On the employ of time series in the numerical treatment of differential equations modeling oscillatory phenomena

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Abstract. The employ of an adapted numerical scheme within the integration of differential equations shows benefits in terms of accuracy and stability. In particular, we focus on differential equations modeling chemical phenomena with an oscillatory dynamics. In this work, the adaptation can be performed thanks to the information arising from existing theoretical studies and especially the observation of time series. Such information are properly merged into the exponential fitting technique, which is specially suitable to follow the a-priori known qualitative behavior of the solution. Some numerical experiments will be provided to exhibit the effectiveness of this approach.

Keywords: oscillating solutions, exponential fitting, parameter estimation, reaction equations, Belousov-Zhabotinsky reaction

1 Introduction

This work aims to solve systems of differential equations modeling oscillatory chemical phenomena. In particular, it highlights how useful can be time series of experimental data when they are properly merged into a numerical scheme. Classic numerical methods could determine a strong reduction in stepsize in order to accurately follow the prescribed oscillations of the exact solution because they are developed in order to be exact (within round-off error) on polynomials up to a certain degree. When the qualitative behavior of the exact solution is a-priori known, it may be worthwhile to employ adapted methods which are constructed in order to be exact on functions other than polynomials, following the well-known strategy of exponential fitting [1–4]. Such functions are assumed to belong to a finite-dimensional space (the so-called fitting space) and are chosen according to the character of the exact solution. As a consequence, the coefficients of the resulting numerical method are no longer constant as in the classic case, but depend on a parameter characterizing the exact solution, whose value is evidently unknown. Therefore, the advantages of this technique can be reached only if the fitting space is suitably chosen and the parameter is properly computed.

We deal with these two challenges by taking into account the existing theoretical studies on the problem and observing the time series of experimental data. The oscillatory dynamics emerging from both these approaches suggests the employ of a trigonometrical fitting space. In this case, the basis functions rely on a parameter which is the time frequency of oscillations of the exact solution. When the time series of experimental data are available, we can estimate the parameter by means of the frequency of observed oscillations, thus avoiding expensive procedures based on solving non-linear systems as in [5, 6].

As an experimental case study, we focus on the Belousov-Zhabotinsky (BZ) reaction, a prototypical oscillatory chemical system whose kinetics is essentially described in the well-known *Oregonator* model developed by Field, Körös and Noyes [7–9]. It consists in a system of ordinary differential equations which we integrate by means of the above-mentioned adapted strategy.
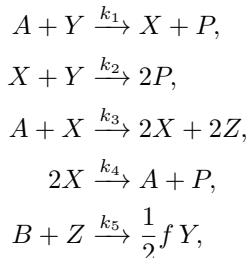
In summary, we describe the main aspects of the Belousov-Zhabotinsky reaction in Section 2, Section 3 is devoted to the development of the numerical scheme used to integrate the Oregonator, while Section 4 shows some numerical experiments and Section 5 exhibits the conclusions.

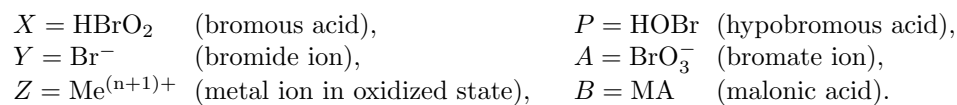## 2   The Belousov Zhabotinsky reaction

The BZ reaction was discovered in 1951 by Boris P. Belousov who observed oscillations in the color of a solution while he was trying to develop a simple chemical model for the oxidation of organic molecules in living cells [10, 11]. His study was confirmed and extended by Zhabotinsky 10 years later [12–14] and now BZ is probably one of the most studied oscillating reaction; the popularity of the BZ is mainly due to the fact that it is the simplest closed macroscopic system that can be maintained far from equilibrium by an internal source of free energy homogeneously distributed in space. Being outside of thermodynamical equilibrium, BZ displays several *exotic* dynamical regimes: periodic, aperiodic and chaotic oscillations [15, 16], autocatalysis and bistability [17], Turing structures and pattern formation [18, 19].

The BZ reaction consists in the oxidation of an organic substrate (generally malonic acid) by bromate ions in an acidic medium, catalyzed by a metal complex (iron, cerium or ruthenium, see [8, 9] and references therein). The oscillations especially occur in the concentrations of the metal ions and become evident through a change in the color of the solution, which is more drastic for the iron. According to Fields, Körös and Noyes, the oscillations are due to the competition between two processes: firstly, the metal ion is mainly in its reduced state and the concentration of bromide ions ($[Br^-]$) is high (Process I); then the bromide ion is consumed up to a certain critical value and the metal ion reverts to the oxidized state (Process II); finally the metal ion reacts to produce bromide ions and changes to its reduced state again. However, from the kinetics point of view, oscillations are due to an Hopf instability arising from the nonlinear chemical mechanism (autocatalysis + inhibition), involved in the reaction. The whole chemical kinetics has been described by Field, Körös and Noyes by means

of the following key reactions

$$A + Y \xrightarrow{k_1} X + P,$$

$$X + Y \xrightarrow{k_2} 2P,$$

$$A + X \xrightarrow{k_3} 2X + 2Z,$$

$$2X \xrightarrow{k_4} A + P,$$

$$B + Z \xrightarrow{k_5} \frac{1}{2} f Y,$$

where

$X = \mathrm{HBrO_2}$	(bromous acid),	$P = \mathrm{HOBr}$	(hypobromous acid),
$Y = \mathrm{Br^-}$	(bromide ion),	$A = \mathrm{BrO_3^-}$	(bromate ion),
$Z = \mathrm{Me^{(n+1)+}}$	(metal ion in oxidized state),	$B = \mathrm{MA}$	(malonic acid).

Applying the law of mass action, the Field-Körös-Noyes model can be converted into the following third order system of kinetic equations [8]:

$$\frac{dx^*}{dt^*} = k_1 \, a \, y^* - k_2 \, x^* y^* + k_3 \, a \, x^* - 2k_4 (x^*)^2, \qquad (1\mathrm{a})$$

$$\frac{dy^*}{dt^*} = -k_1 \, a \, y^* - k_2 \, x^* y^* + \frac{f}{2} \, k_5 \, b \, z^*, \qquad (1\mathrm{b})$$

$$\frac{dz^*}{dt^*} = 2k_3 \, a \, x^* - k_5 \, b \, z^*, \qquad (1\mathrm{c})$$

which is known as *Oregonator* and involve the concentrations of the aforementioned chemical elements. Such concentrations are indicated by letters in lower case henceforth. The occurrence of oscillations in the exact solution depends strongly on the values of the involved parameters, especially k_5 and f. Indeed, if $k_5 = 0$, the bromide ion ($\mathrm{Br^-}$) concentration decays to zero according to the equation (1b), so the system cannot oscillate. With regards to f, oscillations arise only if $0.5 < f < 2.414$, whereas for $f < 0.5$ and $f > 2.414$ the reaction is in a stable steady state, being Process II or Process I dominant, respectively (see [9] and references therein).

It is more convenient to study the Oregonator (1) in its dimensionless form, as follows:

$$\epsilon \frac{dx}{dt} = q \, y - x \, y + x \, (1 - x), \qquad (2\mathrm{a})$$

$$\epsilon' \frac{dy}{dt} = -q \, y - x \, y + f \, z, \qquad (2\mathrm{b})$$

$$\frac{dz}{dt} = x - z, \qquad (2\mathrm{c})$$

where

$$x = \frac{2k_4}{k_3 a} x^*, \quad y = \frac{k_2}{k_3 a} y^*, \quad z = \frac{k_4 k_5 b}{(k_3 a)^2} z^*, \quad t = \frac{t^*}{k_5 b},$$

$$\epsilon = \frac{k_5 b}{k_3 a}, \quad \epsilon' = \frac{2k_4 k_5 b}{k_2 k_3 a}, \quad q = \frac{2k_1 k_4}{k_2 k_3}, \tag{3}$$

or, in a more compact form,

$$\frac{dr}{dt} = F(r; q, f, \epsilon, \epsilon'), \tag{4}$$

where $r = [x, y, z]^T$ and $F(r; q, f, \epsilon, \epsilon') = \begin{bmatrix} \frac{1}{\epsilon} \left(q\, y - x\, y + x\, (1 - x) \right) \\ \frac{1}{\epsilon'} \left(-q\, y - x\, y + f\, z \right) \\ x - z \end{bmatrix}.$

3   An adapted numerical scheme

We aim to integrate the system (4) in a certain interval $[t_0, T]$ provided with the following initial condition

$$r(t_0) = r_0, \tag{5}$$

in a region of the plane $k_5 - f$ where the solution is known to oscillate. For this purpose, we discretize the interval $[t_0, T]$ and we employ an adapted Runge Kutta method, developed in order to be exact (within round-off error) on functions belonging to a particular fitting space. The general expression of a s-stage Runge-Kutta method applied to the system (4) is

$$R_i = r_n + k \sum_{j=1}^{s} a_{i,j}\, F(t_n + c_j k, R_j), \quad i = 1, \ldots, s,$$

$$r_{n+1} = r_n + k \sum_{i=1}^{s} b_i\, F(t_n + c_i k, R_i), \tag{6}$$

where k is the stepsize. We remark that the system (4) is autonomous, so $F(t_n + c_j k, R_j) = F(R_j)$. The scheme (6) is a one-step procedure and each of its stages can be seen as a linear multistep formula on a non-equidistant grid [20]. Following this approach, it can be reformulated by means of the following $s+1$ linear stage representation

$$r_{n+c_i} = r_n + k \sum_{j=1}^{s} a_{i,j}\, F(r_{n+c_j}), \quad i = 1, \ldots, s, \tag{7a}$$

$$r_{n+1} = r_n + k \sum_{i=1}^{s} b_i\, F(r_{n+c_i}), \tag{7b}$$

being (7a) the internal stages and (7b) the final one. In this way, it is possible to associate a linear difference operator with each stage

$$\mathcal{L}_i[\phi(t); k] = \phi(t + c_i k) - \phi(t) - k \sum_{j=1}^{s} a_{i,j}\, \phi'(t + c_j k), \quad i = 1, \ldots, s, \qquad (8a)$$

$$\mathcal{L}[\phi(t); k] = \phi(t + k) - \phi(t) - k \sum_{i=1}^{s} b_i\, \phi'(t + k). \qquad (8b)$$

Annhilating it on a proper fitting space, we can obtain the required adapted Runge Kutta.

The prescribed oscillatory behavior of the exact solution of (4) suggests the employ of a trigonometrical fitting space

$$\mathcal{F}_{trig} = \{1, \sin(\mu\, t), \cos(\mu\, t)\}, \qquad (9)$$

and the above procedure leads to a trigonometrically fitted 2-stage Runge Kutta method having the following coefficients [21]:

$$a_{i1}(z) = \frac{1}{zD(z)}\left(\sin(c_i z)\sin(c_2 z) - \cos(c_2 z)(1 - \cos(c_i z))\right), \; i = 1, 2,$$

$$a_{i2}(z) = \frac{1}{zD(z)}\left(-\sin(c_i z)\sin(c_1 z) + \cos(c_1 z)(1 - \cos(c_i z))\right), \; i = 1, 2,$$

$$\qquad\qquad (10)$$

$$b_1(z) = \frac{1}{zD(z)}\left(\sin(z)\sin(c_2 z) - \cos(c_2 z)(1 - \cos(z))\right),$$

$$b_2(z) = \frac{1}{zD(z)}\left(-\sin(z)\sin(c_1 z) + \cos(c_1 z)(1 - \cos(z))\right),$$

where $z = \mu\, k$ and

$$D(z) = \cos(c_1 z)\sin(c_2 z) - \sin(c_1 z)\cos(c_2 z).$$

We remark that the coefficients (10) rely on the parameter μ, which needs to be properly estimated. For this purpose, we consider the experiment in [22] carried out on an unstirred ferroin catalyzed BZ system and we observe the corresponding time series reported in Figure 1. We focus on the oscillations occurring in the concentration of ferriin, i.e. the oxidized form of the catalyst, $Fe(phen)_3^{3+}$, which corresponds to z in the *Oregonator* model (4). The time series exhibits an initial exponential decay trend corresponding to the start of the reaction. We extract the frequency of the oscillations from the time series as the inverse of the period and we use the obtained value (0.0349) as an estimate of the parameter μ. In this way, we can reach the benefits of the exponential fitting strategy without increasing the computational cost to compute an accurate estimate of μ.
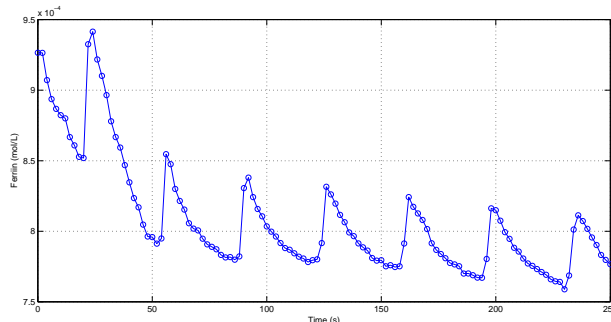
Fig. 1: Time series of concentration of ferriin related to the experiment carried out in [22] on an unstirred ferroin catalyzed BZ system.

4   Numerical experiments

We now show some numerical results arising from the integration of (4) in $[0, 185]$ provided by the initial conditions

$$x(0) = 0.0013, \quad y(0) = 0.2834, \quad z(0) = 0.1984, \tag{11}$$

and with the following values for the parameters

$$f = 1, \quad q = 3.52 \cdot 10^{-5}, \quad \epsilon = 0.3779, \quad \epsilon' = 7.56 \cdot 10^{-4}. \tag{12}$$

We remark that the concentrations in (11) are in their dimensionless form. We employ the trigonometrically fitted Runge Kutta method (10) described in Section 3 with the vector of nodes of the implicit trapezoidal rule ($c = [0, 1]$) and compare it with the corresponding classic Runge Kutta, the Lobatto-IIIA method and the well-known Gauss' Runge Kutta of order 4, which have the following Butcher's arrays [23]

$$
\begin{array}{c|cc}
0 \\
1 & 1/2 & 1/2 \\
\hline
 & 1/2 & 1/2
\end{array}
\qquad
\begin{array}{c|ccc}
0 \\
1/2 & 5/24 & 1/3 & -1/24 \\
1 & 1/6 & 2/3 & 1/6 \\
\hline
 & 1/6 & 2/3 & 1/6
\end{array}
\qquad
\begin{array}{c|cc}
1/2 - \sqrt{3}/6 & 1/4 & 1/4 - \sqrt{3}/6 \\
1/2 + \sqrt{3}/6 & 1/4 + \sqrt{3}/6 & 1/4 \\
\hline
 & 1/2 & 1/2
\end{array}
$$

respectively. Table 1 shows that the trigonometrically fitted Runge Kutta method (10) is more accurate and even stabler than the classic methods. In this table, we consider the relative error with respect to a reference solution, computed by the Matlab routine ode15s with an accuracy equal to 10^{-13}. As reported in Figure 2, the trigonometrically fitted Runge Kutta method (10) follows the oscillations of the solution expected both from theoretical studies [9] and from the observation of time series related to the experiment in [22]. Moreover, Figure 2 shows that the numerical solution obtained by this method and the reference solution computed by the Matlab solver ode15s exhibit totally similar oscillatory profiles. We remark that the variables concentration of ferriin (z) and time (t) have been recast according to the positions (3).

Table 1: Comparison among some classic Runge Kutta methods and the trigonometrically fitted Runge Kutta (10) with nodes $c = [0, 1]$ for the the integration of system (4) with initial condition (5) and parameters chosen as in (12).

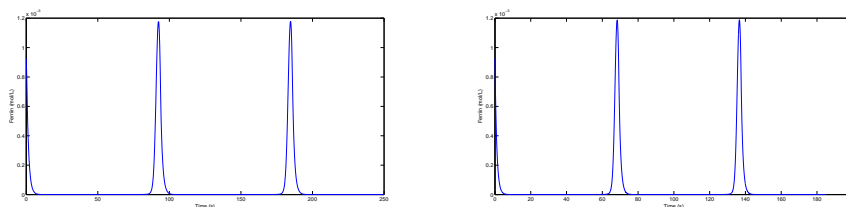|	**Error**		
	$k = 0.25$	$k = 1$	$k = 1.5$
Trapezoidal rule	0.000109	0.750955	0.978572
LobattoIIIA Runge Kutta	0.003356	it blows up	it blows up
Gauss' Runge Kutta	0.002093	1.000013	0.995994
Trigonometrically fitted Runge Kutta	0.000070	0.577778	0.588392

Fig. 2: Numerical solution of (4) obtained by the trigonometrically fitted Runge Kutta method (10) with nodes $c = [0, 1]$ and stepsize $k = 0.25$ (on the left) and numerical solution computed by the Matlab routine `ode15s` with an accuracy equal to 10^{-13} (on the right). The variables concentration of ferriin (z) and time (t) have been recasted according to the positions (3).

5   Conclusions

In this work, we have presented an adapted numerical scheme to integrate systems of ordinary differential equations modeling oscillatory chemical phenomena. In particular, we have employed a trigonometrically fitted Runge Kutta method in order to accurately follow the prescribed oscillations of the exact solution. Indeed, such methods are constructed in order to be exact (within round-off error) on trigonometric functions. However, this strategy usually requires a further computational effort to estimate the parameter which the basis functions depend on. For this reason, we have considered the time series coming from an experiment which can be reasonably modelled by the system we want to integrate. Therefore, we have chosen the frequency of the oscillations observed in time series as an estimate of the parameter, thus avoiding an increase of computational cost. Numerical experiments show the effectiveness of this approach.

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