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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–Skodjie reaction model, to the $CO + H_2$ 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.

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:

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

where: the dependent variables **r** (of dimension n_r) are called primary variables; the variables **u** (of dimension n_u), which are known functions of **r**, are called secondary variables; **S** (of dimension n_r) denotes the rate-of-change of the primary variables due to chemical reactions; and **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 **S** and the transport operator **M**. The operator **S** is independent of time; in the method of lines, the reaction process is separate for each grid point. The operator **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

$$\frac{\mathrm{d}\mathbf{r}^a}{\mathrm{d}t} = \mathbf{S}(\mathbf{r}^a, \mathbf{u}(\mathbf{r}^a)). \tag{2}$$

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 $\mathbf{r}^a(\Delta t/2)$.