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M. van Loon

Department of Numerical Mathematics

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CWI
P.O. Box 94079
1090 GB Amsterdam
The Netherlands

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P.O. Box 94079, 1090 GB Amsterdam (NL)
Kruislaan 413, 1098 SJ Amsterdam (NL)
Telephone +31 20 592 9333
Telefax +31 20 592 4199

Fast and Efficient Solution Methods for Ozone Chemistry *

M. van Loon
e-mail: vanloon@cwi.nl

CWI
P.O. Box 94079, 1090 GB Amsterdam, The Netherlands

Abstract

Two special-purpose solvers for chemical kinetics problems, a QSSA method and TWOSTEP, together with the state-of-the-art stiff solver VODE, provided with sparse matrix routines, are considered for application in an atmospheric model. Of all three methods a short description is given. A comparison is made for a chemical model describing (parametrized) ozone chemistry. The code TWOSTEP turns out to be a good alternative for the QSSA solver as regards accuracy and to outperform VODE with respect to computation time for accuracies near 1%.

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1. INTRODUCTION

Atmospheric models are computationally very expensive. Usually the computational work is dominated by the numerical treatment of systems of ordinary differential equations (ODEs) describing the chemical transformations. One reason is that these systems are *stiff* due to the presence of very fast reacting species. In the numerical stiff ODE field various robust methods are available for solving such systems. However, in air pollution models one often has to solve a system of chemical equations at thousands of grid points. Usually, the accuracy level is quite modest, say at most 1%. Therefore it seems worthwhile to look for special-purpose solvers which satisfy the accuracy requirement and are very fast as well. Such methods may exploit the special form of a chemical kinetics system

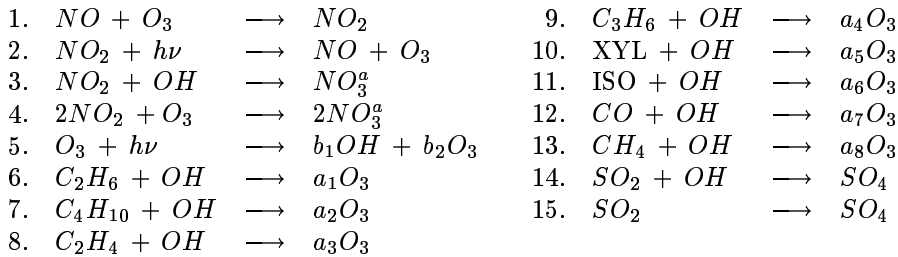
$$\dot{y}(t) = f(t, y) \equiv P(t, y(t)) - L(t, y(t)) y(t), \quad y(0) = y_0, \quad (1.1)$$

where P is an n -vector specifying the production terms and L an $n \times n$ diagonal matrix defining the loss rates. In this paper we will consider two of such solvers. The first is based on the *Quasi Steady State Approximation* approach (QSSA) and the second is the more recent code TWOSTEP, developed by Verwer [8, 11]. These two solvers are tested together with the state-of-the-art stiff solver VODE [1, 2] on a set of reaction equations describing ozone formation. Note that VODE is a BDF code similar as LSODE [3].

2. THE OZONE MODEL

The performance of the methods will be illustrated by the results of the integration of the following set of reactions describing ozone-chemistry, which is currently examined for use in the Dutch Smog Prediction Model.

*This note has been published in the proceedings of the conference AIR POLLUTION III, see [5].



This highly parametrized model has been derived from the EMEP MSC-West model [7] which consists of about 140 reactions between ca. 70 species. A full specification of all parameters can be found in [4] and [9].

3. SOLUTION METHODS

In this section we will describe the methods considered in our investigation. In case the exact solution of system (1.1) is mass conserving in the sense that one or more relations of the kind

$$w^T y(t) = \text{constant} \quad (3.2)$$

hold, with w an n -vector with constant weights, we would like the numerical method to satisfy this relation as well. In case of constant emission terms, the equivalent of (3.2) is

$$w^T y(t) = \text{constant} + w^T Q \cdot t, \quad (3.3)$$

which should be satisfied by the numerical scheme as well. Especially for long range transport models it is of importance that mass is not systematically added to or deleted from the system.

3.1 VODE

The code VODE [1, 2] is a state-of-the art variable step size code developed for stiff ODEs. It is, like TWOSTEP, based on the BDF formulae (3.4). In contrast to TWOSTEP, it varies its order q , where $1 \leq q \leq 5$ for stability reasons. Another difference is that it solves the implicit relation (3.4) with the (modified) Newton method. This involves evaluations and decompositions of Jacobian matrices, which is time consuming. To reduce the linear algebra overhead, in [9] we implemented sparse matrix routines for decomposing the Jacobian matrix and for performing backsolves. We also provided the code with the analytic Jacobian. This prevents the code from approximating the Jacobian by numerical differencing which is computationally more expensive and less accurate.

An advantage of using the (modified) Newton's method with analytic Jacobian is that the resulting solution after an arbitrary number of iterations always satisfies the conservation condition (see e.g. [6]). If the Jacobian is approximated by numerical differencing, this may no longer be true. In the remainder of this paper we only consider VODE provided with the analytic Jacobian. In general, VODE needs only 1 or 2 Newton iterations to (approximately) solve the relation (3.4).

3.2 The TWOSTEP approach

TWOSTEP is based on the second order *Backward Differentiation Formula* (BDF), which can be written in the general form

$$y^{n+1} = Y^n + \gamma \tau f^{n+1}, \quad (3.4)$$

where Y^n is an history vector, depending on the solutions at previous time steps and γ is a scalar variable. The step size is denoted by τ . In case variable step sizes are applied, Y^n and γ also depend on previous step sizes.

General purpose solvers like VODE usually solve the implicit relation (3.4) using the (modified) Newton method. In TWOSTEP the special form (1.1) is exploited to rewrite (3.4) as

$$y^{n+1} = (I + \gamma\tau L^{n+1})^{-1} (Y^n + \gamma\tau P^{n+1}) \quad (3.5)$$

to which explicit Gauss-Seidel iteration is applied. In the experiments below we will apply a fixed number of 2 iterations per time step. We emphasize that this number is (by far) not enough for convergence to the true BDF solution. The starting vector for the iteration process is obtained by first order extrapolation using solutions from previous time levels. When starting up the integration, the second order formula cannot be applied since no values from the past are available. In that case the first order BDF method is applied, i.e. $Y^n = y^n$ in (3.4). In general this will hardly influence the overall result, because only the first step of the integration is done with a first order method.

If solved exactly, the solution y^{n+1} of (3.4) is conservative, provided that the true ODE solution is conservative. However, in case the Gauss-Seidel iteration is not continued until convergence, y^{n+1} is only an approximation for the solution of (3.4) and will not be conservative in general, in contrast to VODE which always produces a conservative solution, independent of the number of iterations used to approximate the solution of the nonlinear system. This disadvantage for Gauss-Seidel iteration can be overcome for our chemistry by lumping (see below).

3.3 The QSSA approach

If P and L in (1.1) are constant, this equation can be solved exactly,

$$y(t + \tau) = e^{-\tau L} y(t) + (I - e^{-\tau L}) L^{-1} P. \quad (3.6)$$

This suggests the associated integration scheme

$$y^{n+1} = e^{-\tau L(\tilde{y})} y^n + (I - e^{-\tau L(\tilde{y})}) L^{-1}(\tilde{y}) P(\tilde{y}). \quad (3.7)$$

where \tilde{y} is still undefined. If we select $\tilde{y} = y^n$, the method is explicit and first order consistent. If we choose $\tilde{y} = \frac{1}{2}(y^n + y^{n+1})$ the method is implicit and of second order. The solution of the implicit equation is then obtained by Picard iteration. The second order scheme may be rewritten as (dropping the argument \tilde{y})

$$y^{n+1} = y^n + 2(I + e^{-\tau L})^{-1} (I - e^{-\tau L}) L^{-1} f. \quad (3.8)$$

Imposing mass conservation results into the condition

$$2w^T (I + e^{-\tau L})^{-1} (I - e^{-\tau L}) L^{-1} = \tau w^T, \quad (3.9)$$

because from (3.2) we have $w^T f = 0$. The above relation is not satisfied for the exact exponential. Often some approximation is used. The only approximation that makes the scheme conservative is

$$e^{-\tau L} \approx \frac{2 - \tau L}{2 + \tau L}, \quad (3.10)$$

which gives the implicit midpoint rule. However, this approximation results into negative solutions for $\tau L > 2$, though it is A -stable. For the first order scheme it is even worse: the corresponding condition for conservation is $e^{-\tau L} = I - \tau L$ which is the Forward Euler method, an inappropriate method to solve stiff systems because of its severe stability restriction.

We therefore select the second order scheme (i.e. $\tilde{y} = \frac{1}{2}(y^{n+1} + y^n)$) and use a very accurate, 6th order approximation of the exponential. This approximation is used instead of the exact exponential

for efficiency reasons only: there is no significant difference in the results, whereas using this approximation, when implemented efficiently, saves 20% or more computation time. The resulting scheme (3.7) can be written in an efficient form:

$$\tilde{y} = \frac{1}{2}(1 + e^{-\tau L(\tilde{y})})y^n + \frac{1}{2}(I - e^{-\tau L(\tilde{y})})L^{-1}(\tilde{y})P(\tilde{y}). \quad (3.11)$$

As no significant differences were observed with Picard iteration, we use, as in TWOSTEP, two Gauss-Seidel iterations to approximate \tilde{y} . The time-stepping mechanism is the same as for TWOSTEP.

3.4 Lumping

A common way to improve the integration process is lumping. The basic idea is to define a 'new' species, being a linear combination of two or more species from the system, that is easier to integrate than the individual species it consists of. Each integration step the 'new' species is integrated together with all other species. At the end of the integration step, the 'new' species is used to re-evaluate one of its components. In our chemical model (specified below), two such new, lumped species may be defined: $NO_x = NO + NO_2$ and $O_x = NO_2 + O_3$. In the TWOSTEP and the QSSA scheme these species are computed at the end of each Gauss-Seidel iteration and then used to re-evaluate the largest component in each lumped species. In [9] we showed that lumping can be seen as an acceleration of the iteration process. In the remainder of this paper, we shall refer to these methods as TWOSTEP2 and QSSA2 whereas the methods without lumping will be referred to as TWOSTEP1 and QSSA1. For implicit methods, which solve the nonlinear system exactly (i.e. very accurately), the lumping trick will not improve the solution, hence we will not apply lumping in VODE.

3.5 Setup of experiment

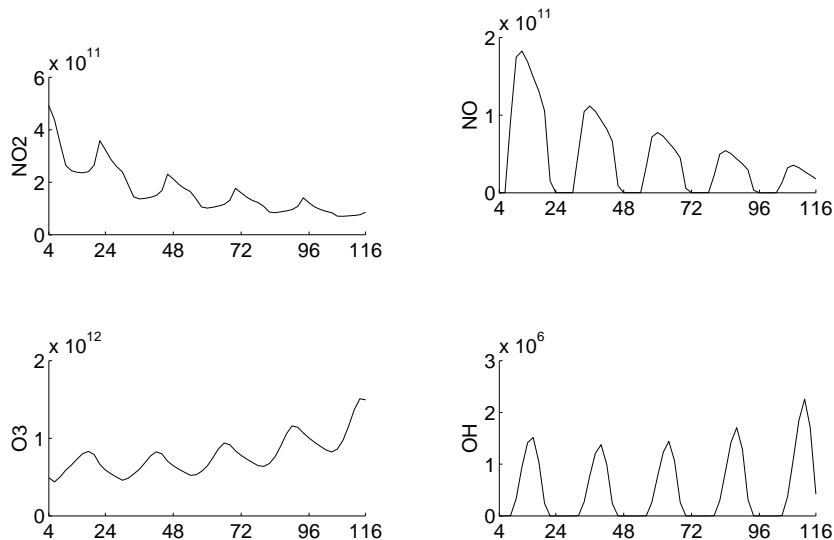


Figure 1: Reference solution for NO_2 , NO , O_3 and OH

The setup of the experiment is completely identical to the one described in [9]. This means that we integrate over a period of 112 hours, so approximately 5 days. The integration starts at 4:00 hour at day one and ends at 20:00 at day five. This time interval is sufficiently large to include a number of diurnal cycles. The integration interval is split up in 56 2-hour subintervals. At the beginning of each subinterval all parameters are updated and the code is restarted. This corresponds to actual applications in atmospheric models where operator splitting (fractional steps) is applied.

Here, however, we only carry out box calculations with the chemical model. In order to get realistic concentration profiles, i.e. representative for ozone episodes, emission terms Q_i (for NO , the VOCs and SO_2) and deposition terms vg_i (for NO_2 , O_3 and SO_2) have been added. A solution plot is given in Figure 1.

For each species k , accuracy is measured by the relative root mean square error $RRMS_k$

$$RRMS_k = \sqrt{\frac{\sum_{n=1}^N (y_k^n - y_k(t_n))^2}{\sum_{n=1}^N (y_k(t_n))^2}}, \quad (3.12)$$

where $N = 56$, $t_n = 14400 + 7200n$ sec. and $y_k(t_n)$ represents a sufficiently accurate reference solution. The average number of significant digits SDA is then defined as

$$SDA = -\log_{10} \left(\frac{1}{m} \sum_{k=1}^m RRMS_k \right). \quad (3.13)$$

Since in air pollution model only modest accuracy is required, our comparison focuses on (relative) accuracies near 1%. For all methods we will use the same set of tolerances, namely $ATOL=1$ and $RTOL=10^{-l}$, $l = 1, 2, 3, 4, 5$ for all species. Moreover, we prescribe a minimum and maximum step size: $\tau_{min}=1$ and $\tau_{max}=900$. In VODE we had to overrule the rejection strategy to enable $\tau_{min}=1$, because the code signals time constants smaller than 1 sec. In general this is all right, of course, but for the present application, with a modest accuracy requirement, smaller time steps seem to be redundant.

In addition we also performed some runs with (large) fixed step sizes and examined the solutions on conservation of NO_x . The system can be made to satisfy a relation of the kind (3.3) if we add an artificial component representing the amount of NO_2 deposition on the earth's surface. Conservation is then measured by $RRMS_{NO_x}$.

4. RESULTS

4.1 variable step sizes

The results of the experiments are plotted in Figure 2. The markers correspond with the first four tolerances for QSSA1/2 and all five tolerances for the other methods. The results clearly show that the QSSA approach is not very favorable in the present application. QSSA1 and QSSA2 are much more inaccurate than both TWOSTEP versions, though QSSA as well as TWOSTEP are second order consistent. Also QSSA needs much more time steps than TWOSTEP as can be seen from Table 1. This time stepping behavior is in accordance with the results reported in [10] for a quite similar QSSA

Table 1: Number of accepted step sizes with number of rejections (in brackets)

RTOL	QSSA1	QSSA2	TWOSTEP1	TWOSTEP2	VODE
10^{-1}	1583 (0)	1588 (0)	1267 (0)	1267 (0)	1062 (13)
10^{-2}	5742 (0)	5749 (0)	2044 (3)	2042 (3)	1465 (12)
10^{-3}	23566 (0)	23584 (0)	4330 (3)	4330 (3)	2035 (65)
10^{-4}	116536 (0)	116539 (0)	10174 (1)	10173 (1)	2722 (41)

scheme. The results reported here also confirm the conclusion in [10] that other tailor-made solution methods may outperform QSSA. In our view TWOSTEP is such a method, at least for the chemical problem considered in this paper. In [9] we applied TWOSTEP and VODE also to two other test problems and TWOSTEP performed satisfactorily in all cases. We should also mention that it was

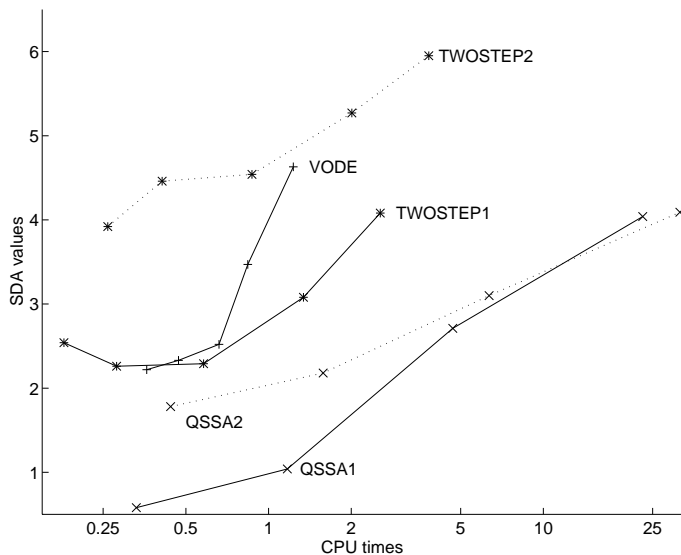


Figure 2: Results for the test problem

found that supplying VODE with sparse matrix routines results in a large decrease in CPU for a large problem size. In [9] results are presented for the EMEP chemistry with 66 species [7]. For this chemical system the sparse matrix routines implemented in VODE reduce the CPU time with about 70% which makes VODE and TWOSTEP competitive for the accuracy range of interest for atmospheric models. However, in the model presented here, with only 15 species, the reduction in CPU time for VODE is only about 20% and for accuracy levels near 1% TWOSTEP still is convincingly the most efficient solver.

4.2 Fixed step sizes

Table 2 presents results for QSSA and TWOSTEP using fixed step sizes. No results for VODE are listed because the code (in its present form) was unable to integrate with such large step sizes over the whole integration interval. The results in Table 2 however indicate that large step sizes can be feasible in a special-purpose implementation.

Table 2: Results for fixed step sizes

τ	QSSA1		QSSA2		TWOSTEP1		TWOSTEP2	
	SDA	SD_{NO_x}	SDA	SD_{NO_x}	SDA	SD_{NO_x}	SDA	SD_{NO_x}
100	1.43	3.08	2.51	10.18	2.26	4.13	3.53	13.83
200	0.86	1.95	2.22	9.51	1.88	3.38	3.42	10.97
300	0.50	1.26	2.05	9.92	1.78	3.24	3.20	10.43
400	unstable		1.93	10.19	1.65	3.08	3.08	9.98
600	unstable		1.76	8.47	1.17	2.17	2.93	9.83
900	unstable		1.59	7.61	0.72	1.38	2.60	9.18
1200	unstable		1.47	6.97	0.48	1.03	2.51	8.48

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