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ORIGINAL PAPER

Integration of chemical stiff ODEs using exponential propagation method

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Abstract In this paper, we study the numerical long time integration of large stiff systems of differential equations arising from chemical reactions by exponential propagation methods. These methods, which typically converge faster, use matrix-vector products with the exponential or other related function of the Jacobian that can be effectively approximated by Krylov sabspace methods. We equip these methods to an automatic stepsize control technique and apply the method of order 4 for numerical integration of some famous stiff chemical problems such as Belousov-Zhabotinskii reaction, the Chapman atmosphere, Hydrogen chemistry, chemical Akzo-Nobel problem and air pollution problem.

Keywords Numerical integrator · Mathematical modeling · Chemical reactions · Exponential method · Krylov subspace method · Stiff systems · Ordinary differential equation

1 Introduction

The construction of an efficient algorithm for the solution of large sets of stiff ordinary differential equations has been a central concern of numerical analysis. A major difficulty in solving large stiff systems of nonlinear differential equations is choosing an efficient time integration scheme. Typically one has to make a decision whether to use an explicit or an implicit method. Explicit schemes require the least amount of computation per time step but the allowable time step is severely restricted by the stability

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requirements. Implicit schemes have much better stability properties and allow significantly larger time steps compared to explicit integrators. However, this advantage comes at the expense of a significant increase in the amount of computation needed at each time iteration.

In this paper, we study exponential propagation methods [13] for the integration of large stiff systems of nonlinear initial value problems

$$y' = f(y), \quad y(t_0) = y_0. \tag{1}$$

These methods use Krylov subspace projections and a Rosenbruck-type methods framework [4] to construct exponential propagation iterative methods. By equipping these methods to an automatic stepsize control technique based on error of the method, we apply the method of order 4 for numerical integration of some famous stiff chemical problems such as Belousov-Zhabotinskii reaction, the Chapman atmosphere, Hydrogen chemistry, chemical Akzo-Nobel problem and air pollution problem. These problems are stiff ODEs in long time integration which the standard numerical methods fail in deal with them. For the especial properties of exponential propagation methods, applying them on the stiff ODEs in long time integration will be successful.

Next sections of this paper are organized as follows: In Sect. 2, we recall the main concepts and construction of exponential propagation technique. In Sect. 3, the methods of classical order 4 are described which have further favorable properties when applied to stiff problems and also they are equipped by an automatic stepsize control technique. In Sect. 4, we apply exponential propagation methods to solve some important initial value problems that arise from mathematical modeling of chemical reaction.

2 Exponential propagation method

In this section, we give a brief review of a general class of exponential integrators introduced in [13]. Starting with y_0 as an approximation to $y(t_0)$, an approximation to $y(t_0 + h)$ is computed with

$$k_i = \varphi(\gamma h A)\left(f(u_i) + hA\sum_{j=1}^{i-1}\gamma_{ij}k_j\right), \qquad i = 1, \ldots, s, \tag{2}$$

$$u_i = y_0 + h\sum_{j=1}^{i-1}\alpha_{ij}k_j, \tag{3}$$

$$y_1 = y_0 + h\sum_{i=1}^{s} b_i k_i. \tag{4}$$

Here $A = f'(y_0), \varphi(z) = (e^z - 1)/z$ and $\gamma, \gamma_{ij}, \alpha_{ij}, b_i$, with $\gamma_{ij} = \alpha_{ij} = 0$ for $i \leq j$, are the coefficients that determine the method. The internal stages $u_1, \ldots, u_s$ can be computed one after other, with one multiplication by $\varphi(\gamma h A)$ and a function

evaluation at each stage. The scheme would become an explicit Runge-Kutta method for $\varphi(z) \equiv 1$ (and $\gamma_{ij} = 0$), and a Rosenbrock method for the choice $\varphi(z) = 1/(1-z)$. The most effective way of approximating the matrix exponential is Krylov subspace projections. The series expansion form of the matrix exponential $e^{\tau A}$ multiplied by a vector v is

$$e^{\tau A}v = v + \frac{(\tau A)}{1!}v + \frac{(\tau A)^2}{2!}v + \cdots + \frac{(\tau A)^m}{m!}v + \cdots, \tag{5}$$

where $\tau \in \mathbb{R}$ is a number which corresponds to the time step and $A \in \mathbb{R}^{N\times N}$. Clearly the vector $e^{\tau A}v$ belongs to an infinite dimensional space of vectors $\{v, Av, A^2v, \ldots, A^m v, \ldots\}$. To approximate (5), we will project the operator $e^{\tau A}$ and the vector v onto a finite dimensional Krylov subspace

$$S_{kry} = Span\{v, Av, A^2v, \ldots, A^{m-1}v\}.$$

In order to do this, we compute an orthonormal basis $\{v_1, \ldots, v_m\}$ of the subspace S_{kry} using the Arnoldi algorithm [11]. If we define the matrix H with elements $h_{ij} = (v_i, Av_j), i, j = 1, \ldots m$, we can rewrite the Arnoldi algorithm in a matrix form as

$$AV_m = V_m H + h_{m+1,m} v_{m+1} e_m^T, \tag{6}$$

where $e_m = [0 \ \ldots \ 0 \ 1]$ is a unit vector in $\mathbb{R}^m$ and $V_m = [v_1, \ldots, v_m]$ is a $m \times m$ matrix with vectors v_i as its columns. It is clear that $V_m^T V_m$ is a $m \times m$ identity matrix and $V_m V_m^T$ is a projector from $\mathbb{R}^N$ onto S_{kry}. Using $V_m^T v_{m+1} = 0$ from (6), we have $H = V_m^T A V_m$ and if we want to use projection onto S_{kry} to approximate Av, we can write $Av \approx V_m V_m^T A V_m V_m^T v = V_m H V_m^T v$. Similarly we can approximate the action of any operator $f(A)$ on a vector v using the Krylov subspace projection as follows

$$f(A)v \approx V_m f(H) V_m^T v = V_m f(H) V_m^T v_1 ||v||_2 = ||v||_2 V_m f(H) e_1, \tag{7}$$

where we use $v_1 = v/||v||_2$. In particular, to approximate the exponential in (5) we write

$$e^{\tau A}v \approx ||v||_2 V_m e^{\tau H} e_1.$$

Even for very large matrices it is possible in cases of interest to obtain desired accuracy by computing only 15–20 Krylov vectors.

2.1 Order conditions

Now we recall the construction of higher-order methods. The order conditions for the exponential methods can be derived similarly to Rosenbrock methods, see [4]. Therefore, we only state the conditions here. For abbreviation we define

$$\beta_{ij} = \alpha_{ij} + \gamma_{ij}. \tag{8}$$

Table 1 Order conditions for the exponential propagation methods up to order 5

Elementary differential τ	$\Phi_j(t)$	$P_t(\gamma)$
f	1	1
$f'f$	$\sum_k \beta_{jk}$	$1/2(1-\gamma)$
$f''(f,f)$	$\sum_{k,l} \alpha_{jk}\alpha_{jl}$	$1/3$
$f'f'f$	$\sum_{k,l} \beta_{jk}\beta_{kl}$	$1/3(1/2-\gamma)(1-\gamma)$
$f'''(f,f,f)$	$\sum_{k,l,m} \alpha_{jk}\alpha_{jl}\alpha_{jm}$	$1/4$
$f''(f'f,f)$	$\sum_{k,l,m} \alpha_{jk}\beta_{kl}\alpha_{jm}$	$1/8-\gamma/6$
$f'f''(f,f)$	$\sum_{k,l,m} \beta_{jk}\alpha_{kl}\alpha_{km}$	$1/12-\gamma/6$
$f'f'f'f$	$\sum_{k,l,m} \beta_{jk}\beta_{kl}\beta_{lm}$	$1/4(1/3-\gamma)(1/2-\gamma)(1-\gamma)$
$f^{(4)}(f,f,f,f)$	$\sum \alpha_{jk}\alpha_{jl}\alpha_{jm}\alpha_{jp}$	$1/5$
$f'''(f'f,f,f)$	$\sum \alpha_{jk}\beta_{kl}\alpha_{jm}\alpha_{jp}$	$1/10-\gamma/8$
$f''(f,f''(f,f))$	$\sum \alpha_{jk}\alpha_{kl}\alpha_{km}\alpha_{jp}$	$1/15$
$f''(f'f'f,f)$	$\sum \alpha_{jk}\beta_{kl}\beta_{lm}\alpha_{jp}$	$1/30-\gamma/8+\gamma^2/9$
$f''(f'f,f'f)$	$\sum \alpha_{jk}\beta_{kl}\alpha_{jm}\beta_{mp}$	$1/20-\gamma/8+\gamma^2/12$
$f'f'''(f,f,f)$	$\sum \beta_{jk}\alpha_{kl}\alpha_{km}\alpha_{kp}$	$1/20-\gamma/8$
$f'f''(f'f,f)$	$\sum \beta_{jk}\alpha_{kl}\beta_{lm}\alpha_{kp}$	$1/40-5\gamma/48+\gamma^2/12$
$f'f'f''(f,f)$	$\sum \beta_{jk}\beta_{kl}\alpha_{lm}\alpha_{lp}$	$1/60-\gamma/12+\gamma^2/9$
$f'f'f'f'f$	$\sum \beta_{jk}\beta_{kl}\beta_{lm}\beta_{mp}$	$1/5(1/4-\gamma)(1/3-\gamma)(1/2-\gamma)(1-\gamma)$

Theorem 2.1 *[6] An exponential method (2)–(4) with $A = f'(y_0)$ is of order p iff*

$$\sum_{j=1}^{s} b_j \Phi_j(\tau) = P_\tau(\gamma),$$

for elementary differentials τ up to order p. Here, $\Phi_j(\tau)$ and the polynomials $P_\tau(\gamma)$ are listed in Table 1 for $p \le 5$.

The only difference to the order conditions for Rosenbrock methods is in the polynomials $P_\tau(\gamma)$.

Theorem 2.2 *[6] The method (2)–(4) is exact for linear differential equations iff for all $n = 1, 2, 3, \ldots$*

$$\sum b_{j_1}\beta_{j_1,j_2}\beta_{j_2,j_3}\cdots\beta_{j_{n-1},j_n} = \frac{1}{n}\left(\frac{1}{n-1}-\gamma\right)\left(\frac{1}{n-2}-\gamma\right)\cdots\left(\frac{1}{2}-\gamma\right)(1-\gamma).$$

These conditions can be fulfilled if γ be the reciprocal of an integer. Then only a finite number of these conditions are needed. The others are satisfied automatically because for sufficiently large n, both sides of the above equation then vanish.

2.2 Stability

Applying a perturbed method (2)–(4) to the linear test problem $y' = Ay$ gives

$$\tilde{k}_i = \varphi(\gamma hA)\left(A\tilde{y}_0 + b + hA\sum_{j=1}^{i-1}\beta_{ij}\tilde{k}_j\right) + \delta_i,$$
$$\tilde{y}_1 = \tilde{y}_0 + h\sum_{i=1}^{s} b_i\tilde{k}_i.$$

Here, δ_i is a perturbation at the ith stage and y_0 is a perturbed starting value. Subtracting from the unperturbed scheme yields for the error $\varepsilon_1 = \tilde{y}_1 - y_1$ that

$$l_i = \varphi(\gamma hA)\left(A\varepsilon_0 + hA\sum_{j=1}^{i-1}\beta_{ij}l_j\right) + \delta_i,$$
$$\varepsilon_1 = \varepsilon_0 + h\sum_{i=1}^{s} b_i l_i,$$

where $l_j = \tilde{k}_j - k_j$ and $\varepsilon_0 = \tilde{y}_0 - y_0$. It is easy to see that

$$\varepsilon_1 = e^{hA}\varepsilon_0 + h\sum_{i=1}^{s} b_i\, p_{s-i}\left(e^{\gamma hA} - I\right)\delta_i,$$

where $p_k(z)$ is a polynomial of degree k with $p_k(0) = 1$, whose coefficients are products of β_{ij}/γ. In particular, when the numerical range of A is contained in the left half-plane, then we have the stable error recurrence

$$\|\varepsilon_1\| \le \|\varepsilon_0\| + Ch\sum_{i=1}^{s}\|\delta_i\|.$$

The stability analysis could be extended to nonlinear problems $y' = Ay + g(y)$ in a similar way to what has been done for Rosenbrock methods, cf. [8].

3 Construction of fourth-order methods

3.1 Reduced methods

We recall that one step of the exponential propagation method evaluated in the form (2)–(4) contains s multiplications of $\varphi(\gamma hA)$ with a vector. Since this vector is different in each of these s steps, the approximation with a Krylov subspace method requires the construction of bases of s Krylov spaces with respect to the same matrix

A but with different vectors. We study an alternative formulation of the method for computing $\varphi(jz)$, $j = 2, 3, \ldots$, recursively from $\varphi(z)$

$$\varphi(jz) = \frac{j-1}{j}\left(z\varphi(z)+1\right)\varphi\left((j-1)z\right) + \frac{1}{j}\varphi(z), \quad j = 2, 3, \ldots \tag{9}$$

Therefore if we approximate $\varphi(\gamma hA)v$ by the Krylov subspace projection to get

$$\varphi(\gamma hA)v \approx V_m \varphi(\gamma h H_m) V_m^T v,$$

then rather than performing the Krylov projection again to compute $\varphi(j\gamma hA)v$, we can use recurrence (9). For $j = 2, 3, \ldots$

$$\begin{aligned}&\varphi(j\gamma hA)v \approx V_m \varphi(j\gamma h H_m) V_m^T v\\ &= V_m \left[\frac{j-1}{j}\left(\gamma h H_m \varphi(\gamma h H_m) + I_m\right)\varphi\left((j-1)\gamma h H_m\right) + \frac{1}{j}\varphi(\gamma h H_m)\right] V_m^T v.\end{aligned}$$

We introduce auxiliary vectors

$$d_i = F(u_i) - F(y_0) - hA\sum_{j=1}^{i-1}\alpha_{ij}k_j. \tag{10}$$

Note that for $A = f'(y_0)$, this corresponds to a first-degree Taylor expansion of f around y_0, hence the vectors d_i are usually small in norm. From (8) and (10) we have

$$k_i = k_1 + \varphi(\gamma hA)d_i + \varphi(\gamma hA)hA\sum_{j=1}^{i-1}\beta_{ij}k_j.$$

Because of (9), we can choose β_{kl} such that for $\gamma = 1/n$ and $i = 1, \ldots, n$

$$\begin{aligned}k_i &= \varphi\left(i\gamma hA\right) f(y_0),\\ k_{nj+i} &= k_1 + \varphi\left(i\gamma hA\right) d_{nj+i}, \quad j \geq 1.\end{aligned} \tag{11}$$

All the coefficients β_{kl} are uniquely determined by (11). In order to apply the recurrence formulas (9) in (11), we further choose

$$\alpha_{nj+i,l} = \alpha_{nj+1,l}, \quad i = 1, \ldots, n, \quad l, j \geq 1,$$

which gives

$$\begin{aligned}u_{nj+i} &= u_{nj+1},\\ d_{nj+i} &= d_{nj+1}, \quad i = 1, \ldots, n, \quad j \geq 1.\end{aligned}$$

This reduces the number of f-evaluations and of evaluations of $\varphi(\gamma hA)$ by a factor of n compared to the general scheme (2)–(4). This is particularly important when this reduced method is combined with a Krylov process for approximating $\varphi(\gamma hA)v$, since in this case we need to compute a basis of a new Krylov space only at every nth intermediate step.

3.2 Method of order 4

We derive one specific seven stage method of order four with $\gamma = 1/3$. The reduced version of this scheme is given by

$$
\begin{aligned}
k_1 &= \varphi\left(\frac{1}{3}hA\right) f(y_0),\\
k_2 &= \varphi\left(\frac{2}{3}hA\right) f(y_0),\\
k_3 &= \varphi(hA) f(y_0),\\
w_4 &= -\frac{7}{300}k_1 + \frac{97}{150}k_2 - \frac{37}{300}k_3,\\
u_4 &= y_0 + hw_4,\\
d_4 &= f(u_4) - f(y_0) - hAw_4,\\
k_4 &= \varphi\left(\frac{1}{3}hA\right) d_4,\\
k_5 &= \varphi\left(\frac{2}{3}hA\right) d_4,\\
k_6 &= \varphi(hA) d_4,\\
w_7 &= \frac{59}{300}k_1 + \frac{7}{75}k_2 - \frac{269}{300}k_3 + \frac{2}{3}(k_4 + k_5 + k_6),\\
u_7 &= y_0 + hw_7,\\
d_7 &= f(u_7) - f(y_0) - hAw_7,\\
k_7 &= \varphi\left(\frac{1}{3}hA\right) d_7,\\
y_1 &= y_0 + h\left(k_3 + k_4 - \frac{4}{3}k_5 + k_6 + \frac{1}{6}k_7\right).
\end{aligned}
\tag{12}
$$

The scheme (12) requires only three function evaluations. When using Krylov approximations, the computational cost is dominated by computing k_1. As discussed before, the reason is that k_2, k_3, k_5, and k_6 can be computed recursively from (9) or the more stable recurrence (15) below.

3.3 Embedded method

Embedded methods are schemes that have same matrices of coefficients α_{ij}, β_{ij} and γ_{ij} and parameter γ which differ only by the coefficients b_j. Since the parameters b_j are only used to compute the final approximation

$$y_1 = y_0 + h \sum_{j=1}^{s} b_j k_j,$$

once all the vectors k_j are computed, it is cheap to calculate two approximations to solution at the cost of $s - 1$ extra vector additions.

We derive two embedded methods for the fourth-order seven stage method (12) which differs from (12) only by the last formula

$$\hat{y_1} = y_0 + h \left(k_3 - \frac{1}{2}k_4 + \frac{2}{3}k_5 + \frac{1}{2}k_6 + \frac{1}{2}k_7 \right), \tag{13}$$

and

$$\hat{y_1} = y_0 + h(-k_1 + 2k_2 - k_4 + k_7). \tag{14}$$

The first method has order three and the later has order two. So, since it is important to us to make the time step as large as possible given the accuracy requirements we choose to use method (12) with an embedded method (13).

3.4 Stopping criterion for the Krylov method

We need to decide when the Krylov approximation (7) is to be considered sufficiently accurate. The error estimates are derived from applying the Cauchy integral formula to the expression $f(\tau A)v$, that is

$$\varepsilon_m = f(\tau A)v - V_m f(\tau H_m)e_1 = \frac{1}{2\pi i} \int_{\Gamma} f(\lambda) e_m(\lambda) d\lambda$$

with

$$e_m(\lambda) = (\lambda I - \tau A)^{-1} v - V_m (\lambda I - \tau H_m)^{-1} e_1.$$

Since exact errors are inaccessible, the stopping criterion is usually based on the residual instead of error of the mth iteration. Therefore we use

$$\rho_m = \frac{1}{2\pi i} \int_{\Gamma} f(\lambda) r_m(\lambda) d\lambda$$

with

$$r_m(\lambda) = -\|v\|_2 h_{m+1,m} v_{m+1} \left[(\lambda I - \tau H_m)^{-1} \right]_{m,1}.$$

It was proposed in [6,10] to use the norm of the generalized residual defined by

$$\rho_m = \frac{1}{2\pi i} \int_\Gamma f(\lambda) r_m(\lambda) d\lambda = -\|v\|_2 h_{m+1,1} \left[f(\tau H_m) \right]_{m,1} v_{m+1},$$

as an accuracy check.

3.5 Computing of $\varphi(\tau H_m)$

If A is Hermitian, then H_m is Hermitian tridiagonal. In this case, one can simply diagonalize and easily compute eigenvalues and eigenvectors of H_m and approximate $\varphi(\tau H_m)$.

In the non-Hermitian case, we it is suggested to use Padé approximation to compute the matrix exponential [9]. Here, since the roundoff error and the cost of computing Padé approximates both increase as $\|h_m\|$ grows, the matrix is first scaled by a factor of 2^{-k} such that $\|2^{-k}\tau H_m\| < 1/2$. Then we evaluate the (6,6) Padé approximation to $\varphi(z)$ for the scaled matrix

$$\varphi(z) = \frac{1 + \frac{1}{26}z + \frac{5}{156}z^2 + \frac{1}{858}z^3 + \frac{1}{5720}z^4 + \frac{1}{205920}z^5 + \frac{1}{8648640}z^6}{1 - \frac{6}{13}z + \frac{5}{52}z^2 - \frac{5}{429}z^3 + \frac{1}{1144}z^4 - \frac{1}{25740}z^5 + \frac{1}{1235520}z^6} + O\left(z^{13}\right).$$

Next, $\varphi(\tau H_m)$ is computed recursively from $\varphi(2^{-k}\tau H_m)$ by applying the following coupled recurrences

$$\begin{aligned} \varphi(2z) &= \frac{1}{2}\left(e^z + 1\right)\varphi(z), \\ e^{2z} &= e^z e^z. \end{aligned} \tag{15}$$

This recurrence is stable for all z in the left half-plane, whereas (9) becomes unstable for large $|z|$ because of the multiplication with z.

3.6 Automatic error control Gustafson's approach

Error estimation is a crucial point in constructing a good exponential propagation method. We have already described how the generalized residuals can be used to assess the error of the Arnoldi algorithm in approximation of $\varphi(\gamma h A)$. Now, we also need a mechanism to estimate error of the new approximation to the solution at the next time step y_1 so that we can adjust the time stepsize based on this calculation. An approach proposed first by Gustafson for the Runge-Kutta methods can be naturally extended to the exponential propagation methods.

Suppose we derived an exponential method of order q with certain coefficients $\gamma, \alpha_{ij}, \beta_{ij}, \gamma_{ij}$ and b_j, which we then compute an approximate solution y^{n+1} to the system of differential equations. Assume also that we found an embedded exponential method of order $\hat{q}$ with coefficients $\gamma, \alpha_{ij}, \beta_{ij}, \gamma_{ij}$ and $\hat{b}_j$, which gives us another approximation to the solution $\hat{y}^{n+1}$. We want the error between approximations y^{n+1} and $\hat{y}^{n+1}$ to be within a predefined tolerance componentwise, i.e.

$$|y_i^{n+1} - \hat{y}_i^{n+1}| \leq sc_i, \quad sc_i = Atol_i + \max\left(|y_i^n|, |y_i^{n+1}|\right) \cdot Rtol_i,$$

where $Atol_i$ and $Rtol_i$ are the desired absolute and relative tolerances per component prescribed by the user. The measure of the total error ε is defined as

$$\varepsilon = \left\| \frac{y_i^{n+1} - \hat{y}_i^{n+1}}{sc} \right\|,$$

where the norm $\|.\|$ is taken to be either the normalized 2-norm or the maximum norm depending on which of these provide a better error estimate for a particular problem. Since the used numerical methods are of orders q and $\hat{q}$, we expect the error to behave as

$$\varepsilon \approx C \cdot h^r, \quad r = \min(q, \hat{q}).$$

The optimal stepsize h_{opt} would ensure that $C \cdot h_{opt}^r \approx 1$. From the last two equations we can compute the optimal stepsize as

$$h_{opt} = h \cdot \sqrt[r]{\frac{1}{\varepsilon}}.$$

The error control mechanism therefore, proceeds as follows. First, we set some starting values for the time step h and compute the approximations to the solution y^{n+1} and $\hat{y}^{n+1}$. Then, we calculate the error. If the error is larger than 1, we reduce the size of the time step and compute the approximate solution again with the new time step. Otherwise the solution is advanced with y^{n+1} and the new time stepsize is calculated according to the above formula.

Coupling the procedure described above with the error control mechanism for the Arnoldi algorithm in the general scheme, we estimate the new time stepsize h_{kry} based on the residual in the Krylov subspace projection and the time step h_{opt} and pick the minimum of these to be the new time stepsize

$$h_{new} = \min\left(h_{kry}, h_{opt}\right).$$

With this new value for the time stepsize, we proceed with integrating the system of equations in time.

4 Numerical experiments

The main aim of this paper is introduce in this section by applying the mentioned method on some famous chemical problems and showing its efficiency. We have implemented the method of order four in a Matlab code.

4.1 Belousov-Zhabotinskii reaction

The Belousov-Zhabotinskii reaction [12] may be represented by the following scheme of homogeneous chemical reactions

$$\begin{array}{lll}
(1) & A + Y \to X, & k_1 = 4.72 \\
(2) & X + Y \to P, & k_2 = 3 \times 10^9 \\
(3) & B + X \to 2X + Z, & k_3 = 1.5 \times 10^4 \\
(4) & 2X \to Q, & k_4 = 4 \times 10^7 \\
(5) & Z \to Y, & k_5 = 1
\end{array}$$

Letters $A, \ldots, Z$ denote species taking part in the reactions and constants k_i denote the reaction rates. Since the Belousov-Zhabotinskii reaction is homogeneous (meaning that all species are uniformly distributed in the reaction space), we only need to consider variations of the concentrations in time. Each reaction step is characterised by its reaction rate constant. Obviously, the rate constants differ by several orders of magnitude which indicates the likeliness of the corresponding ODE system being stiff. The initial conditions are given by initial concentrations of species at $t = 0$

$$A = B = 0.066, \quad Y = X = P = Q = 0, \quad Z = 0.002.$$

The ODEs system modeling of the reaction scheme is

$$\begin{array}{ll}
y_1' = -k_1 y_1 y_2, & y_1(0) = 0.066, \\
y_2' = -k_1 y_1 y_2 - k_2 y_3 y_2 + k_1 y_6, & y_2(0) = 0, \\
y_3' = -k_2 y_3 y_2 + k_3 y_3 y_5 - 2k_4 y_3^2 + k_1 y_1 y_2, & y_3(0) = 0, \\
y_4' = k_2 y_3 y_2, & y_4(0) = 0, \\
y_5' = -k_3 y_5 y_3, & y_5(0) = 0.066, \\
y_6' = -k_3 y_5 y_3 - k_5 y_6, & y_6(0) = 0.002, \\
y_7' = -k_4 y_3^2, & y_7(0) = 0.
\end{array}$$

The latter is considered at the interval $t \in [0, 40]$ and solved using exponential propagation method. The obtained solution of this problem at the end of time interval is reported in Table 2. Plots in the Fig. 1 show the concentration of A, Y, P and Z computed using the exponential propagation method.

Table 2 The results of problem Belousov-Zhabotiskii reaction at $t = 40$

y_i	Solution at $t = 40$
y_1	0.063596056700909
y_2	0.000000285915255
y_3	0.000000000104847
y_4	0.003065397855150
y_5	0.062530274724733
y_6	0.000000098205770
y_7	0.001402126415417

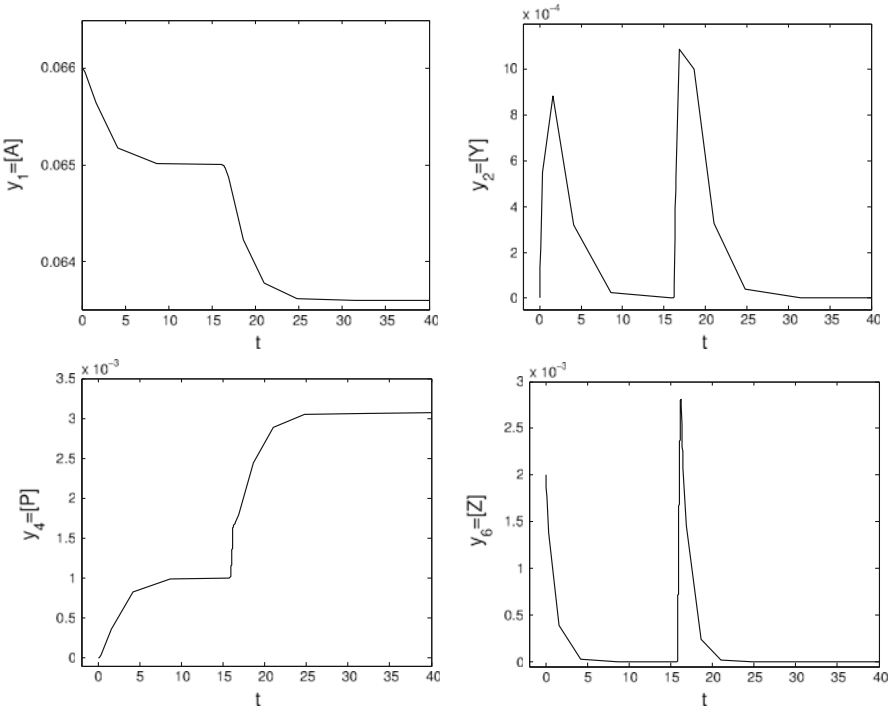

Fig. 1 Concentration of A, Y, P and Z computed using the exponential propagation method

4.2 The Chapman atmosphere

Consider the equations describing the generation and destruction of ozone in the simple Chapman model, with conditions valid for the low to middle stratosphere. In this case, the atmosphere includes only the chemistry of O_2, O and O_3 [1]. In this situation there are four chemical reactions

$$\begin{array}{lll} O + O_2 + M \rightarrow O_3 + M & k_1 \\ O + O_3 \rightarrow 2O_2 & k_2 \\ O_2 + h\nu \rightarrow 2O & k_3 \\ O_3 + h\nu \rightarrow O + O_2 & k_4 \end{array}$$

Table 3 Results of the Chapman atmosphere problem at $t = 172,800$

y_i	Solution at $t = 172,800$
y_1	0
y_2	$1.154675314113236 \times 10^{12}$
y_3	$0.000000171230962 \times 10^{12}$

where the k_i denote the reaction rates, M denotes an extra molecule required to carry off excess energy and $h\nu$ denotes the absorption of light (a photochemical reaction). Ozone formation occurs through the first reaction while ozone destruction occurs in the second and last reactions. For this problem, the concentration of molecular oxygen, O_2, is held constant (a reasonable assumption in the atmosphere). The first two reaction rates are fixed (functions of temperature only) while the latter two (being driven by the absorption of light) will vary diurnally. If we set y_1, y_2, y_3 to be the concentrations of O, O_3, O_2, respectively, then the resulting system of ordinary differential equations takes the form

$$\begin{aligned} y_1' &= -k_1 y_1 y_3 - k_2 y_1 y_2 + 2k_3 y_3 + k_4 y_2, \quad && y_1(0) = 10^6, \\ y_2' &= k_1 y_1 y_3 - k_2 y_1 y_2 - k_4 y_2, && y_2(0) = 10^{12}, \end{aligned}$$

with the constant values

$$y_3 = 3.7 \times 10^{16}, \quad k_1 = 1.63 \times 10^{-16}, \quad k_2 = 4.66 \times 10^{-16},$$

and

$$k_i = \begin{cases} \exp\left(\dfrac{-a_i}{\sin wt}\right), & \sin wt > 0, \\ 0, & \sin wt \le 0, \end{cases} \quad i = 3, 4$$

with

$$a_3 = 22.62, \quad a_4 = 7.601, \quad w = \frac{\pi}{43,200}.$$

The constant 43,200 is just 12 h in seconds, so that the diurnally varying rates (k_3 and k_4) have 24-h periods. The obtained solution of this problem at t $= 172,800$ is reported in Table 3. Behavior of the solution components in time interval [0, 172,800 = 48-h] is shown in Fig. 2.

4.3 More complexity: hydrogen chemistry

In this section we use a slightly more complicated mechanism that includes the quadratic behavior found in many reaction problems. We shall use the following chemical species [2], again with conditions valid for the lower to middle stratosphere, which are represented by the variables $y_1 = [O]$, $y_2 = [O_3]$, $y_3 = [OH]$, $y_4 = [HO_2]$, $y_5 =$

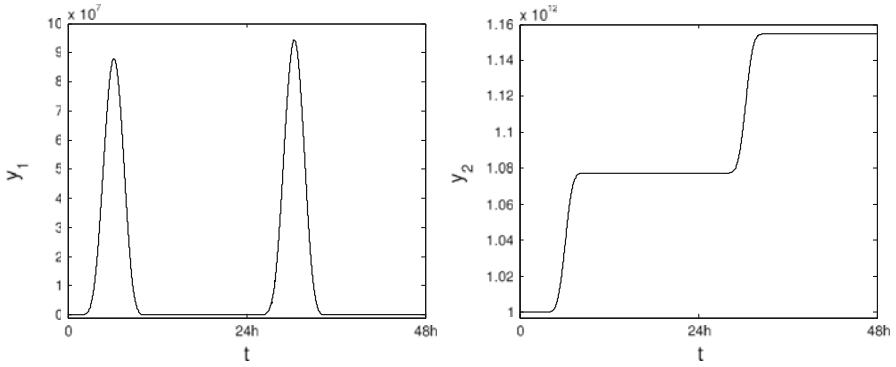

Fig. 2 Chapman atmosphere: numerical solution obtained by exponential propagation method

$[H_2O_2]$, $y_6 = [N_2]$, $y_7 = [O_2]$, $y_8 = [H_2O]$, $y_9 = [O(^1D)]$. A total of 15 chemical reactions will be modeled

$$\begin{array}{lll}
O + O_2 + M & \rightarrow O_3 + M & k_1 \\
O + O_3 & \rightarrow 2O_2 & k_2 \\
O(^1D) + N_2 & \rightarrow O + N_2 & k_3 \\
O(^1D) + O_2 & \rightarrow O + O_2 & k_4 \\
O(^1D) + H_2O & \rightarrow 2OH & k_5 \\
OH + O_3 & \rightarrow HO_2 + O_2 & k_6 \\
HO_2 + O & \rightarrow OH + O_2 & k_7 \\
HO_2 + O_3 & \rightarrow OH + 2O_2 & k_8 \\
HO_2 + OH & \rightarrow H_2O + O_2 & k_9 \\
HO_2 + HO_2 & \rightarrow H_2O_2 + O_2 & k_{10} \\
H_2O_2 + OH & \rightarrow H_2O + HO_2 & k_{11} \\
O_2 + h\nu & \rightarrow 2O & k_{12} \\
O_3 + h\nu & \rightarrow O + O_2 & k_{13} \\
O_3 + h\nu & \rightarrow O(^1D) + O_2 & k_{14} \\
H_2O_2 + h\nu & \rightarrow 2OH & k_{15}
\end{array}$$

The constant reaction rates are

$k_1 = 1.46 \times 10^{-16}$, $k_4 = 4.20 \times 10^{-11}$, $k_7 = 6.00 \times 10^{-11}$, $k_{10} = 2.30 \times 10^{-12}$,
$k_2 = 2.12 \times 10^{-15}$, $k_5 = 2.20 \times 10^{-10}$, $k_8 = 1.50 \times 10^{-15}$, $k_{11} = 1.50 \times 10^{-12}$.
$k_3 = 2.80 \times 10^{-11}$, $k_6 = 3.70 \times 10^{-14}$, $k_9 = 1.20 \times 10^{-10}$,

The diurnally varying reaction rates ($k_{12}, k_{13}, k_{14}, k_{15}$) are again mathematically idealized and take the same form as in the Chapman problem with

$$a_{12} = 22.62, \quad a_{13} = 7.601, \quad a_{14} = 7.500, \quad a_{15} = 10.40, \quad w = \frac{\pi}{43200}.$$

Table 4 Results of the Chapman atmosphere problem at $t = 172{,}800$

y_i	Solution at $t = 172{,}800$
y_1	0
y_2	$1.000000999850914 \times 10^{12}$
y_3	$0.000000051603041 \times 10^{12}$
y_4	$0.000001283441007 \times 10^{12}$
y_5	$0.000112887143925 \times 10^{12}$

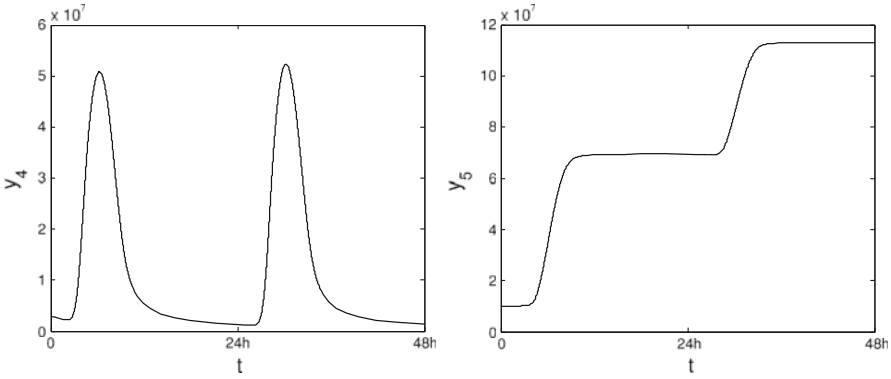

Fig. 3 Hydrogen chemistry: numerical solution obtained by exponential propagation method

We hold three of the species constant $y_6 = 1.3\times10^{17}$, $y_7 = 3.4\times10^{16}$, $y_8 = 9.4\times10^{11}$ and assume one to be in instantaneous equilibrium

$$y_9 = \frac{k_{14}y_2}{k_3y_6 + k_4y_7 + k_5y_8}.$$

The five remaining species react according to the differential system

$$\begin{aligned}
y_1' &= (k_3y_9y_6 + k_4y_9y_7 + 2k_{12}y_7 + k_{13}y_2) \\
&\quad - (k_1y_7 + k_2y_2 + k_7y_4)\, y_1, && y_1(0) = 10^6, \\
y_2' &= k_1y_1y_7 - (k_2y_1 + k_6y_3 + k_8y_4 + k_{13} + k_{14})\, y_2, && y_2(0) = 10^{12}, \\
y_3' &= (2k_5y_8y_9 + k_7y_1y_4 + k_8y_2y_4 + 2k_{15}y_5) \\
&\quad - (k_6y_2 + k_9y_4 + k_{11}y_5)\, y_3, && y_3(0) = 10^6, \\
y_4' &= (k_6y_2y_3 + k_{11}y_3y_5) - (k_7y_1 + k_8y_2 + k_9y_3)\, y_4 - 2k_{10}y_4^2, && y_4(0) = 2\times10^6, \\
y_5' &= k_{10}y_4^2 - (k_{11}y_3 + k_{15})\, y_5, && y_5(0) = 10^7.
\end{aligned}$$

The obtained solution of this problem at $t = 172{,}800$ using exponential propagation method is reported in Table 4. Plots given in the Fig. 3 show behavior of the solution $y_4 = [HO_2]$ and $y_5 = [H_2O_2]$ in time interval [0,172,800 = 48-h].

4.4 Chemical Akzo Nobel problem

This IVP is a stiff system of 6 non-linear differential equations. It has been taken from [3].

Mathematical description of the problem: The problem is of the form

$$\frac{dy}{dt} = f(y), \quad y(0) = y_0, \quad y \in \mathbb{R}^6, \ 0 \le t \le 180$$

and the function f is defined by

$$f = \begin{pmatrix} -2r_1 + r_2 - r_3 - r_4 \\ -\frac{1}{2}r_1 - r_4 - \frac{1}{2}r_5 + F_{in} \\ r_1 - r_2 + r_3 \\ -r_2 + r_3 - 2r_4 \\ r_2 - r_3 + r_5 \\ -r_5 \end{pmatrix}$$

where the r_i and F_{in} are auxiliary variables, given by

$$\begin{aligned} r_1 &= k_1 \cdot y_1^4 \cdot y_2^{\frac{1}{2}}, \quad k_1 = 18.7, \\ r_2 &= k_2 \cdot y_3 \cdot y_4, \quad k_2 = 0.58, \\ r_3 &= \frac{k_2}{K} \cdot y_1 \cdot y_5, \quad K = 34.4, \\ r_4 &= k_3 \cdot y_1 \cdot y_4^2, \quad k_3 = 0.09, \\ r_5 &= k_4 \cdot y_6^2 \cdot y_2^{\frac{1}{2}}, \quad k_4 = 0.42, \\ F_{in} &= klA \cdot \left(\frac{p(O_2)}{H} - y_2 \right), \quad klA = 3.3, \ p(O_2) = 0.9, \ H = 737. \end{aligned}$$

Finally the initial vector y_0 is given by $y_0 = (0.437, 0.00123, 0, 0, 0, 0.367)^T$.

Origin of the problem: The problem originates from Akzo Nobel Central Research in Arnhem, The Netherlands. It describes a chemical process, in which 2 species, *MBT* and *CHA*, are mixed, while oxygen is continuously added. The resulting species of importance is *CBS*. The reaction equations, as given by Akzo Nobel, are

$$\begin{aligned} &2MBT + \tfrac{1}{2}O_2 \xrightarrow{k_1} MBTS + H_2O \\ &CBS + MBT \underset{k_2}{\overset{k_2/K}{\rightleftarrows}} MBTS + CHA \\ &MBT + 2CHA + O_2 \xrightarrow{k_3} BT + sulfate \\ &MBT + CHA + \tfrac{1}{2}O_2 \xrightarrow{k_4} CBS + H_2O \\ &MBT + CHA \rightleftarrows MBT.CHA. \end{aligned}$$

The last equation describes an equilibrium

$$Ks^1 = \frac{[MBT.CHA]}{[MBT] \cdot [CHA]},$$

while the others describe reactions, whose velocities are given by

$$\begin{aligned} r_1 &= k_1 \cdot [MBT]^4 \cdot [O_2]^{\frac{1}{2}}, \\ r_2 &= k_2 \cdot [MBTS] \cdot [CHA], \\ r_3 &= \frac{k_2}{K} \cdot [MBT] \cdot [CBS], \\ r_4 &= k_3 \cdot [MBT] \cdot [CHA]^2, \\ r_5 &= k_4 \cdot [MBT.CHA]^2 \cdot [O_2]^{\frac{1}{2}}, \end{aligned}$$

respectively. Here the square brackets '[ ]' denote concentrations. The inflow of oxygen per volume unit is denoted by F_{in}, and satisfies

$$F_{in} = klA \cdot \left(\frac{p(O_2)}{H} - [O_2] \right),$$

where klA is the mass transfer coefficient, H is the Henry constant and $p(O_2)$ is the partial oxygen pressure. $p(O_2)$ is assumed to be independent of $[O_2]$. The parameters $k_1, k_2, k_3, k_4, K, klA, H$ and $p(O_2)$ are given constants. The process is started by mixing 0.437 mol/L $[MBT]$ with 0.367 mol/L $[MBT.CHA]$. The concentration of oxygen at the beginning is 0.00123 mol/L. Initially, no other species are present. The simulation is performed on the time interval [0 180 min].

Identifying the concentrations $[MBT], [O_2], [MBTS], [CHA], [CBS], [MBT.CHA]$ with $y_1, \ldots, y_6$, respectively, one easily arrives at the mathematical formulation of the preceding subsection. Solution of this problem at $t = 180$ using exponential propagation method is reported in Table 5. Behavior of the solution components is shown in Fig. 4.

Table 5 Results of the Chemical Akzo Nobel problem at $t = 180$

y_i	Solution at $t = 180$
y_1	0.116158370478195
y_2	0.001119409155633
y_3	0.162126567728322
y_4	0.003395915545571
y_5	0.164618513734356
y_6	0.198954389941537

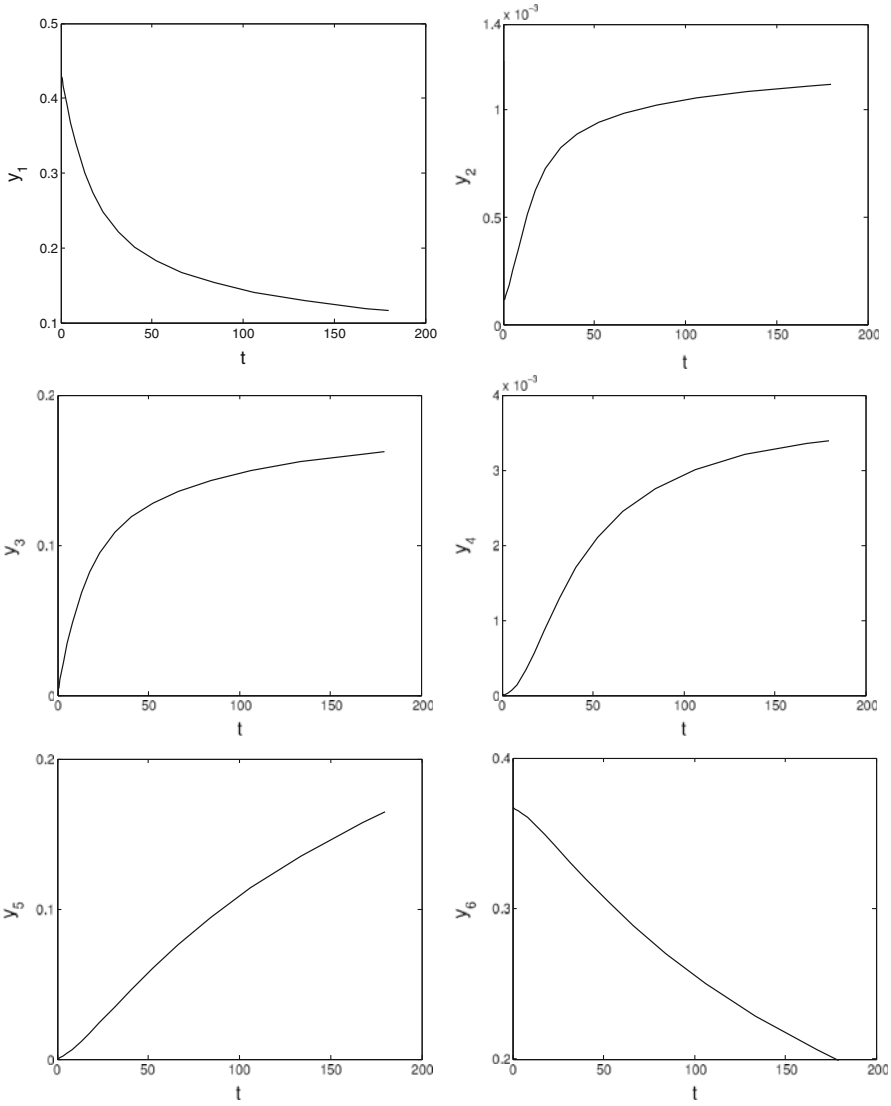

Fig. 4 Chemical Akzo Nobel problem: numerical solution obtained by exponential propagation method

4.5 A simple air pollution problem

In this test, we illustrate the mass action law by three reactions between oxygen O_2, atomic oxygen O, ozone O_3, nitrogen oxide NO and nitrogen dioxide NO_2. It is important, first, to consider the primary chemical reactions that are involved

$$NO_2 + h\nu \xrightarrow{\mu_1(t)} NO + O$$

$$O + O_2 \xrightarrow{\mu_2} O_3$$

$$NO + O_3 \xrightarrow{\mu_3} O_2 + NO_2$$

The first photochemical reaction says that during the light hours, due to the solar radiation indicated here by $h\nu$, NO_2 is photo-dissociated into NO and O; this reaction is regulated by $\mu_1(t)$ as specified below. We assume that the oxygen concentration O_2 is constant, which is a realistic hypothesis.

Setting the concentrations $y_1 = [O]$, $y_2 = [NO]$, $y_3 = [NO_2]$ and $y_4 = [O_3]$, a simple model for the air pollution in the lower troposphere is given below [7]

$$\begin{aligned}
y_1' &= \mu_1(t)y_3 - \mu_2 y_1, & y_1(t_0) &= 0,\\
y_2' &= \mu_1(t)y_3 - \mu_3 y_2 y_4 + s_2, & y_2(t_0) &= 1.3 \times 10^8,\\
y_3' &= \mu_3 y_2 y_4 - \mu_1(t)y_3, & y_3(t_0) &= 5 \times 10^{11},\\
y_4' &= \mu_2 y_1 - \mu_3 y_2 y_4, & y_4(t_0) &= 8 \times 10^{11}.
\end{aligned}$$

The concentrations are given in molecules for cm^3 and time in seconds. Note that μ_2 is the total number of oxygen molecules per cm^3 and as a consequence is much larger than $\mu_1(t)$ and μ_3. Moreover, a constant source term s_2 is used to simulate the emission of nitrogen oxide. The reported numerical results use following involved parameters:

$$\mu_1(t) = \begin{cases} 10^{-40} & \text{night} - \text{hours} : \text{8p.m.} - \text{4a.m.},\\ 10^{-5} e^{7sec(t)} & \text{day} - \text{hours} : \text{4a.m.} - \text{8p.m.}, \end{cases}$$

$$\mu_2 = 10^5, \quad \mu_3 = 10^{-16}, \quad s_2 = 10^6,$$

where

$$sec(t) = \left(\sin\left(\frac{\pi}{16}(t_h - 4)\right)\right)^{0.2}, \quad t_h = th - 24\left[\frac{th}{24}\right], \quad th = \frac{t}{3,600},$$

here $[z]$ stands for the floor function.

Figure 5 shows the results for a period of 5 days, that is, from 4 a.m. ($t_0 = 144, 00$) up to 4 a.m. of the next 5 days ($t_{end} = 504, 000$), obtained with exponential propagation method.

5 Conclusion

The primary objective of using exponential propagation methods is to avoid the restrictive stability condition which constrains the maximum allowed time step for explicit schemes. This becomes important if system of differential equations is stiff. Because of the stability condition, the time step in an explicit scheme has to be very small in order to obtain a stable method. Thus, the time step restriction becomes severe if the

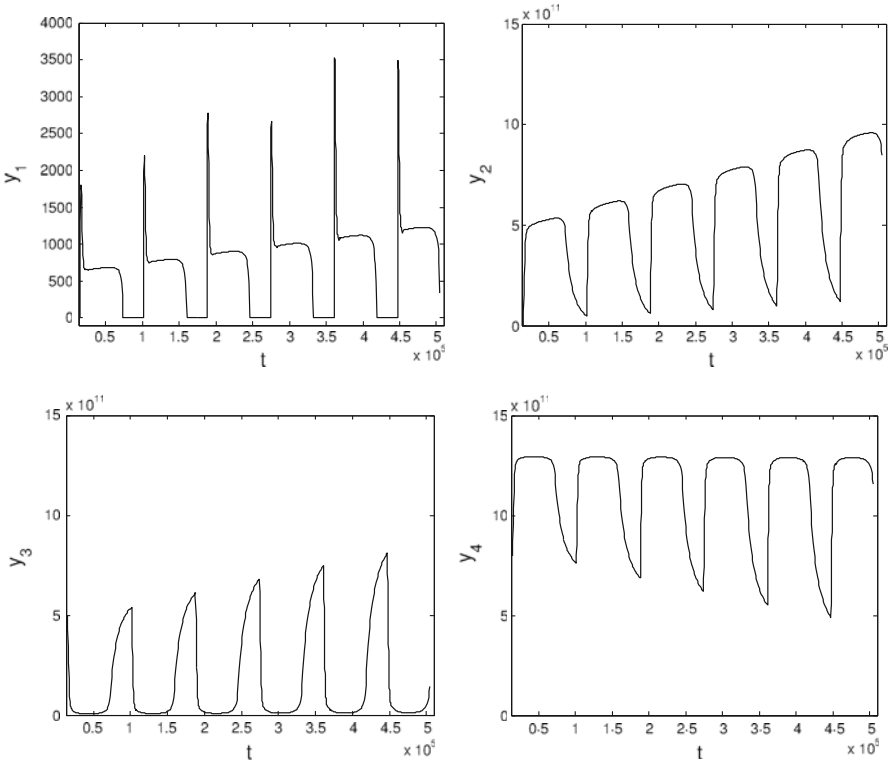

Fig. 5 The air pollution model: numerical solution obtained by exponential propagation method

system has to be integrated over long periods of time. In implicit scheme since the problems we are interested in are large, a Krylov projection based iterative method has to be used to invert a matrix. Due to the stiffness of the Jacobian matrix we can expect the convergence of an iterative method to be very slow, so that the larger time step advantage of an implicit methods is overweighed by the number of iterations required to invert the matrix.

Since the selected systems of ODEs in this paper are stiff systems in long periods of time, we suggested applying exponential propagation methods on them. These methods provide an alternative to avoid the limitations of both explicit and implicit methods. First, they allow a stable time integration to be performed with the time step greatly exceeding the stability bound. Second, as was shown in [5], the convergence of the Krylov projection method used in an exponential propagation scheme exceeds that of the same Krylov projection technique used to invert a matrix in an implicit method.

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