

Adapted numerical modelling of the Belousov-Zhabotinsky reaction

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Abstract Adapted numerical schemes for the integration of differential equations generating periodic wavefronts have reported benefits in terms of accuracy and stability. This work is focused on differential equations modelling chemical phenomena which are characterized by an oscillatory dynamics. The adaptation is carried out through the exponential fitting technique, which is specially suitable to follow the a-priori known qualitative behavior of the solution. In particular, we have merged this strategy with the information coming from existing theoretical studies and especially the observation of time series. Numerical tests will be provided to show the effectiveness of this problem-oriented approach.

Keywords Oscillating solutions · exponential fitting · adapted Runge-Kutta methods · parameter estimation · reaction equations · Belousov-Zhabotinsky reaction · chemical oscillators

1 Introduction

This treatise is devoted to the integration of systems of differential equations modelling oscillatory chemical phenomena. In particular, it shows the benefits of merging time series of experimental data and theoretical studies about the problem into an adapted numerical scheme.

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In case of problems having oscillating solutions, standard numerical methods could require a very small stepsize in order to accurately follow the prescribed oscillations. Indeed, they are constructed in order to be exact (within round-off error) on polynomials up to a certain degree. When some information about the qualitative behaviour of the exact solution are a-priori available, it may be more convenient to employ adapted methods which are developed in order to be exact on functions other than polynomials, following the well-known technique of exponential fitting [4, 5, 8, 11, 11, 12, 19, 20, 24]. These basis functions are supposed to belong to a finite-dimensional space, the so-called fitting space, and are selected according to the prescribed character of the exact solution. Consequently, the coefficients of the resulting numerical scheme are no longer constant, as in the classic case, but rely on a parameter characterising the exact solution, whose value is clearly unknown. Hence, the major issues arising from the exponential fitting are the choice of a suitable fitting space and the estimate of the parameter.

In this work, extending the ideas presented in [9], we take on these two challenges by exploiting the existing theoretical studies about the problem and observing the time series of experimental data. Since both these approaches show that the considered problem has an oscillatory dynamics, it may be worthwhile using a trigonometrical fitting space. The whole behaviour observed in time series also suggests a modification of this fitting space, based on a combination of trigonometric and logarithmic functions. In both cases, the basis functions depend on a parameter, characterising the exact solution, which needs to be approximated. When the time series of experimental data are available, we can estimate this parameter by employing the frequency of observed oscillations. We can also approximate the parameter by using the inverse of the period, when its analytic expression is known. In both strategies, we avoid expensive procedures involving non-linear systems employed, for instance, in [6, 7].

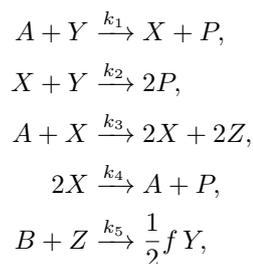
As an experimental case study, we consider the Belousov-Zhabotinsky (BZ) reaction, a prototypical oscillatory chemical system whose kinetics is basically described by the well-known *Oregonator* model proposed by Field, Körös and Noyes [13, 22, 36]. This model is a system of first-order ordinary differential equations which we integrate by employing the above-mentioned adapted strategy. In particular, we take into account information coming from the theoretical studies presented in [35, 36] and the observation of time series of experimental data related to the experiment carried out in [26] on an unstirred BZ system.

In summary, we present the key features of the Belousov-Zhabotinsky reaction in Section 2 and we describe the adapted numerical scheme used to integrate the Oregonator in Section 3. Section 4 reports some numerical tests and Section 5 is devoted to the conclusions.

2 The Belousov Zhabotinsky reaction

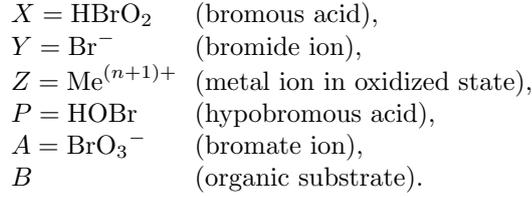
The Belousov-Zhabotinsky reaction, shortly indicated as BZ reaction [2, 15, 37–39], is an outstanding example of self-organizing chemical system, widely studied in different scientific disciplines. BZ reaction is, in fact, one of the simplest closed macroscopic system that can be maintained far from equilibrium by an internal source of free energy homogeneously distributed in space. Since it is outside of thermodynamic equilibrium, BZ can exhibit several dynamical regimes: periodic, aperiodic and chaotic oscillations [21, 25], autocatalysis and bistability [31], Turing structures and pattern formation [3, 27]. Most of the recent research concerning BZ reaction is devoted to stimuli-responsive smart materials [14, 29, 30] and the simulation of complex biological communication [32–34]. In this work, we focus on cases where a BZ system displays periodic oscillations and we aim to reproduce them along the numerical solution.

In the BZ reaction, an organic substrate (generally malonic acid) is oxidised by bromate ions in an acidic medium. The process is catalysed by one-electron metal ion oxidants with standard reduction potentials of 1 – 1.5V, for instance metal ions complexes such as ferroin, cerium sulphate, and so on (see [22, 36] and references therein). Under proper conditions, the system displays self-sustained temporal oscillations in the concentrations of the intermediates, which can be observed through a colour change of the solution (more evident in case of ferroin as catalyst). Fields, Körös and Noyes found that these oscillations derive from the competition between two processes: firstly, the metal ion is mainly in its reduced state and the bromide ions ($[\text{Br}^-]$) have a high concentration (Process I, inhibitory step); then the bromide ion is consumed up to a certain critical value and the metal ion is converted to the oxidised state (Process II, autocatalytic step); finally, the metal ion reacts to produce bromide ions and reverts to its reduced state again. From a dynamical point of view, the linear stability analysis of the kinetic model reveals that oscillations occur through an Hopf instability stemming from the nonlinear chemical mechanism (autocatalysis + inhibition). Although the whole chemical kinetics involves several reactions, the fundamental mechanistic features are captured in the FKN model proposed by Field, Körös and Noyes in [16] and used here in the following simplified formulation [17, 28]:



where the rate constants k_1, \dots, k_5 are known, f is a stoichiometric factor representing the number of bromides produced when metal ions are reduced,

and the key chemical elements are:



Concentrations of the reactant and product species P , A and B are in general much higher than those of the dynamical intermediate species X , Y and Z , so they are assumed to be constant on the time scale of a few oscillations.

Applying the law of mass action, the FKN model leads to the following system of kinetic equations [22, 28, 36]:

$$\frac{dx^*}{dt^*} = k_1 a y^* - k_2 x^* y^* + k_3 a x^* - 2k_4 (x^*)^2, \quad (2.1a)$$

$$\frac{dy^*}{dt^*} = -k_1 a y^* - k_2 x^* y^* + \frac{f}{2} k_5 b z^*, \quad (2.1b)$$

$$\frac{dz^*}{dt^*} = 2k_3 a x^* - k_5 b z^*. \quad (2.1c)$$

This system of first-order differential equations is known as *Oregonator* and involves the concentrations of the aforementioned chemical elements, which we indicate through letters in lower case henceforth. The oscillatory behaviour of the exact solution strongly relies on the values of the parameters in (2.1), especially k_5 and f . Indeed, oscillations arise only if $0.5 < f < 2.414$ and $k_5 \neq 0$. In case of $k_5 = 0$, the bromide ion (Br^-) concentration decays to zero according to the equation (2.1b), so the system cannot oscillate. On the other side, for $f < 0.5$ and $f > 2.414$ the reaction is in a stable steady state, being Process II or Process I dominant, respectively. However, for $f > 2.414$ (but not too much larger) the system is excitable and, when it is spatially distributed, can generate waves of oxidation, whereas when $f < 0.5$ (but not too much smaller) the steady state is excitable and can propagate waves of reduction (see [36] and references therein).

In case of $0.5 < f < 2.414$ and $k_5 \neq 0$, it has been proved that the amplitude \mathcal{A} and the period \mathcal{T} of the oscillations can be estimated as follows [36]:

$$\mathcal{A} \approx \frac{[\text{Me}^{(n+1)+}]_{\max}}{[\text{Me}^{(n+1)+}]_{\min}} = \frac{1}{4q(3 + 2\sqrt{2})}, \quad (2.2a)$$

$$\mathcal{T} \approx \frac{1}{k_5 b} \left(\ln \frac{1}{4q(3 + 2\sqrt{2} - f)} + \frac{2f - 1}{1 - f} \ln \frac{2f - 1}{2f} + \frac{1}{1 - f} \ln 2 \right). \quad (2.2b)$$

Let us consider the Oregonator (2.1) in its dimensionless form [28]:

$$\epsilon \frac{dx}{dt} = qy - xy + x(1-x), \quad (2.3a)$$

$$\epsilon' \frac{dy}{dt} = -qy - xy + fz, \quad (2.3b)$$

$$\frac{dz}{dt} = x - z, \quad (2.3c)$$

where

$$\begin{aligned} x &= \frac{2k_4}{k_3a} x^*, & y &= \frac{k_2}{k_3a} y^*, & z &= \frac{k_4k_5b}{(k_3a)^2} z^*, & t &= t^*k_5b, \\ \epsilon &= \frac{k_5b}{k_3a}, & \epsilon' &= \frac{2k_4k_5b}{k_2k_3a}, & q &= \frac{2k_1k_4}{k_2k_3}, \end{aligned} \quad (2.4)$$

or, in a more compact form,

$$\frac{dr}{dt} = F(r; q, f, \epsilon, \epsilon'), \quad (2.5)$$

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

In the following Section, we present an adapted integration of this system of ordinary differential equations.

3 Adapted numerical integration of Oregonator

The goal of this section is integrating system (2.5) in a certain interval $[t_0, T]$, provided with the initial condition

$$r(t_0) = r_0, \quad (3.6)$$

in a region of the plane $k_5 - f$ where the solution is known to oscillate. Therefore, we discretize the interval $[t_0, T]$ by employing N points

$$t_n = t_0 + nk, \quad n = 0, \dots, N-1,$$

where k is the stepsize. The general expression of a s -stage Runge-Kutta method applied to the system (2.5) to step from t_n to t_{n+1} is

$$R_i = r_n + k \sum_{j=1}^s a_{ij} F(t_n + c_jk, R_j), \quad i = 1, \dots, s, \quad (3.7a)$$

$$r_{n+1} = r_n + k \sum_{i=1}^s b_i F(t_n + c_ik, R_i). \quad (3.7b)$$

Let us assume that system (2.5) is autonomous, so we can simplify the right-hand-side: $F(t_n + c_j k, R_j) = F(R_j)$.

We aim to construct an adapted Runge-Kutta method in order to be exact (within round-off error) on a set of linearly independent functions. This means that each stage equation (3.7a) and the final step one (3.7b) have to integrate exactly these functions. For this purpose, we recast the Runge-Kutta method (3.7) following Albrecht's approach [1], i.e. as a linear multistep formula on a non-equidistant grid:

$$r_{n+c_i} = r_n + k \sum_{j=1}^s a_{ij} F(r_{n+c_j}), \quad i = 1, \dots, s, \quad (3.8a)$$

$$r_{n+1} = r_n + k \sum_{i=1}^s b_i F(r_{n+c_i}), \quad (3.8b)$$

being (3.8a) the internal stages and (3.8b) the final one. In this way, it is easy to define a linear difference operator for each stage

$$\mathcal{L}_i[A; k]\phi(t) = \phi(t + c_i k) - \phi(t) - k \sum_{j=1}^s a_{ij} \phi'(t + c_j k), \quad i = 1, \dots, s, \quad (3.9a)$$

$$\mathcal{L}[b; k]\phi(t) = \phi(t + k) - \phi(t) - k \sum_{i=1}^s b_i \phi'(t + c_i k). \quad (3.9b)$$

We observe that if $\phi(t)$ is a constant, the linear difference operator is null both for internal and final stages:

$$\mathcal{L}_i[A; k]\phi(t) = 0 = \mathcal{L}[b; k]\phi(t), \quad (3.10)$$

so a RK method always integrates a constant in an exact way.

Classic Runge-Kutta methods are constructed in order to be exact (within round-off error) on polynomials up a certain degree q . This is equivalent to annihilating the difference operator (3.9) on the polynomial fitting space

$$\mathcal{F} = \{1, x, x^2, \dots, x^q\}, \quad (3.11)$$

i.e. solving the linear systems

$$\begin{aligned} c_i^m - m \sum_{j=1}^s a_{ij} c_j^{m-1} &= 0, \quad i = 1, \dots, s, \quad m = 1, \dots, M-1, \\ 1 - m' \sum_{i=1}^s b_i c_i^{m'-1} &= 0, \quad m' = 1, \dots, M'-1, \end{aligned} \quad (3.12)$$

considering a_{ij} and b_i as unknowns and c_i as free parameters. For instance, standard two-stage Runge-Kutta methods have the following coefficients

$$\begin{aligned} a_{11} &= \frac{2c_2c_1 - c_1^2}{2(c_2 - c_1)}, & a_{12} &= -\frac{c_1^2}{2(c_2 - c_1)}, \\ a_{21} &= \frac{c_2^2}{2(c_2 - c_1)}, & a_{22} &= \frac{c_2^2 - 2c_2c_1}{2(c_2 - c_1)}, \\ b_1 &= \frac{2c_2 - 1}{2(c_2 - c_1)}, & b_2 &= \frac{1 - 2c_1}{2(c_2 - c_1)}, \end{aligned} \quad (3.13)$$

and they have order 2 for arbitrary c_i .

Following this approach, the coefficients of the required adapted Runge-Kutta method are derived by annihilating the difference operator (3.9) on a suitable fitting space, different from the polynomial one (3.11). As a consequence, they are no longer constant, but depend on a parameter μ , which characterises the basis functions of the fitting space. For the resulting scheme, it is possible to derive order conditions as an extension of the standard order conditions for a classic Runge-Kutta method. Indeed, we recall that a Runge-Kutta method has order 2 if its coefficients verify the conditions

$$\sum_{i=1}^s b_i = 1, \quad \sum_{i=1}^s b_i c_i = \frac{1}{2}, \quad (3.14)$$

whereas it has order 3 if the further conditions are satisfied

$$\sum_{i=1}^s b_i c_i^2 = \frac{1}{3}, \quad \sum_{i,j=1}^s b_i a_{ij} c_j = \frac{1}{6}, \quad (3.15)$$

and it has order 4 if the following conditions are also fulfilled

$$\begin{aligned} \sum_{i=1}^s b_i c_i^3 &= \frac{1}{4}, & \sum_{i,j=1}^s b_i c_i a_{ij} c_j &= \frac{1}{8}, \\ \sum_{i,j=1}^s b_i a_{ij} c_j^2 &= \frac{1}{12}, & \sum_{i,j,k=1}^s b_i a_{ij} a_{jk} c_k &= \frac{1}{24}. \end{aligned} \quad (3.16)$$

Therefore, an adapted Runge-Kutta method has algebraic order 2 if

$$\sum_{i=1}^s b_i(z) = 1 + \mathcal{O}(z^2), \quad (3.17a)$$

$$\sum_{i=1}^s b_i(z) c_i = \frac{1}{2} + \mathcal{O}(z^2), \quad (3.17b)$$

whereas it has algebraic order 3 if the further conditions hold

$$\sum_{i=1}^s b_i(z) c_i^2 = \frac{1}{3} + \mathcal{O}(z^2), \quad (3.18a)$$

$$\sum_{i,j=1}^s b_i(z) a_{ij}(z) c_j = \frac{1}{6} + \mathcal{O}(z^2), \quad (3.18b)$$

and it has algebraic order 4 if its coefficients verify also the following conditions:

$$\sum_{i=1}^s b_i(z) c_i^3 = \frac{1}{4} + \mathcal{O}(z^2), \quad (3.19a)$$

$$\sum_{i,j=1}^s b_i(z) c_i a_{ij}(z) c_j = \frac{1}{8} + \mathcal{O}(z^2), \quad (3.19b)$$

$$\sum_{i,j=1}^s b_i(z) a_{ij}(z) c_j^2 = \frac{1}{12} + \mathcal{O}(z^2), \quad (3.19c)$$

$$\sum_{i,j,l=1}^s b_i(z) a_{ij}(z) a_{jl}(z) c_l = \frac{1}{24} + \mathcal{O}(z^2), \quad (3.19d)$$

where $z = \mu k$. The knot points c_i are generally treated as free parameters and the order of the adapted scheme depends on them.

For a generic adapted Runge-Kutta method, we can also define the *adapted order* extending the definition of *trigonometric order*, given in [23], as follows:

Definition 1 An adapted Runge-Kutta method, constructed in order to be exact (within round-off error) on functions belonged to the fitting space

$$\mathcal{F} = \{1, \psi_1(m \mu t), \psi_2(m \mu t), \quad m = 1, \dots, q\},$$

has *adapted order* q if the corresponding linear difference operator (3.9) fulfils the following conditions for $m = 1, \dots, q$:

$$\mathcal{L}_i[A; k] 1 = 0, \quad i = 1, \dots, s, \quad (3.20a)$$

$$\mathcal{L}[b; k] 1 = 0, \quad (3.20b)$$

$$\mathcal{L}_i[A; k] \psi_1(m \mu t) = \mathcal{L}_i[A; k] \psi_2(m \mu t) = 0, \quad i = 1, \dots, s, \quad (3.20c)$$

$$\mathcal{L}[b; k] \psi_1(m \mu t) = \mathcal{L}[b; k] \psi_2(m \mu t) = 0. \quad (3.20d)$$

This definition advances the definitions concerning linear multistep methods presented in [18]. In this work, a functional \mathcal{L} is said to have *algebraic order* p if it is null on all algebraic polynomials of degree less or equal than p . On the other hand, \mathcal{L} has *trigonometric order* p , for a fixed period \mathcal{T} , if it is null on all trigonometric polynomials of degree less or equal than p and period \mathcal{T} . We have already observed that a Runge-Kutta exactly integrates constants, so conditions (3.20a) and (3.20b) always hold.

3.1 Trigonometrically fitted Runge Kutta methods

Since we aim to solve the Oregonator (2.5) in a certain region of the k_5 - f plane where the solution is known to oscillate, it may be convenient to employ an adapted Runge-Kutta method which exactly integrates (within round-off error) problems having trigonometric solutions. As described in Section 3, this is equivalent to annihilating the difference operator (3.9) on the following basis functions:

$$\mathcal{F}_{T,q} = \{1, \sin(m \mu t), \cos(m \mu t), \quad m = 1, \dots, q\}. \quad (3.21)$$

We recall that a RK method is said to have *trigonometric order* q (see [23] and reference therein), related to the frequency μ , if the corresponding linear difference operator verifies conditions (3.20) on the trigonometrical fitting space (3.21). In particular, conditions (3.20a) and (3.20b) always hold, whereas conditions (3.20c) and (3.20d) can be written in terms of the coefficients of the method, as follows:

$$\begin{aligned} \sum_{j=1}^s a_{ij} \sin(m c_j z) &= \frac{1 - \cos(m c_i z)}{m z}, \quad i = 1, \dots, s, \\ \sum_{j=1}^s a_{ij} \cos(m c_j z) &= \frac{\sin(m c_i z)}{m z}, \quad i = 1, \dots, s, \\ \sum_{i=1}^s b_i \sin(m c_i z) &= \frac{1 - \cos(m z)}{m z}, \\ \sum_{i=1}^s b_i \cos(m c_i z) &= \frac{\sin(m z)}{m z}, \end{aligned} \quad (3.22)$$

where $z = \mu k$ and $m = 1, \dots, q$. The knot points c_i are generally treated as free parameters and they must verify the conditions

$$c_i \neq c_j, \quad \forall i \neq j \quad \text{and} \quad c_i \in (0, 1) \quad (3.23)$$

to guarantee the non-singularity of system (3.22), which has the coefficients of the desired adapted Runge-Kutta method having trigonometric order q as solutions.

For instance, solving system (3.22) with $q = 1$ and $s = 2$, we can construct the following family of trigonometrically fitted 2-stage Runge-Kutta methods,

as in [23]:

$$\begin{aligned}
a_{i1}(z) &= \frac{1}{zD(z)} \left(\sin(c_i z) \sin(c_2 z) - \cos(c_2 z)(1 - \cos(c_i z)) \right), \quad i = 1, 2, \\
a_{i2}(z) &= \frac{1}{zD(z)} \left(-\sin(c_i z) \sin(c_1 z) + \cos(c_1 z)(1 - \cos(c_i z)) \right), \quad i = 1, 2, \\
b_1(z) &= \frac{1}{zD(z)} \left(\sin(z) \sin(c_2 z) - \cos(c_2 z)(1 - \cos(z)) \right), \\
b_2(z) &= \frac{1}{zD(z)} \left(-\sin(z) \sin(c_1 z) + \cos(c_1 z)(1 - \cos(z)) \right),
\end{aligned} \tag{3.24}$$

where

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

When μ tends to 0, these coefficients tend to the classic ones (3.13), as expected. The adapted Runge-Kutta method (3.24) has trigonometric order 1. Moreover, it has been shown in [23] that a 2-stage Runge-Kutta method of trigonometric order 1 has always algebraic order 2 and it has order 3 if its knot points verify the following condition

$$2 - 3(c_1 + c_2) + 6 c_1 c_2 = 0, \tag{3.25}$$

which does not necessarily guarantee order 4, as proved in the following theorem.

Theorem 1 *A trigonometrically-fitted Runge-Kutta method (3.24) of order 3 has algebraic order 4 if its knot points satisfy the following condition:*

$$c_1 c_2 = \frac{1}{6}. \tag{3.26}$$

Proof: An adapted method has algebraic order 4 if its coefficients verify equations (3.19). Conditions (3.19a) and (3.19b) hold if

$$\begin{aligned}
1 - 4 \sum_{i=1}^2 b_i c_i &= 1 - 2(c_1^2 + c_2^2) - 2c_1 c_2 + 4c_1 c_2 (c_1 + c_2) + \mathcal{O}(z^2) = \mathcal{O}(z^2), \\
1 - 8 \sum_{i,j=1}^2 b_i c_i a_{ij} c_j &= 1 - 2(c_1^2 + c_2^2) - 2c_1 c_2 + 4c_1 c_2 (c_1 + c_2) + \mathcal{O}(z^2) = \mathcal{O}(z^2),
\end{aligned}$$

which are satisfied if the knot points fulfil the following condition:

$$1 - 2(c_1^2 + c_2^2) - 2c_1 c_2 + 4c_1 c_2 (c_1 + c_2) = 0. \tag{3.27}$$

Combining this last equation with condition (3.25), which is satisfied because the method has order 3, we obtain the thesis (3.26). Conditions (3.19c) and (3.19d) are verified whether

$$1 - 12 \sum_{i,j=1}^2 b_i a_{ij} c_j^2 = 1 + 6c_1 c_2 (c_1 + c_2) - 3(c_1^2 + c_2^2) + \mathcal{O}(z^2) = \mathcal{O}(z^2),$$

$$1 - 24 \sum_{i,j,l=1}^2 b_i a_{ij} a_{jl} c_l = 1 + 6c_1 c_2 (c_1 + c_2) - 3(c_1^2 + c_2^2) + \mathcal{O}(z^2) = \mathcal{O}(z^2),$$

which lead to the following relation among the knot points

$$(c_1 + c_2)(6c_1 c_2 - 3(c_1 + c_2) + 2) - 2(c_1 + c_2) + 6c_1 c_2 + 1 = 0. \quad (3.28)$$

This last equation is verified if conditions (3.25) and (3.26) hold.

□

Solving system (3.25)-(3.26), it is easy to show that the only fourth order 2-stage Runge-Kutta method adapted on the trigonometric fitting space (3.21) with $q = 1$ has Gauss' knot points

$$c_1 = \frac{3 - \sqrt{3}}{6}, \quad c_2 = \frac{3 + \sqrt{3}}{6}. \quad (3.29)$$

3.2 Logarithmically-trigonometrically fitted Runge-Kutta methods

The concentrations of the key chemical elements in the Oregonator can exhibit oscillations which decay in time, as it is observed, for instance, in the time series related to the experiment in [26]. This behaviour is more similar to the profile of a function given by a linear combination of logarithmic and trigonometric functions. Therefore, it may be worthwhile constructing an adapted Runge-Kutta method in order to be exact (within round-off error) on an alternative fitting space:

$$\mathcal{F}_{LT,q} = \{1, \cos(m\mu t), \log(1 + m\mu t), \quad m = 1, \dots, q\}. \quad (3.30)$$

Annihilating the difference operator (3.9) on these basis functions, as described in Section 3, leads to the following system having coefficients a_{ij} and b_i as

unknowns:

$$\sum_{j=1}^s \frac{a_{ij}}{1 + m c_j z} = \frac{\log(1 + m c_i z)}{m z}, \quad i = 1, \dots, s, \quad (3.31a)$$

$$\sum_{j=1}^s a_{ij} \sin(m c_j z) = \frac{1 - \cos(m c_i z)}{m z}, \quad i = 1, \dots, s, \quad (3.31b)$$

$$\sum_{i=1}^s \frac{b_i}{1 + m c_i z} = \frac{\log(1 + m z)}{m z}, \quad (3.31c)$$

$$\sum_{i=1}^s b_i \sin(m c_i z) = \frac{1 - \cos(m z)}{m z}, \quad (3.31d)$$

where $z = \mu k$ and $m = 1, \dots, q$. The knot points c_i are generally treated as free parameters and they must verify conditions (3.23) to guarantee the non-singularity of the obtained system.

For example, solving system (3.31) with $q = 1$ and $s = 2$, we obtain the following family of 2-stage adapted Runge-Kutta methods:

$$a_{i1}(z) = \frac{1}{zG(z)} \left(\log(1 + c_i z) \sin(c_2 z) - \frac{1 - \cos(c_i z)}{1 + c_2 z} \right), \quad i = 1, 2, \quad (3.32a)$$

$$a_{i2}(z) = \frac{1}{zG(z)} \left(\frac{1 - \cos(c_i z)}{1 + c_1 z} - \log(1 + c_i z) \sin(c_1 z) \right), \quad i = 1, 2, \quad (3.32b)$$

$$b_1(z) = \frac{1}{zG(z)} \left(\log(1 + z) \sin(c_2 z) - \frac{1 - \cos(z)}{1 + c_2 z} \right), \quad (3.32c)$$

$$b_2(z) = \frac{1}{zG(z)} \left(\frac{1 - \cos(z)}{1 + c_1 z} - \log(1 + z) \sin(c_1 z) \right), \quad (3.32d)$$

where

$$G(z) = \frac{\sin(c_2 z)}{1 + c_1 z} - \frac{\sin(c_1 z)}{1 + c_2 z}.$$

Also in this case, for μ tending to 0, these coefficients tend to the classic ones (3.13), as expected. The adapted order of the presented fitted method is 1 and the algebraic order depends on the knot points c_i . In particular, the order conditions are the same of 2-stage trigonometrically fitted Runge-Kutta method (3.24), as shown in the following theorem.

Theorem 2 *An adapted Runge-Kutta method belonged to the family (3.32) has always algebraic order 2, it has algebraic order 3 and 4 if conditions (3.25) and (3.26) hold, respectively.*

Proof: The Runge-Kutta method (3.32) with z -dependent coefficients has always algebraic order 2 because conditions (3.17) hold:

$$\sum_{i=1}^2 b_i = 1 + \left(c_1 c_2 - \frac{c_1 + c_2}{2} + \frac{1}{3} \right) z^2 + \mathcal{O}(z^3),$$

$$1 - 2 \sum_{i=1}^2 b_i c_i = \frac{1}{3} \left((c_1 + c_2) \left(c_1 c_2 - \frac{c_1 + c_2}{2} \right) + \frac{1 + 2c_1 c_2}{4} \right) z^2 + \mathcal{O}(z^3).$$

Third-order conditions (3.18) are satisfied whether

$$1 - 3 \sum_{i=1}^2 b_i c_i^2 = \frac{6c_1 c_2 - 3(c_1 + c_2) + 2}{2} + \mathcal{O}(z^2) = \mathcal{O}(z^2),$$

$$1 - 6 \sum_{i,j=1}^2 b_i a_{ij} c_j = \frac{6c_1 c_2 - 3(c_1 + c_2) + 2}{2} + \mathcal{O}(z^2) = \mathcal{O}(z^2),$$

i.e. if condition (3.25) holds, which gives the first part of the thesis.

Finally, let us assume that the considered adapted scheme has algebraic order 3. It has order 4 if its coefficients verify the further equations (3.19). Conditions (3.19a) and (3.19b) are equivalent to

$$1 - 4 \sum_{i=1}^2 b_i c_i = 1 - 2(c_1^2 + c_2^2) - 2c_1 c_2 + 4c_1 c_2 (c_1 + c_2) + \mathcal{O}(z^2) = \mathcal{O}(z^2),$$

$$1 - 8 \sum_{i,j=1}^2 b_i c_i a_{ij} c_j = 1 - 2(c_1^2 + c_2^2) - 2c_1 c_2 + 4c_1 c_2 (c_1 + c_2) + \mathcal{O}(z^2) = \mathcal{O}(z^2),$$

which are satisfied if the knot points fulfil the following condition:

$$1 - 2(c_1^2 + c_2^2) - 2c_1 c_2 + 4c_1 c_2 (c_1 + c_2) = 0. \quad (3.33)$$

As in the proof of Theorem 1 for the trigonometric case, we observe that condition (3.25) is satisfied because the method has order 3, so (3.33) becomes (3.26). Conditions (3.19c) and (3.19d) can be recast in

$$1 - 12 \sum_{i,j=1}^2 b_i a_{ij} c_j^2 = 1 + 6c_1 c_2 (c_1 + c_2) - 3(c_1^2 + c_2^2) + \mathcal{O}(z^2) = \mathcal{O}(z^2),$$

$$1 - 24 \sum_{i,j,l=1}^2 b_i a_{ij} a_{jl} c_l = 1 + 6c_1 c_2 (c_1 + c_2) - 3(c_1^2 + c_2^2) + \mathcal{O}(z^2) = \mathcal{O}(z^2),$$

and, as in the trigonometric case, are satisfied if

$$(c_1 + c_2)(6c_1 c_2 - 3(c_1 + c_2) + 2) + 6c_1 c_2 + 1 - 2(c_1 + c_2) = 0.$$

This last equation is verified if (3.25) and (3.26) hold.

□

As in the trigonometric case, the only fourth order 2-stage Runge-Kutta method adapted on the fitting space (3.30) with $q = 1$ has Gauss' knot points (3.29).

3.3 Parameter estimation

The coefficients of the adapted Runge-Kutta methods (3.24) and (3.32) presented in the previous paragraphs are no longer constant, as in the classic case, but depend on the parameter μ , which has to be properly estimated. We first can approximate it as the inverse of the period (2.2b) of the oscillations, as follows [36]:

$$\mu_t = \frac{k_5 b (1 - f)}{\ln 2 + (2f - 1) \ln \left(\frac{2f - 1}{2f} \right) - (1 - f) \ln (4q (3 + 2\sqrt{2} - f))}. \quad (3.34)$$

When experimental data are available, it may be worthwhile estimating the parameter μ through the frequency of the oscillations observed in time series. For this purpose, we consider the experiment performed in [26] on an unstirred BZ system, where the organic substrate is the malonic acid ($B = MA$) and the catalyst is the redox couple ferriin/ferroin ($\text{Fe}(\text{phen})_3^{3+}/\text{Fe}(\text{phen})_3^{2+}$). The related time series are recorded spectrophotometrically in [26] by following the absorbance of ferroin and ferriin at wavelength equal to 510 nm and 630 nm, being the molar extinction coefficient equal to $1.1 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ and $620 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$, respectively. In the experimental conditions and time frame considered for the estimation of μ , the BZ reaction behaves as an open well-stirred system, i.e. the reaction is only under kinetic control and the *pool chemical approximation* (reactants' concentration in stationary state) applies [21]. We use these data to construct the corresponding time series related to the concentration of ferriin, i.e. the catalyst in its oxidised state, which is the third component of the solution in system (2.5). Such time series exhibits an initial exponential decay trend which corresponds to the start of the reaction and is followed by periodic oscillations (see Figure 1). Extracting the oscillation frequency as inverse of the period, we obtain the following estimate for the parameter μ :

$$\mu_e = 0.0625 \text{ Hz}. \quad (3.35)$$

Both the theoretical (3.34) and the experimental (3.35) approaches do not highly increase the computational cost, as is the case in procedures involving non-linear systems [6, 7].

4 Numerical experiments

We now present some numerical tests arising from the integration of system (2.5) in $[0, 250]$ provided by the initial conditions

$$x(0) = 0.0013, \quad y(0) = 0.2834, \quad z(0) = 0.1984, \quad (4.36)$$

and with the following values for the parameters

$$f = 1.00001, \quad q = 3.52 \cdot 10^{-5}, \quad \epsilon = 0.3779, \quad \epsilon' = 7.56 \cdot 10^{-4}, \quad (4.37)$$

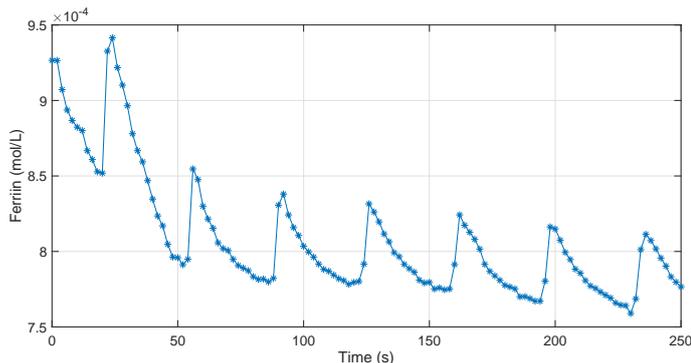


Fig. 1: Time series of concentration of ferrin related to the experiment carried out in [26] on an unstirred ferriin catalysed BZ system.

computed according to the real experimental conditions. We remark that the concentrations in (4.36) are in their dimensionless form.

In the following, we indicate the trigonometrically fitted Runge-Kutta method (3.24) as TRK and the logarithmically-trigonometrically fitted Runge-Kutta method (3.32) as LTRK. We employ the knot points of implicit trapezoidal rule and 2-stage Gauss method, which have the following expressions

$$c_t = [0, 1], \quad c_g = \left[\frac{3 - \sqrt{3}}{6}, \frac{3 + \sqrt{3}}{6} \right], \quad (4.38)$$

respectively. For both methods, the first choice ensures only second order, whereas Gauss knot points c_g lead to 4-order adapted schemes, as shown in Section 3. In the following, we adopt suffices TR- and GL- to indicate the kind of knot points used (c_t and c_g , respectively). The resulting adapted numerical methods are compared with their classic counterpart, i.e. the implicit trapezoidal rule and 2-stage Gauss-Legendre Runge-Kutta method, and also with 3-stage Gauss-Legendre, RadauIA and RadauIIA methods. The comparison is carried out in terms of CPU time, function evaluations and relative error computed in the final point with respect to a reference solution (obtained by the Matlab routine `ode15s` with an accuracy equal to 10^{-13}). Table 1 shows that the adapted schemes are always more accurate than their classic counterpart and both the presented estimates for the parameter do not increase a lot the computational cost. Moreover, the adapted schemes are in general more accurate also than 3-stage RadauIA and RadauIIA, which have algebraic order 5, and they are competitive with 3-stage Gauss-Legendre method, which has order 6. However, employing high order schemes increases the number of function evaluations, so it may be worthwhile using the presented lower-order fitted methods. Among the adapted schemes, the highest accuracy is achieved by using GL-TRK and GL-LTRK (fitted methods with Gauss' knot points), which have order 4, except for the case of GL-TRK with the theoretical estimate for

the parameter (3.34). On the other hand, the theoretical estimate seems the best choice when combined with the nodes of the implicit trapezoidal rule (in TR-TRK and TR-LTRK). Therefore, it appears clear how challenging is the problem of properly estimating the parameter. The quantitative comparison has been performed by considering a reference solution and not the time series because the model (2.3) is not perfectly suitable to describe the complex dynamics of BZ reaction. Therefore, the quantitative check is provided in order to highlight the benefits in accuracy and efficiency gained in the numerical integration of the considered model.

From a qualitative point of view, the adapted schemes follow much more accurately the prescribed oscillations of the solution than their classic counterpart, as shown in Figure 2 for methods with Gauss' knot points. Indeed, classic Gauss-Legendre method (see Figure 2(a)) provides a chaotic solution assuming also negative values (not allowed for chemical concentrations). Also in case of trigonometrically-fitted Gauss-Legendre method (GL-TRK) joined with the theoretical estimate μ_t (3.34) for the parameter (see Figure 2(c)), the numerical solution assumes some negative values but they are few and smaller in modulus than the values observed in the numerical solution computed by the classic Gauss-Legendre method (Figure 2(a)) and the periodic behaviour is more accurately reproduced. After all, also Table 1 reports this loss in accuracy for GL-TRK combined with the theoretical estimate μ_t for the parameter. Among adapted schemes, the best matching with the reference solution, depicted in Figure 3, is obtained by employing the logarithmically-trigonometrically fitted Runge-Kutta method LTRK (3.32). We remark that in these plots the concentrations of ferriin (z) and time (t) have been recast according to the positions (2.4). However, the period of the numerical solution represented in this Figure does not totally correspond to the period observed in the experimental time series. The families of Runge-Kutta methods (3.24) and (3.32) are actually constructed in order to be exact on functions belonged to the fitting spaces (3.21) and (3.30). After all, we do not know the analytical expression of the solution of system (2.3) and we infer it from the observation of the time series. For this reason, the exact solution of the considered model (2.3) may be not simply a linear combination of functions (3.21) and (3.30) and also the Oregonator could be too simple to describe the complex dynamics of the BZ system in contest. Nevertheless, this paper aims to show how the observation of time series may allow to overcome the crucial issue of estimating the parameter within exponential fitting technique without increasing the computational burden. As a future work, we aim to complicate the model to improve the matching with the time series. An initial investigation in this perspective has been carried out in [10].

Finally, we estimate the order p of the presented fitted schemes (3.24) and (3.32) employing the following relations

$$p = \lim_{k \rightarrow 0} p(k), \quad p(k) \approx \log_2 \left(\frac{E(k)}{E(k/2)} \right), \quad (4.39)$$

where $E(k)$ and $E(k/2)$ are the errors obtained with a stepsize k and $k/2$, respectively. As reported in Table 2, the estimated orders $p(k)$ of the presented adapted methods (3.24) and (3.32) are 2 or 4, according to the choice of knot points (nodes of the implicit trapezoidal rule or Gauss' ones, respectively), as expected.

Table 1: Comparison among the presented adapted schemes (3.24) and (3.32) (combined with theoretical μ_t (3.34) and experimental μ_e (3.35) estimates for the parameter and with different choices for the knot points), their classic counterpart and some higher order classic Runge-Kutta methods in terms of relative error (computed with respect to a reference solution obtained by the Matlab solver `ode15s` with a tolerance of 10^{-13}), CPU time and function evaluations (fe) within the the integration of system (2.5) with initial conditions (4.36) and parameters chosen as in (4.37). The step size is $k = 0.75$.

	p	μ	Error	CPU time (s)	fe
Trapezoidal Rule	2	—	$1.21 \cdot 10^{-1}$	17.60	2952
TR-TRK	2	μ_e	$7.79 \cdot 10^{-2}$	18.05	2958
		μ_t	$4.24 \cdot 10^{-2}$	17.94	2962
TR-LTRK	2	μ_e	$7.18 \cdot 10^{-2}$	21.31	2960
		μ_t	$5.06 \cdot 10^{-2}$	23.87	2964
2-stage Gauss-Legendre	4	—	$9.96 \cdot 10^{-1}$	16.74	2952
GL-TRK	4	μ_e	$3.79 \cdot 10^{-2}$	7.63	2958
		μ_t	$2.44 \cdot 10^{-1}$	9.98	2962
GL-LTRK	4	μ_e	$4.09 \cdot 10^{-2}$	7.74	2960
		μ_t	$3.84 \cdot 10^{-2}$	7.55	2964
3-stage RadauIA	5	—	$2.55 \cdot 10^{-1}$	11.06	4428
3-stage RadauIIA	5	—	$2.21 \cdot 10^{-1}$	14.66	4428
3-stage Gauss-Legendre	6	—	$4.11 \cdot 10^{-2}$	13.51	4428

5 Conclusions

In this treatise, we have presented adapted numerical schemes to integrate systems of ordinary differential equations modelling oscillatory chemical reactions. Since we aimed to accurately follow the prescribed oscillations of the exact solution, we have developed these methods in order to be exact (within round-off error) on trigonometric functions, following the exponential fitting strategy. Moreover, since the concentrations of the chemical elements can exhibit oscillations which decay in time, we have proposed an alternative version of trigonometrically-fitted methods, which are exact (within round-off error) on trigonometric and logarithmic functions. However, the exponential fitting usually requires a further computational effort to estimate the parameter which

Table 2: Estimated orders $p(k)$ and errors of the presented adapted schemes (3.24) and (3.32) (combined with theoretical μ_t (3.34) and experimental μ_e (3.35) estimates for the parameter and with different choices for the knot points) within the integration of system (2.5) provided with initial conditions (4.36) and parameters chosen as in (4.37).

Knot points	Fitted scheme	μ	k	Error	p(k)
Trapezoidal Rule	TRK	μ_e	0.1	$7.31 \cdot 10^{-4}$	-
			0.05	$1.83 \cdot 10^{-4}$	2.00
	LTRK	μ_t	0.1	$7.62 \cdot 10^{-4}$	-
			0.05	$1.90 \cdot 10^{-4}$	2.00
		μ_e	0.1	$6.67 \cdot 10^{-4}$	-
			0.05	$1.66 \cdot 10^{-4}$	2.00
Gauss	TRK	μ_e	0.1	$2.61 \cdot 10^{-7}$	-
			0.05	$1.51 \cdot 10^{-8}$	4.11
	LTRK	μ_t	0.1	$2.60 \cdot 10^{-7}$	-
			0.05	$1.51 \cdot 10^{-8}$	4.10
		μ_e	0.1	$2.63 \cdot 10^{-7}$	-
			0.05	$1.49 \cdot 10^{-8}$	4.14
	μ_t	0.1	$2.67 \cdot 10^{-7}$	-	
		0.05	$1.47 \cdot 10^{-8}$	4.18	

the basis functions rely on. For this reason, we have taken into account experimental time series which can be reasonably modelled by the system we aim to integrate and existing theoretical studies about the considered model. Therefore, we have estimated the parameter with the frequency of the oscillations observed in time series and the frequency approximated in [36], thus avoiding an increase of computational burden. We have applied this problem-oriented approach to adapt 2-stage Runge-Kutta methods and we have studied the corresponding order conditions. Numerical experiments exhibit the effectiveness of this approach, which can be easily applied to every system of differential equations modelling chemical oscillators and to every method used for its numerical treatment. Indeed, for a general system, the presented strategy essentially consists in merging the a-priori known information about the problem in contest (coming from existing literature and experimental data) into the numerical scheme chosen to integrate the corresponding model. Consequently, it first prescribes to a-priori analyse the considered oscillator, especially observing the time series of experimental data, when they are available. Such investigation, combined with the existing studies about the problem, can then suggest the proper adaptation that has to be carried out on the numerical scheme (for instance, a Runge-Kutta method) in order to improve accuracy

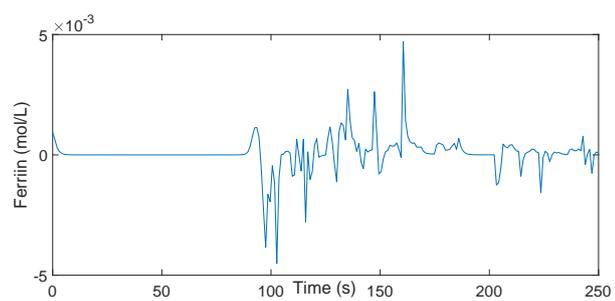
and stability. The adaptation is performed by following the exponential fitting strategy, which consists in developing formulae exact (within round-off error) on functions other than polynomials and can be applied by annihilating the linear difference operator related to the considered method on the basis functions chosen according to the a-priori knowledge about the problem. Solving the resulting system allows to obtain the coefficients of the desired adapted method. However, they depend on an unknown parameter, which can be approximated by employing existing theoretical estimates of the oscillation frequency or by extracting the frequency from the time series.

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(a) 2-stage Gauss-Legendre

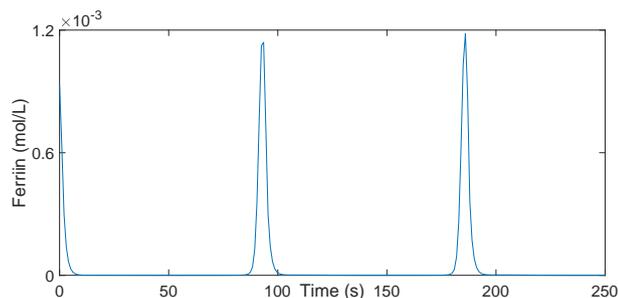
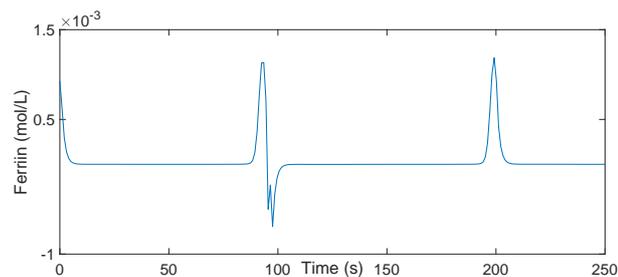
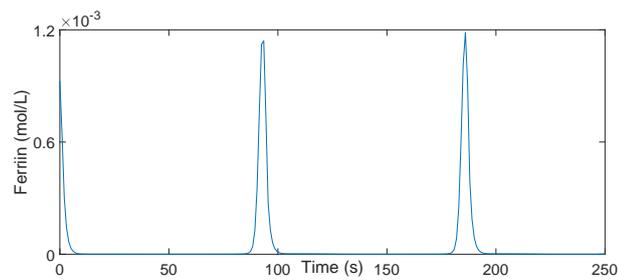
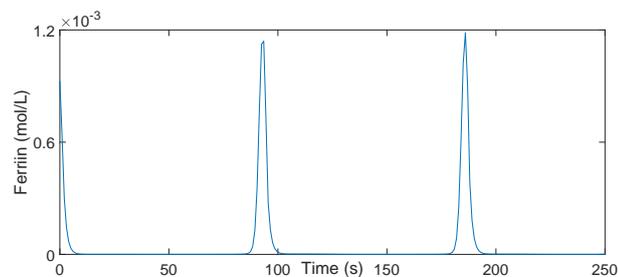
(b) GL-TRK, μ_e (c) GL-TRK, μ_t (d) GL-LTRK, μ_e (e) GL-LTRK, μ_t

Fig. 2: Numerical solution of the Oregonator (2.5), provided with initial conditions (4.36) and parameters (4.37), computed with a step size $k = 0.75$ by the classic Gauss-Legendre schemes and its corresponding adapted methods (3.24) and (3.32) combined with the experimental μ_e (3.35) and theoretical μ_t (3.34) estimates for the parameter.

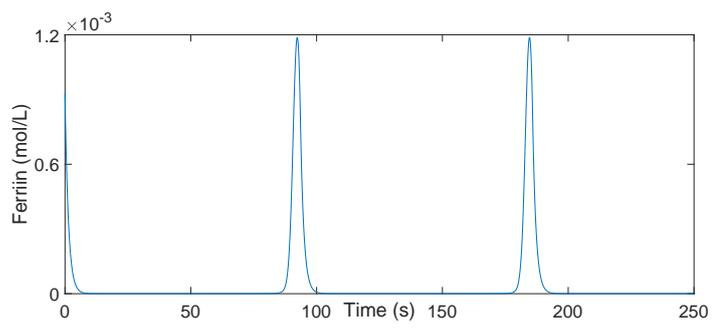


Fig. 3: Reference solution of the Oregonator (2.5) with initial conditions (4.36) and parameters (4.37) computed by the Matlab solver `ode15s` with a tolerance equal to 10^{-13} .