

Analysis of split operator methods applied to reactive transport with Monod kinetics

Matthew J. Simpson ^{*}, Kerry A. Landman

Department of Mathematics and Statistics, University of Melbourne, Victoria 3010, Australia

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Abstract

Split operator approaches are commonly used to solve coupled nonlinear reactive transport problems. The benefits of split operator algorithms come with the cost of an $\mathcal{O}(\Delta t)$ truncation error. This error has two components: (i) an error strictly associated with the boundary, and (ii) an error occurring within the domain. Previous analyses of split operator methods for Monod reactions are incomplete and conflicting. First, previous analyses have focused only on the boundary error while ignoring the internal error. This is problematic as the boundary error is irrelevant in many practical applications. Second, conflicting results regarding the accuracy of alternating split operator methods have been reported. This new work exactly characterizes the net splitting error for an arbitrary system of nonequilibrium reactive transport equations showing that both the boundary and internal error can always be removed with alternating methods for sufficiently small Δt . Numerical results are presented for reactive transport governed by single and multiple species with Monod kinetics.

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1. Introduction

The benefits of solving coupled nonlinear reactive transport equations using split operator approaches are well-known and extensively documented [1,2,7,8,10,13–15,17–19,21,22,24–26,28–30]. Split operator approaches are particularly useful for solving reactive transport problems where the coupling and nonlinearities are restricted to the reaction terms. Reactive transport equations of this kind are ubiquitous in many applied science disciplines. For example, simulating aquifer bioremediation processes typically involves multicomponent reactive transport with reactions governed by coupled nonlinear Monod kinetics [3,4,6,11,12,15,16,20,27,29].

Several variations of split operator approaches are available [9,25], but the noniterative two step method is the most commonly used in practical algorithm design

[4,13,19,23,29]. In these algorithms, the entire system is advanced through each discrete time step in two stages. First, the uncoupled linear transport equations are integrated over Δt to yield an intermediate solution. Second, the intermediate solution is used as an initial condition to integrate the ordinary differential equations associated with the reaction terms. Completing these two steps approximately advances the whole system through the time interval. This kind of splitting can be achieved in one of two ways. Either the transport terms are integrated followed by the reaction terms (TR), or the reaction terms are integrated followed by the transport terms (RT) [22,24].

It is well-known that splitting transport and reaction processes introduces an $\mathcal{O}(\Delta t)$ truncation error [1,2,7,22,24,26]. The characteristics of this error have been deduced for certain problems. For example, the error associated with single species linear nonequilibrium reactive transport [1,21,26] and reactive transport with equilibrium reactions [1,2,7] have been reported by several previous investigators. Recently, the exact mathematical characteristics of the

^{*} Corresponding author. Tel.: +61 3 8344 6517; fax: +61 3 8344 4599.
E-mail address: m.simpson@ms.unimelb.edu.au (M.J. Simpson).

$\mathcal{O}(\Delta t)$ error associated with TR and RT splitting for an arbitrary system of nonequilibrium reactive transport equations have been deduced [24]. This analysis is relevant for (i) arbitrary spatial dimensions, (ii) any linear transport mechanism, (iii) arbitrary initial and boundary conditions, (iv) any differentiable kinetic functions and (v) any number of reacting species.

Prior analyses of the split operator error for reactive transport with Monod kinetics have been restricted to heuristic numerical–numerical comparisons [3,17]. It is difficult to draw general conclusions from these analyses since comparisons are typically reported for a particular set of initial and boundary conditions together with a limited range of parameters [3,8,17]. It is not clear how these kinds of case-by-case results generalize. Therefore, this study will complement, integrate and extend these previous heuristic investigations which are incomplete and conflicting. We present a framework for mathematically characterizing the splitting error for a general system. Specific results are demonstrated for reactive transport problems involving single and two-species Monod reactions.

2. Previous investigations

Morshed and Kaluarachchi [17] considered 1D reactive transport involving single and two-species Monod reactions. Fully-coupled fine mesh solutions were compared with TR split operator solutions. This analysis focussed on a “time lag” error associated with a specified-flux inlet boundary condition. This error was reduced using an alternating split operator method where the order of sequential integration was swapped in each subsequent step. That is, the splitting is carried out (i) time step 1 TR, (ii) time step 2 RT, (iii) time step 3 TR and so on. This leads to a TRT alternating algorithm. Alternatively, the splitting can be achieved as (i) time step 1 RT, (ii) time step 2 TR, (iii) time step 3 RT and so on. This leads to an RTR alternating algorithm [24].

More recently Bell and Binning [3] used a split operator approach to simulate 1D multiple Monod reactive transport. Their analysis used a specialized numerical technique relevant for advection-dominant problems. These simulations also identified an error associated with the domain boundary. Curiously, these results showed that an alternating algorithm amplified the splitting error relative to a standard TR algorithm. Therefore, it is unclear whether alternating algorithms are useful since the conclusions of Bell and Binning [3] are at odds with those of Morshed and Kaluarachchi [17].

One important difficulty in interpreting the practical significance of these previous studies is that the error analyzed is relevant when a contaminant is introduced through an inlet-type boundary [3,17]. This has application for simulating 1D laboratory-scale column tests where a known concentration or specified-flux is introduced at the boundary. However the real beauty of split operator methods becomes apparent for simulating large-scale multidimensional field

applications involving multicomponent reactive transport [4,5,11,20,29]. For these applications simulations are often aimed at predicting the fate of existing reactive plumes. In such applications, it is common to construct the spatial mesh so that it extends well-beyond the edge of the plumes [4,5,11]. Under these conditions inlet-type boundary conditions are not imposed, therefore the previously identified boundary error is irrelevant. For this kind of simulation, we are interested to know whether splitting causes other errors that act independently of the boundary. If such an error exists, then it would be useful to have an appreciation of its characteristics to understand how the error will manifest in the numerical solution. Moreover, it is also relevant to ask whether the splitting algorithm can be altered to minimize or remove such “internal” splitting errors. All of these questions will be answered in this work using a very general mathematical approach.

3. Splitting analysis

A system of n -dimensional reactive transport equations with m components is written as

$$\frac{\partial u_i}{\partial t} = L_i(u_i) + F_i(u_1, u_2, \dots, u_m) \quad \forall i = 1, 2, \dots, m, \quad (1)$$

where u_i is the concentration of the i th species. Here L_i is an arbitrary n -dimensional linear transport operator and F_i is a time dependent kinetic process.

The transport operator is written in an equivalent vector form representing the system after spatial discretization, $L_i(u_i) = \mathbf{A}_i \mathbf{u}_i + \mathbf{b}_i$. The $\mathbf{A}_i \mathbf{u}_i$ term is the discretized transport operator and \mathbf{b}_i is the discretized boundary conditions in conjunction with the discretized transport operator [1,2]. Note $\mathbf{b}_i = \mathbf{0}$ for homogeneous Dirichlet boundary conditions. The system is integrated across a time step from t^k to t^{k+1} with $\Delta t = t^{k+1} - t^k$. The reaction and transport terms are integrated separately and combined by using the result from the first step as the initial condition in the second step. The temporal integration of the transport and reaction steps is done with an $\mathcal{O}[(\Delta t)^2]$ Crank–Nicolson approximation. At each step in the integration process Δt is assumed to be small and the equations are expanded in a Taylor series about the time point $t^{k+1/2} = t^k + \Delta t/2$ [24]. For TR splitting, the equivalent system at $t^{k+1/2}$ can be written as

$$\left(\frac{\partial u_i}{\partial t} \right)^{k+1/2} = L_i(u_i)^{k+1/2} + F_i(u_1, u_2, \dots, u_m)^{k+1/2} + (E_i^{\text{TR}})^{k+1/2} \quad \forall i = 1, 2, \dots, m, \quad (2)$$

where the last term represents a truncation error. This error contains an $\mathcal{O}(\Delta t)$ component corresponding to the error introduced by splitting:

$$E_i^{\text{TR}} = \frac{\Delta t}{2} \left[\sum_{j=1}^m \frac{\partial F_i}{\partial u_j} (\mathbf{A}_j \mathbf{u}_j + \mathbf{b}_j) - \mathbf{A}_i F_i \right] + \mathcal{O}[(\Delta t)^2] \quad \forall i = 1, 2, \dots, m. \quad (3)$$

Similar results can be derived for RT splitting where the equivalent $\mathcal{O}(\Delta t)$ component is equal and opposite to the term in (3) [24]. That is, $E_i^{\text{TR}} = -E_i^{\text{RT}} + \mathcal{O}[(\Delta t)^2] \quad \forall i = 1, 2, \dots, m$. These expressions allow the exact characteristics of the splitting error to be deduced from the structure of the governing equations. The error terms can be interpreted as additional terms in the conservation equations allowing the characteristics of the truncation error to be physically anticipated *a priori*. This analysis is completely general since the results can be applied reactive transport problems with (i) arbitrary spatial dimensions, (ii) any linear transport mechanism, (iii) arbitrary initial and boundary conditions, (iv) any differentiable kinetic functions and (v) any number of reacting species. Furthermore the analysis is applicable for both RT and TR splitting algorithms.

The expression for the splitting error can be rewritten to emphasize that the net error has two components:

$$E_i^{\text{TR}} = \underbrace{\frac{\Delta t}{2} \left[\sum_{j=1}^m \frac{\partial F_i}{\partial u_j} \mathbf{b}_j \right]}_{\text{Boundary error}} + \underbrace{\frac{\Delta t}{2} \left[\sum_{j=1}^m \frac{\partial F_i}{\partial u_j} \mathbf{A}_j \mathbf{u}_j - \mathbf{A}_i F_i \right]}_{\text{Internal error}} \quad \forall i = 1, 2, \dots, m. \quad (4)$$

The first term in (4) represents the error due to effects at the boundary. The second term represents an internal error which acts independently of the boundary. For any problem with homogeneous Dirichlet boundary conditions $\mathbf{b}_i = \mathbf{0}$ and the boundary error is removed [1]. However even when $\mathbf{b}_i = \mathbf{0}$, there is still an internal error associated with \mathbf{A}_i . The influence of this internal error in the context of biological invasion and pattern formation models has only recently been identified and demonstrated [24]. The influence of this internal error for reactive transport with Monod kinetics will be demonstrated here for the first time. This analysis provides important insights into previous analyses which focused only on the boundary error [3,17].

4. Single species reactive transport with Monod kinetics

A single species reactive transport model corresponds to (1) with $m = 1$ and a general kinetic function $F_1(u)$. Combining a three-dimensional advection–diffusion transport operator $L(u) = D_x \frac{\partial^2 u}{\partial x^2} + D_y \frac{\partial^2 u}{\partial y^2} + D_z \frac{\partial^2 u}{\partial z^2} - v_x \frac{\partial u}{\partial x} - v_y \frac{\partial u}{\partial y} - v_z \frac{\partial u}{\partial z}$ with the internal error term in (4) gives

$$E_1^{\text{TR}} = \frac{\Delta t}{2} \frac{dF_1}{du} \left[D_x \frac{\partial^2 u}{\partial x^2} + D_y \frac{\partial^2 u}{\partial y^2} + D_z \frac{\partial^2 u}{\partial z^2} - v_x \frac{\partial u}{\partial x} - v_y \frac{\partial u}{\partial y} - v_z \frac{\partial u}{\partial z} \right] - \frac{\Delta t}{2} \left[D_x \frac{\partial^2 F_1}{\partial x^2} + D_y \frac{\partial^2 F_1}{\partial y^2} + D_z \frac{\partial^2 F_1}{\partial z^2} - v_x \frac{\partial F_1}{\partial x} - v_y \frac{\partial F_1}{\partial y} - v_z \frac{\partial F_1}{\partial z} \right]. \quad (5)$$

Noting that $F_1 = F_1(u)$ and $u = u(x, y, z)$ the derivatives in the second line of (5) are expanded giving

$$E_1^{\text{TR}} = \frac{\Delta t}{2} \frac{dF_1}{du} \left[D_x \frac{\partial^2 u}{\partial x^2} + D_y \frac{\partial^2 u}{\partial y^2} + D_z \frac{\partial^2 u}{\partial z^2} - v_x \frac{\partial u}{\partial x} - v_y \frac{\partial u}{\partial y} - v_z \frac{\partial u}{\partial z} \right] - \frac{\Delta t}{2} \frac{d^2 F_1}{du^2} \left[D_x \left(\frac{\partial u}{\partial x} \right)^2 + D_y \left(\frac{\partial u}{\partial y} \right)^2 + D_z \left(\frac{\partial u}{\partial z} \right)^2 \right] - \frac{\Delta t}{2} \frac{dF_1}{du} \left[D_x \frac{\partial^2 u}{\partial x^2} + D_y \frac{\partial^2 u}{\partial y^2} + D_z \frac{\partial^2 u}{\partial z^2} - v_x \frac{\partial u}{\partial x} - v_y \frac{\partial u}{\partial y} - v_z \frac{\partial u}{\partial z} \right]. \quad (6)$$

Written in this form it is clear that some terms associated with diffusive transport and all terms associated with advective transport cancel. This gives the simplified expression for the internal splitting error for any single species reactive transport problem subject to 3D advection–diffusion,

$$E_1^{\text{TR}} = -\frac{\Delta t}{2} \frac{d^2 F_1}{du^2} \left[D_x \left(\frac{\partial u}{\partial x} \right)^2 + D_y \left(\frac{\partial u}{\partial y} \right)^2 + D_z \left(\frac{\partial u}{\partial z} \right)^2 \right]. \quad (7)$$

This expression shows that the internal error is independent of advection and vanishes unless $F_1(u)$ is nonlinear. Therefore single species reactive transport with a constant or linear kinetic function does not involve any $\mathcal{O}(\Delta t)$ internal splitting error [1,21]. We note that this expression is very general and valid for *any* single species nonequilibrium reactive transport problem regardless of the boundary and initial conditions.

An expression for the internal error associated with the Monod kinetic function is obtained by setting $F_1(u) = -\alpha u / [K + u]$. The half saturation concentration is given by K and α is the characteristic reaction rate. The internal error expression for the Monod kinetic function is

$$E_1^{\text{TR}} = -\frac{\Delta t K \alpha}{(K + u)^3} \left[D_x \left(\frac{\partial u}{\partial x} \right)^2 + D_y \left(\frac{\partial u}{\partial y} \right)^2 + D_z \left(\frac{\partial u}{\partial z} \right)^2 \right]. \quad (8)$$

This gives $E_1^{\text{TR}} < 0$, while $E_1^{\text{RT}} > 0$. Therefore TR splitting will underestimate the solution and RT splitting will overestimate the solution. The error is directly proportional to α and varies with K in a more complicated manner.

We note that the Monod kinetic function relaxes to (i) a linear kinetic function in the limit $K \rightarrow \infty$, and (ii) a constant kinetic function when $K = 0$ [29]. In these two special limiting cases $d^2 F_1 / du^2 = 0$ giving $E_1^{\text{TR}} = 0$. Naturally, Eq. (8) is consistent with this when either $K = 0$ or $K \rightarrow \infty$.

To demonstrate the splitting error, we solve

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} - \frac{\alpha u}{(K + u)}, \quad (9)$$

on $0 < x < 50$. A 1D problem is chosen for clarity and simplicity. Advective transport is neglected as the internal splitting error is independent of advection. Homogeneous Dirichlet boundaries are considered on both boundaries so the boundary error is removed. The initial condition is $u(x, 0) = e^{-(x-25)^2}$, which represents an existing localized mass of contaminant in the domain. The domain extends

well-beyond the extent of $u(x, 0)$ so the plume will not interact with the boundaries during the numerical simulation.

Fully-coupled solutions will be compared to TR and RT split operator solutions. Fully-coupled solutions are obtained with fine discretizations ensuring grid-independent results [17]. To generate the fully-coupled solutions, we replace the spatial derivatives with a standard finite difference approximation and use an implicit Crank–Nicolson $\mathcal{O}(\Delta t)^2$ temporal integration [21] to integrate through time. The resulting nonlinear systems are solved with Newton–Raphson iteration imposed with a strict absolute convergence tolerance τ . The grid-independent fully-coupled solutions will be considered “exact” [1]. The fully-coupled solutions are exact in the sense that they are not subject to the $\mathcal{O}(\Delta t)$ splitting error. This is convenient as we can compare various $\mathcal{O}(\Delta t)$ split operator solutions with the exact solutions to demonstrate and investigate the splitting error.

The split operator solutions will be obtained using a moderate value of Δt so that the splitting error will be visually detectable. In the split operator algorithms, the transport term is solved with a standard finite difference approximation and an implicit Crank–Nicolson $\mathcal{O}(\Delta t)^2$ temporal integration. The ordinary differential equations associated with the reaction term are solved using a fourth order Runge–Kutta method [21]. Although the analysis in Section 3 is based on a second order Crank–Nicolson time integration method, we will use a fourth order Runge–Kutta method for the reaction terms. This has no influence on the applicability of the analysis as the analysis is valid for any time integration method which is at least second order accurate.

Results are given in Fig. 1a at $t = 1$ where the initial Gaussian distribution has spread symmetrically about $x = 25$. The profile has undergone significant decay. The TR and RT profiles are symmetric about the exact solution emphasizing that $E^{\text{TR}} = -E^{\text{RT}} + \mathcal{O}[(\Delta t)^2]$. The TR solution

underestimates the exact solution and the RT solution overestimates the exact solution as predicted. This simulation clearly shows that the internal error can influence the accuracy of a split operator algorithm even when the previously identified boundary error is absent.

The question of whether the $\mathcal{O}(\Delta t)$ error can be removed is now addressed. Theoretically since $E_i^{\text{TR}} = -E_i^{\text{RT}} + \mathcal{O}[(\Delta t)^2] \quad \forall i = 1, 2, \dots, m$, it is always possible to remove the error using an alternating scheme. This is because the error incurred in one step, say E^{TR} , will be exactly removed in the following step by incurring a further error of E^{RT} . This will remove the error after every second step provided that Δt is sufficiently small so that the series expansions in Section 3 are valid. To demonstrate this, the same problem was resolved using identical discretizations with both a TRT and an RTR alternating algorithm [24]. Results are shown in Fig. 1b where the alternating profiles are visually indistinguishable from the exact solution. Therefore, these results are concordant with the analysis and previous numerical evidence by Morshed and Kaluarachchi [17]. This is an important result since alternating algorithms are easy to code, require no additional computational overhead compared to standard TR or RT algorithms and provide a simple way to remove the splitting error.

The fact that alternating split operator algorithms are more accurate than standard TR or RT algorithms for Monod reactions is important since previous analyses and discussions are conflicting. For example, Barry et al. [1] showed that alternating methods do not perform well for reactive transport with linear equilibrium reactions. Similarly, Bell and Binning’s [3] study showed that results from an alternating algorithm performed poorly relative to a standard TR algorithm. These results are at odds with those reported by Morshed and Kaluarachchi [17] and Fig. 1b. The reason for this discrepancy will be explained after a practical case of coupled reactive transport is analyzed.

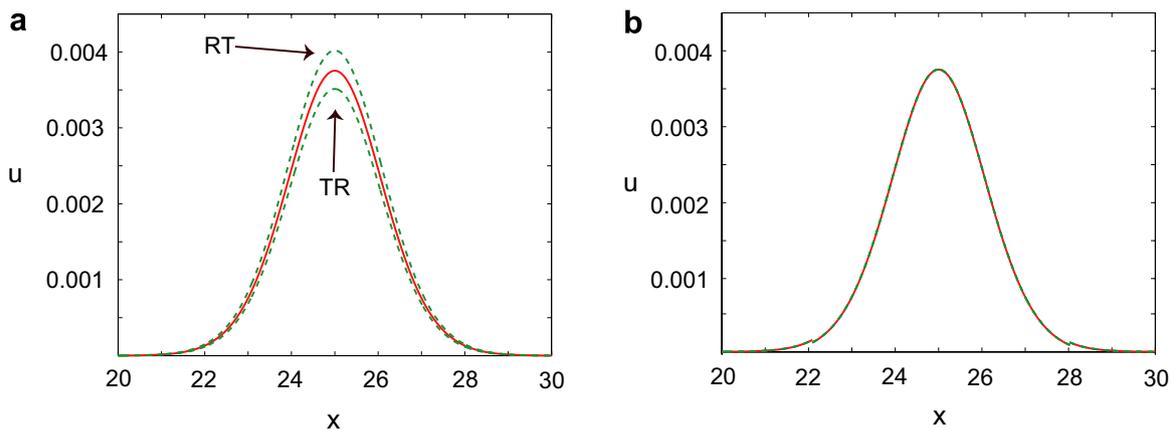


Fig. 1. Fully-coupled and split operator solutions for the single species Monod decay problem for $u(x, t)$ at $t = 1$. Profiles in (a) show the exact solution (solid red line) superimposed on the TR and RT solutions (dashed green lines). Results in (b) show the same exact solution (solid red line) superimposed on the TRT and RTR solutions (dashed green lines). All results are evaluated using $\Delta x = 0.01$. The fine mesh exact solutions are evaluated with $\Delta t = 0.001$ and a convergence tolerance of $\tau = 1 \times 10^{-9}$. All split operator solutions are evaluated with $\Delta t = 0.05$. The decay parameters are $\alpha = 1$ and $K = 0.1$. The transport parameter is $D = 1$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5. Two-species reactive transport with coupled Monod kinetics

Practical implementation of splitting algorithms is virtually always restricted to coupled multicomponent reactive transport [4,6,11–13,15,20,23,27]. Therefore further analysis and results will be presented for a coupled problem. For clarity, we focus on a 1D problem with two coupled species; however, equivalent expressions for multidimensional equations with an arbitrary number of reacting species or a different linear transport operator can be derived from (3) using the same procedure. A 1D conservation system associated the reactive transport of two coupled species is given by

$$\frac{\partial u}{\partial t} = D_1 \frac{\partial^2 u}{\partial x^2} - v_1 \frac{\partial u}{\partial x} + F_1(u, v), \quad (10)$$

$$\frac{\partial v}{\partial t} = D_2 \frac{\partial^2 v}{\partial x^2} - v_2 \frac{\partial v}{\partial x} + F_2(u, v). \quad (11)$$

Expanding (3) for (10) and (11), and assuming the mixed second order partial derivatives commute yields

$$E_1^{\text{TR}} = \frac{\Delta t}{2} \left[(v_1 - v_2) \frac{\partial F_1}{\partial v} \frac{\partial v}{\partial x} + (D_2 - D_1) \frac{\partial F_1}{\partial v} \frac{\partial^2 v}{\partial x^2} - D_1 \frac{\partial^2 F_1}{\partial v^2} \left(\frac{\partial v}{\partial x} \right)^2 - D_1 \frac{\partial^2 F_1}{\partial u^2} \left(\frac{\partial u}{\partial x} \right)^2 - 2D_1 \frac{\partial^2 F_1}{\partial v \partial u} \left(\frac{\partial u}{\partial x} \frac{\partial v}{\partial x} \right) \right], \quad (12)$$

$$E_2^{\text{TR}} = \frac{\Delta t}{2} \left[(v_2 - v_1) \frac{\partial F_2}{\partial u} \frac{\partial u}{\partial x} + (D_1 - D_2) \frac{\partial F_2}{\partial u} \frac{\partial^2 u}{\partial x^2} - D_2 \frac{\partial^2 F_2}{\partial u^2} \left(\frac{\partial u}{\partial x} \right)^2 - D_2 \frac{\partial^2 F_2}{\partial v^2} \left(\frac{\partial v}{\partial x} \right)^2 - 2D_2 \frac{\partial^2 F_2}{\partial v \partial u} \left(\frac{\partial u}{\partial x} \frac{\partial v}{\partial x} \right) \right]. \quad (13)$$

These expressions for the internal splitting error are valid for *any* two-species reactive transport problems with linear advection–diffusion transport and arbitrary differentiable coupling kinetics $F_1(u, v)$ and $F_2(u, v)$.

Clearly the error expressions for (12) and (13) are more complex than for the single species case. For the coupled problem the internal error can depend on the advective velocity only if the two-species undergo different rates of advection $v_1 \neq v_2$. The error also has an additional component arising when the two-species undergo diffusive transport at different rates $D_1 \neq D_2$. Unfortunately, unlike the simpler single species expression, it is not possible to say whether the TR or RT solutions will always underestimate or overestimate the exact solution. This is because the net truncation error depends on the relative magnitudes of the transport coefficients, the first and second order partial derivatives of the kinetic functions and the shapes of $u(x, t)$ and $v(x, t)$ in a much more complicated way than for the single species problem.

From a practical point of view, the most important property of the error expressions is that $E_i^{\text{TR}} = -E_i^{\text{RT}} + \mathcal{O}[(\Delta t)^2] \quad \forall i = 1, 2, \dots, m$. This means that for *any* system of nonequilibrium reactive transport equations, the splitting error can always be removed with an alternating

scheme provided Δt is sufficiently small. This is true for both the boundary and internal errors in (4).

To demonstrate the splitting error we solve (10) and (11) with $F_1(u, v) = -\alpha_1 uv / [(K_1 + u)(K_2 + v)]$ and $F_2(u, v) = -\alpha_2 uv / [(K_1 + u)(K_2 + v)]$. Exact solutions are obtained with a fine mesh fully-coupled algorithm and compared to TR and RT solutions obtained with a moderate value of Δt . For this problem, $u(x, t)$ is a decaying contaminant (e.g., a carbon source). The decay of $u(x, t)$ is coupled to the uptake of an indigenous background species $v(x, t)$ (e.g., dissolved oxygen). The domain, initial and boundary conditions for $u(x, t)$ are the same as for the previous single species problem. A uniform initial concentration of $v(x, t) = 0.1$ is specified and the boundary conditions for $v(x, t)$ are no flux conditions on both boundaries. Advective transport will be ignored as this makes little difference to the splitting error. Each species undergoes different rates of diffusion with $D_1 < D_2$.

It is possible to predict some properties of the truncation error introduced by splitting *a priori* according to (12) and (13). For the initial conditions considered here, the maximum absolute value of the gradient term $|\partial^2 u / \partial x^2|$, is much larger than all other gradient terms in (12) and (13). Accordingly for a short simulation we expect the term proportional to $\partial^2 u / \partial x^2$, which appears in the E_2^{TR} expression, to dominate the net splitting error. Therefore, the splitting error will be more prominent in the $v(x, t)$ profile. The term $(D_1 - D_2)(\partial F_2 / \partial u)(\partial^2 u / \partial x^2)$, is negative locally about $x = 25$. Hence the TR solution for $v(x, t)$ will underestimate the exact solution and the RT solution for $v(x, t)$ will overestimate the exact solution. Numerical results are given in Fig. 2.

Profiles in Fig. 2a show that the $u(x, t)$ species spreads symmetrically about $x = 25$ while simultaneously decaying. The decay of $u(x, t)$ is coupled with the uptake of $v(x, t)$ as shown in Fig. 2b. As predicted, the influence of the splitting error is more obvious in the $v(x, t)$ profile. The $v(x, t)$ solutions show that the TR and RT solutions are symmetric about the exact solution with the TR solution underestimating the exact solution and the RT solution overestimating the exact solution as predicted. These simulations were repeated with both an RTR and TRT alternating algorithms implemented with identical discretizations. Both alternating solutions for $u(x, t)$ and $v(x, t)$ were visually indistinguishable from the exact solutions, hence they are not shown here.

Similar results for both the single and two-species Monod problems are obtained when a combined advection and diffusion transport mechanism is used in (9)–(11) rather than pure diffusion as in Figs. 1 and 2. For combined advection and diffusion the TR and RT solutions are symmetric about the exact solution and the TRT and RTR alternating algorithms remove the splitting error. The profiles in Figs. 1 and 2 are shown for pure diffusive transport as this allowed more flexibility in selecting a moderate value of Δt to visually demonstrate the influence of the splitting error. Ignoring advection gives us the freedom to select Δt without the

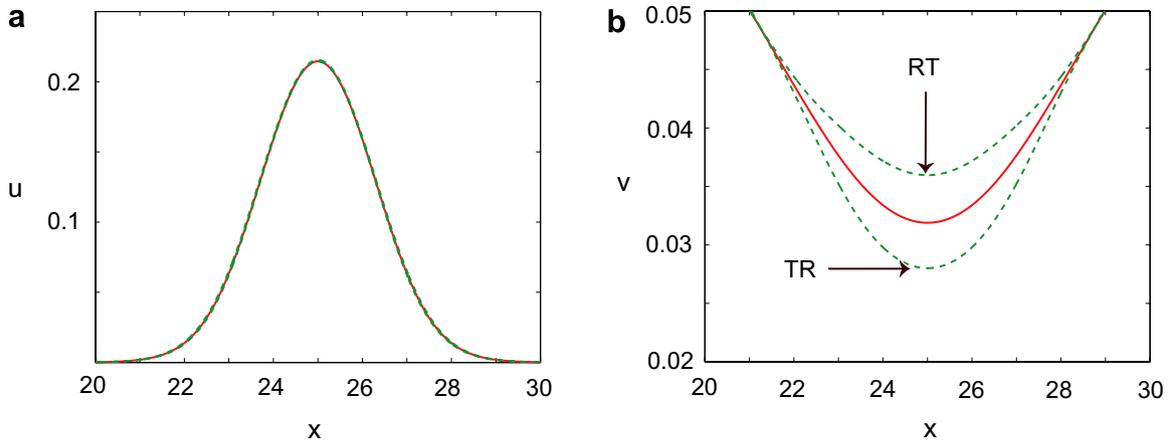


Fig. 2. Fully-coupled and split operator solutions for the two-species Monod decay problem showing $u(x, t)$ and $v(x, t)$ at $t = 1$. Results in (a) for $u(x, 1)$ show the exact solution (solid red line) superimposed on the TR and RT solutions (dashed green lines). Results in (b) for $v(x, 1)$ show the exact solution (solid red line) superimposed on the RT and TR solutions (dashed green lines). All results are evaluated using $\Delta x = 0.01$. The fine mesh exact solutions are evaluated with $\Delta t = 0.001$ and a convergence tolerance of $\tau = 1 \times 10^{-9}$. All split operator solutions are evaluated with $\Delta t = 0.05$. The decay parameters are $\alpha_1 = \alpha_2 = 1$ and $K_1 = K_2 = 0.1$. The transport parameters are $v_1 = v_2 = 0$, $D_1 = 1$ and $D_2 = 50$ (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

need to satisfy additional constraints imposed by the Courant number constraint [29].

A further point regarding the generality of our analysis can be made. In certain applications the system of transport equations contains both mobile and immobile components [3,4]. The application of the analysis in Section 3 to these problems is straightforward. For example, if one of the components in (10) and (11) were immobile then the same error expressions (12) and (13) are valid except that the transport coefficients of the immobile species will be set to zero.

6. Guidelines for using alternating splitting methods

Results presented here show that the splitting error can be removed with an alternating method. This is concordant with the findings of Morshed and Kaluarachchi [17] yet at odds with those of Bell and Binning [3]. We note that Morshed and Kaluarachchi's governing equations were slightly different to those considered by Bell and Binning. Morshed and Kaluarachchi considered a two-species product form Monod reaction while Bell and Binning considered a coupled problem without the product form. They also included an immobile third species. Regardless of these differences, both systems are of the form given by Eq. (1). Therefore, according to the analysis in Section 3, the splitting error can be removed with an alternating algorithm provided that Δt is sufficiently small. What now remains to be established is how "small" Δt needs to be to ensure this.

We note that in cases where Δt is not sufficiently small the truncated Taylor series in Section 3 are not necessarily valid. In these cases it may not be true that $E_i^{\text{TR}} = -E_i^{\text{RT}} + \mathcal{O}[(\Delta t)^2] \quad \forall i = 1, 2, \dots, m$, and it is unclear whether alternating methods will remove the $\mathcal{O}(\Delta t)$ splitting error. We will now investigate the transition from Δt being sufficiently small to sufficiently large and quantify this transition to

aid practical implementation of alternating algorithms. The transition from sufficiently small to sufficiently large Δt has not been considered or quantified by previous analyses of splitting algorithms [1,2,7,22,24].

A dimensionless number reflecting the ratio of the numerical time scale to the reaction time scale will be used to indicate the size of Δt . The reaction time scale can be written as

$$t_r = \frac{\hat{u}}{\max[\alpha_i]}, \quad (14)$$

where \hat{u} is the maximum characteristic concentration associated with the system. The ratio of numerical to reaction time scales is given by

$$\bar{T} = \frac{\Delta t}{t_r} = \frac{\max[\alpha_i] \Delta t}{\hat{u}}. \quad (15)$$

We anticipate that \bar{T} is a useful indicator of the splitting error as the expressions for E_1^{TR} and E_2^{TR} , given by (8), (12) and (13), are directly proportional to \bar{T} . When $\bar{T} \ll 1$ the numerical time scale is small compared to the reaction time scale. We would like to propose a particular limit on \bar{T} to aid practical implementation of alternating algorithms. For both examples considered in this work $\bar{T} = 0.05$. In these cases Δt was sufficiently small so that alternating algorithms outperformed standard TR and RT splitting algorithms.

Morshed and Kaluarachchi [17] provided several data sets reporting splitting-induced mass balance error as a function of \bar{T} . (See Table 1 and 2 in Morshed and Kaluarachchi [17], note that $\hat{u} = 1$ for all cases considered.) For their simulations, all results with $\bar{T} < 1$ show that the alternating methods had a reduced mass balance error compared to standard TR splitting. Conversely, all results with $\bar{T} \geq 1$ showed that the alternating methods had an increased mass balance error compared standard splitting [17]. To investigate this trend, we resimulated the problem

in Fig. 1 over a wide range of \bar{T} values. These results also showed that alternating solutions outperformed standard splitting when $\bar{T} < 1$ while standard splitting outperformed alternating methods when $\bar{T} \geq 1$. Therefore, $\bar{T} = 1$ appears to be a critical value.

The algorithm developed by Bell and Binning was designed to be used in advection-dominant conditions with large Δt [3]. The numerical time scale was large compared to the advective time scale as defined by the Courant number. The critical simulation in Bell and Binning's analysis where results from a standard TR splitting method were compared with results from a TRT alternating method was conducted for $\Delta t = 17$, $\alpha = 2$ and $\hat{u} = 10$, giving $\bar{T} > 1$. For this simulation, the numerical time scale is faster than the reaction time scale and the TRT alternating algorithm performed poorly relative to the standard TR algorithm.

These observations suggest it is possible to define an *a priori* estimate of Δt for which an alternating algorithm will outperform standard two step algorithms:

$$\Delta t < \frac{\hat{u}}{\max[\alpha_i]}. \quad (16)$$

Therefore, when using an alternating algorithm for reactive transport with Monod kinetics, a time step satisfying (16) ought to be selected. Of course, it would then be prudent to check that the algorithm produces grid-independent results with this time step.

It is also possible to define other relevant dimensionless numbers such as the ratio of the numerical time scale to the time scale of diffusive transport t_d ($t_d = L^2/D$, where L is a characteristic length). To maintain overall accuracy $\Delta t/t_d$ ought to be small. However numerical experiments indicate that the performance of splitting algorithms is much more sensitive to the reaction rate rather than the diffusivity. Eq. (7) shows that the splitting error increases with both the diffusivity and the spatial gradient of the solution. However increasing the diffusivity has the effect of reducing spatial gradients. Therefore these two opposing effects mean that the splitting error is relatively insensitive to the diffusivity compared to the reaction rate, justifying that the proposed time step limit (16) is independent of t_d .

Although the analysis in this work focuses on reactive transport with nonequilibrium kinetic models, splitting methods are also used for reactive transport with equilibrium (time independent) reactions [7,18]. For equilibrium reactions, the reaction occurs instantaneously. For any equilibrium reaction model it makes no sense to split the equations using an RT approach since no reaction will take place. Therefore $E_i^{\text{TR}} \neq -E_i^{\text{RT}} + \mathcal{O}[(\Delta t)^2] \quad \forall i = 1, 2, \dots, m$, and alternating methods should *never* be used for reactive transport with equilibrium reactions.

7. Conclusions

Split operator algorithms are convenient for solving coupled nonlinear reactive transport equations. Existing

analyses of these algorithms are incomplete and conflicting. These analyses showed that the splitting error is associated with inlet boundary conditions. While these previous results are insightful, they are not practical for simulations aimed at predicting the fate of existing plumes where inlet boundary conditions are irrelevant.

The present analysis shows that the net splitting error has two components. The first is associated with the boundary while the second acts independently of the boundary. This second error is referred to as an internal error. For single species reactive transport the internal error is proportional to the second derivative of the kinetic function, hence there is no internal error for single species reactive transport with constant or linear kinetics. Furthermore, for single species reactive transport the internal error is independent of advection regardless of the kinetic function. For multicomponent problems the internal error can depend on advection only if the various components are subject to different rates of advection.

The general error analysis is used to derive expressions for the details of the internal splitting error for reactive transport with Monod kinetics. These specific error expressions significantly extend previous heuristic analyses as they are applicable for arbitrary parameters, initial conditions and boundary conditions. The properties of the internal splitting error are demonstrated through numerical experimentation. These properties are accurately predicted by the analysis.

A mathematical analysis of the splitting error shows that $E_i^{\text{TR}} = -E_i^{\text{RT}} + \mathcal{O}[(\Delta t)^2] \quad \forall i = 1, 2, \dots, m$. This result is applicable for any number of reacting species undergoing any type of nonequilibrium reaction. This means that there is no advantage in using TR splitting compared to RT splitting for these problems. Moreover both the boundary and internal error can *always* be removed with an alternating scheme provided that Δt is sufficiently small. This explains why previous heuristic analyses have reported conflicting results. Those analyses that found alternating methods favorable used a sufficiently small Δt while those that found alternating methods unfavorable used a sufficiently larger Δt . A dimensionless number \bar{T} reflects the ratio of the numerical time scale to the reaction time scale. Numerical evidence for Monod kinetics suggests that alternating algorithms will remove the splitting error for $\bar{T} < 1$.

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