

Mass conservative, positive definite integrator for atmospheric chemical dynamics

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ABSTRACT

Air quality models compute the transformation of species in the atmosphere undergoing chemical and physical changes. The numerical algorithms used to predict these transformations should obey mass conservation and positive definiteness properties. Among all physical phenomena, the chemical kinetics solver provides the greatest challenge to attain these two properties. In general, most chemical kinetics solvers are mass conservative but not positive definite. In this article, a new numerical algorithm for the computation of chemical kinetics is presented. The integrator is called Split Single Reaction Integrator (SSRI). It is both mass conservative and positive definite. It solves each chemical reaction exactly and uses operator splitting techniques (symmetric split) to combine them into the entire system.

The method can be used within a host integrator to fix the negative concentrations while preserving the mass, or it can be used as a standalone integrator that guarantees positive definiteness and mass conservation. Numerical results show that the new integrator, used as a standalone integrator, is second order accurate and stable under large fixed time steps when other conventional integrators are unstable.

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1. Introduction

The use of operator splitting in the atmospheric advection–diffusion equation separates the solution of pollution dynamics into four key operators: the advection–diffusion operator, the chemical dynamics, the emissions and deposition, and the aerosol transport and formation (Carmichael et al., 1986; Lansner and Verwer, 1999).

It is important that numerical solutions to all processes describing pollutant formation should be mass conservative and positive definite. The advection–diffusion operator (Nguyen and Dabdub, 2001; Bott, 1989), the emissions, and the aerosols operators (Nguyen and Dabdub, 2002; Landry et al., in press) are solved with algorithms that ensure higher-order, accurate, positive definite and mass conservative properties through flux formulations. The exception is the operator related to the numerical solution to stiff chemical dynamics, for which these properties are more difficult to obtain, as illustrated in Sandu et al. (1997a,b). Most traditional solutions to chemical dynamics are mass conservative, as in Verwer et al. (1998), but the addition of the strict positive

definiteness property is difficult to achieve. There has been some research presented in the literature; for example, Sandu (2001) developed a method using projection to convert negative concentrations into non-negative concentrations via an optimization routine under a mass conservative constraint.

This paper presents a novel alternative algorithm to attain mass conservative and positive definite integration of chemical dynamics. The algorithm developed here solves exactly each chemical reaction, and uses an operator splitting approach (Yanenko, 1971) to combine them in order to solve the entire system of reactions. We prove that the exact solution to each chemical reaction is positive definite and mass conservative, and consequently the solution to the entire system also shares those properties. This new method is called *Split Single Reaction Integrator* (SSRI). It can be used independently of other integrators or in conjunction with an host integrator, in which SSRI is invoked only when the host integrator provides negative concentrations. SSRI is second order accurate (Strang, 1968)—which is the limit of the order of accuracy of all air quality models that employ the operator splitting theory. Numerical results show that the method is stable for integrations with large fixed time steps.

The structure of this article is as follows. Section 2 develops the conservation statements. In Section 3, SSRI is presented and the properties of mass conservation and positiveness are detailed. In

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Section 4, test cases and numerical results are presented to show the efficiency and stability of SSRI.

2. Chemical dynamics and conservation statements

In order to gauge the mass conservation capabilities of a chemical kinetics solver, a set of conservation measures must be established. Establishing such conservation relations defines the quantities to conserve and provides useful constraints for the solvers.

To illustrate the framework of conservation relations, consider a simple set of atmospheric reactions as in Seinfeld and Pandis (1998):



Let the time-dependent concentration vector be $c(t) = (\text{NO}, \text{NO}_2, \text{O}, \text{O}_3, \text{O}_2)^T$ and the vector of reaction rates be $R(t) = (k_1 \text{NO}_2, k_2 \text{OO}_2, k_3 \text{O}_3 \text{NO})^T$, where t denotes the time. The system of ordinary differential equations governing the evolution of the chemical species in this set of reactions can be represented as

$$\frac{dc(t)}{dt} = \omega R(t), \quad \text{where} \quad \omega := \begin{pmatrix} 1 & 0 & -1 \\ -1 & 0 & 1 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & 1 \end{pmatrix}. \quad (4)$$

Here ω is the stoichiometric matrix of the system of chemical reactions (1)–(3). In order to determine all appropriate conservation equations, all linear combinations of species that are conserved have to be found. For these species, the time derivative $dc(t)/dt$ vanishes. Thus we consider a matrix M that contains all linear combinations of derivatives that are zero.

$$M \frac{dc(t)}{dt} = 0, \quad (5)$$

and substituting (4) into (5) yields

$$M \frac{dc(t)}{dt} = M \omega R(t) = 0. \quad (6)$$

Since the relation (6) is true for all times, it follows that

$$M \omega = 0 \quad \text{and} \quad \omega^T M^T = 0.$$

Namely, M^T belongs to the null-space of ω^T , denoted by $\mathcal{N}(\omega^T)$, and therefore

$$M \in \mathcal{N}(\omega^T)^T.$$

The matrix M^T is a matrix containing a basis of the null-space $\mathcal{N}(\omega^T)$. In particular, the matrix M for the sample reactions (1)–(3) is given by:

$$M = \begin{pmatrix} 1 & 0 & -1 & 0 & 1 \\ -1 & 0 & 1 & 1 & 0 \\ 1 & 1 & 0 & 0 & 0 \end{pmatrix},$$

which implies that the mass conservation relations for this simple system (1)–(3) are

$$\text{NO} - \text{O} + \text{O}_2 = \text{NO}^0 - \text{O}^0 + \text{O}_2^0$$

$$\text{O} + \text{O}_3 - \text{NO} = \text{O}^0 + \text{O}_3^0 - \text{NO}^0$$

$$\text{NO} + \text{NO}_2 = \text{NO}^0 + \text{NO}_2^0,$$

where the superscript 0 denotes the initial concentrations at time $t = 0$. The relations given by M are used to quantify the mass conservation properties of the SSRI integrator. Note that there are more conservation relationships than just the obvious conservation of nitrogen and oxygen species.

The use of conservation relations can reduce the number of differential equations, by replacing them by algebraic relations. In addition, the use of conservation relations can transform non-mass conservative integrators into conservative integrators.

3. Numerical algorithm

3.1. An operator splitting approach

Among the existing chemical integrators, there are algorithms that are positive definite but not mass conservative, e.g. CHEMEQ2 (Mott et al., 2000). On the other hand, there are also many algorithms that are mass conservative but not positive definite (Verwer et al., 1998). It seems that having both properties is elusive for higher-order integrators in the literature.

The problem of losing the positive definiteness and mass conservative characters come either from the numerical approximation of the ordinary differential equations or from the interpolation and smoothing of the solution. These two artifacts arise since nonlinear systems of coupled ordinary differential equations are complex and exact solutions are virtually impossible to derive.

The proposed method relies on explicit exact solutions of a decoupled set of ordinary differential equations. The coupled set of chemical reactions is decoupled into a *sequence of single reactions*. Each reaction is represented by a system of ordinary differential equations that is considered independently. Moreover, the exact solution to each single chemical reaction can be derived and allows to construct a solution that is mass conservative and positive definite. The solution to the entire mechanism is computed via an operator splitting scheme using the exact solution of each chemical reaction. Since the solution associated with each chemical reaction is mass conservative and positive definite, as we prove later, the solution to the entire system shares the same properties.

To illustrate the decomposition according to the chemical reactions, consider three arbitrary chemical reactions:



Strang (1968) operator splitting techniques can be used to split fast chemical reactions from slow chemical reactions.

Let us explain briefly how the splitting of reactions can be achieved. Assume that the reaction (9) is slower than the reaction (8), which is slower than the reaction (7). The chemical dynamics can be split as follows. Let Δt be a given time step. First, we solve the fast reaction (7) for a time step of $\Delta t/2$ and the solution is used as the initial condition for solving the other fast reaction (8) for a time step of $\Delta t/2$. Then, the slow reaction (9) is solved for a time step Δt . Once the slow reaction (8) is solved, the split is completed by solving the fast reactions in reverse order, i.e. successively (8), then (7), for a time step of $\Delta t/2$. The splitting of the reactions into a fast-slow-fast sketch is a symmetric split.

When dealing with an arbitrary number of reactions in practice, the chemical reactions are sorted according to their reaction speeds (from the fastest to the slowest). Starting with the fastest, each of them is solved for a time step of $\Delta t/2$. Once the slowest is solved, the order is reversed and the procedure is repeated, to solve each of them with a time step of $\Delta t/2$ from the slowest to the fastest.

This symmetric split is a second order accurate time splitting scheme (see Glowinski, 2003; Marchuk, 1990; Strang, 1968). This means that an additional numerical error of order $\mathcal{O}(\Delta t^2)$ is introduced by the operator splitting, independently of the method used for the solution of each individual reactions. Introducing this error is consistent with the global convergence order of atmospheric models, and it allows to treat each chemical reaction independently of the others, and independently of the total number of reactions.

Remark 3.1. A ‘classical’ splitting strategy for a system of ordinary differential equations typically solves each ODE sequentially. The proposed strategy splits the chemical reactions (groups of ODEs) instead of the equations themselves (species).

In the following subsections, the solution of each chemical reaction is discussed, independently of the reaction speeds. The exact solution to each chemical reaction, and therefore the solution of the corresponding system of differential equations, depends on the number of reactants, but the complexity of the resolution does not depend on the number of products. The solution to systems with one or two reactants is discussed first. The number of products is arbitrary and therefore will be restricted to two for the sake of clarity. Then the solution method is extended to an arbitrary number of reactants and products in Section 3.4. The exact solution to each reaction is proved to be *mass conservative* and *positive definite*.

3.2. Explicit solution to individual reactions: the case of one reactant

Consider the reaction



where $a, b, c \in \mathbf{N}$ (lower cases) represent the stoichiometric coefficients of the reaction and A, B and C (capital letters) represent the concentrations of the species. The corresponding reaction speed is denoted by k . Note that $k > 0$. The time evolution of the concentrations in reaction (10) is described by the following system of differential equations

$$\frac{dA(t)}{dt} = -kA(t)^a \quad (11)$$

$$\frac{dB(t)}{dt} = -b \frac{dA(t)}{dt} = bkA(t)^a \quad (12)$$

$$\frac{dC(t)}{dt} = -c \frac{dA(t)}{dt} = ckA(t)^a. \quad (13)$$

The conservation relations corresponding to (11)–(13) are obtained as in Section 2. For the case of this single reaction, $\omega = (-1, b, c)$ and the associated null-space matrix is

$$M = \begin{pmatrix} b & 1 & 0 \\ c & 0 & 1 \end{pmatrix}.$$

Since the product of M and the vector $[A, B, C]^T$ is conserved, the following relations arise

$$B(t) + bA(t) = B^0 + bA^0 = \text{constant} \quad (14)$$

$$C(t) + cA(t) = C^0 + cA^0 = \text{constant}, \quad (15)$$

where the superscript 0 represents the initial concentrations at time $t = 0$. The use of these conservation relations guarantees that mass is conserved. It remains to be seen that the exact solution to (11)–(13) leads to a positive solution. Using the conservation relations, the system of equations (11)–(13) can be solved explicitly. The exact solution for the reactant in (11) when $a > 1$ is

$$A(t) = [(1-a)kt + (A^0)^{1-a}]^{\frac{1}{1-a}}. \quad (16)$$

The concentration A remains positive for all times if $A^0 \geq 0$ (which is satisfied for chemical dynamics). When $a = 1$, the exact solution for A is a decaying exponential $A(t) = A^0 \exp(-kt)$ with the same properties. Equation (16) reveals that A is a non-increasing function in time. Given A , the products are computed from the conservation equations (14) and (15):

$$B(t) = B^0 + b(A^0 - A(t))$$

$$C(t) = C^0 + c(A^0 - A(t)).$$

Since $A(t)$ is a non-increasing function of time, the concentrations $B(t)$ and $C(t)$ are non-decreasing functions in time, and therefore positive when the initial values B^0 and C^0 are positive. In conclusion, all species are non-negative at all times.

Remark 3.2. The number of products is not important, since each product is linked to a conservation relation similar to (14) and (15) that states that the concentration of each product is increasing in time. In Section 3.4, notations are introduced to address the general case of n reactants and m products.

3.3. Explicit solution to individual reactions: the case of two reactants

Subsection 3.2 shows that the solution to a reaction involving only one reactant is mass conservative and positive definite. Here, the behavior of a reaction with two reactants is derived and similar properties are obtained. Consider the general chemical reaction



The differential equations describing the evolution of the concentrations are

$$\frac{dA(t)}{dt} = -kA(t)^a B(t)^b \quad (18)$$

$$\frac{dB(t)}{dt} = b \frac{dA(t)}{dt} = -bkA(t)^a B(t)^b \quad (19)$$

$$\frac{dC(t)}{dt} = -c \frac{dA(t)}{dt} = ckA(t)^a B(t)^b \quad (20)$$

$$\frac{dD(t)}{dt} = -d \frac{dA(t)}{dt} = dkA(t)^a B(t)^b. \quad (21)$$

For this reaction, $\omega = (-1, -b, c, d)$ and the null-space matrix is

$$M = \begin{pmatrix} -b & 1 & 0 & 0 \\ c & 0 & 1 & 0 \\ d & 0 & 0 & 1 \end{pmatrix}. \quad (22)$$

The resulting conservation relations are

$$B(t) - bA(t) = B^0 - bA^0 = \text{constant}, \quad (23)$$

$$C(t) + cA(t) = C^0 + cA^0 = \text{constant}, \quad (24)$$

$$D(t) + dA(t) = D^0 + dA^0 = \text{constant}. \quad (25)$$

Note that adding a product E with stoichiometric coefficients e is either equivalent to adding a differential equation to the Equations (18)–(21), adding a line in the matrix M , or adding the relation $E(t) + eA(t) = E^0 + eA^0$. Therefore, the analysis is independent of the number of products.

The decoupled differential equation for A is found by substituting Equation (23) into Equation (18):

$$\frac{dA(t)}{dt} = -kA(t)^a(\alpha + bA(t))^b, \quad \alpha = B^0 - bA^0. \quad (26)$$

In most cases, reactions in the atmosphere involve two molecules reacting (Morris and Myers, 1990), i.e. $a = 1$ and $b = 1$. In this case, the solution to (26) is

$$A(t) = \frac{A^0 \alpha}{A^0(e^{k\alpha t} - 1) + e^{k\alpha t} \alpha}. \quad (27)$$

Equations (23)–(25) provide mass conservation in the system, while Equation (27) states the positiveness of A .

We analyze the behavior of the differential equations to prove the positiveness of the general solution of (26). We consider the two cases $\alpha > 0$ and $\alpha \leq 0$. For the first case, $\alpha > 0$, there is enough of B to react with all of A , and A disappears before B . Provided that the initial conditions satisfy $A^0 > 0$ and $B^0 > 0$, Equation (26) implies that

$$\left. \frac{dA(t)}{dt} \right|_{t=0} = -k(A^0)^a(\alpha + bA^0)^b < 0,$$

and A is decreasing in a neighborhood of $t = 0$.

Thus, the derivative is initially negative and changes sign at time t if and only if $A(t) = 0$ or $\alpha + bA(t) = 0$. If $\alpha > 0$, $A(t)$ approaches 0 before $\alpha + bA(t)$ does. When the concentration $A(t)$ equals zero, Equation (17) only contains one reactant, the reactant B . Moreover, when A tends to zero, the differential equation (26) is approximated by

$$\frac{dA(t)}{dt} = -kA(t)^a(\alpha + bA(t))^b \approx -k_s A(t)^a, \quad k_s = k\alpha^b$$

and treated the same way as the case with one reactant in Subsection 3.2 to conclude that $A(t)$ is a decreasing positive function. In summary, when $\alpha > 0$, the concentration $A(t)$ decreases to zero monotonically, while the concentration of B is given by Equation (23), $B(t) = \alpha + bA(t) > 0$.

In the second case, $\alpha \leq 0$, the role of the reactants A and B are exchanged. The concentration B decreases monotonically to zero and is consumed totally according to the differential equation

$$\frac{dB(t)}{dt} = -bk\left(\frac{1}{b}(B(t) - \alpha)\right)^a B(t)^b.$$

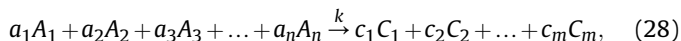
The concentration A is positive since $A(t) = \frac{1}{b}(B(t) - \alpha) \geq 0$. In both cases, the concentrations of all reactants are decreasing positive functions. The concentration of the products are derived from Equations (24) and (25),

$$C(t) = C^0 + c(A^0 - A(t)) \quad \text{and} \quad D(t) = D^0 + d(A^0 - A(t)).$$

Since A is decreasing, C and D are increasing and non-negative.

3.4. Explicit solution to individual reactions: the case of n reactants and m products

The behavior of a reaction with more than two reactants is derived and similar properties are obtained. Consider the general chemical reaction with n reactants A_i , $i = 1, \dots, n$ and m products C_j , $j = 1, \dots, m$,



where $a_1, \dots, a_n, c_1, \dots, c_m$ are the stoichiometric coefficients. The differential equations describing the evolution in time of the concentrations are

$$\frac{dA_1(t)}{dt} = -k \prod_{j=1}^n A_j(t)^{a_j}$$

$$\frac{dA_i(t)}{dt} = a_i \frac{dA_1(t)}{dt}, \quad i = 2, \dots, n$$

$$\frac{dC_j(t)}{dt} = -c_j \frac{dA_1(t)}{dt}, \quad j = 1, \dots, m$$

implying that the conservation relations for reaction (28) are

$$A_i(t) - a_i A_1(t) = A_i^0 - a_i A_1^0, \quad i = 2, \dots, n$$

$$C_j(t) + c_j A_1(t) = C_j^0 + c_j A_1^0, \quad j = 1, \dots, m$$

The demonstration of the positiveness occurs by induction on the reactants. Let A_K be the first reactant that gets consumed and goes to zero. The index K is equal to one if A_1 gets consumed first; otherwise it is given by the index such that $A_K^0 - a_K A_1^0 \leq A_j^0 - a_j A_1^0$ for all $j = 1, \dots, n$. Therefore A_K is a decreasing concentration, that goes to zero, whose evolution is given by the differential equation:

$$\frac{dA_K(t)}{dt} \approx -k_s A_K(t)^a, \quad k_s = k \prod_{j=1, j \neq K}^n a_j^{a_j}, \quad \alpha_j = A_j^0 - a_j A_K^0.$$

By using similar arguments than in Section 3.3, $A_K(t)$ is positive and decreasing. When $A_K(t) = 0$, A_K is consumed and the number of reactants is reduced by one. By induction, the same arguments can be repeated for all reactants in order of their disappearance from the system. The solution to the chemical dynamics is therefore positive definite and mass conservative. The concentrations of the products are given by $C_j(t) = C_j^0 + c_j(A_1^0 - A_1(t))$, $j = 1, \dots, m$; they are increasing by using the same arguments as in Section 3.3.

3.5. Global time splitting algorithm

The proposed SSRI algorithm computes the exact solution to each reaction independently, within an operator splitting framework, to couple all the reactions together. Strang (1968) showed that a symmetric operator splitting leads to second order accuracy, provided that the approximation of the solution to each step is at least of second order. The solution to each reaction outlined in Subsections 3.2–3.4 being exact, this method's symmetric split is at least second order. Note that the order of convergence of symmetric operator splitting schemes could be higher (see e.g. Goldman and Kaper, 1996). However, higher-order chemical integrators in atmospheric models may not be useful since the other operators, in particular the transport dynamics, are only second order.

For the simulations presented in Section 4, the order of operations inside the splitting scheme is as follows. The chemical reactions are split up into fast and slow reactions via the reaction rates

for each time step. Let Δt be a given time step, and $t^0, t^1, \dots$ a sequence of discrete times, such that $t^n = n\Delta t$. At each time step, the reactions are ordered according to their reaction speeds (using a bubble sort algorithm). The fast reactions are first solved for a time step of $\Delta t/2$; then sequentially from the faster to the slowest reactions, each reaction is solved for a time step of $\Delta t/2$. Finally the slowest reaction is solved for a time step of Δt . Then the order is reversed and, going from the slower to the faster, the reactions are solved again for a time step of $\Delta t/2$ to complete the symmetric split. The fast reactions are computed twice at each time step to account for larger transient responses.

Let $c(t)$ be the time-dependent concentration vector of the species in the system. Let c^n denote the approximation of the concentration vector $c(t)$ at time t^n , and let L_f and L_s represent the operators corresponding to the fast reactions and slow reactions respectively. One time step of the time-evolution algorithm can be represented as follows:

$$c^{n+1} = L_f \left[\frac{\Delta t}{2} \right] L_s \left[\frac{\Delta t}{2} \right] L_f \left[\frac{\Delta t}{2} \right] c^n.$$

For $N > 0$ given, Strang (1968) implies that there exists a constant $C > 0$, independent of Δt such that (second order accuracy):

$$\|c^N - c(t^N)\| \leq C(\Delta t)^2,$$

since the individual reactions are solved exactly, as shown in Subsections 3.2–3.4.

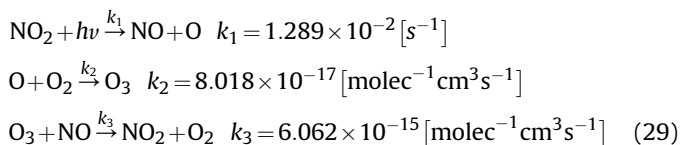
Remark 3.3. An adaptive time integration procedure can be established by checking the convergence of the splitting algorithm. More precisely, for a given relative tolerance $\varepsilon > 0$, the time increment Δt is decreased if $\|L_f[\frac{\Delta t}{2}]L_s[\Delta t]L_f[\frac{\Delta t}{2}]c^n - L_s[\frac{\Delta t}{2}]L_f[\Delta t]L_s[\frac{\Delta t}{2}]c^n\| \geq \varepsilon\|c\|$. In an adaptive scheme, the relative tolerance ensures an accurate solution, independently of the splitting among chemical reactions.

The present algorithm (SSRI) inherits mass conservation and positive definiteness at each time step since the solution to each chemical reaction has such properties. The proposed solution splits according to the chemical reactions, instead of the chemical species. Since atmospheric models tend to have more chemical reactions than chemical species, this algorithm might be computationally expensive when used as a standalone integrator. For better efficiency, it can be inserted into a host integrator, like CHEMEQ2 (Mott et al., 2000), RODAS-3 (Sandu et al., 1997a), or ROS-2 (Verwer et al., 1999), and be invoked to correct negative concentrations produced by the host model. Although the proposed algorithm SSRI may be used inside an host integrator, it is used as a standalone solver in the sequel in order to fairly evaluate its performance. The corresponding numerical results are presented in the next section.

4. Numerical experiments

4.1. Benchmark example

In order to validate the proposed algorithm, let us first consider the simple system (1)–(3):



This set of chemical reactions corresponds to the following system of differential equations:

$$\begin{aligned} \frac{d\text{NO}}{dt} &= k_1 \text{NO}_2 - k_3 \text{O}_3 \text{NO} \\ \frac{d\text{NO}_2}{dt} &= -k_1 \text{NO}_2 + k_3 \text{O}_3 \text{NO} \\ \frac{d\text{O}}{dt} &= k_1 \text{NO}_2 - k_2 \text{OO}_2 \\ \frac{d\text{O}_3}{dt} &= k_2 \text{OO}_2 - k_3 \text{O}_3 \text{NO} \\ \frac{d\text{O}_2}{dt} &= -k_2 \text{OO}_2 + k_3 \text{O}_3 \text{NO} \end{aligned} \quad (30)$$

We consider the initial condition $[\text{NO}^0, \text{NO}_2^0, \text{O}^0, \text{O}_3^0, \text{O}_2^0] = [8.725 \cdot 10^8, 2.24 \cdot 10^8, 6.624 \cdot 10^8, 5.326 \cdot 10^{11}, 1.697 \cdot 10^{16}]$. All concentrations are in $[\text{molec cm}^{-3}]$. The exact solution to (30) is not known explicitly. In order to validate the SSRI algorithm, the solution of (29) and (30) is compared with classical integrators such as the explicit Runge-Kutta method of order 4 (RK44), and the two-steps backward differentiation formula (BDF-2), see e.g. Hairer and Wanner (1996).

Fig. 1 illustrates the stability of the three integrators (RK44, BDF-2 and SSRI) for various (large) values of the time step Δt . It visualizes the concentrations of NO_2 and O_3 respectively. For small time steps ($\Delta t = 1$ [s]), all methods are stable and provide similar results. For larger time steps ($\Delta t = 100$ [s]), the solutions obtained with the RK44 and BDF-2 methods grow without bound (as already stated in (Sandu (2001))), while the one obtained with the SSRI remains bounded.

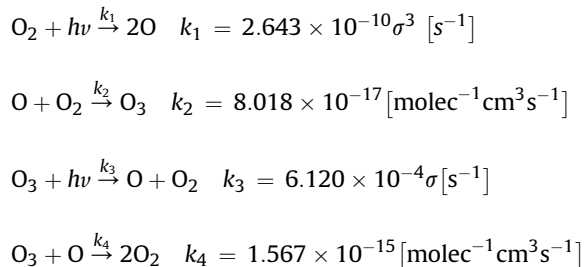
Fig. 2 visualizes only the solution of the SSRI algorithm for various time steps. Keeping in mind that reasonable time steps in the field of atmospheric chemical reactions are around 1000 [s], it shows that the proposed algorithm provides a bounded, although oscillating, solution, that may be incorporated into global 3D atmospheric simulation models.

Finally the convergence of the SSRI algorithm is studied. Since the exact analytical solution of (29) and (30) is not known explicitly, we consider the solution obtained by the BDF-2 scheme on a time interval of 1 h with $\Delta t = 0.01$ [s] as the reference solution. Fig. 3 visualizes, on a log–log plot, the maximal error between the reference solution and the solution obtained with SSRI when the time step decreases. Both the error for the concentrations of NO_2 and O_3 behave approximately like $\mathcal{O}(\Delta t^2)$, which confirms that SSRI is second order accurate.

Numerical experiments on this simple system confirm the second order accuracy of the proposed scheme, as well as its good stability properties. A more complicated, stringent, system is considered in the following.

4.2. Stringent test case

The new method is evaluated on a real chemical system, that is described in details in Sandu (2001). This stringent test case consists of integrating the following set of stratospheric chemical reactions, by using large fixed time steps of 15 and 30 min respectively.



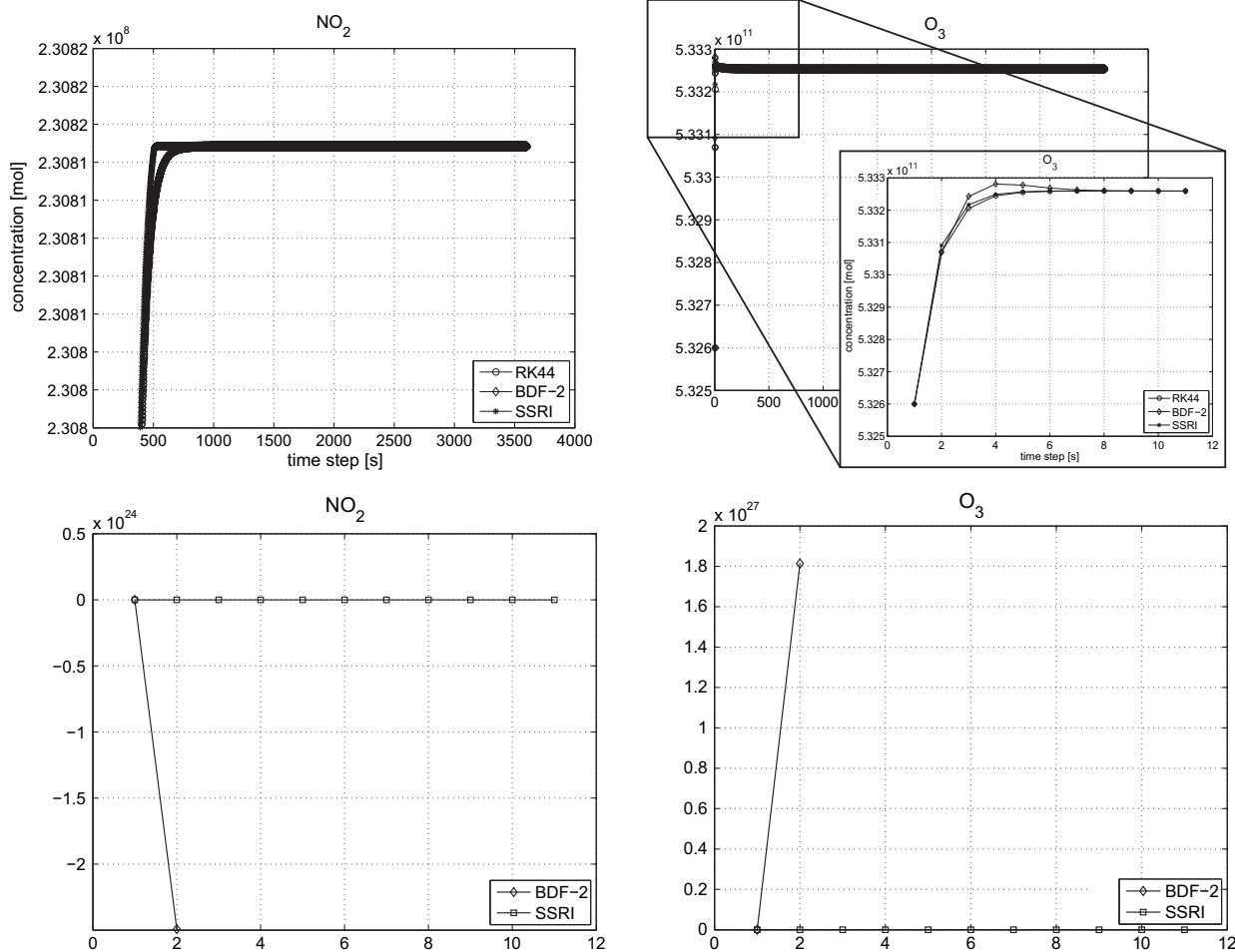


Fig. 1. Stability of the SSRI algorithm and comparison with the RK44 and BDF-2 schemes. Top: Evolution for 1 h and $\Delta t = 1$ [s] of the concentrations of NO_2 (left), O_3 with zoom on the trajectories for the concentration of O_3 (right); all solutions are close to each other. Bottom: Evolution for 1 h and $\Delta t = 100$ [s] of the concentrations of NO_2 (left), O_3 (right); the solution obtained with BDF-2 is unstable; the one obtained with the RK44 scheme is not represented.

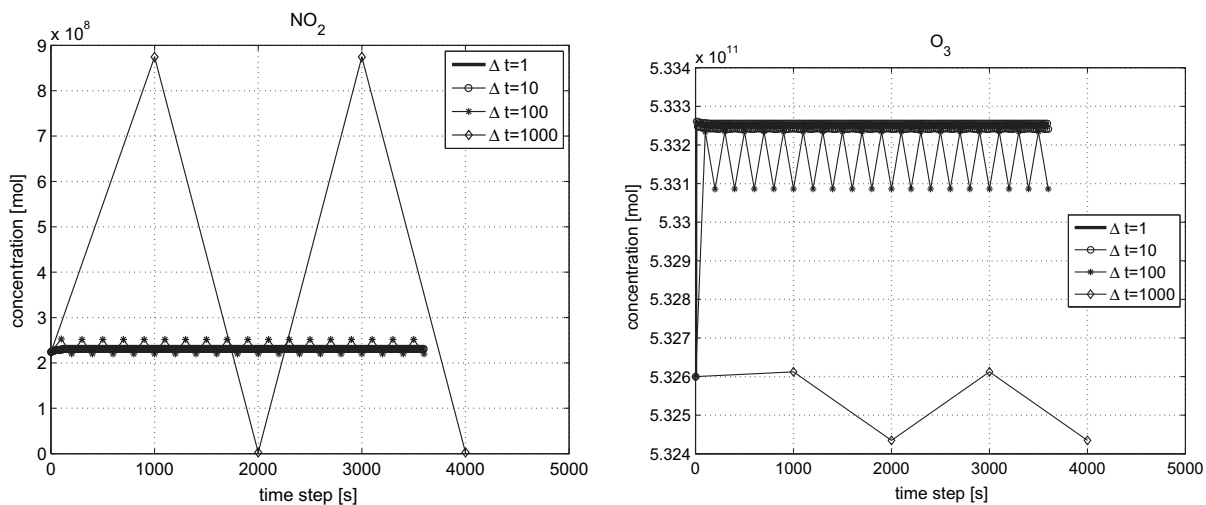


Fig. 2. Stability of the SSRI algorithm. Evolution for 1 h and various time steps Δt of the concentrations of NO_2 (left) and O_3 (right).

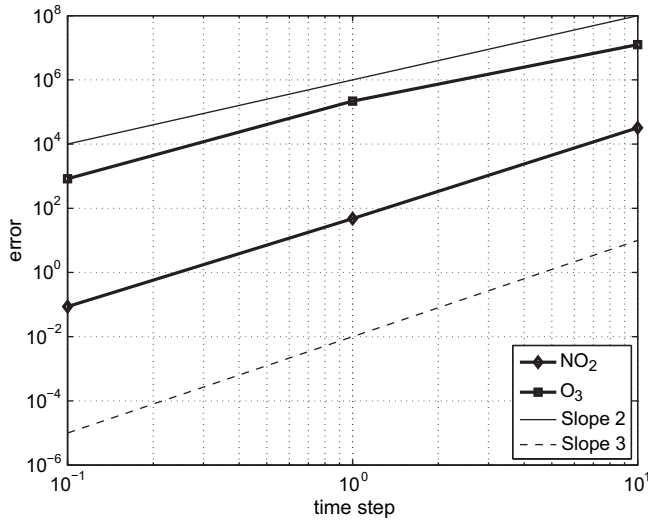
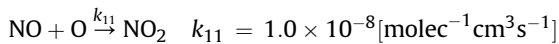
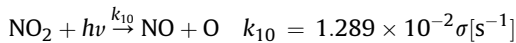
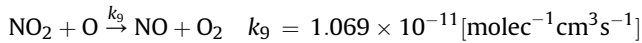
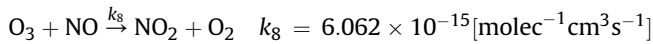
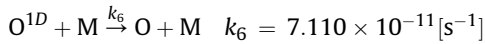
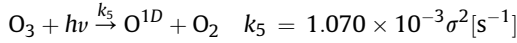


Fig. 3. Convergence (log-log plot) of the concentrations of NO_2 and O_3 obtained with the SSRI algorithm towards the reference solution. The second order of accuracy corresponds to the splitting error.



where $M = 8.120E + 16 [\text{molec cm}^{-3}]$ is the atmospheric number density, and $\sigma = \sigma(t)$ is the normalized sunlight intensity given by:

$$\sigma(t) = \begin{cases} \frac{1}{2} + \frac{1}{2} \cos\left(\pi \left| \frac{2t - T_R - T_S}{T_S - T_R} \right| \left(\frac{2t - T_R - T_S}{T_S - T_R} \right) \right), & \text{if } T_R \leq t \leq T_S \\ 0, & \text{otherwise,} \end{cases}$$

where we assume that the sun rises at $T_R = 4.5$ (4:30 am) and disappears at $T_S = 19.5$ (7:30 pm), giving 15 h of light per day, with a maximum intensity at 12:00 pm (noon). The coefficient $\sigma(t)$ is adimensional and between 0 and 1 for all times t (Sandu (2001)).

Remark 4.1. The characteristic time scales of such chemical systems arising in atmospheric chemistry range from 10^{-4} s for the fastest reactions to several weeks or months for the slowest ones, i.e. typically the O_2 species.

The simulation starts at 12:00 pm (noon) and runs for 72 h. In order to quantify the mass conservation properties of the solvers, the following mass conservation relations are computed:

$$\alpha_N = \text{NO}_2^0 + \text{NO}^0$$

$$\alpha_O = \text{NO}^0 + 2\text{NO}_2^0 + \text{O}^{1D,0} + 2\text{O}_2^0 + 3\text{O}_3^0 + \text{O}^0,$$

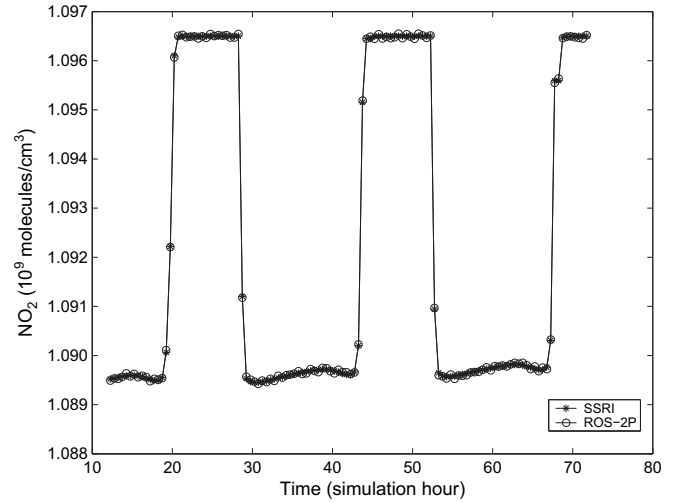


Fig. 4. Evolution of NO_2 with an adaptive step control of $\varepsilon = 10^{-4}$ for ROS-2P and SSRI. The results for ROS-2P and SSRI are nearly identical. Neither exhibits negative concentrations. Both require extremely small time steps of 10^{-5} s at the beginning of the simulation.

where the superscript 0 indicates the quantities at the initial time. The norm chosen to measure the mass conservation property of the algorithm is

$$\text{MC} = \frac{|\text{NO}_2 + \text{NO} - \alpha_N| + |\text{NO} + 2\text{NO}_2 + \text{O}^{1D} + 2\text{O}_2 + 3\text{O}_3 + \text{O} - \alpha_O|}{\text{NO}_2 + \text{NO} + \text{NO} + 2\text{NO}_2 + \text{O}^{1D} + 2\text{O}_2 + 3\text{O}_3 + \text{O}} \quad (31)$$

This chemical system is difficult to solve when considering large time steps, since a stable integrator is required to accommodate the wide range of eigenvalues of the system. In addition, the reaction $\text{NO} + \text{O} \rightarrow \text{NO}_2$ is called a *non-correcting* reaction, in which the species NO and O are destroyed without bound, permitting NO_2 to grow indefinitely. As a result, the analysis of numerical tests presented here focuses on NO_2 .

Large time steps are commonly used in stratospheric chemical simulations. However, most solvers (like BDF-2, RODAS-3, ROS-2,

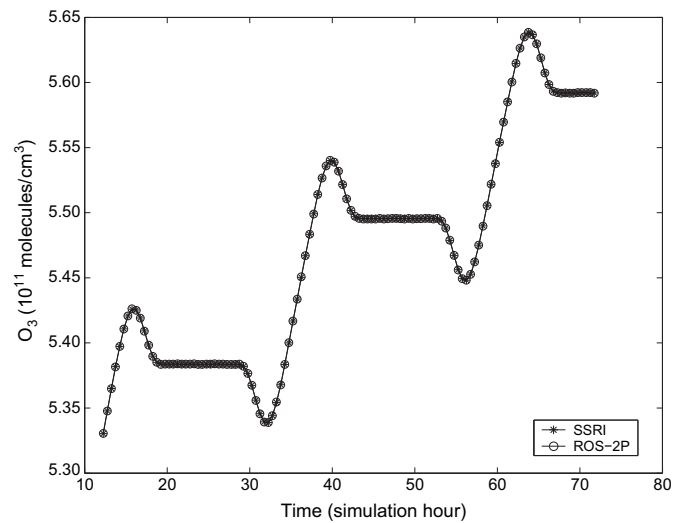


Fig. 5. Evolution of O_3 with an adaptive step control of $\varepsilon = 10^{-4}$ for ROS-2P and SSRI. The results for ROS-2P and SSRI are nearly identical. Neither exhibits negative concentrations. Both require extremely small time steps of 10^{-5} s at the beginning of the simulation.

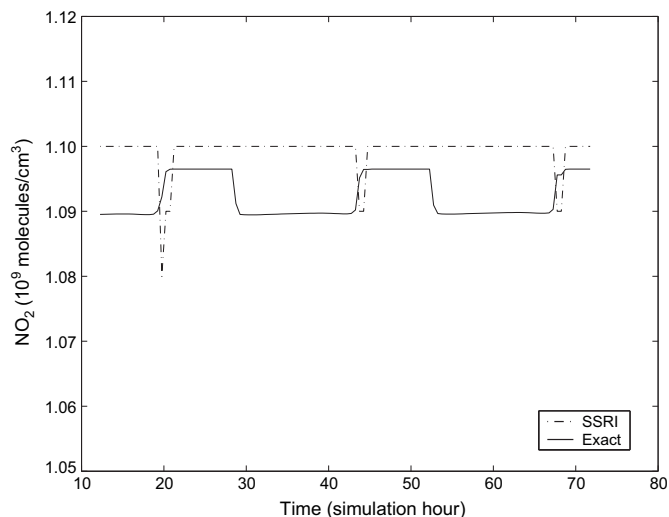


Fig. 6. SSRI approximation of the concentration of NO_2 with a time step of 15 [mn].

and CHEMEQ2) yield meaningless results for a time step of 30 min. In particular, NO_2 concentrations are divergent for all mentioned schemes; according to the current literature, this instability is largely due to oscillations and negative values of the concentrations (Sandu, 2001).

Stability can be achieved by clipping the negative concentrations and setting them to zero. Clipping, however, is not mass conservative. To avoid violations in the mass conservation, Sandu (2001) proposed a projection method that projects the negative concentration into positive concentrations via an optimization problem under a mass conservation constraint. However, such projection methods may be computationally expensive, and, either projection or stabilization methods require a host integrator since they are not directly based on chemical dynamics. Sandu (2001) showed that the integrator ROS-2P with the positive projection (denoted here as ROS-2P) produce the most desired result. Taking the solver ROS-2P as a reference, we compare it to the Split Single Reaction Integrator (SSRI) presented in this article.

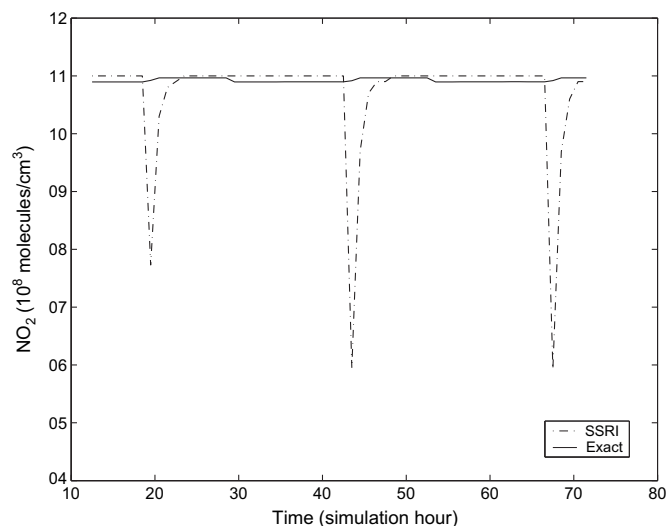


Fig. 7. SSRI approximation of the concentration of NO_2 with a time step of 30 [mn]. The large time step provides a stringent test for the stability and accuracy of the algorithm. SSRI captures the general behavior of cyclic ultra violet radiation. More importantly, SSRI is stable with a relative error less than 2%. All other tested schemes (BDF2, RODAS3 and CHEMEQ2) are unstable and not plotted.

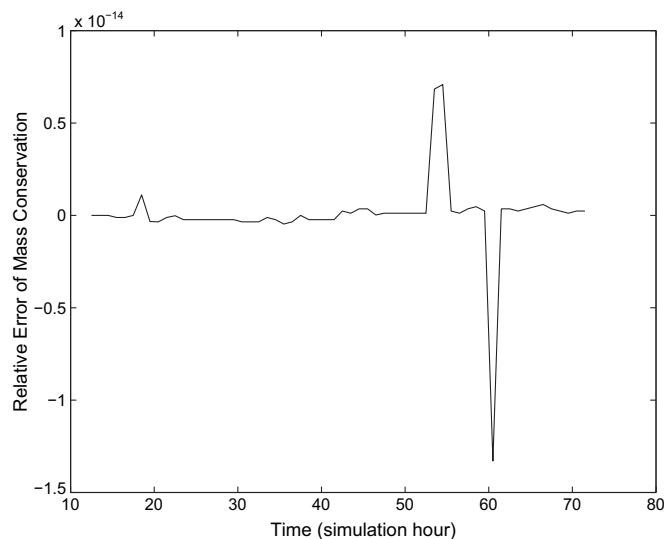


Fig. 8. Mass conservation of the SSRI algorithm. The quantity MC is conserved exactly (up to the machine precision), and the relative error is less than 1.5×10^{-14} .

The reference solution is computed by using a relative time step integration using SSRI and ROS-2P with a relative error of $\varepsilon = 10^{-4}$ (see Remark 3.3). The solution computed with both integrators are almost identical and the approximation of the concentrations of NO_2 and O_3 is presented in Figs. 4 and 5.

It is interesting to note that, with a variable time step integration, ROS-2P does not use any projection since ROS-2 does not accrue any negative mass. However, very small time steps are needed to provide such an accurate integration. In particular, a time step of 10^{-5} s is needed at the beginning of the simulation for both SSRI and ROS-2P to capture the rapid transient region. Negative concentrations only occur with sufficiently large time steps.

When using fixed time steps of 15 and 30 min, a stringent test case is obtained. For a fixed time step of 15 min, all non-positive definite methods (ROS-2, BDF, RK44 and RODAS3) are unstable, while SSRI is stable. Fig. 6 visualizes the stable evolution of NO_2 .

For a fixed time step of 30 min, SSRI still produces stable results. Fig. 7 visualizes the evolution of NO_2 , and shows that SSRI still captures the general behavior of cyclic ultra violet radiation, while being stable with a relative error less than 2%. All other methods, including the projected ROS-2P, are unstable and grow without bound, and are not represented. Naturally, when the time step increases, SSRI's error grows (due to the splitting error) but the algorithm still maintains positive definiteness. Finally Fig. 8 visualizes the conservation of the mass MC defined by (31); it shows that the SSRI is exactly mass conservative, up to round-off errors, and allows to conclude to the strong stability of the SSRI scheme.

5. Conclusions

A novel approach for the integration of chemical dynamics has been presented in this article. It provides a positive definite, mass conservative, and stable numerical solution. This new method is called Split Single Reaction Integrator (SSRI). It relies on an operator splitting approach to decouple chemical reactions and solve each reaction exactly. The exact solutions for each chemical reaction are symmetrically combined using the Strang operator splitting approach to compute the solution of the entire chemical mechanism.

SSRI is easy to implement because it only depends on the number of reactants; it is even easier when chemical systems have

only one or two reactants in each chemical reactions as it is usually the case in most atmospheric systems.

Numerical results have confirmed that SSRI is a second order accurate algorithm with excellent stability properties for large fixed time steps. They have also shown that SSRI (as a standalone solver) is accurate when used as a variable step integrator. In particular, it provides stable results for a stringent test case involving large time steps, when all other integrators tested (BDF, RK44, ROS-2, RODAS3, CHEMEQ2 and projected positive definite ROS-2) are unstable.

The chemical dynamics operator being usually the operator that suffers the most from a lack of mass conservation and/or positiveness in atmospheric 3D solvers, SSRI provides an efficient alternative method to ensure that the solution to consistent chemical dynamics is mass conservative and positive definite.

Acknowledgments

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