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Reduced Atmospheric Chemistry Models

by Sensitivity Matrix Approach

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– Short Communication –

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Abstract

Simulation of chemical kinetics typically claims about 80 to 90% of the total computational time in three dimensional atmospheric chemistry-transport models; to alleviate this computational burden reduced chemical models are often employed. Reduced models are build via a dynamical analysis that results in the elimination of the fastest time scales, or by tuning a simpler model to reproduce the input-output relations of the kinetic system.

The sensitivity matrix is a linear entity associated with the dynamics of a nonlinear system. In this communication we show that sensitivity matrices can be used to identify low-dimensional linear evolution manifolds and to construct reduced kinetic models.

Keywords: Atmospheric chemistry, reduced kinetic models, sensitivity matrix.

1 Introduction

Air quality models are used to enhance the understanding of the chemical composition of the atmosphere, in particular with regard to the relation between emissions and the resulting distributions of primary and secondary pollutant species. These models can be mathematically described as time-dependent, three-dimensional partial differential equations. Simulation of the stiff and highly nonlinear chemical kinetics requires implicit integration schemes and typically claims about 80 to 90% of the total computational time. To alleviate this computational burden reduced chemical models are often employed. Reduced models are able to reproduce the behavior of the full models using a smaller number of variables.

The traditional way to build reduced models is based on a dynamical system analysis. As the fast time scales reach equilibrium, the dynamics of the system becomes confined to lower dimensional manifolds in the phase space. Parameterizing the (slow) motion along the lower-dimensional manifold results in a reduced model; this model is less stiff due to the elimination of the fastest time scales. Maas and Pope explicitly build an orthogonal local basis for the slow manifold in their fundamental work [6]. Lam and Goussis [4] propose a singular perturbation approach to the construction of simplified kinetic models.

Lowe and Tomlin [5] use time-scale analysis to show that the intrinsic dimension of a tropospheric chemical model is low (between 2 and 9). The repro-modeling technique which fits multivariate polynomials to a data set representative for the chemical system is employed; tests performed with CBM-IV chemical mechanism show excellent agreement between the full and the reduced models.

Sportisse and Djouad [9] take a novel view of lumping from the perspective of singular

perturbation theory. They are able to build reduced tropospheric models by using linear lumping to eliminate the fastest timescales.

A different approach is taken by Wang, Levy II, Li and Rabitz [10]. The authors build fully equivalent operational models using a hierarchical correlated-function expansion that captures the input-output relationships of the chemical system.

Previous work [6, 9] used linear transformations to decouple the fast components from the slow ones. The fundamental question is how to compute this decoupling linear transformation. In [6] the Schur decomposition of the Jacobian is employed, while in [9] information on the stoichiometric matrix and on the rate coefficients is used.

Finding linear transformations that decouple the dynamics of a nonlinear system is a challenging task. A linear entity associated with nonlinear system dynamics is the sensitivity matrix. In this technical communication we show that the sensitivity matrix holds information useful to identify a linear, lower dimensional evolution manifold.

The communication is organized as follows. Section 2 reviews sensitivity matrices and their numerical calculation; Section 3 presents the use of sensitivity matrices to build simplified models. Numerical results for a tropospheric and for a stratospheric chemical models are presented in Section 4.

2   The sensitivity matrix

Consider the description of the chemical kinetic system by a smooth initial value problem:

$$y' = f(t, y) , \qquad y(t_0) = y_0 . \tag{1}$$

The flow uniquely maps y_0 to $y(t)$; the sensitivity matrix (of the solution with respect to the initial values) is the differential of the flow

$$\Psi(t_0; t) = \frac{\partial y(t)}{\partial y_0} \ . \tag{2}$$

Differentiating (1) with respect to the initial conditions results in an initial-value problem for the sensitivity matrix:

$$\Psi'(t_0; t) = J(t, y) \, \Psi(t_0; t) \ , \qquad \Psi(t_0; t_0) = I \ . \tag{3}$$

In the above $J(t, y) = f_y(t, y)$ is the Jacobian of the derivative function in (1), and I represents the identity matrix. In the direct method equations (1) and (3) are solved together forward in time to obtain both the concentrations $y(t)$ and the sensitivities $\Psi(t_0; t)$. A very efficient numerical process can be devised based on the fact that both equations share the same Jacobian (the direct decoupled method of Dunker [1]).

3   Reduced model analysis

A small change in the initial conditions Δy_0 will produce a change $\Delta y(t)$ in the solution at time t

$$\Delta y(t) = \Psi(t; t_0) \, \Delta y_0 \ .$$

Clearly, if $\Delta y_0 \in \text{null}(\Psi)$ (the perturbation is in the nullspace of Ψ) then no changes are induced in the solution at time t. Conversely, the perturbations along $\text{range}(\Psi)$ will cause changes in $y(t)$.

We can take a dynamical point of view as follows. Assume the solution of the chemical system has collapsed onto a reduced manifold. Perturbations that pull the initial conditions

outside the attracting manifold will fade away under the system dynamics and will not influence $y(t)$; perturbations inside the manifold on the other hand will produce visible changes in the solution.

Consider S an orthonormal basis for range(Ψ), and N and orthonormal basis for null(Ψ^T)

$$S^T S = I \ , \quad \text{range}(S) = \text{range}(\Psi) \ , \qquad N^T N = I \ , \quad \text{range}(N) = \text{null}(\Psi^T) \ .$$

S stands for "significant" directions and "N" for non-significant (insignificant) directions. We can describe the system dynamics in the new orthonormal basis $[NS]^T$ as

$$\begin{bmatrix} N^T \\ S^T \end{bmatrix} y' = \begin{bmatrix} N^T y' \\ S^T y' \end{bmatrix} = \begin{bmatrix} z' \\ x' \end{bmatrix} = \begin{bmatrix} N^T f(t, y) \\ S^T f(t, y) \end{bmatrix} = \begin{bmatrix} N^T f(t, x, z) \\ S^T f(t, x, z) \end{bmatrix} \ .$$

The reduced system is obtained by setting the non-significant directions to steady-state

$$\begin{bmatrix} 0 \\ x' \end{bmatrix} = \begin{bmatrix} F^T f(t, x, z) \\ S^T f(t, x, z) \end{bmatrix} \ .$$

For linear autonomous systems the sensitivity matrix is exponential

$$y' = J y \quad \Rightarrow \quad \Psi(t_0; t_0 + \tau) = e^{\tau J} \ .$$

This means that Ψ and J share the same the eigenvector set; in this case the sensitivity matrix analysis is similar to the method of Maas and Pope. The eigenvalues of Ψ and J are related by

$$\lambda_i(\Psi) = e^{\tau \lambda_i(J)} \ ,$$

therefore the eigenvalues of J with large negative parts will result in zero eigenvalues of Ψ; this provides a direct relationship between fast dynamics (J-analysis) and insignificant directions (Ψ-analysis).

In practice the chemical system has a multitude of time scales; we can decide the "cut" between significant (slow) and insignificant (fast) directions by using a singular value decomposition

$$\Psi = U \, \Sigma \, V^T \, ,$$

Once a tolerance level ϵ is chosen, S is given by the columns of U that correspond to the singular values larger than ϵ, and N by the remaining columns. If we relax the condition that the new basis is orthonormal, N can be taken to be a basis for the null(Ψ), or the columns of V that correspond to those singular values smaller than ϵ. However this approach needs extra precautions, which is why we do not pursue it further.

Finally let us mention that the dimension of the reduced system depends on the time horizon τ used to compute the sensitivity matrix $\Psi(t_0; t_0 + \tau)$; τ should be chosen of the order of time scale of interest.

4   Numerical Results

For the numerical tests we consider one tropospheric and one stratospheric model.

The tropospheric model is the Carbon Bond Mechanism IV (CBM-IV) [2], consisting of 32 chemical species interacting in 70 thermal and 11 photolytic reactions. The concentration of H_2O was held fixed throughout simulation. The CBM-IV mechanism was designed for the numerical simulation of chemical processes in urban and in regional scale models. The urban scenario simulates a heavily polluted atmosphere, while the rural scenario simulates a clean atmosphere. The values of initial concentrations are those given in [7, 8] and are not reproduced here. No emissions are considered.

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The stratospheric test problem [3] is based on the chemical mechanism that has been used in the NASA HSRP/AESA stratospheric models intercomparison. There are 34 species[*] interacting in 84 thermal and 25 photolytic reactions. The initial concentrations are those given in [7, 8].

For both models matlab simulations were carried out for 24 hours, i.e. a full photo-chemical cycle. We used the matlab integration routine ode15s, which is based on numerical differentiation formulas and is able to integrate both ordinary differential equations (for the reference solutions) and differential algebraic equations of index 1 (for the reduced solutions). We used the tight tolerances rtol = 1.E-8 and atol = 100 molecules per cubic centimeter. The concentrations were recorded every 15 minutes, and the root mean square (rms) norm of the difference between the reference and the reduced solutions were computed for every species according to

$$E_i = \sqrt{\frac{1}{n} \sum_{k=1}^{n} \left| \frac{y_i^{\mathrm{ODE}}(t_k) - y_i^{\mathrm{DAE}}(t_k)}{\max\{y_i^{\mathrm{ODE}}(t_k), \mathrm{atol}\}} \right|^2} \, .$$

The results for the stratospheric problem are shown in Table 1. For time scales of up to 1 minute the reduced solution reproduces the exact solution extremely well for all species in the system; the dimension decreases from 34 to 27. For a time horizon of 1 hour, however, significant differences appear between the full and the reduced solutions for several species.

Two different scenarios (rural and urban) are tested with the tropospheric model and the results are presented in Table 2. We notice that, as expected, the fast and slow bases depend on the initial conditions, i.e. on the specific regime. The results of the full and the reduced models agree well for time scales of up to 1 hour; the single large errors are seen in ISOP for

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[*]Plus 6 species whose concentrations were held fixed throughout simulation: H_2O, CO, O_2, H_2, N_2, CH_4.

a time horizon of 1 hour and for the urban scenario only. The reduced system dimensions are down to 24 (urban) and 27 (rural) as compared to the full system dimension of 32.

5 Conclusions and future work

The sensitivity matrix is a linear entity associated with nonlinear chemical kinetics. In this work we used the sensitivity matrix information to build reduced kinetic models. Specifically, the range of the sensitivity matrix is a subspace that contains the reduced manifold where chemical dynamics takes place. Consequently, the construction of a reduced systems is possible by restricting the system dynamics to this subspace. Numerical experiments were performed with the CBM-IV mechanism (both rural and urban conditions) and with a stratospheric system. In both cases reduced models were constructed that capture well the full system dynamics.

The purpose of this communication is to show that sensitivity matrix information can be useful for reducing chemical kinetics. However, the resulting models are not yet operational. More work is needed to better understand the relationships between the sensitivity matrix and the lower dimensional evolution manifold, and to build fully operational reduced models.

Acknowledgements

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τ	1/60 sec	1 sec	1 min	1 hour
Dimension	31	30	27	23
CH3	3.8e-09	3.9e-09	2.3e-07	2.6e-05
Cl2	4.4e-05	4.5e-05	3.6e-03	1.6e-01
Cl2O2	1.3e-04	1.4e-04	1.2e-02	8.3e-01
ClOO	9.0e-07	9.0e-07	5.6e-05	2.6e-03
OClO	8.9e-05	8.0e-05	2.4e-03	4.5e+02
BrCl	4.6e-05	4.7e-05	1.9e-03	6.4e+00
HOBr	1.5e-06	1.3e-06	7.1e-04	4.4e+00
BrONO2	2.3e-05	2.4e-05	9.3e-04	4.6e+00
HCO	4.5e-11	4.6e-11	1.4e-09	2.1e-07
CH3O	2.4e-07	2.5e-07	1.4e-05	1.2e-03
O1D	3.9e-08	4.0e-08	1.1e-06	2.1e-04
N2O5	1.9e-04	2.2e-04	1.9e-04	1.0e+00
HBr	9.6e-07	9.8e-07	7.4e-05	2.6e+00
CH3OOH	2.0e-06	2.2e-06	1.7e-04	9.4e-02
HNO4	8.9e-06	9.2e-06	2.9e-04	4.8e-02
HCl	5.9e-07	5.9e-07	5.0e-05	2.0e-03
H2O2	9.9e-07	1.1e-06	1.3e-05	2.6e-02
HOCl	7.4e-06	7.2e-06	8.7e-04	1.3e-01
HNO3	2.2e-06	2.3e-06	2.8e-05	2.0e-02
H	3.1e-07	3.5e-07	2.4e-05	1.6e-02
CH3O2	1.0e-05	1.0e-05	1.9e-03	5.7e+00
ClONO2	4.7e-05	4.9e-05	3.8e-03	6.6e-02
NO3	5.6e-05	5.0e-05	9.1e-04	4.5e-01
CH2O	2.2e-06	2.2e-06	1.9e-04	9.7e-03
Br	5.0e-05	5.2e-05	9.1e-04	6.4e+00
OH	3.4e-04	3.4e-04	4.1e-03	4.9e+00
Cl	3.2e-05	3.1e-05	2.1e-03	5.7e-02
ClO	6.0e-05	6.0e-05	5.6e-03	6.4e-02
O3	2.5e-07	2.6e-07	3.4e-05	1.6e-03
NO	5.6e-04	2.9e-04	1.4e-03	2.2e-02
BrO	7.7e-04	7.8e-04	4.3e-03	2.1e+01
O	8.8e-07	2.9e-07	2.2e-05	5.9e-02
HO2	1.4e-03	1.5e-03	1.2e-02	2.9e+00
NO2	5.2e-06	5.2e-06	1.8e-04	3.1e-03

Table 1: The rms errors in species predictions for different time horizons with STRATO model. The dimension of the full system is 34.

Scenario	Urban				Rural			
τ	1/60 sec	1 sec	1 min	1 hour	1/60 sec	1 sec	1 min	1 hour
Dimension	31	29	28	24	30	30	29	27
O1D	5.1e-12	1.9e-12	1.4e-09	9.7e-09	2.5e-13	3.4e-13	1.9e-13	4.7e-11
H2O2	6.4e-08	5.2e-08	2.6e-04	3.9e-03	2.4e-07	2.6e-07	1.0e-07	2.9e-05
PAN	1.2e-07	2.8e-08	1.7e-04	4.5e-04	5.2e-07	6.8e-07	5.9e-07	1.6e-04
CRO	2.3e-06	1.3e-06	3.2e-03	4.8e-02	2.3e-08	5.4e-08	2.1e-07	2.1e-03
TOL	8.9e-08	1.3e-08	5.8e-05	3.2e-04	1.9e-08	2.1e-08	8.5e-09	2.2e-02
N2O5	2.8e-06	2.2e-06	4.6e-03	2.5e-02	1.9e-05	3.5e-05	3.1e-05	3.6e-03
XYL	3.7e-07	5.7e-08	2.3e-04	1.3e-03	2.7e-08	9.7e-08	4.5e-07	7.4e-02
XO2N	8.2e-07	3.0e-07	1.2e-03	4.9e-03	1.2e-06	1.7e-06	9.6e-07	1.3e-04
HONO	4.5e-07	2.1e-06	4.9e-04	1.5e-03	1.7e-06	2.5e-06	2.0e-06	2.3e-03
PNA	1.3e-06	8.6e-07	3.7e-03	1.1e-02	3.2e-06	8.4e-06	4.2e-06	3.3e-03
TO2	6.9e-07	4.3e-07	3.7e-03	1.1e-02	3.1e-09	2.3e-10	4.4e-12	5.9e-06
HNO3	5.2e-08	1.4e-08	3.2e-05	5.1e-04	5.7e-06	8.5e-06	7.3e-06	1.2e-04
ROR	6.2e-08	2.5e-08	9.9e-05	4.8e-04	1.1e-11	1.9e-11	1.6e-10	3.8e-08
CRES	1.8e-06	1.3e-06	3.6e-03	2.0e-02	1.4e-07	3.4e-07	7.0e-06	5.3e-02
MGLY	4.5e-07	1.0e-07	1.0e-04	8.7e-04	5.7e-06	5.2e-06	5.1e-06	2.0e-04
CO	1.4e-08	1.8e-09	5.5e-06	3.8e-05	3.8e-09	4.5e-09	2.7e-09	6.6e-07
ETH	1.4e-07	1.8e-08	7.5e-05	4.4e-04	4.1e-07	5.4e-07	2.1e-07	1.2e-04
XO2	8.2e-07	5.3e-07	1.3e-03	6.3e-03	3.7e-06	1.1e-05	6.8e-06	1.5e-03
OPEN	3.7e-07	1.3e-07	1.8e-04	2.3e-03	4.9e-07	8.0e-07	2.7e-06	7.2e-02
PAR	2.2e-08	3.2e-09	1.1e-05	7.2e-05	1.2e-07	1.9e-07	8.3e-07	2.9e-04
HCHO	9.8e-08	3.2e-08	1.9e-04	4.4e-04	1.4e-07	1.7e-07	9.0e-08	1.3e-04
ISOP	1.5e-05	9.2e-06	6.9e-02	2.6e+00	3.8e-05	5.3e-05	2.6e-05	2.4e-04
OLE	1.0e-06	2.1e-07	3.3e-04	1.6e-03	4.1e-06	5.4e-06	2.0e-06	3.2e-04
ALD2	1.8e-07	1.3e-08	1.3e-04	5.1e-04	3.2e-07	3.9e-07	1.3e-07	1.2e-04
O3	1.2e-07	3.0e-08	2.1e-05	2.5e-04	3.5e-08	3.3e-08	1.6e-08	2.8e-06
NO2	1.7e-06	1.1e-06	2.9e-03	7.2e-03	3.3e-06	4.8e-06	4.0e-06	3.4e-04
OH	7.6e-07	4.3e-07	4.0e-03	1.2e-02	2.4e-06	8.2e-06	3.7e-06	5.3e-03
HO2	4.8e-07	3.0e-07	1.6e-03	1.4e-02	2.3e-06	8.1e-06	3.6e-06	3.3e-03
O	7.8e-08	5.2e-08	8.8e-05	2.9e-04	1.8e-08	3.1e-08	2.0e-08	5.1e-06
NO3	1.2e-06	1.1e-06	1.8e-03	1.9e-02	1.6e-05	2.2e-05	2.0e-05	1.1e-03
NO	2.8e-06	1.7e-06	3.5e-03	9.6e-03	2.3e-05	1.6e-05	1.5e-05	8.4e-03
C2O3	1.7e-06	1.1e-06	3.1e-03	7.4e-03	3.2e-06	4.5e-06	3.7e-06	3.1e-04

Table 2: The rms errors in species predictions for different time horizons with CBM4 model. The dimension of the full system is 32.