator is based on the second-order split operator algorithm.^{15,16} One of the interesting properties of the second-order split operator is that it conserves the norm of the wavepacket, even when an unphysically large time step is used. As a result, the propagation is exceedingly stable. The adopted time step can be varied to some extent, which is decided by the desired accuracy of the results. Thus, the numerical effort is flexible to a certain degree. There are also other methods, such as the second-order differencing scheme, the Crank–Nicholson method, and the iterative Lanczos propagator, for integrating the time-dependent Schrödinger equation.^{17–20}

Currently, most reactive scattering calculations were performed with the second-order split operator^{2,23–27} before the introduction of the Chebyshev real wavepacket method.⁵ In order to find which approach is more efficient, Sun et al.²⁸ have made a comparison between the second-order split operator method and the Chebyshev real wavepacket method. They found that the second-order split operator method is more efficient when the wavepacket is propagated on the flat PES. While for the PES with a deep potential well, which supports long-lived resonance states, the Chebyshev real wavepacket method becomes more efficient. However, in such a calculation, to obtain fully converged scattering information, the Chebyshev real wavepacket method also requires a large number of iterations.

There is much interest in investigating the application of the higher-order split operators in solving the Schrödinger equation.^{29–55} Blanes and his co-workers derived many higher-order symplectic integrators for numerically solving ordinary differential equations and also applied the one-dimensional Schrödinger equation.^{56,57} In 2013, Bader et al. proposed higher-order time-splitting integrators with complex parameters for finding the eigenvalue of the one-dimensional Schrödinger equation with a time-independent potential.³³ Bandrauk and his co-workers proposed higher-order exponential time-splitting integrators with complex parameters for solving the Schrödinger equation.³⁴ In recent years, there is focused interest for exploring efficient higher-order time-splitting integrators for solving the nonlinear Schrödinger equation, which are derived based upon the Magnus expansion and have a form both with and without a potential gradient.^{35–37,39–42} Along with the development of attosecond physics, numerical simulation of electronic dynamics with a Coulomb potential by the Schrödinger equation raises increasing interest. However, the potential involving singularity and application of a higher-order time-splitting method needs special exploration.^{40,41}

In the past, application of a higher-order time-splitting method for solving the Schrödinger equation describing chemical reactive processes is rather rare. This may be due to the fact that the Hamiltonian describing the molecular reaction is much more complicated than that in a one-dimensional model, and the real PESs exhibit various shapes; the numerical performance of the proposed higher-order integrator in the literature, which was mostly obtained on a one-dimensional model, may be not reliable. Therefore, a direct application of

the higher-order integrator is not possible, and numerical examination of them on real systems is necessary.

Sun et al.⁵⁵ in 2012 made an extensive numerical test with the higher-order time-splitting integrators reported in the literature on several typical triatomic reactive scattering processes. In their work, the integrators in an exponential VTV form (splitting in the potential–kinetic–potential form; please see below) were employed, without paying special attention to their original theoretically required form due to the nature of numerical training with complicated real systems. This is reasoned by the following numerical results. We note here that we have no interest in the higher-order integrators in the symplectic form,³² which usually have strict requirement with the largest allowed time and are not useful in a practical low-accuracy reactive scattering calculations.

In the work by Sun et al.,⁵⁵ some higher-order split operator in the VTV form, which in general are more efficient than the Chebyshev real wavepacket method, are recommended for a reactive scattering involving a deep potential well. The second-order split operator in the VTV form can be written as

$$e^{-i\hat{H}\Delta t/\hbar} = e^{-i(\hat{T}+\hat{V})\Delta t/\hbar} \approx e^{-i\hat{V}\Delta t/2\hbar} e^{-i\hat{T}\Delta t/\hbar} e^{-i\hat{V}\Delta t/2\hbar}$$

where the kinetic operator is at the central position. It is known that there is some, even slight, difference between the performance of the second-order split operator method in the TVT and VTV forms. The second-order split operator in the TVT form can be written as

$$e^{-i\hat{H}\Delta t/\hbar} = e^{-i(\hat{T}+\hat{V})\Delta t/\hbar} \approx e^{-i\hat{T}\Delta t/2\hbar} e^{-i\hat{V}\Delta t/\hbar} e^{-i\hat{T}\Delta t/2\hbar}$$

where the potential operator is at the central position.⁵⁸ Due to the mathematically compact structure of the coefficients of the higher-order split operators,⁵⁶ it may be expected that there is a substantial difference between the higher-order split operators in the VTV and TVT forms. For instance, the positions of the kinetic and potential operators in higher-order split operators of a partitioned Runge–Kutta (PRK) type are interchangeable; however, in a Runge–Kutta–Nyström type, theoretically, the positions are not interchangeable. Therefore, it is highly desirable to make a thorough comparison between the efficiency of the higher split operators in both forms, on several typical reactive scatterings. From the investigation, more efficient time propagators for a general time-dependent wavepacket calculation may be found, which brings about the motivation of the present work.

This paper is organized as follows: Section 2 introduces the related theoretical methods. In section 3, the higher-order split operators constructed in the TVT form are examined on the typical $\text{H} + \text{H}_2$, $\text{H} + \text{H}_2^+$, $\text{H} + \text{O}_2$, $\text{H} + \text{NH}$, and $\text{F} + \text{HD}$ reactions. We then make a comparison of the numerical efficiency of these higher-order split operators in the VTV form and in the TVT form. Section 4 concludes our present work.

2. THEORY

The theoretical methods adopted in the present work are similar to those in the work by Sun et al.;⁵⁵ therefore, we will only make a brief introduction here.

Second-Order Split Operator Method. A time-dependent Schrödinger equation can be generally written as

$$i\frac{\partial}{\partial t}\Psi(\vec{r}, t) = \hat{H}\Psi(\vec{r}, t) = (\hat{T} + \hat{V})\Psi(\vec{r}, t) \quad (1)$$

where V is a function of \vec{r} and is time-independent in describing a reactive scattering process. By the second-order split operator method approximation, its numerical solution can be written as

$$\Psi(\vec{r}, t + \Delta t) = e^{-i\hat{H}\Delta t}\Psi(\vec{r}, t) = S_2(\Delta t)\Psi(\vec{r}, t) + O(\Delta t^3) \quad (2)$$

where

$$S_2(\Delta t) = \exp\left(-\frac{i\Delta t V}{2}\right) \exp(-i\Delta t T) \exp\left(-\frac{i\Delta t V}{2}\right) \quad (3)$$

or

$$S_2(\Delta t) = \exp\left(-\frac{i\Delta t T}{2}\right) \exp(-i\Delta t V) \exp\left(-\frac{i\Delta t T}{2}\right) \quad (4)$$

We define a higher-order split operator, which is constituted by a series of combination of eq 3, that is in the VTV form, but a higher-order split operator, which is constituted by a series of combination of eq 4, is in the TVT form.

Higher-Order Split Operators. There are various ways to construct a higher-order split operator, as reported in the literature.^{29–55} For any desired order split operator, the simplest way is by combining a basic lower-order integrator with carefully designed coefficients,^{44–46} and one can obtain a higher-order integrator by the following formula

$$S_n(\Delta t) = S_2(\omega_k \Delta t) \dots S_2(\omega_1 \Delta t) S_2(\omega_0 \Delta t) S_2(\omega_1 \Delta t) \dots S_2(\omega_k \Delta t) \quad (5)$$

The optimization of the coefficients ω_k is intricate. Many higher-order split operators were reported in the literature following this procedure.^{47–49} One can also construct a higher-order split operator in a more general form

$$S_n(\Delta t) = \exp(-i\alpha_{k+1}T) \exp(-i\beta_k V) \exp(-i\alpha_k T) \\ \exp(-i\beta_{k-1}V) \dots \exp(-i\alpha_2 T) \exp(-i\beta_1 V) \\ \exp(-i\alpha_1 T) \quad (6)$$

A number of higher-order split operators constructed in this way were reported also in the literature,^{47,49–51} and the parameters in this form are more flexible for obtaining efficient results.

Following work by Sun et al.,⁵⁵ the higher-order split operator constructed in a form of eq 5 are categorized as class S series because their parameters have center-reflection symmetry. The higher-order integrators, 4S5, 4S7, and 4S9, examined in the present work are all constructed in this way. These three integrators are put forward in the work by Suzuki,⁴⁴ and their parameters are defined by the following equations

$$\alpha = \frac{1}{(2n - (2nm^{2k})^{1/(2k+1)})} \quad \beta = \frac{1}{(1 - 2n\alpha/m)}$$

where for the 4S5, 4S7, and 4S9, $n = 2, 3$, and 4 , respectively, but $k = m = 1$, $\omega_0 = \beta$, and $\omega_{i \neq 0} \equiv \alpha$.

The higher-order split operators constructed by eq 6 are categorized as class A series. The higher-order split operators, 4A4a, 4A6a, 4A6b, and 6A8, examined in this work are all constructed according to eq 6. We note here that the names of the higher-order split operators exactly follow the definition in the work by Sun et al.⁵⁵ The 4A4a propagator is put forward by McLachlan and has parameters as follows:⁵³

$$\alpha_1 = \frac{1}{2} - \frac{\sqrt{7/8}}{3} \quad \alpha_2 = -\frac{1}{3} + \frac{\sqrt{7/8}}{3} \\ \alpha_3 = 1 - 2(\alpha_1 + \alpha_2) \quad \alpha_4 = \alpha_2 \quad \alpha_5 = \alpha_1 \\ \beta_1 = 1 \quad \beta_2 = \frac{1}{2} - \beta_1 = -\frac{1}{2} \quad \beta_3 = \beta_2 \quad \beta_4 = \beta_1$$

The 4A6a and 4A6b were reported by Blanes and Moan.⁵⁰ The parameters for 4A6a are

$$\alpha_1 = 0.0792036964311957 \\ \alpha_2 = 0.353172906049774 \\ \alpha_3 = -0.0420650803577195 \\ \alpha_4 = 1 - 2(\alpha_1 + \alpha_2 + \alpha_3) \\ \alpha_5 = \alpha_3, \alpha_6 = \alpha_2, \alpha_7 = \alpha_1 \\ \beta_1 = 0.209515106613362 \\ \beta_2 = -0.143831773179818 \\ \beta_3 = \frac{1}{2} - (\beta_1 + \beta_2) \\ \beta_4 = \beta_3, \beta_5 = \beta_2, \beta_6 = \beta_1$$

and those for 4A6b are

$$\alpha_1 = 0.0829844064174052 \\ \alpha_2 = 0.396309801498368 \\ \alpha_3 = -0.0390563049223486 \\ \alpha_4 = 1 - 2(\alpha_1 + \alpha_2 + \alpha_3) \\ \alpha_5 = \alpha_3, \alpha_6 = \alpha_2, \alpha_7 = \alpha_1 \\ \beta_1 = 0.245298957184271 \\ \beta_2 = 0.604872665711080 \\ \beta_3 = \frac{1}{2} - (\beta_1 + \beta_2) \\ \beta_4 = \beta_3, \beta_5 = \beta_2, \beta_6 = \beta_1$$

The 6A8 integrator was put forward in the work by Schlier and Seiter⁵¹ and has parameters as

$$\alpha_1 = 0.06942944346252987735848865824703402 \\ \alpha_2 = -0.13315519831598209409961309951373512 \\ \alpha_3 = 0.00129038917981078974230481746443284 \\ \alpha_4 = 0.42243536567364142699881962380226825 \\ \alpha_5 = 1 - 2(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4) \\ \alpha_6 = \alpha_4, \alpha_7 = \alpha_3, \alpha_8 = \alpha_2, \alpha_9 = \alpha_1 \\ \beta_1 = 0.28487837717280084052745346456657828 \\ \beta_2 = 0.32783975759612945412054678367325547 \\ \beta_3 = -0.38122104271932629475622784374211274 \\ \beta_4 = 12 - (\beta_1 + \beta_2 + \beta_3) \\ \beta_5 = \beta_4, \beta_6 = \beta_3, \beta_7 = \beta_2, \beta_8 = \beta_1$$

In a practical implementation, the 4S7 propagator is a fourth-order propagator with seven stages (one time step needs seven times action of H on the wave function), which can be written as

$$S_4(\Delta_t) = S_2(\omega_3\Delta_t)S_2(\omega_2\Delta_t)S_2(\omega_1\Delta_t)S_2(\omega_0\Delta_t)S_2(\omega_1\Delta_t)S_2(\omega_2\Delta_t)S_2(\omega_3\Delta_t) \quad (7)$$

but the 4A4a is a fourth-order propagator with four stages (one time step needs four times action of H on the wave function), which can be written as

$$S_n(\Delta_t) = \exp(-i\alpha_5 T) \exp(-i\beta_4 V) \exp\left(-i\alpha_4 \frac{T}{2}\right) \exp\left(-i\alpha_4 \frac{T}{2}\right) \exp(-i\beta_3 V) \exp\left(-i\alpha_3 \frac{T}{2}\right) \exp\left(-i\alpha_3 \frac{T}{2}\right) \exp(-i\beta_2 V) \exp\left(-i\alpha_2 \frac{T}{2}\right) \exp\left(-i\alpha_2 \frac{T}{2}\right) \exp(-i\beta_1 V) \exp(-i\alpha_1 T) \quad (8)$$

The implementation of a higher-order split operator simply is a continuous combination of a second-order split operator, which suggests the easy programming of a higher-order split operator in practice.

In order to make a clear comparison between the efficiency of higher-order split operators, we define the numerical error as a function of Δ_t^s . The Δ_t^s is defined as a normalized time step or effective time step, which is the time step Δ_t divided by the number of the coordinate-momentum representation switches required in the calculation, that is, divided by the number of stages of the propagator

$$\Delta_t^s = \frac{\Delta_t}{N_s} \quad (9)$$

as defined in the work by Sun et al.⁵⁵ The normalized time step Δ_t^s is the averaged time step for each evaluation of Hamiltonian action on the wave function of the split operator. For example, the normalized time step Δ_t^s of the 4A4a is equal to $\Delta_t/4$ with $N_s = 4$. The normalized time step has a direct relation to the computational efficiency of a higher-order split operator.

Triatomic Reactive Scattering Theory in Reactant Jacobi Coordinate. In this section, we describe the basic theoretical details for a triatomic reactive scattering calculation using time-dependent wavepacket method related to the current work. For more details, one may refer to our previous work.²⁷

The propagation of the wavepacket is propagated exclusively in reactant Jacobi coordinates in the body-fixed frame by the second-order split operator or a higher-order propagator. In the reactant coordinates, the Hamiltonian for a given total angular momentum J can be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu_{R_a}} \frac{\partial^2}{\partial^2 R_a} - \frac{\hbar^2}{2\mu_{r_a}} \frac{\partial^2}{\partial^2 r_a} + \frac{(J-j)^2}{2\mu_{R_a} R_a^2} + \frac{j^2}{2\mu_{r_a} r_a^2} + V \quad (10)$$

where μ_{R_a} is the reduced mass between the center of mass of A and BC, J is the total angular momentum operator, j is the rotational angular momentum operator of BC, and μ_{r_a} is the reduced mass of BC.

A direct product sinc-discrete variable representation is adopted for the two radial degrees of freedom, and a finite basis representation of spherical harmonic basis $y_{jk}(\theta_\alpha)$ is used for the angular degree of freedom. Thus, the time-dependent wave function in the body-fixed frame representation can be written as^{2,44}

$$\Psi^{JMe}(R_\alpha, r_\alpha, t) = \sum_{K_\alpha} D_{MK_\alpha}^{J\epsilon*}(\Omega_\alpha) \psi_\alpha(t, R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}; K_\alpha) \quad (11)$$

where $D_{MK_\alpha}^{J\epsilon*}(\Omega_\alpha)$ is the parity-adapted normalized rotation matrix, depending only on the Euler angles Ω_α . In eq 11, the wave function $\psi_\alpha(t, R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}; K_\alpha)$, which depends on three internal coordinates of the system and projection of the total angular momentum K_α on the body-fixed frame z axis, can be expanded as

$$\psi_\alpha(t, R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}; K_\alpha) = \sum_{n,m,j} F_{nmj}^{K_\alpha}(t) u_n(R_\alpha) \phi_m(r_\alpha) y_{jk_\alpha}(\theta_\alpha) \quad (12)$$

where n and m are the translational basis labels, $u_n(R_\alpha)$ and $\phi_m(r_\alpha)$ are the translational basis functions for R and r , respectively, and $y_{jk_\alpha} = [(2j+1)/4\pi]^{1/2} d_{K_\alpha 0}^{j0}$ are spherical harmonics. $d_{K_\alpha K_\nu}^j$ is a reduced Wigner rotational matrix⁵⁹ with $K_\nu = 0$.

Time Propagation of the Initial Wavepacket. In a wavepacket calculation, the initial wavepacket should be constructed first. For a triatomic reaction scattering, the initial wavepacket in the SF representation ($\nu_{0j_0l_0}$)^{60,61} can be constructed simply as

$$\Psi_{\alpha\nu_0 j_0 l_0}^{JMe}(t=0) = G(R_\alpha) \phi_{\nu_0 j_0}(r_\alpha) |JMj_0 l_0 \epsilon\rangle \quad (13)$$

Where $|JMj_0 l_0 \epsilon\rangle$ is the total angular momentum eigenfunction in the SF representation with parity of the system $\epsilon = (-1)^{j_0+l_0}$, $\phi_{\nu_0 j_0}(r_\alpha)$ is the rovibrational eigenfunction of the diatomic reactant BC, and $G(R_\alpha)$ is a Gaussian shape function.

During the wavepacket propagation, the fast sine transform is used to evaluate the action of the radial Hamiltonian operators on the wavepacket. The action of the angular kinetic operators on the wavepacket can be evaluated straightforwardly in a finite basis representation of spherical harmonics. The corresponding discrete variable representation technique^{6,28,62} is used to evaluate the action of the potential energy operator in the angular degree of the freedom.

The propagation of the wave function is carried out by the second-order split operator method in the TVT form as

$$\begin{aligned} \Psi(R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}, t + \Delta_t; K_\alpha) &= S_S(\Delta_t) \Psi(R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}, t; K_\alpha) \\ &\approx e^{-iT\Delta_t/2\hbar} e^{-iV\Delta_t/\hbar} e^{-iT\Delta_t/2\hbar} \Psi(R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}, t; K_\alpha) \end{aligned} \quad (14)$$

where V is the PES of the triatomic system

$$e^{-iT\Delta_t/\hbar} = S_2^T(\Delta_t) \approx e^{-iT_j\Delta_t/2\hbar} e^{-i(T_r+T_R)\Delta_t/\hbar} e^{-iT_j\Delta_t/2\hbar} \quad (15)$$

and

$$T_j = \frac{(J-j)^2}{2\mu_{R_a} R_a^2} + \frac{j^2}{2\mu_{r_a} r_a^2}$$

is the angular momentum operator.

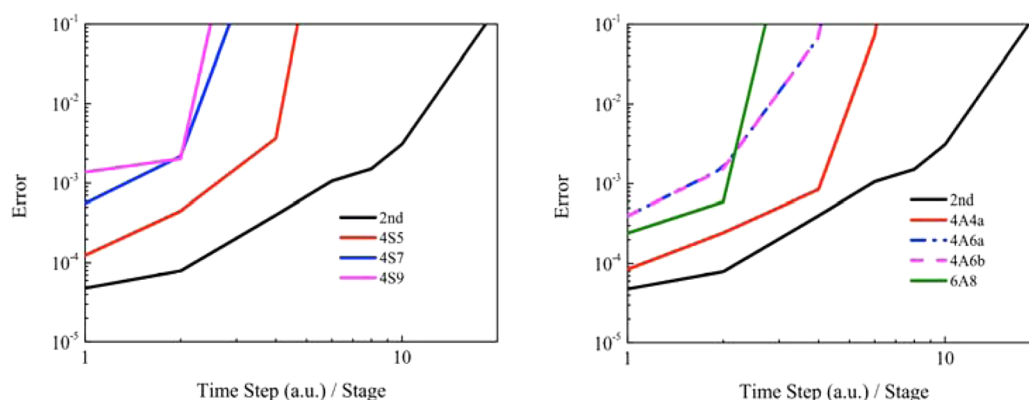


Figure 1. $\log_{10}(\text{error})$ versus $\log_{10}(\text{normalized time step})$ associated with the higher-order split operator methods on the 3D H + H₂ reactive scattering calculations with $J = 0$. (The higher-order split operators in the left panel are of the S series, but those in the right panel are of A series.)

$$T_r = -\frac{\hbar^2}{2\mu_\alpha} \frac{\partial^2}{\partial^2 r_\alpha} \quad \text{and} \quad T_R = -\frac{\hbar^2}{2\mu_{R_\alpha}} \frac{\partial^2}{\partial^2 R_\alpha}$$

are the radial kinetic operators of the triatomic system.

As shown in eq 15, the kinetic operator T has been split using the second-order split operator with respect to the kinetic operators T_r and T_R to reduce the computational effort. The propagation carried out by the second-order split operator method in the VTV form can be expressed in a similar way.

The implementation of a higher-order split operator is straightforward by a combination of a series of the second-order split operator, either in the TVT or VTV form, but with a carefully designed local time step, as in the work by Sun et al.⁵⁵

What is need to be noted here is that there is an upper limit of the time step for a higher-order split operator due to the requirement of the time–energy transform. The time step should meet the condition $2\pi/\Delta t > E_{\max} - E_{\min}$ (where $E_{\max} - E_{\min}$ is the maximal energy distribution of the wavepacket), which suggests that a higher-order split operator with more than eight stages is hardly useful because of the effective time step cannot be large and its numerical efficiency cannot be high.

Finally, a damping function, which has the same form as that in the work by Sun et al.,⁵⁵ is employed to prevent the wavepacket reflecting back from the boundaries.

3. RESULT AND DISCUSSION

In order to measure the efficiency of higher-order split operators, the H + H₂, H + H₂⁺, H + NH, H + O₂, and F + HD reactions are taken as the training samples in this work. We estimate the error from the total reaction probabilities, which is calculated by the flux formalism as

$$P(E) = \frac{1}{\mu_f} \text{Im} \left[\left\langle \Psi(\vec{R}, \vec{r}; E) \left| (r - r_E) \frac{\partial}{\partial r} \right| \Psi(\vec{R}, \vec{r}; E) \right\rangle \right] \quad (16)$$

where

$$\Psi(\vec{R}, \vec{r}; E) = \frac{1}{a(E)} \int \exp(iEt) \Psi(\vec{R}, \vec{r}; E) dt \quad (17)$$

and $a(E)$ is determined by the initial wavepacket.^{23,28}

The error is calculated according to

$$\sigma = \frac{1}{M} \sum_{k=1}^M \frac{|P(E_k) - P^0(E_k)|}{P^0(E_k)} \quad (18)$$

where M is the number of the measured collision energies E_k . For the H + H₂ reaction, M is 680, and the measured E_k evenly distribute in the range of [0.1, 3.5] eV. For the H + H₂⁺, H + NH, H + O₂, and F + HD reactions, M is chosen as 600, 451, 530, and 790, and E_k evenly distribute in the range of [0.2, 0.8], [0.1, 1.0], [0.67, 1.2], and [0.001, 0.08] eV, respectively.

A quantum reactive scattering calculation is quite different from a determination of bound states. Often, resonance peaks are difficult to assign in experimental results of reactive scattering because the summation of many different partial waves usually smears out any resonance peak features appearing in a single partial wave calculation. Therefore, accurate determination of the energy position usually is unnecessary. On the other hand, overcomplete basis functions usually are difficult to apply for a reaction involving a deep potential well due to the limitation of available computational resources. Further, due to the complicated distribution of the kinetic energy of the wave function in a reactive scattering calculation, a perfect absorption potential is hard to find. Another fact is that it is still difficult to obtain an accurate enough PES to predict the resonance peaks with small enough error, regardless of the advances in ab initio calculations on small molecules. Altogether, we conclude that an error of 10^{-2} of the total reaction probabilities may be acceptable for most purposes of a reactive scattering calculation.⁵⁵ In the present work, we adopt an error of 10^{-2} as the standard to judge how efficient the examined higher-order split operator is. The “converged” numerical results P^0 are calculated by an eighth HOSO with a small time step.

In the following numerical calculations searching for a generally efficient higher-order split operator in the TVT form, we do not make numerical examination for all of the higher-order split operators that appeared in the literature, as listed in the work by Sun et al.⁵⁵ Only very limited optimal ones will be examined, with the reference from the 1D numerical convergence trend reported in the work by Sun et al.⁵⁵ These higher-order split operators examined in the following numerical calculations are expected to be among the most efficient higher-order split operators for a reactive scattering calculation.

H + H₂ Reaction. In order to identify the effectiveness of the higher-order split operator in the TVT form for the direct reaction type, the simplest H + H₂ system is taken as the prototype in the present work. This reaction is a typical direct

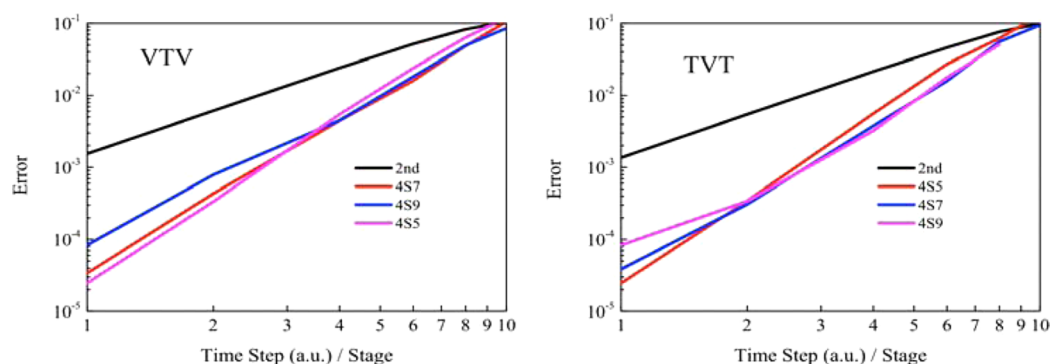


Figure 2. $\text{Log}_{10}(\text{error})$ versus $\text{log}_{10}(\text{normalized time step})$ associated with the higher-order split operator methods of the S series on the 3D $\text{H} + \text{H}_2^+$ reactive scattering calculations with $J = 0$. (The higher-order split operators in the left panel are in the VTV form, and those in the right panel are in the TVT form.)

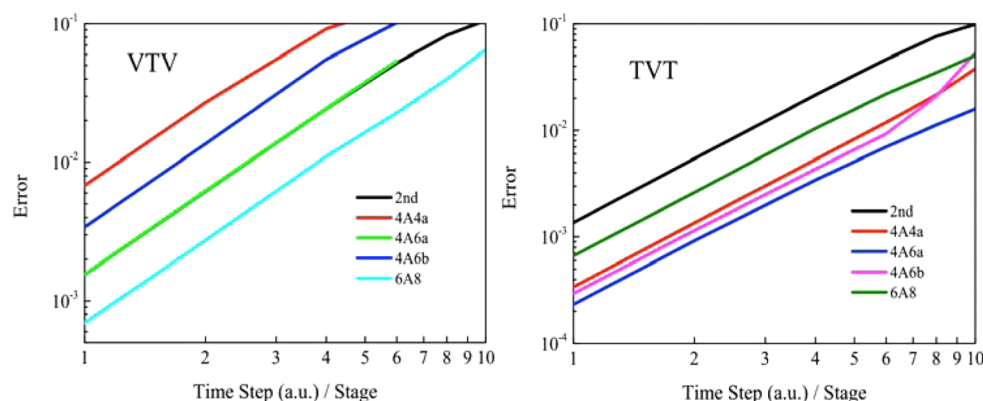


Figure 3. $\text{Log}_{10}(\text{error})$ versus $\text{log}_{10}(\text{normalized time step})$ associated with the higher-order split operator methods of the A series on the 3D $\text{H} + \text{H}_2^+$ reactive scattering calculations with $J = 0$. (The higher-order split operators in the left panel are in the VTV form, and those in the right panel are in the TVT form. Note the different ranges for the y axis of the two panels.)

reaction, and the adiabatic BKMP2⁶³ PES is employed in the reaction scattering calculation.

The numerical results of the higher-order split operators of the S series and A series for this reaction are collected in the left panel and right panel of Figure 1, respectively. As shown in Figure 1, the higher-order split operators of both S series and A series are all less effective than the second-order split operator if we chose the convergence of 10^{-2} as a tolerable error limit. Because the reaction $\text{H} + \text{H}_2$ is direct with no potential well on the reaction path and does not involve a long-lived complex, we do not need to worry much about an accumulation error of the propagators. As we expect, the second-order split operator is always the optimal choice for the direct type reaction. This conclusion is consistent with the literature report delivered by Sun et al.²⁸

$\text{H} + \text{H}_2^+$ System. In order to identify the efficiency of the higher-order split operators for the ion–molecule type reaction, the PPKT2 PES⁶⁴ of the $\text{H} + \text{H}_2^+$ reaction system is chosen for numerical examination because we found that the higher-order split operators in the VTV form are hardly more effective than the second-order split operator; as shown below, even it has a deep potential well. The convergence of the A series and S series higher-order split operators in the TVT and VTV forms for the $\text{H} + \text{H}_2^+$ reaction are shown in Figures 2 and 3, respectively.

From the plots in Figure 2, we can find that all of these S series higher-order split operator have better numerical efficiency than the second-order split operator, regardless of

the TVT or VTV form. However, there is a small difference between the performances of the S series in the TVT and VTV form for this reaction, which can be effectively ignored in a real reactive scattering calculation. These higher-order split operators are about two times faster than the second-order split operator for obtaining numerical results with the tolerable error as 10^{-2} .

However, as shown in Figure 3, there is substantial difference between the efficiency of the A series higher-order split operators in the VTV and TVT forms for this reaction. For the higher-order split operator in the VTV form, the 4A4a and 4A6b propagators are less effective than the second-order split operator. The efficiency of the 4A6a propagator is nearly the same as the second-order split operator. Only the 6A8 propagator is slightly more efficient than the second-order split operator. These four higher-order split operators are among the best ones in the VTV form, and numerical results of other higher-order split operators are not shown here. Therefore, it looks that the A series higher-order split operator in the VTV form is not a good choice for the $\text{H} + \text{H}_2^+$ reaction, and we should turn to the S series higher-order split operators; even they are only about 2 times faster than the second-order split operator.

In contrast, from the right panel of Figure 3, we can easily find that the higher-order split operators in the TVT form of the A series all are much more efficient than the higher-order split operators. Especially, the 4A6a propagator is most efficient, which is about 3 times faster than the second-order

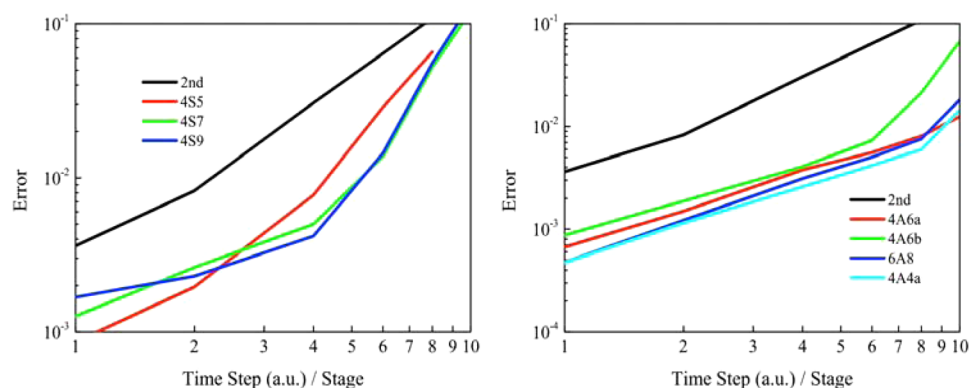


Figure 4. $\text{Log}_{10}(\text{error})$ versus $\text{log}_{10}(\text{normalized time step})$ associated with the higher-order split operator methods on the 3D H + NH reactive scattering calculations with $J = 0$. (The higher-order split operators in the left panel belong to the S series, but those in the right panel belong to the A series.)

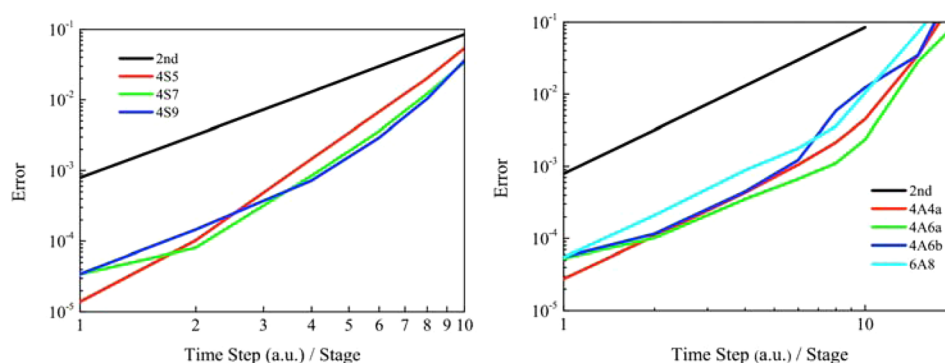


Figure 5. $\text{Log}_{10}(\text{error})$ versus $\text{log}_{10}(\text{normalized time step})$ associated with the higher-order split operator methods on the 3D H + O₂ reactive scattering calculations with $J = 0$. (The higher-order split operators in the left panel belong to the S series, but those in the right panel belong to the A series.)

split operator. Apparently, the higher-order split operators of the A series in the TVT form are more efficient than those in the VTV form for the H + H₂⁺ reaction, and the 4A6a propagator in the TVT form is the most optimal choice.

H + NH System. The H + NH reaction, which is a typical reaction that has a deep well on the PES,⁶⁵ is difficult for the higher-order split operators in the VTV form, as shown in the work by Sun et al.⁵⁵ In their work, they found that the best higher-order split operator in the VTV form is only 2 times faster than the second-order split operator. Also, the S series higher-order split operators are more efficient than the A series in the VTV form for this reaction, as reported by Sun et al.⁵⁵

Anyway, a closer comparison between the results of the S series higher-order split operators in the VTV and TVT forms indicates that there is only a slight difference between them. For the higher-order split operators of the S series in the TVT form, the 4S7 and 4S9 propagators are most efficient, which only are about 2.5 times faster than the second-order split operator. However, as shown in Figure 4, the higher-order split operators of the A series in the TVT form are much faster. Especially, the 4A6a and 4A4a are the best and about 4.3 times faster than the second-order split operator. Apparently, for this reaction, the 4A6a and 4A4a in the TVT form are the optimal choices for this reaction.

H + O₂ System. There is a potential well of about 2.3 eV in the PES of the H + O₂ reaction, which is a little shallower than that in the H + NH reaction. It is well-known that the total reaction probabilities for the H + O₂ and H + NH reactions at a

specified J are characterized by many resonance peaks. The higher-order split operators in the TVT form have been proved to be efficient for the H + O₂ reaction. The numerical convergence of higher-order split operators in the TVT form of the S series and A series is listed in the left and right panels of Figure 5, respectively. As shown in Figure 5, we observe again that the A series higher-order split operators are more efficient than S series ones in the TVT form. The situations are very similar to those of the H + H₂⁺ and H + NH reactions, and we found that the 4A6a propagator is the most efficient among the A series higher order split operators and the 4S9 propagator is the most efficient propagator among the S series higher-order split operator.

In the work by Sun et al.,⁵⁵ the best propagator of the S series higher-order split operators of the VTV form for this reaction is the 4S7 propagator, and we need an effective time step of 6.5 au to obtain results with an error of 10^{-2} . However, for the S series propagators in the TVT form, the 4S9 propagator is the most efficient and with an effective time step of 8.0 au to reach the numerical results with an error of 10^{-2} . For the A series higher-order split operators in the VTV form, the best propagator is 4A6b, and we need an effective time step of 16.5 au to obtain numerical results with an error of 10^{-2} , whereas for the higher-order split operator in the TVT form here, the 4A6a propagator is most efficient, and the effective time step of 13.6 au can give results with an error of 10^{-2} .

From the above discussion, we can find that the S series higher-order split operators in the TVT form are more efficient

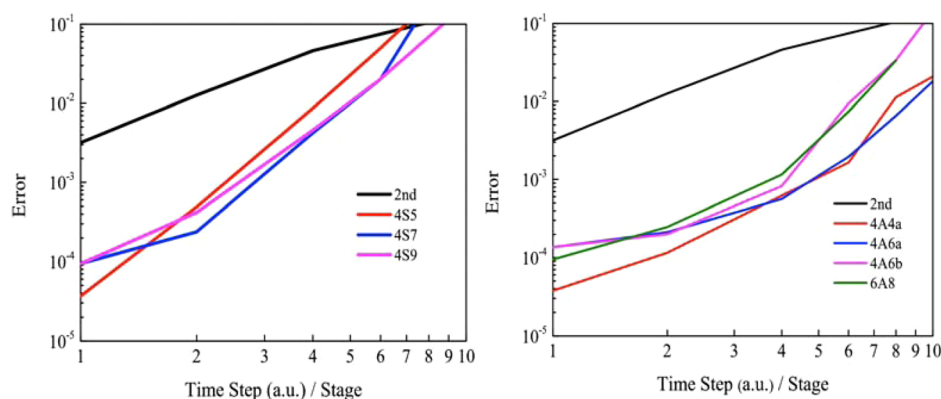


Figure 6. $\log_{10}(\text{error})$ versus $\log_{10}(\text{normalized time step})$ associated with the higher-order split operator methods on the 3D F + HD reactive scattering calculations with $J = 0$. (The left panel is the higher-order split operators of the S series, but those in the right panel are the higher-order split operators of the A series.)

Table 1. Most Efficient Propagators in the VTV and TVT Forms for the $\text{H} + \text{H}_2^+$, $\text{H} + \text{NH}$, $\text{H} + \text{O}_2$, and $\text{F} + \text{HD}$ Reactions^a

reaction	TVT form		VTV form ⁵⁵	
	A series/time step (au)	S series/time step (au)	A series/time step (au)	S series/time step (au)
$\text{H} + \text{H}_2^+$	4A6a/8.0	4S7, 4S9/5.1	6A8/3.8	4S7, 4S9/5.1
$\text{H} + \text{NH}$	4A6a, 4A4a/9.1	4S7, 4S9/5.2	6A8/2.5	4S9/5.0
$\text{H} + \text{O}_2$	4A6a/13.6	4S9/8.0	4A6b/16.5	4S7/6.5
$\text{F} + \text{HD}$	4A6a/9.0	4S7, 4S9/5.1	6A8/10.0	4S7/4.5

^aFor these propagators, the effective time steps (au), which give numerical results with an error of 10^{-2} , are also listed in the table.

than those in the VTV form for this reaction. The A series propagators in the TVT form are a little less efficient than those in the VTV form. Anyway, the higher-order split operators of the A series in both the TVT and VTV forms are very efficient for the $\text{H} + \text{O}_2$ reaction and much more efficient than the S series higher-order split operators.

F + HD System. The F + HD reaction is a typical direct reaction without any intermediate potential well but having dynamical Feshbach resonances.⁶⁶ The FXZ PES^{67,68} is applied in the following calculations, and the convergence test results are given in Figure 6. As shown in Figure 6, the situations are very similar to those of the other reactions $\text{H} + \text{NH}$ and $\text{H} + \text{O}_2$. The higher-order split operators of the A series are more efficient than the S series propagators. The 4A6a and 4S9 propagators are the best in the A series and S series propagators, respectively.

For the S series propagators in the VTV form,⁵⁵ the 4S7 propagator is the most efficient for this reaction, and the effective time step of 4.5 au can give numerical results with an error of 10^{-2} , whereas for the S series propagators in the TVT form, the 4S9 is the best, and the effective time step of 5.1 au can reach a convergence error of 10^{-2} . For the A series higher-order split operators in the VTV and TVT forms, the best propagators are 6A8 and 4A6a, respectively. The effective time steps of 10.0 and 9.0 au are able to present results with an error of 10^{-2} , respectively.

Therefore, the S series higher-order split operators in the TVT form are a little better than those in the VTV form, whereas for the A series propagators, the higher-order split operators in the VTV form are a little better than those in the TVT form for the F + HD reaction. However, we can find that the difference in the numerical efficiency of the best higher-order split operator in the TVT form and VTV form is rather small, whether of the A series or the S series higher-order split operators.

4. DISCUSSION AND CONCLUSION

In order to present a clear picture for the results obtained above and reported by Sun et al.,⁵⁵ the most efficient propagators in the TVT form and in the VTV form are collected in Table 1, along with the corresponding effective time steps that are able to give numerical results with an error of 10^{-2} .

As shown in Table 1, we can find that for the higher-order split operators of the S series, the best ones in the TVT form for these reactions are all more efficient than those in the VTV form, whereas for the higher-order split operators of the A series, the VTV form is a little better than the TVT form for the $\text{H} + \text{O}_2$ and F + HD reactions, but the difference may be ignored in a practical molecular reaction scattering dynamics calculation. However, the higher-order split operators in the TVT form have significant improvement in the numerical efficiency, as compared with the higher-order split operators in the VTV form, for the $\text{H} + \text{H}_2^+$ and $\text{H} + \text{NH}$ reactions.

From Table 1, we can also find some interesting rules of the higher-order split operators for these reactions, such as, for the S series propagators in the TVT form, the 4S9 propagator is always best and the 4A6a propagator is the most efficient for the A series propagators in the TVT form. In the TVT form, the best A series propagators are always more efficient than the best S series propagators, whereas, the higher-order split operators in the VTV form do not follow such rules. The best S series propagators are not always more efficient than the best A series propagators. At the same time, for these reactions, there are two best higher-order split operators of the A series, 4A6b and 6A8. Therefore, when we adopt the higher-order split operator in the VTV form in a real reaction scattering calculation, we may need to test several higher-order split operators of both the A and S series to determine which one is an optimal propagator. In contrast, we do not need to do so many test calculations to determine the optimal higher-order

split operators in the TVT form. We can simply choose the 4A6a propagator for a real reaction scattering calculation. Of course, this conclusion is drawn within our limited training reactions. In the future, with more applications of these higher-order split operators, the conclusion might possibly be altered.

In short, the convergence of the higher-order split operators implemented in the VTV or TVT form is quite different, which may be due to the mathematical properties⁵⁶ and the features of the applied PES. Within the limited training reactions examined in this work, we have seen that the higher-order split operators in the TVT form are always more efficient than those in the VTV form, regardless of the higher-order split operator of the S series or A series (except for the H + O₂ and F + HD reactions, but the 4A6a in the VTV and TVT forms are both very efficient), and the best one is the fourth-order split operator, 4A6a.

The implementation of the 4A6a propagator in a quantum dynamics code is given in eq 6, which can be coded straightforward from the implementation of the second-order split operator. We emphasized here that the convergence behavior of the 4A6a in the TVT form for all of the examined reactions is rather stable and should be a generally efficient 4A6a.

We hope that our present work will stimulate more applications of the higher-order split operators in a quantum dynamic calculation, and our investigations may suggest that the higher-order split operators mathematically have developed into a very mature stage.

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Notes

The authors declare no competing financial interest.

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