

Second-order splitting schemes for a class of reactive systems

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ABSTRACT

We consider the numerical time integration of a class of reaction–transport systems that are described by a set of ordinary differential equations for primary variables. In the governing equations, the terms involved may require the knowledge of secondary variables, which are functions of the primary variables. Specifically, we consider the case where, given the primary variables, the evaluation of the secondary variables is computationally expensive. To solve this class of reaction–transport equations, we develop and demonstrate several computationally efficient splitting schemes, wherein the portions of the governing equations containing chemical reaction terms are separated from those parts containing the transport terms. A computationally efficient solution to the transport sub-step is achieved through the use of linearization or predictor–corrector methods. The splitting schemes are applied to the reactive flow in a continuously stirred tank reactor (CSTR) with the Davis–Skodjic reaction model, to the CO + H₂ oxidation in a CSTR with detailed chemical kinetics, and to a reaction–diffusion system with an extension of the Oregonator model of the Belousov–Zhabotinsky reaction. As demonstrated in the test problems, the proposed splitting schemes, which yield efficient solutions to the transport sub-step, achieve second-order accuracy in time.

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1. Introduction

In this study, we consider the numerical solution of the time dependent reaction–transport systems described by the following set of nonlinear ordinary differential equations:

$$\frac{d\mathbf{r}}{dt} = \mathbf{S}(\mathbf{r}, \mathbf{u}(\mathbf{r})) + \mathbf{M}(\mathbf{r}, \mathbf{u}(\mathbf{r}), t), \quad (1)$$

where: the dependent variables \mathbf{r} (of dimension n_r) are called primary variables; the variables \mathbf{u} (of dimension n_u), which are known functions of \mathbf{r} , are called secondary variables; \mathbf{S} (of dimension n_r) denotes the rate-of-change of the primary variables due to chemical reactions; and \mathbf{M} (of dimension n_r) denotes the rate-of-change of the primary variables due to transport processes such as diffusion, heat loss, or inflow/outflow. For general reaction–diffusion systems described by a set of partial differential equations (PDEs), the governing PDEs can be transformed into a set of ODEs of the form of Eq. (1) by the method of lines. That is, by discretizing in space only, one transforms the PDEs into a set of ODEs for the variables at the grid nodes. It is important to appreciate the mathematical difference between the reaction operator \mathbf{S} and the transport operator \mathbf{M} . The operator \mathbf{S} is independent of time; in the method of lines, the reaction process is separate for each grid point. The operator \mathbf{M} may depend on time because of external interactions or time-dependent boundary conditions; in the method of lines, the

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transport process is not separate for different grid points. As shown in Eq. (1), the reaction and transport terms may require the knowledge of the secondary variables, which are functions of primary variables. In this study, we focus on the circumstance in which the evaluation of the function $\mathbf{u}(\mathbf{r})$ is computationally expensive. Moreover we assume that the reaction operator \mathbf{S} is stiff whereas \mathbf{M} is not.

Equations of the form of Eq. (1) arise in the formulation of a variety of physical problems. One example is the description of reactive flows with enthalpy being the (primary) energy variable. The governing equations are solved for the primary variables \mathbf{r} consisting of the velocities, pressure, enthalpy and the concentrations of the chemical species involved. The secondary variables \mathbf{u} may consist of density and temperature. The knowledge of density and temperature is needed for evaluating transport properties and the corresponding terms in the energy equation (if heat loss due to convection or radiation is present). For a mixture of thermally perfect gases, the standard nonlinear polynomial dependencies of enthalpy on temperature (see CHEMKIN [1]) are often used for all chemical species involved. Due to this nonlinear relationship, given the enthalpy of the mixture and species concentrations, an iteration procedure has to be employed to obtain temperature. This may incur a significant computational burden for certain simulations.

Another example where equations of the form of Eq. (1) arise is in the reduced description of reactive flows. (For simplicity, we consider the reduced description of reactive flows, where the pressure is taken to be constant and uniform.) In the reduced description, the reactive system is described in terms of the primary variables \mathbf{r} , which can be taken to be enthalpy, concentrations of some species and linear combinations of the concentrations of all the species (depending on the method used). For example, the primary variables \mathbf{r} can consist of enthalpy and the concentrations of specified “major” species. The secondary variables \mathbf{u} can consist of the concentrations of the “minor” species and temperature. In the reduced description, the secondary variables \mathbf{u} , which are functions of the primary variables \mathbf{r} , are needed for evaluating chemical reactions. The knowledge of \mathbf{u} is also needed for evaluating transport properties and heat loss processes (if heat loss due to convection or radiation is present) in the transport term. In the reduced description provided by different dimension-reduction methods such as the quasi-steady state assumption (QSSA) method [2], the rate-controlled constrained equilibrium (RCCE) method [3], and the ICE-PIC method [4], the evaluation of $\mathbf{u}(\mathbf{r})$ is computationally expensive. For example, in the RCCE method, given the primary variables \mathbf{r} , a constrained equilibrium problem must be solved to obtain the secondary variables $\mathbf{u}(\mathbf{r})$. In ICE-PIC \mathbf{u} is obtained from \mathbf{r} by a yet more expensive process involving the solution of stiff ODEs.

Eq. (1) can be efficiently solved by numerical schemes based on an operator-splitting approach. These schemes split the governing equation into sub-equations, usually with each having a single operator capturing only a portion of the physics present, and integrate each separately and sequentially in time to advance to the next time step [5,6]. In [7,8], for example, operator-splitting schemes are used to separate chemical reaction processes from transport processes in atmospheric modeling simulations. The results from the sub-steps are then combined in such a way that the final solution accurately approximates the solution to the original equation. In recent years, operator-splitting schemes have been widely applied in reactive flow calculations [9–16]. More recently, operator-splitting schemes are combined with the storage/retrieval method, known as *in situ* adaptive tabulation (ISAT) [17], for unsteady reactive flow calculations with detailed chemistry [18,19]. In this study, we develop and demonstrate several computationally efficient, second-order accurate in time, splitting schemes for solving Eq. (1).

The outline of the remainder of the paper is as follows. In Section 2, we first describe the Strang splitting scheme [20] for solving Eq. (1). Then computationally more efficient methods for the transport sub-step are proposed. In Section 2, we also propose splitting schemes based on staggered time steps. Numerical tests are reported in Section 3. Section 4 provides a discussion and conclusions.

2. Splitting schemes

To solve Eq. (1) numerically, the time is discretized in increments $\Delta t \equiv (t_f - t_0)/n_t$, where t_0 and t_f are the initial and final simulation time respectively, and $n_t + 1$ is the total number of time steps. (For simplicity, non-constant Δt is not discussed here.) Then, time is discretely represented by $t_n = t_0 + n\Delta t$, where $n = 0, 1, 2, \dots, n_t$. The integration of Eq. (1) forward in time is then performed as follows: starting from $n = 0$, the schemes march in time steps Δt from t_n to t_{n+1} . In the following, we describe different splitting schemes.

2.1. Strang splitting scheme

With the Strang splitting scheme [20], reaction is separated from the transport process, and Eq. (1) is integrated over a time step Δt as follows:

- Sub-step 1. The reaction terms are integrated over a time interval $\Delta t/2$ by solving

$$\frac{d\mathbf{r}^a}{dt} = \mathbf{S}(\mathbf{r}^a, \mathbf{u}(\mathbf{r}^a)). \quad (2)$$

The initial condition $\mathbf{r}^a(0)$ is taken to be the final state \mathbf{r} from the previous time step, and the solution to Eq. (2) is denoted by $\mathbf{r}^a(\Delta t/2)$.

- Sub-step 2. The transport terms are integrated over a time interval Δt by solving

$$\frac{d\mathbf{r}^b}{dt} = \mathbf{M}(\mathbf{r}^b, \mathbf{u}(\mathbf{r}^b), t). \tag{3}$$

The initial condition $\mathbf{r}^b(0)$ corresponds to the final state of the system from the previous sub-step, $\mathbf{r}^d(\Delta t/2)$, and the solution to Eq. (3) is denoted by $\mathbf{r}^b(\Delta t)$.

- Sub-step 3. A sub-step identical to Sub-step 1 is performed taking as the initial condition the final state of the system from Sub-step 2, $\mathbf{r}^b(\Delta t)$. At the completion of this sub-step, the final state of the system is given by $\mathbf{r}^c(\Delta t/2)$. This is the solution at the end of the current time step and serves as the initial condition for the next time step.

The classical analysis [11,20] (which considers the limit $\Delta t \rightarrow 0$) shows that the splitting error in the Strang splitting scheme is of order Δt^2 . If each of the three sub-steps in the above splitting procedure is solved accurately (with at least second-order accuracy in time), the Strang splitting scheme is second-order accurate in time. As discussed by Sportisse [11], the classical analysis of the splitting error may fail when the Strang scheme is applied to a stiff system with Δt in practice being much larger than the smallest time scales. This is the case here where a large time step is sought for solving the above sub-steps, in particular, larger than the smallest chemical time scales. Under this circumstance, the accuracy of the Strang scheme is determined by numerical tests [11,18,19].

The reaction and transport sub-steps can be solved accurately using an ODE solver such as DDASAC [33]. However in the Strang splitting scheme, both the reaction sub-steps and transport sub-step are expensive to integrate due to the required expensive function evaluation of the secondary variables (and stiffness in the reaction term). For the reaction sub-steps, the governing equation Eq. (2) is autonomous. Given the initial condition $\mathbf{r}(0)$, the state of the system $\mathbf{r}(\Delta t/2)$ after fixed $\Delta t/2$ depends only on $\mathbf{r}(0)$, and can be efficiently computed by a storage/retrieval method such as ISAT [17–19]. That is, ISAT tabulates $\mathbf{r}(\Delta t/2)$ as a function of $\mathbf{r}(0)$. Given a new initial condition, whenever possible, ISAT uses a linear approximation to obtain the primary variables after the reaction sub-step, which is accurate to within a user-specified error tolerance. Only when needed, new table entries (consisting of the primary variables before and after reaction sub-step) are added for possible later use, where the primary variables after reaction are obtained by integrating Eq. (2) using the ODE integrator DDASAC.

In this study, we focus on the efficient solution to the transport sub-step (Sub-step 2). Splitting schemes are introduced with modifications to Sub-step 2. The purpose is to obtain a more efficient solution to the transport sub-step by minimizing the number of expensive function evaluations $\mathbf{u}(\mathbf{r})$, while at the same time achieving second-order accuracy in time for solving the reactive system Eq. (1). In Section 3 the numerical accuracy of the proposed splitting schemes is demonstrated through different numerical tests.

2.2. Modified Strang splitting schemes with a predictor–corrector for the transport sub-step

To simplify notation, Eq. (3) is rewritten as

$$\frac{d\mathbf{r}}{dt} = \mathbf{M}(\mathbf{r}, \mathbf{u}(\mathbf{r}), t). \tag{4}$$

The initial condition is denoted by \mathbf{r}^0 , which corresponds to the final state of the system from the previous sub-step $\mathbf{r}^d(\Delta t/2)$ (i.e., $\mathbf{r}^0 \equiv \mathbf{r}^d(\Delta t/2)$). The solution to the transport sub-step (i.e., Eq. (4)) after a time step Δt is denoted by $\mathbf{r}(\Delta t)$. In the following, two modified Strang splitting schemes are described with modifications to the transport sub-step based on predictor–corrector methods.

2.2.1. Predictor–corrector method PC1

The second-order accurate solution for the transport sub-step (Sub-step 2) can be obtained through the following predictor–corrector method, referred to as PC1.

- Predictor: The predictor for $\mathbf{r}(\Delta t)$ given by Eq. (4) is obtained by integrating over a time interval Δt by solving

$$\frac{d\mathbf{r}}{dt} = \mathbf{M}(\mathbf{r}, \mathbf{u}^0, t), \tag{5}$$

with the initial condition being $\mathbf{r}^0 = \mathbf{r}^d(\Delta t/2)$ and the secondary variables $\mathbf{u}^0 \equiv \mathbf{u}(\mathbf{r}^0)$ being fixed at the values obtained after Sub-step 1. The solution to Eq. (5) after time step Δt is denoted by \mathbf{r}^p . The secondary variables evaluated based on \mathbf{r}^p are denoted by \mathbf{u}^p , i.e.,

$$\mathbf{u}^p \equiv \mathbf{u}(\mathbf{r}^p). \tag{6}$$

- Corrector: The corrector for $\mathbf{r}(\Delta t)$ given by Eq. (4) is then obtained by integrating over a time interval Δt by solving

$$\frac{d\mathbf{r}}{dt} = \frac{1}{2}\mathbf{M}(\mathbf{r}, \mathbf{u}^0, t) + \frac{1}{2}\mathbf{M}(\mathbf{r}, \mathbf{u}^p, t) \tag{7}$$

with initial condition \mathbf{r}^0 . The solution to Eq. (7) is $\mathbf{r}(\Delta t)$, which is the final state of the system after Sub-step 2.

The scheme PC1 requires the knowledge of the secondary variables \mathbf{u}^0 and \mathbf{u}^p , respectively, which are obtained by directly performing two expensive function evaluations, i.e., $\mathbf{u}^0 \equiv \mathbf{u}(\mathbf{r}^0)$ and $\mathbf{u}^p \equiv \mathbf{u}(\mathbf{r}^p)$. Notice that the secondary variables in the governing ODEs (Eqs. (5) and (7)) for the predictor and corrector are fixed. With \mathbf{u}^0 and \mathbf{u}^p having been obtained, without additional expensive function evaluations of the secondary variables, Eqs. (5) and (7) can be solved accurately (either analytically or using an ODE solver) or they can be solved using computationally more efficient but less accurate numerical schemes. In this study, the ODEs (Eqs. (5) and (7)) are solved accurately, i.e., with numerical errors that are small compared to the splitting error, so that (over the range of Δt considered) the only significant numerical error is the splitting error.

2.2.2. Predictor–corrector method PC2

An alternative method, referred to as PC2, is to use an approximation to \mathbf{u}^p obtained from the following linear extrapolation (instead of using Eq. (6))

$$\mathbf{u}^p \approx \mathbf{u}^0 + (\mathbf{r}^p - \mathbf{r}^0) \cdot \nabla_{\mathbf{r}} \mathbf{u} |_{\mathbf{r}=\mathbf{r}^0}, \quad (8)$$

where $\nabla_{\mathbf{r}} \mathbf{u}$ are the gradients, i.e., $\partial u_i / \partial r_j$. This scheme requires the expensive function evaluation $\mathbf{u}^0 \equiv \mathbf{u}(\mathbf{r}^0)$, but does not need the expensive function evaluation for \mathbf{u}^p after the predictor step. However it requires the evaluation of $\nabla_{\mathbf{r}} \mathbf{u}$. When divided differences are employed to evaluate $\nabla_{\mathbf{r}} \mathbf{u}$, at least $n_r + 1$ function evaluations of $\mathbf{u}(\mathbf{r})$ are required. For example, when a two-point stencil (with one point at \mathbf{r}^0) is used for the gradient operator, $n_r + 1$ function evaluations of $\mathbf{u}(\mathbf{r})$ are needed. Hence in general, compared to PC1, the scheme PC2 requires at least n_r more function evaluations of $\mathbf{u}(\mathbf{r})$ in the transport sub-step (Sub-step 2). However, there are some circumstances (e.g., in the reduced description of reactive flows [21,22]) in which the gradient $\nabla_{\mathbf{r}} \mathbf{u}$ is known from the previous reaction sub-step. Under these circumstances, compared to PC1, the scheme PC2 requires one less function evaluation $\mathbf{u}(\mathbf{r})$ in the transport sub-step (Sub-step 2).

2.3. Modified Strang splitting scheme with linearization for the transport sub-step

The second-order accurate solution for transport sub-step (Sub-step 2) can be obtained through the following linearization method, referred to as Lin. With \mathbf{r}^0 being the initial condition (for the transport fractional sub-step) and $\mathbf{u}^0 \equiv \mathbf{u}(\mathbf{r}^0)$ being the corresponding secondary variables, the transport term \mathbf{M} , linearized about the initial condition is

$$M_i(\mathbf{r}, \mathbf{u}(\mathbf{r}), t) \approx M_i(\mathbf{r}^0, \mathbf{u}^0, t) + \frac{\partial M_i}{\partial r_k} (r_k - r_k^0) + \frac{\partial M_i}{\partial u_j} \frac{\partial u_j}{\partial r_k} (r_k - r_k^0) = M_i^0 + D_{ik}^0 (r_k - r_k^0), \quad (9)$$

where

$$M_i^0 \equiv M_i(\mathbf{r}^0, \mathbf{u}^0, t), \quad (10)$$

$$D_{ik}^0 \equiv \frac{\partial M_i}{\partial r_k} + \frac{\partial M_i}{\partial u_j} \frac{\partial u_j}{\partial r_k}, \quad (11)$$

the summation convention applies, and all the derivatives are evaluated at $(\mathbf{r}, \mathbf{u}) = (\mathbf{r}^0, \mathbf{u}^0)$.

Thus with this linearization, the governing equation for the transport sub-step (Eq. (3)) becomes

$$\frac{dr_i}{dt} = M_i^0 + D_{ik}^0 (r_k - r_k^0), \quad (12)$$

which has an analytic solution (when \mathbf{M} is independent of t). The linearization method requires only one function evaluation $\mathbf{u}(\mathbf{r})$ in the transport sub-step, i.e., $\mathbf{u}^0 \equiv \mathbf{u}(\mathbf{r}^0)$. However it requires the evaluation of the matrix \mathbf{D}^0 , which is in general computationally expensive. Under certain circumstances (e.g., in the reduced description of reactive flows [21,22]) \mathbf{D}^0 is known from the previous reaction sub-step, and compared to PC1 the scheme Lin requires one less function evaluation $\mathbf{u}(\mathbf{r})$ in the transport sub-step.

2.4. Splitting schemes based on staggered time steps

All the splitting schemes described above are based on the Strang splitting scheme with two reaction sub-steps of length $\Delta t/2$ and one transport sub-step of length Δt per time step. Under some circumstances [22], a single reaction fractional step of length Δt and a single transport sub-step of length Δt per time step is preferable (while still maintaining second-order accuracy in time). For example when ISAT [17] is employed for reaction sub-steps in PDF [23] modeling of turbulent combustion, the computational cost scales with the number of reaction sub-steps that need to be performed. Hence it is computationally significant to decrease the number of reaction sub-steps by a factor of two. This can be achieved based on staggered time steps. Fig. 1 illustrates the proposed staggered splitting scheme for solving Eq. (1). On the time axis, time is discretely represented by $t_n = t_0 + n\Delta t$, where $n = 0, 1, 2, \dots, n_t$: the full time steps are labeled $n, n + 1, \dots$, and the middle points are labeled $n + 1/2, n + 3/2, \dots$. The primary variables at the full time step $n + 1$ are denoted by \mathbf{r}^{n+1} and are obtained by integrating Eq. (1) forward in time as follows:

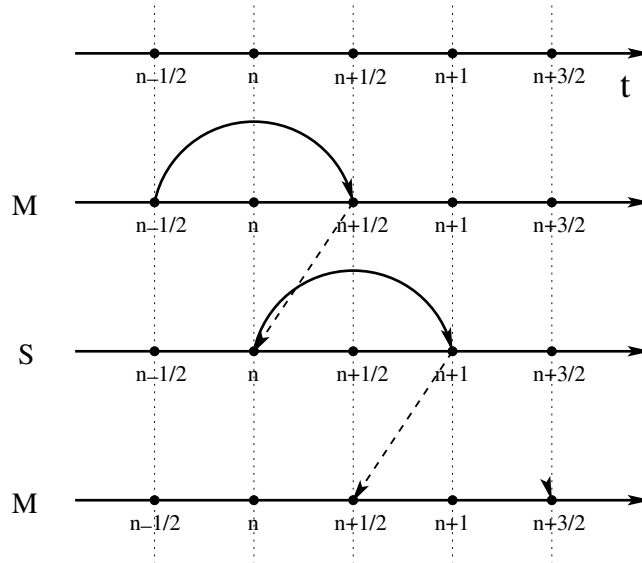


Fig. 1. The time axis showing the staggered splitting scheme for solving Eq. (1). The time is discretized in increments $\Delta t/2$. Symbols *S* and *M* denote reaction sub-step (of length Δt) and transport sub-step (of length Δt), respectively.

- From time step n to $n + 1$, a reaction sub-step of length Δt is performed. The initial conditions are taken to be the final state of the system from the previous transport sub-step from $n - 1/2$ to $n + 1/2$. The solution to this reaction sub-step is denoted by \mathbf{r}_S^{n+1} .
- Following the reaction sub-step, a transport sub-step (of length Δt) is performed from $n + 1/2$ to $n + 3/2$, with the initial conditions being the final state of the system from the previous reaction sub-step, \mathbf{r}_S^{n+1} . The solution to this transport sub-step is denoted by $\mathbf{r}_M^{n+3/2}$. For the transport sub-step, all the methods described in the previous subsections can be applied.

For the first time step (i.e., $n = 0$), the initial conditions for the reaction sub-step need special treatment and are taken to be the final state of the system from the first transport sub-step, which is of length $\Delta t/2$ and from 0 to $1/2$. The initial conditions for the first transport sub-step is specified as the initial conditions for a particular system.

The primary variables \mathbf{r}^{n+1} , i.e., the state of the system at time step $n + 1$ are obtained as

$$\mathbf{r}^{n+1} \approx \frac{1}{2} (\mathbf{r}_S^{n+1} + \mathbf{r}_M^{n+3/2}). \tag{13}$$

As demonstrated below, splitting schemes based on the above staggered time steps achieve second-order accuracy in time (even with a single reaction fractional step of length Δt and a single transport sub-step of length Δt per time step).

2.5. Discussion

In the above, we introduce two classes of splitting schemes: one is based on the Strang splitting scheme, and the other is based on staggered time steps. For schemes based on the Strang splitting scheme, for each time step Δt , it involves two reaction sub-steps of length $\Delta t/2$ and one transport sub-step of length Δt . For schemes based on staggered time steps, for each time step Δt , it involves a single reaction fractional step of length Δt and a single transport sub-step of length Δt .

For the transport sub-step, either method PC1, method PC2, or method Lin can be employed. For PC1, two function evaluations $\mathbf{u}(\mathbf{r})$ are required to obtain \mathbf{u}^a and \mathbf{u}^b in the transport sub-step. For PC2 and Lin, only one function evaluation (for evaluating \mathbf{u}^a) is required. However they require the evaluation of other information such as the derivatives $\nabla_{\mathbf{r}}\mathbf{u}$ or the matrix \mathbf{D}^0 , which is in general computationally expensive. Under certain circumstances [21,22] where $\nabla_{\mathbf{r}}\mathbf{u}$ and \mathbf{D}^0 are known from the previous reaction sub-step, compared to PC1, schemes PC2 and Lin require one less function evaluation $\mathbf{u}(\mathbf{r})$ and are computationally advantageous. It is worth mentioning that for some problems such as the reduced description of reactive flows [22], even \mathbf{u}^a may be known from the previous reaction sub-step, and therefore no function evaluation is needed for evaluating \mathbf{u}^a during the transport sub-step.

3. Numerical tests

In this Section, we apply the various splitting methods to three test problems and examine their performance.

3.1. Extension of the Davis–Skodjje model

The first test considered is the following model system

$$\begin{bmatrix} dr_1/dt \\ dr_2/dt \end{bmatrix} = \begin{bmatrix} -r_1 u \exp(-r_2) \\ 0 \end{bmatrix} + \begin{bmatrix} (r_1^{in} - r_1)/t_{res} \\ (r_2^{in} - r_2)/t_{res} + r_1 u^2 \end{bmatrix}, \quad (14)$$

where $\mathbf{r} \equiv [r_1; r_2]$ are the primary variables, u (a function of \mathbf{r}) is the secondary variable, t_{res} is the specified residence time, and \mathbf{r}^{in} is the specified inflow condition. The first term on the right-hand side represents reaction and the second term on the right-hand side represents transport (i.e., inflow/outflow). This model is an abstraction of the reduced description of the Davis–Skodjje reactive model [24,25] in a continuously stirred tank reactor. In this model, r_1 and u correspond to chemical species, and r_2 corresponds to temperature. For the particular case considered, the residence time is taken to be $t_{res} = 2$, the inflow conditions are $\mathbf{r}^{in} = [1; 1]$ and the initial conditions are $\mathbf{r} = [1; 1]$. For simplicity, the secondary variable u is taken to be related to the primary variables through

$$u = \frac{r_1}{1 + r_1}. \quad (15)$$

We pretend that the above function is computationally expensive to evaluate. The purpose is to demonstrate different splitting schemes in a simple model problem.

The solution to Eq. (14) can be obtained with high accuracy by directly integrating Eq. (14) forward in time using an ODE solver. Fig. 2 shows the evolution of the primary variables with time. After the initial transient, the system reaches a steady state. To demonstrate the different splitting schemes described in Section 2, Eq. (14) is alternatively solved using the splitting schemes with reaction being separated from inflow/outflow. For this model system, the Strang scheme, modified Strang schemes and Staggered schemes can be straightforwardly applied. In each of the sub-steps, the governing ODEs are integrated accurately using an ODE solver so that (over the range of Δt considered) the only significant numerical error is the splitting error. We define

$$\varepsilon_{\max}(\Delta t) \equiv \frac{1}{|\mathbf{r}^{DI}(t_{\text{end}})|} \max(|\mathbf{r}^{DI}(t) - \mathbf{r}^{SP}(t, \Delta t)|), \quad \text{for } 0 < t < t_{\text{end}}, \quad (16)$$

to be the normalized measure of the maximum two-norm error between the accurate solution $\mathbf{r}^{DI}(t)$ from the direct integration of the fully coupled equations (Eq. (14)) and the solution $\mathbf{r}^{SP}(t, \Delta t)$ from one of the splitting schemes with time step Δt . (For the results presented below $t_{\text{end}} = 10$.) Fig. 3 shows the numerical errors against the time step. As shown in the plot, for this system, schemes Strang-PC1, Strang-PC2 and Strang-Lin achieve comparable accuracy to the original Strang scheme. The Staggered-PC1 scheme is less accurate compared to other schemes. Nevertheless, for all the splitting schemes considered, over a wide range of Δt , the error decreases with Δt , essentially as Δt^2 , thus illustrating their second-order accuracy in time. For this system, the number of function evaluations per mixing sub-step is about 40 for the Strang scheme, 2 for Strang-PC1 and Staggered-PC1 and 1 for Strang-PC2 and Strang-Lin. (For this system, the knowledge of derivatives necessary for Strang-PC2 and Strang-Lin is known and requires no extra function evaluations.)

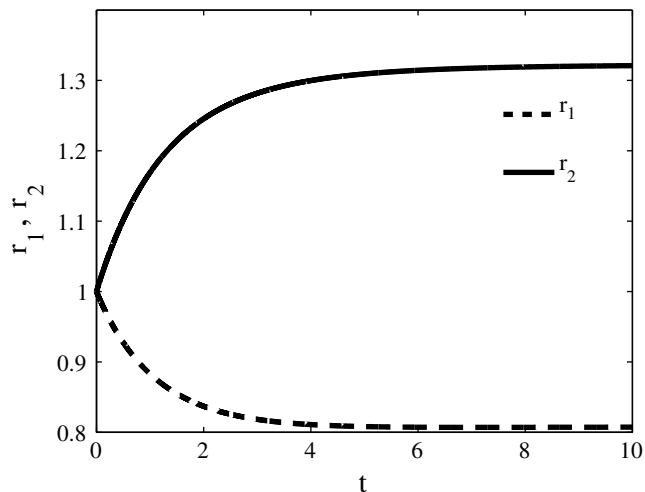


Fig. 2. The primary variables r_1 and r_2 against time in the model system Eq. (14).

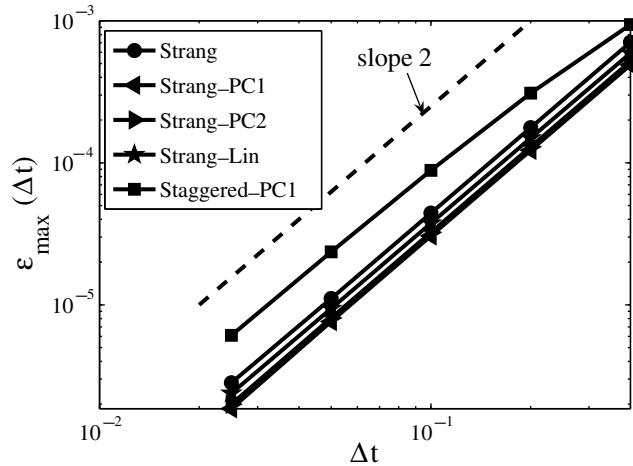
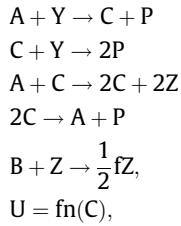


Fig. 3. Demonstration of the accuracy of different splitting schemes for the model system Eq. (14): the splitting error defined by Eq. (16) against time step Δt . Also shown is the dashed line of slope 2 corresponding to second-order accuracy ($\epsilon_{\max}(\Delta t) \sim \Delta t^2$).

3.2. Extension of the Oregonator model of the Belousov–Zhabotinsky reaction

The second test is a one-dimensional reaction–diffusion system capable of generating periodic patterns. The chemical reaction model employed is an extension of the Oregonator model of the Belousov–Zhabotinsky reaction [26–28] appending a general functional relation between the activator and its nonreactive form,



where $A = [\text{HBrO}_3^-]$, $B = \text{malonic acid}$, $P = \text{HOBr}$, $C = [\text{HBrO}_2]$, $Y = [\text{Br}^{-1}]$ and U is the nonreactive form of C . As denoted in the reaction scheme, U is assumed to be a function of C . As shown in [28], by using a quasi-steady-state approximation for Y , a two variable reaction–diffusion model describing this system is given by the following PDEs

$$\begin{bmatrix} \partial c / \partial t \\ \partial z / \partial t \end{bmatrix} = \begin{bmatrix} \frac{1}{\epsilon} (c - c^2 - fz \frac{c-q}{c+q}) \\ c - z \end{bmatrix} + \begin{bmatrix} D_c(c, z, u(c, z)) \partial^2 c / \partial x^2 \\ D_z(c, z, u(c, z)) \partial^2 z / \partial x^2 \end{bmatrix}, \tag{17}$$

where: the variables $c(x, t)$, $z(x, t)$ and u (which is a function of c and z) are the non-dimensionalized concentrations of species C , Z and U , respectively; D_c and D_z (which depend on c , z and u) are the non-dimensional diffusivities of c and z respectively; and ϵ , f and q are related kinetic parameters with values $\epsilon = 0.343$, $f = 0.94$ and $q = 0.009$. In Eq. (17), the first term on the right-hand side represents reaction, and the second term on the right-hand side represents diffusion. The primary variables are $\mathbf{r} \equiv [c; z]$, and the secondary variable is $\mathbf{u} \equiv u$. The diffusivities are given by

$$\begin{aligned}
 D_c(c, z, u(c, z)) &= 0.05c / (c + z + u) \\
 D_z(c, z, u(c, z)) &= 0.4z / (c + z + u).
 \end{aligned} \tag{18}$$

The secondary variable u is related to the primary variables c and z through

$$u = 0.2c^{1/2}. \tag{19}$$

We pretend that the above function is computationally expensive to evaluate.

The solution domain is set to be $0 \leq x \leq L = 5$. The boundary conditions are given by $[c(t, 0) \ z(t, 0)]^T = [0.4 \ 0.15]^T$ and $[c(t, L) \ z(t, L)]^T = [0.4 \ 0.15]^T$, and the initial condition is taken to be $[c(0, x) \ z(0, x)]^T = [0.4 \ 0.15]^T$.

The governing PDEs (Eq. (17)) are transformed into a set of ODEs of the form of Eq. (1) by performing central finite differencing of the diffusion term over a mesh consisting of 201 equally spaced grid nodes in x -space. We define $\mathbf{r}_f(t)$ (of dimension 402) to be the dependent variables of the resulting set of ODEs, i.e., $\mathbf{r}_f(t)$ is the collection of all the primary variables \mathbf{r} at the 201 grid nodes at time t . The solution to the resulting set of ODEs can be obtained by integrating forward in time using an

ODE solver. Fig. 4 shows the evolution of the primary variables from this extended Oregonator model in x - t space. After the initial transient ($t < 20$), as may be seen, sustained patterns form in this reactive system.

The resulting ODEs after spatial discretization can be alternatively solved using the splitting schemes described in Section 2 with reaction being separated from the diffusion. To investigate the splitting error, in each of the sub-steps, the governing ODEs are integrated accurately using an ODE solver so that (over the range of Δt considered) the only significant numerical error is the splitting error. We define

$$\varepsilon_{\max}(\Delta t) \equiv \frac{1}{\max(|\mathbf{r}_f^{DI}(t)|)} \max(|\mathbf{r}_f^{DI}(t) - \mathbf{r}_f^{SP}(t, \Delta t)|), \quad \text{for } 0 < t < t_{\text{end}}, \quad (20)$$

to be the normalized measure of the maximum two-norm error between the accurate solution $\mathbf{r}_f^{DI}(t)$ (from the direct integration of the resulting ODEs after spatial discretization of Eq. (17)) and the solution $\mathbf{r}_f^{SP}(t, \Delta t)$ from one of the splitting schemes with time step Δt . (For the results presented below $t_{\text{end}} = 35$.) Fig. 5 shows the numerical errors against the time step. As shown in the plot, for Δt less than 0.2, the errors of all the five splitting schemes decrease with Δt , essentially as Δt^2 , thus illustrating their second-order accuracy. When the time step Δt is greater than about 0.2, the accuracy of all the splitting schemes deteriorates. For this system, schemes Strang-PC1, Strang-PC2 and Staggered-PC1 achieve comparable accuracy as the original Strang scheme. The Strang-Lin scheme is less accurate compared to other schemes. For this system, the number of function evaluations per mixing sub-step is about 230 for the Strang scheme, 2 for Strang-PC1 and Staggered-PC1 and 1 for Strang-PC2 and Strang-Lin. (For this system, the knowledge of derivatives necessary for Strang-PC2 and Strang-Lin is known and requires no extra function evaluations.)

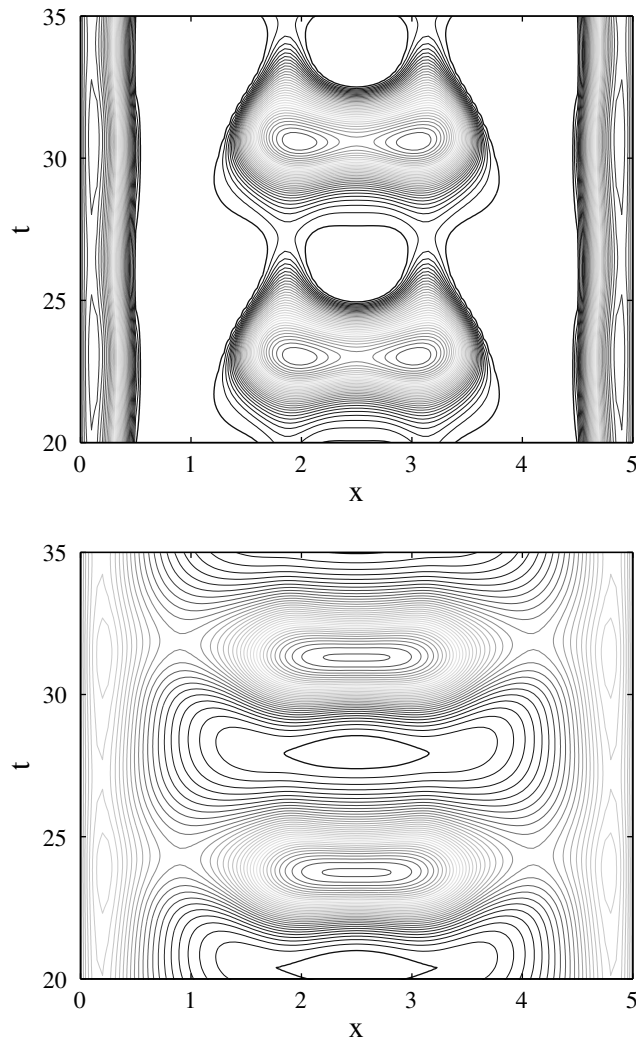


Fig. 4. Contour plots of the primary variables $r_1 \equiv c$ (top figure) and $r_2 \equiv z$ (bottom figure) from the extended Oregonator model in x - t space.

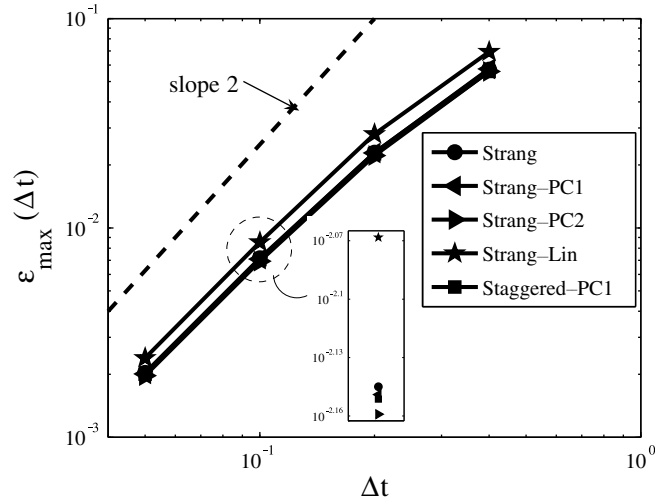


Fig. 5. Demonstration of the accuracy of different splitting schemes for the extended Oregonator model: the splitting error defined by Eq. (20) against time step Δt . Also shown is the dashed line of slope 2 corresponding to second-order accuracy ($\epsilon_{\max}(\Delta t) \sim \Delta t^2$).

3.3. CO + H₂ oxidation in a continuously stirred tank reactor

The third test is the reaction of a CO/H₂/O₂ mixture in an isobaric continuously stirred tank reactor. As shown in [29,30], at low pressures and moderate ambient temperatures, the system may sustain oscillatory ignition. The detailed chemical kinetics mechanism employed for CO + H₂ oxidation is the CO + H₂ subset of the Leeds methane mechanism [31,32], which involves 11 species and 33 reactions. The chemical species are H₂, O₂, H₂O, H₂O₂, CO, CO₂, H, O, OH, HO₂ and HCO. The reactive system at time t is fully described by $\{h(t), \mathbf{z}(t)\}$, where $h(t)$ is the specific enthalpy and the composition $\mathbf{z}(t)$ is taken to be the species specific moles (mass fractions divided by the corresponding species molecular weights). With the assumption of perfect mixing in the reactor, the dynamics in a non-isothermal CSTR are governed by the following set of ordinary differential equations (ODEs):

$$\begin{bmatrix} d\mathbf{z}/dt \\ dh/dt \end{bmatrix} = \begin{bmatrix} \mathbf{S}(\mathbf{z}, T(\mathbf{z}, h)) \\ 0 \end{bmatrix} + \begin{bmatrix} (\mathbf{z}^{\text{in}} - \mathbf{z})/t_{\text{res}} \\ (h^{\text{in}} - h)/t_{\text{res}} + (T_a - T(\mathbf{z}, h))Q/\rho(\mathbf{z}, T(\mathbf{z}, h)) \end{bmatrix}, \quad (21)$$

where: the primary variables $\mathbf{r} \equiv [\mathbf{z}; h]$ are the species specific moles and specific enthalpy; the secondary variables $\mathbf{u} \equiv [T; \rho]$ are the temperature and the density of the mixture in the reactor; $\mathbf{z}^{\text{in}}, h^{\text{in}}$ are the species specific moles and enthalpy of the inflowing stream; t_{res} is the residence time; T_a is the ambient temperature; Q is the heat loss coefficient; and the vector \mathbf{S} (determined by the detailed chemical kinetics) is the rate of change of the composition due to chemical reactions. In Eq. (21), the first term on the right-hand side represents reaction, and the second term on the right-hand side represents transport i.e., inflow/outflow and heat loss. As indicated by the notation, T, ρ are functions of \mathbf{z} and h . Due to the nonlinear relationship between temperature and enthalpy, it requires iterations to obtain temperature from $\{h, \mathbf{z}\}$, which is computationally expensive.

For the particular case considered, the heat loss coefficient Q is taken to be $160 \text{ J K}^{-1} \text{ m}^{-3} \text{ s}^{-1}$, the residence time is taken to be $t_{\text{res}} = 8 \text{ s}$, and the pressure is $P = 25 \text{ Torr}$. The inflow mixture considered is 0.5% H₂, 49.5% CO and 50% O₂ (by volume) at the ambient temperature $T_a = 760 \text{ K}$, the initial conditions are taken to be $\mathbf{z}(t=0) = [6.42 \times 10^{-6}; 9.29 \times 10^{-3}; 1.6 \times 10^{-4}; 6.23 \times 10^{-9}; 1.84 \times 10^{-3}; 1.47 \times 10^{-2}; 8.73 \times 10^{-7}; 8.36 \times 10^{-6}; 3.06 \times 10^{-7}; 1.12 \times 10^{-7}; 1.18 \times 10^{-11}] \text{ kmol/kg}$ and $T(t=0) = 800.43 \text{ K}$. The initial enthalpy $h(t=0)$ is determined from $\mathbf{z}(t=0)$ and $T(t=0)$.

The solution to Eq. (21) can be obtained by integrating it forward in time by using the ODE solver DDASAC [33]. As shown in Fig. 6, the system exhibits a periodic sequence of ignition events separated by periods of relatively little chemical activity, but during which the mixture composition changes under the influence of inflow and outflow. However this direct integration is computationally expensive due to the required expensive temperature and density evaluations. Alternatively, Eq. (21) can be efficiently solved by splitting schemes with reaction being separated from inflow/outflow. (With this operator splitting, an efficient solution to the reaction sub-step can be obtained using a storage/retrieval methods such as ISAT [17], and efficient solution to the transport sub-step can be obtained by methods described in Section 2.2.) For this system, the Strang, Strang-PC1 and Staggered-PC1 splitting schemes can be applied straightforwardly for solving Eq. (21). For this particular system, the other splitting schemes such as Strang-PC2 and Strang-Lin described in Section 2 are not computationally advantageous due to the cost and difficulties in obtaining the required gradient information. For this particular system, this gradient information cannot readily be obtained from the previous reaction substep.

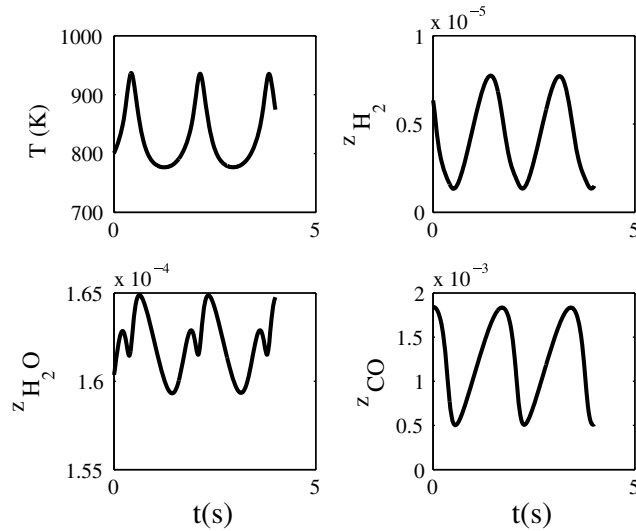


Fig. 6. Temperature and specific moles (kmole/kg) of H_2 , H_2O and CO during oscillatory ignition of $\text{CO} + \text{H}_2$ mixture in a CSTR obtained from Eq. (21).

To investigate the splitting error, the governing ODEs in each of the sub-steps are solved accurately (either using DDASAC or solved analytically) so that (over the range of Δt considered) the only significant numerical error is the splitting error. We define

$$\varepsilon_{\max}(\Delta t) \equiv \frac{1}{\max(|\mathbf{z}^{DI}(t)|)} \max(|\mathbf{z}^{DI}(t) - \mathbf{z}^{SP}(t, \Delta t)|), \quad \text{for } 0 < t < t_{\text{end}}, \quad (22)$$

to be the normalized measure of the maximum two-norm error between the accurate solution $\mathbf{z}^{DI}(t)$ from the direct integration of the full coupled equations (Eq. (21)) and the solution $\mathbf{z}^{SP}(t, \Delta t)$ from one of the splitting schemes with time step Δt . For the results presented below $t_{\text{end}} = 3\text{ s}$.

Fig. 7 shows the numerical errors against the time step during the oscillatory ignition. As shown in the plot, for Δt less than 0.06 s, the errors of all the three splitting schemes decrease with Δt , essentially as Δt^2 , thus illustrating their second-order accuracy. When the time step Δt is greater than 0.06 s, the accuracy of all the splitting schemes deteriorates. One thing worth mentioning is that the governing equation (Eq. (21)) for the $\text{CO} + \text{H}_2$ oxidation in a CSTR is highly stiff. Fig. 8 shows the chemical time scales during the oscillatory ignition. As may be seen, the system contains a wide range of

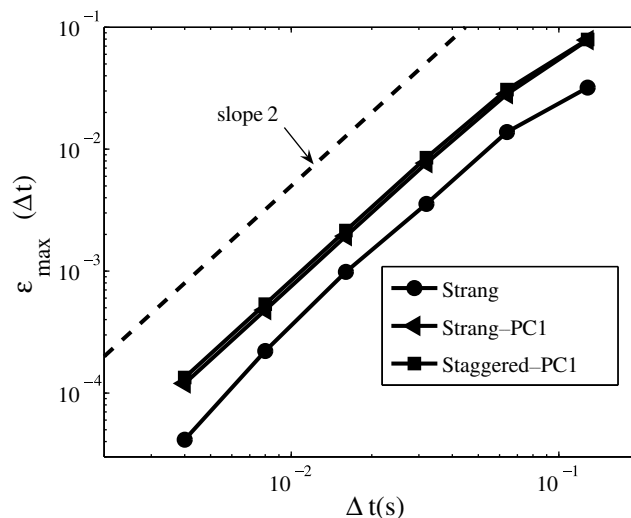


Fig. 7. Demonstration of the accuracy of different splitting schemes for the oscillatory ignition of $\text{CO} + \text{H}_2$ mixture in a CSTR according to Eq. (21). The splitting error defined by Eq. (22) against time step Δt . Also shown is the dashed line of slope 2 corresponding to second-order accuracy ($\varepsilon_{\max}(\Delta t) \sim \Delta t^2$).

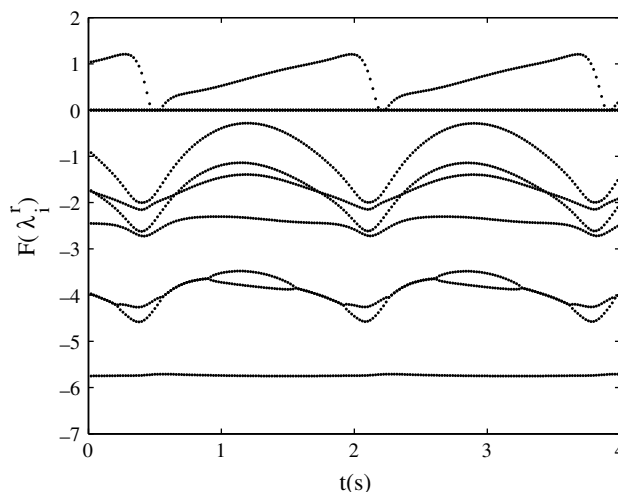


Fig. 8. Chemical time scales during oscillatory ignition. For a reactive system, the eigenvalues of the Jacobian matrix $J_{ij}(\mathbf{z}) \equiv \partial S_i / \partial z_j$ of the reaction source term are related to the chemical time scales τ_i by $\tau_i = 1/|\lambda_i^r|$, where λ_i^r denotes the real part of the i th eigenvalue. There are n_e eigenvalues which are exactly zero due to the conservation of elements. Figure showing the real parts of the eigenvalues of the Jacobian matrix as $F(\lambda_i^r)$, where for $\lambda_i^r \leq -1$, $F(\lambda_i^r) = -\log_{10}(\max(-\lambda_i^r, 1))$, for $\lambda_i^r \geq 1$, $F(\lambda_i^r) = \log_{10}(\max(\lambda_i^r, 1))$, and for $-1 < \lambda_i^r < 1$, $F(\lambda_i^r) = 0$.

chemical time scales. The time step Δt (order of 0.01 s) employed in practice for the splitting schemes is much larger than the smallest chemical time scales (order of 10^{-6} s). Nevertheless, even with this large time step, the splitting schemes achieve second order accuracy in time.

For this system, schemes Strang-PC1 and Staggered-PC1 achieve comparable accuracy, but are less accurate than the original Strang scheme.

4. Conclusions

In this study, we develop computationally efficient splitting schemes for solving a class of reaction–transport problems. The systems are described by a set of governing equations for primary variables, and the terms involved may require the knowledge of secondary variables, which are computationally expensive to evaluate. The schemes are based on the splitting technique wherein the portions of the governing equations containing chemical reaction terms are separated from those parts containing the transport terms. We introduce two classes of splitting schemes: one is based on the Strang splitting scheme, and the other is based on staggered time steps. For each time step Δt , schemes based on Strang splitting require two reaction sub-steps of length $\Delta t/2$ and one transport sub-step of length Δt . Schemes based on staggered time steps require a single reaction fractional step of length Δt and a single transport sub-step of length Δt .

For the reaction sub-steps, efficient solutions can be obtained using the storage/retrieval methods such as ISAT [17]. In this work, a computationally efficient solution to the transport sub-step is achieved through predictor–corrector methods or linearization, namely, methods PC1, PC2, and Lin, described in Sections 2.2,2.3. For splitting schemes with PC1 for the transport sub-step, two function evaluations $\mathbf{u}(\mathbf{r})$ are required to obtain \mathbf{u}^a and \mathbf{u}^p in the transport sub-step. For splitting schemes with PC2 or Lin for the transport sub-step, only one function evaluation (for evaluating \mathbf{u}^a) is required. However they require the evaluation of other information such as derivatives, which is in general computationally expensive. Under certain circumstances where this information is known from the previous reaction sub-step, compared to PC1, schemes PC2 and Lin require one less function evaluation and are computationally advantageous.

The splitting schemes are applied to solve the reactive flow in a continuously stirred tank reactor (CSTR) with the Davis–Skodjie reaction model, to solve the CO + H₂ oxidation in a CSTR with detailed chemical kinetics, and to solve a reaction–diffusion system with an extension of the Oregonator model of the Belousov–Zhabotinsky reaction. As demonstrated in the test problems, the proposed splitting schemes, which yield efficient solutions to the transport sub-step, achieve second-order accuracy in time. Their relative accuracy, cost and ease of implementation is problem dependent. For problems without particular structure, splitting schemes with PC1 for the transport sub-step are easiest to implement and hence are recommended.

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