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MODIFIED RUNGE-KUTTA ALGORITHM FOR OSCILLATORY CHEMICAL KINETICS

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Abstract. Oscillatory dynamics frequently arise in the kinetics of chemical reactions, posing significant challenges to traditional numerical methods in capturing the dynamics. In this study, we introduce a class of modified Runge-Kutta methods specifically designed to solve such oscillatory chemical kinetics problems. Based on exponential fitting conditions for Runge-Kutta methods, we adapt several classical Runge-Kutta methods to better accommodate oscillatory behaviour. Three distinct classes of these modified methods based on some choosen parameters are proposed and presented. To evaluate their effectiveness, we conduct numerical experiments on two practical problems characterised by oscillatory chemical reactions. The results clearly demonstrate that the modified Runge-Kutta methods outperform their classical counterparts when applied to oscillatory systems.

1. Introduction

In recent decades, the mathematical modelling of chemical reactions has seen substantial progress, particularly through the use of ordinary differential equations (ODEs). These models enable the simulation, quantitative evaluation, and a deeper theoretical understanding of the dynamics of complex chemical systems. In some cases, bifurcation analysis has been employed to examine how system behaviour changes with respect to variations in control parameters, thereby enhancing the sensitivity analysis of such models. These developments have been facilitated by the advent of sophisticated mathematical software tools, which have significantly simplified both symbolic and numerical computations.

Oscillatory behaviour is a well-documented phenomenon in chemical kinetics, where the concentration of one or more chemical species fluctuates periodically over time. Several prototypical systems that exhibit such behaviour include the Bray–Liebhafsky reaction, the Belousov–Zhabotinsky reaction, Goodwin's enzymatic oscillators, and the Lotka–Volterra predator-prey model. These systems

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have long been of interest to both chemists and applied mathematicians due to their inherent nonlinearity and complex temporal dynamics.

Using stoichiometric laws and the law of mass action, chemical reaction mechanisms can be systematically converted into systems of coupled nonlinear ODEs that faithfully describe the evolution of species concentrations over time. When these models exhibit oscillatory or periodic solutions, they present additional challenges for numerical simulation. In such cases, classical numerical methods, such as the well-known Runge-Kutta family, often fail to maintain accuracy and stability over extended integration intervals. This is especially evident when the numerical solution is expected to preserve the amplitude and phase of the oscillations inherent in the system.

While many practitioners in chemistry and related sciences rely on established mathematical packages that implement standard integration techniques, these methods were not originally designed with oscillatory dynamics in mind. Consequently, they may yield results that are either inaccurate or computationally inefficient. As a result, there is a growing demand for the development of new numerical algorithms that are specifically tailored to capture the oscillatory characteristics of these systems.

One fruitful approach involves adapting numerical schemes to mimic the analytical structure of known solutions. For example, the exact solution of the simple harmonic oscillator is described in terms of sine and cosine functions. This insight motivates the incorporation of trigonometric fitting techniques into Runge-Kutta methods, leading to modified schemes capable of reproducing the qualitative and quantitative features of oscillatory systems. In this study, we extend the classical fourth-order Runge-Kutta-Gill method by constructing a trigonometrically-fitted version whose coefficients depend explicitly on the time step and an estimate of the system's oscillation frequency. Unlike conventional Runge-Kutta methods with constant coefficients, the proposed method is adaptive and dynamically aligns with the oscillatory nature of the underlying system.

The modelling of oscillatory chemical reactions dates back to the pioneering work of Bray and Liebhafsky [7]. Since then, oscillatory chemical reactions have gained significant attention, notably from Belousov [5] and Zhabotinsky [35]. Other notable examples include the Goodwin [19] enzymatic reactions, the Briggs-Rauscher reaction Briggs and Rauscher [8], and many more. Cardelli [11] explored the transformation of chemical reaction systems into ODEs, while Petrusevski et al. [28] demonstrated oscillating reactions experimentally, providing two analogies.

In the numerical analysis community, there has been significant effort to adapt classical methods for oscillatory problems. Van den Berghe et al. [33] proposed a class of exponentially-fitted Runge-Kutta methods, while Calvo et al. [10] and Simos [30] explored similar adaptations. Van de Vyver [32] developed explicit Runge-Kutta schemes for Schrödinger-type equations, and more recently, Zhang et al. [37] introduced phase-fitted splitting methods for simulating chemical oscillators. Furthermore, Ehigie et al. [15] presented exponentially-fitted diagonal implicit Runge-Kutta schemes for Hamiltonian systems, and Naseri et al. [26] implemented oscillatory simulations using spreadsheet based macros. Several researchers have made significant contributions to the development of exponentially fitted numerical methods, particularly for solving oscillatory differential equations. Lee et al. [24] introduced high-order exponentially and trigonometrically fitted explicit two-derivative Runge–Kutta-type methods tailored for third-order oscillatory problems. Similarly, Chen et al. [12] developed exponentially fitted two-derivative Runge–Kutta methods specifically for simulating oscillatory genetic regulatory systems. Ehigie et al. [16] proposed a class of exponentially fitted two-derivative diagonally implicit Runge–Kutta (DIRK) methods for general oscillatory problems, offering improved accuracy. Al-Fayyadh et al. [3] extended this approach by constructing an exponentially fitted DIRK method for the direct solution of fifth-order ordinary differential equations. Conte and Frasca-Caccia [13] presented exponentially fitted methods that also preserve conservation laws, ensuring better long-term stability. Zhai et al. [36] introduced implicit symmetric symplectic and exponentially fitted Runge–Kutta–Nyström methods for oscillatory systems, combining structural preservation with improved fitting. Senu et al. [29] proposed an improved Runge–Kutta method incorporating trigonometrically fitted techniques to address oscillatory dynamics. Ghawadri et al. [18] developed a fourth-order explicit modified Runge–Kutta-type method with exponential fitting for third-order ODEs. Amiri [4] applied drift exponentially fitted stochastic Runge–Kutta methods to Itô stochastic differential systems, extending the approach to the stochastic domain. Finally, Tiwari and Pandey [31] revised and enhanced a pseudo-Runge–Kutta method with exponential fitting, demonstrating its effectiveness in oscillatory simulations.

Despite these advancements, accurately estimating the frequency of oscillations, which is essential for frequency-dependent methods, remains a major challenge. To address this, we adopt frequency estimation strategies as proposed by Van de Vyver [32] and Vigo-Aguiar and Ramos [34]. Although several adaptations of classical Runge-Kutta methods for oscillatory problems have been developed, In this paper, we present the modified Runge-Kutta-Gill method by adapting the exponential fitting conditions of modified Runge-Kutta methods to specially handle oscillatory systems.

2. OSCILLATORY CHEMICAL REACTIONS

A system of chemical reactions is a finite set of reactions between a finite set of chemical species. It is commonly assumed that chemical reactions are well-stirred solutions such that the dynamics of chemical reactions depends only on concentrations of the species (and on other factors, such as temperature, that are assumed fixed). A system of ordinary differential equations can be extracted from any chemical system of reaction by product of the stoichiometric matrix and the vectors of rate laws, see (Horn and Jackson [22], Cardelli [11]). An N-species chemical reaction system involving M reactions can be described by the following reaction formula:

$$R_j : \qquad m_{1,j}S_1 + \ldots m_{N,j}S_N \rightarrow m'_{1,j}S_1 + \ldots + m'_{N,j}S_N, \qquad j = 1, \ldots, M \quad (2.1)$$

The dynamics of a chemical reaction systems can be modelled by a system of ordinary differential equations (called the reaction rate equations (RREs)) given by

$$\frac{d[S_i]}{dt} = \sum_{j=1}^{M} v_{ij}. \qquad i = 1, \ldots, N, \tag{2.2}$$

where $[S_i(t)]$ is the concentration of the species S_i at time t, v_{ij} represents the contribution of reaction R_j to the reaction rate of species S_i. By the law of mass action, the reaction rate v_{ij} takes the form

$$v_{ij} = r_{ij} k_j [S_i]^{m_{1,j}} \ldots [S_N]^{m_{N,j}}, \qquad i = 1, \ldots, N, \tag{2.3}$$

and k_j are the reaction rate constant which are reaction-dependent,

$$r_{ij} = \operatorname{sgn}(m'_{ij} - m_{ij}) = \begin{cases} 1 & \text{if} \quad m'ij > m_{ij} \\ 0 & \text{if} \quad m'ij = m_{ij} \\ -1 & \text{if} \quad m'ij < m_{ij} \end{cases} \tag{2.4}$$

In this paper, we study the quantitative analysis of some class of Runge-Kutta algorithms for some well known oscillatory chemical kinetics models. We shall consider models such as the Oregenator, Lotka-Volterra and the Brusselator system.

2.1. **Lotka-Volterra Model.** Consider the chemical reaction system consisting three reactions between two reactants S_1 and S_2 (Hering [21], Hairer [20], Bibik [6], Zhang et al. (2017)):

$$S_1 \to 2S_1, \quad S_1 + S_2 \to 2S_2, \quad S_2 \to \emptyset.$$

The reaction rates of the three reactions are r, k and d, respectively. Let $u(t)$ and $v(t)$ denote the concentrations of S_1 and S_2 at time t. By the mass-action law, the evolution of the reactants is governed by the following Lotka-Volterra system

$$\dot{u} = (r - kv)u, \quad \dot{v} = (ku - d)v. \tag{2.5}$$

For the parameter values $k = d = 1$, $r = 2$, the logarithmic transformation $p = \log u$, $q = \log v$ of the Lotka-Volterra system (2.5) results in a Hamiltonian problem of the form

$$\dot{p} = 1 - \mathrm{e}^q, \quad \dot{p} = \mathrm{e}^p - 2, \tag{2.6}$$

with the Hamiltonian

$$H(p, q) = \mathrm{e}^p + \mathrm{e}^q - (2p + q). \tag{2.7}$$

2.2. **Brusselator System.** The brusselator is an autocatalytic chemical reaction model that characterizes an oscillatory chemical reactiion derived by Nicholis and Prigogine [27] with chemical reaction of the form

$$A \to X$$

$$2X + Y \to 3X$$

$$B + X \to Y + D$$

$$X \to E$$

These reactions describe the interaction and transformation chemical species, leading to oscillatory dynamics under certain conditions. Using the RREs, the transformation of the reaction network into a mathematical framework for analysis, results in the following system of nonlinear differential equation:

$$\begin{aligned} \dot{y}_1 &= A + y_1^2(t)y_2 - (B+1)y_1 \quad & y_1(0) = y_1^0 \\ \dot{y}_2 &= By_1 - y_1^2 y_2 & y_2(0) = y_2^0, \end{aligned} \tag{2.8}$$

where $y_1(t)$ and $y_2(t)$ represent the concentrations of key chemical species at time t, while A and B are positive real constants associated with the system's parameters. The variation between the constants A and B significantly influences the system's stability. The equations captures the complex feedback mechanism that drives the autocatalytic nature of the reaction.

3. Modified Runge-Kutta Algorithms

Suppose the solution of the non-dimensionless form of the RREs is known to oscillate for some given parameters r_{ij}, k_{ij} with initial condition $[S_i](t_0) = [S_i](0)$, we simulate the system by discretizing the interval $[t_0, T]$ such that $t_n = t_0 + nh$, $n = 0, \dots, N-1$, where h is the stepsize.

Consider an initial value problem of the systems of ODE

$$y' = f(t, y), \quad y(t_0) = y0 \tag{3.1}$$

which represents a general form of (2.2), where $f : R \times R^N \Rightarrow R^N$ is a smooth function ensuring that the problem is well posed, that is, it satisfies the conditions of existence and uniqueness of solution. With the assumption that the system is autonomous, we define the following:

Definition 3.1 (Butcher [9])**.** The s-stage Runge-Kutta method for the numerical solution of (3.1) is given by

$$\begin{aligned} Y_i &= y_n + h\sum_{j=1}^{s} a_{ij} f(t_n + c_j h, Y_j), \qquad i = 1, \dots, s \\ y_{n+1} &= y_n + h\sum_{i=1}^{s} b_i f(t_n + c_j h, Y_j) \end{aligned} \tag{3.2}$$

Suppose the IVP (3.1) has oscillatory solution of a certain frequency ω. The idea of a modified Runge-Kutta method is to introduce coefficients depending on $z = \mathrm{i}\omega h$. Hence, we define the following:

Definition 3.2 (Ehigie et al. [15])**.** An s-stage *modified Runge-Kutta (RK) method* for solving the system (3.1) has the scheme

$$\begin{aligned} Y_i &= \eta_i(z) y_n + h\sum_{j=1}^{s} a_{ij}(z) f(t_n + c_j(z)h, Y_j), \quad i = 1, \dots, s, \\ y_{n+1} &= y_n + h\sum_{i=1}^{s} b_i(z) f(t_n + c_j(z)h, Y_i), \end{aligned} \tag{3.3}$$

where h is the stepsize, $\eta_i(z), b_i(z), a_{ij}(z), c_i(z)$, $1 \le j \le i$, $i = 1, \dots, s$ are assumed to be even functions of $z = \mathrm{i}\omega h$.

It is usually assumed that $\lim\limits_{z\to 0}\eta_i(z) = 1$ so that as $z \to 0$, the scheme (3.3) reduces to a traditional Runge-Kutta method.

The scheme (3.3) can be compactly expressed using the Butcher tableau

$$\begin{array}{c|c|c} c(z) & \eta(z) & A(z) \\ \hline & & b^T \end{array} = \begin{array}{c|c|ccc} c_1(z) & \eta_1(z) & a_{11}(z) & \dots & a_{1s}(z) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ c_s(z) & \eta_s(z) & a_{s1}(z) & \dots & a_{ss}(z) \\ \hline & & b_1(z) & \dots & b_s(z) \end{array}.$$

3.1. **Exponentially fitting conditions.** The basic idea of exponential fitting is to introduce fitting coefficients to the scheme of a traditional Runge-Kutta method so that the method can integrate without truncation error differential equations with solution of a exponential function $\exp(\lambda x)$, $\lambda \in \mathbb{C}$. Exponentially fitted (EF) algorithms have been systematically studies by Ixaru and Vanden Berghe [23]. Vanden Berghe et al. [33] presented the exponential fitting conditions for the Runge-Kutta methods and derived some practical explicit EFRK methods. We follow the approach of Albrecht [1, 2] and view each internal stage of the scheme (3.3) as a linear multistep method on a non-equidistant grid. In what follows:

- to the internal stages of (3.3), we associate the linear operators

$$\mathcal{L}_i[A(z),h]y(t) = y(t + c_i(z)h) - \eta_i(z)y(t) - h\sum_{j=1}^{s} a_{ij}(z)y'(t + c_jh), \quad i = 1, \dots, s; \tag{3.4}$$

- to the update of (3.3), we associate a linear operator

$$\mathcal{L}[b(z),h]y(t) = y(t + h) - y(t) - h\sum_{i=1}^{s} b_i(z)y'(t + c_ih). \tag{3.5}$$

Requiring that the operators $\mathcal{L}_i$ and $\mathcal{L}$ to vanish for the functions $\{\exp(\pm\lambda x)\}$ leads to the following equations:

$$\begin{aligned} &\sum_{j=1}^{s} a_{ij}(z)\sinh(c_j(z)z) = \frac{\cosh(c_i(z)z) - \eta_i(z)}{z}, \quad i = 1, \dots, s, \\ &\sum_{j=1}^{s} a_{ij}(z)\cosh(c_j(z)z) = \frac{\sinh(c_i(z)z)}{z}, \quad i = 1, \dots, s, \\ &\sum_{i=1}^{s} b_i(z)\sinh(c_i(z)z) = \frac{\cosh(z) - 1}{z}, \\ &\sum_{i=1}^{s} b_i(z)\cosh(c_i(z)z) = \frac{\sinh(z)}{z}, \end{aligned} \tag{3.6}$$

where $z = \lambda h$. Equations (3.6) are called the *exponential fitting conditions.*

Theorem 3.3. *A modified method is at least of order two.*

3.2. **Modified Explicit Runge-Kutta Methods.** Using(3.6), we present the coefficients for some 4-stage modified Runge-Kutta methods. We give the analysis for the choice of free parameters for obtaining the adapted coefficients of the modified Runge-Kutta methods in Table 1.

TABLE 1. Choice of free parameters and additional equations

RK4	$\eta_1 = \eta_4 = 1,\ a_{31} = 0,\ a_{41} = a_{42} = 0,\ b_2 = b_3,\ b_1 + b_2 + b_3 + b_4 = 1$
RK38	$\eta_1 = 1,\ a_{31} = -\frac{1}{3},\ a_{41} = a_{43},\ a_{42} = -1,\ b_2 = b_3,\ b_1 + b_2 + b_3 + b_4 = 1$
RK-Gill	$\eta_1 = \eta_4 = 1,\ a_{31} = \frac{1}{2}\left(\sqrt{2} - 1\right),\ a_{41} = 0,\ a_{42} = -\frac{\sqrt{2}}{2},\ b_2 = \frac{2-\sqrt{2}}{6},$ $b_1 = b_4,\ b_1 + b_2 + b_3 + b_4 = 1$

Remark 3.4. For $s = 4$, substitute the parameters from Table 1 into equation (3.6) and solve for the remaining coefficients. The resulting coefficients of the modified Runge-Kutta methods are given below:

Modified Classical Runge-Kutta method.

$$\begin{aligned}
\eta_2 &= 1 + \frac{z^2}{8} + \frac{z^4}{384} + \frac{z^6}{46080} + \frac{z^8}{10321920} + \mathcal{O}(z^{10}) \\
\eta_3 &= 1 - \frac{z^2}{8} + \frac{5z^4}{384} - \frac{61z^6}{46080} + \frac{277z^8}{2064384} + \mathcal{O}(z^{10}) \\
a_{21} &= \frac{1}{2} + \frac{z^2}{48} + \frac{z^4}{3840} + \frac{z^6}{645120} + \frac{z^8}{185794560} + \mathcal{O}(z^{10}) \\
a_{32} &= \frac{1}{2} - \frac{z^2}{24} + \frac{z^4}{240} - \frac{17z^6}{40320} + \frac{31z^8}{725760} + \mathcal{O}(z^{10}) \\
a_{43} &= 1 + \frac{z^2}{24} + \frac{z^4}{1920} + \frac{z^6}{322560} + \frac{z^8}{92897280} + \mathcal{O}(z^{10}) \\
b_1 = b_4 &= \frac{1}{6} - \frac{z^2}{720} + \frac{z^4}{80640} - \frac{z^6}{9676800} + \frac{z^8}{1226244096} + \mathcal{O}(z^{10}) \\
b_2 = b_3 &= \frac{1}{3} + \frac{z^2}{720} - \frac{z^4}{80640} + \frac{z^6}{9676800} - \frac{z^8}{1226244096} + \mathcal{O}(z^{10})
\end{aligned} \tag{3.7}$$

Modified Classical Runge-Kutta-$\frac{3}{8}$ method.

$$\begin{aligned}
\eta_2 &= 1+\frac{z^2}{18}+\frac{z^4}{1944}+\frac{z^6}{524880}+\frac{z^8}{264539520}+\mathcal{O}(z^{10})\\
\eta_3 &= 1-\frac{z^2}{9}+\frac{z^4}{243}-\frac{2z^6}{10935}+\frac{17z^8}{2066715}+\mathcal{O}(z^{10})\\
\eta_4 &= 1+\frac{z^2}{6}-\frac{z^4}{648}+\frac{7z^6}{58320}-\frac{461z^8}{88179840}+\mathcal{O}(z^{10})\\
a_{21} &= \frac{1}{3}+\frac{z^2}{162}+\frac{z^4}{29160}+\frac{z^6}{11022480}+\frac{z^8}{7142567040}+\mathcal{O}(z^{10})\\
a_{32} &= 1-\frac{z^2}{162}+\frac{z^4}{1080}-\frac{85z^6}{2204496}+\mathcal{O}(z^8)\\
a_{41} = a_{43} &= 1+\frac{z^4}{3240}+\frac{z^6}{204120}-\frac{z^8}{1088640}+\mathcal{O}(z^{10})\\
b_1 = b_4 &= \frac{1}{8}-\frac{z^2}{1440}+\frac{z^4}{181440}-\frac{31z^6}{587865600}+\frac{13z^8}{23279477760}+\mathcal{O}(z^{10})\\
b_2 = b_3 &= \frac{3}{8}+\frac{z^2}{1440}-\frac{z^4}{181440}+\frac{31z^6}{587865600}-\frac{13z^8}{23279477760}+\mathcal{O}(z^{10})
\end{aligned} \tag{3.8}$$

Modified Runge-Kutta-Gill method.

$$\begin{aligned}
\eta_2 &= 1+\frac{z^2}{8}+\frac{z^4}{384}+\frac{z^6}{46080}+\frac{z^8}{10321920}+\mathcal{O}(z^{10})\\
\eta_3 &= 1+\left(\tfrac{1}{2\sqrt{2}}-\tfrac{3}{8}\right)z^2+\left(\tfrac{13}{384}-\tfrac{1}{24\sqrt{2}}\right)z^4+\left(\tfrac{1}{240\sqrt{2}}-\tfrac{157}{46080}\right)z^6\\
&\quad+\left(\tfrac{1187}{3440640}-\tfrac{17}{40320\sqrt{2}}\right)z^8+\mathcal{O}(z^{10})\\
a_{21} &= \frac{1}{2}+\frac{z^2}{48}+\frac{z^4}{3840}+\frac{z^6}{645120}+\frac{z^8}{185794560}+\mathcal{O}(z^{10})\\
a_{32} &= \left(1-\tfrac{1}{\sqrt{2}}\right)+\left(\tfrac{1}{8\sqrt{2}}-\tfrac{5}{48}\right)z^2+\left(\tfrac{41}{3840}-\tfrac{5}{384\sqrt{2}}\right)z^4+\left(\tfrac{61}{46080\sqrt{2}}-\tfrac{233}{215040}\right)z^6\\
&\quad+\left(\tfrac{20401}{185794560}-\tfrac{277}{2064384\sqrt{2}}\right)z^8+\mathcal{O}(z^{10})\\
a_{43} &= \left(1+\frac{1}{\sqrt{2}}\right)+\frac{z^2}{24}+\frac{z^4}{1920}+\frac{z^6}{322560}+\frac{z^8}{92897280}+\mathcal{O}(z^{10})\\
b_1 = b+4 &= \frac{1}{6}-\frac{z^2}{720}+\frac{z^4}{80640}-\frac{z^6}{9676800}+\frac{z^8}{1226244096}+\mathcal{O}(z^{10})\\
b_3 &= \frac{1}{6}\left(2+\sqrt{2}\right)+\frac{z^2}{360}-\frac{z^4}{40320}+\frac{z^6}{4838400}-\frac{z^8}{613122048}+\mathcal{O}(z^{10})
\end{aligned} \tag{3.9}$$

Remark 3.5. We note that the coefficients (3.7) appeared in Vanden Berghe [33]. Generally the coefficients derived are subject to cancellations for small values of z, hence we present their Taylor series expansions which must be used. Furthermore, we have verified the order conditions of the methods to be of order four using the order conditions derived in Ehigie et al. [15].

4. A note on frequency estimation

Accurate frequency estimation is vital for the numerical simulation of initial value problems using modified-coefficient methods, as the coefficients depend on both the step size and the frequency ω. D'Ambrosio et al. [14] proposed a frequency-based formula for simulating Belousov–Zhabotinsky reactions using experimental data, and various researchers have addressed this issue in the context of oscillatory ODEs.

Ixaru et al. [23] introduced a frequency estimation approach based on the leading term of the local truncation error, later refined by Van de Vyver [32]. More recently, Vigo-Aguiar and Ramos [34] developed a method for determining an optimal frequency noting its dependence on the numerical method, integration interval, and step size.

Ehigie and Okunuga [17] applied this optimisation to the Fermi–Pasta–Ulam system, achieving high accuracy by minimising the Hamiltonian error via the Golden Section Search technique:

$$F(\omega) = |H(y_0, x_0) - H(y_N, x_N)|,$$

where $H(x_N, y_N)$ is the total energy function.

In this study, we adopt this frequency estimation strategy for the chemical systems introduced in Section 2.

5. Numerical Analysis

To demonstrate the effectiveness of the newly derived methods, we apply them to two practical chemical reaction kinetics problems. The new methods are referred to as follows: the Modified Classical Runge-Kutta method, Modified Classical Runge-Kutta $\frac{3}{8}$, Trigonometrically fitted Runge-Kutta Method Simos [30], Modified Runge-Kutta-Gill, denoted as EFRK4A, EFRK4B, EFRK4C and EFRK4D, respectively. For comparison, the Classical Runge-Kutta method, Classical Runge-Kutta $\frac{3}{8}$, and Runge-Kutta-Gill method are denoted as RK4A, RK4B and RK4C, respectively.

The accuracy of the methods is evaluated based on the stepsizes and their corresponding maximum global error. Additionally, the time evolution of the reacting species and their phase plots are presented.

First, we analyse the Lotka-Volterra system, described by (2.1), which exhibits oscillatory behaviour and autocatalysis–a phenomenon where the growth rate of chemical species S_1 increases with its own concentration. The system (2.1) has a unique steady state at $([S_2]^*,[S_2]^*)=(d/k, r/k)$.

The Jacobian matrix at the steady state is given by

$$J = \begin{pmatrix} r - k[S_2] & -k[S_1] \\ k[S_2] & k[S_1] - d \end{pmatrix} |_{([S_1^*],[S_2^*])} = \begin{pmatrix} 0 & -d \\ r & 0 \end{pmatrix}.$$

The eigenvalues of J are $\lambda_{1,2} = \mathrm{i} \pm \sqrt{rd}$, where ($\mathrm{i}^2 = -1$). These purely imaginary eigenvalues indicate that the steady state ($[S_1]^*$, $[S_2]^*$) is a centre, and the system's trajectories form a closed periodic orbit orbits around this steady state. Thus, for any initial value $([S_1]_0, [S_2]_0)$, the system exhibits a periodic solution.

To verify this, we simulate the system using parameter values $r = 1$, $k = 1$, $d = 1$. These parameters result in a period solution with an approximate period of $T \doteq 4.61487051945103$. The initial concentration of the species are set to $([S_1]_0, [S_2]_0) = [2, 2]$.

The simulation is performed on the time interval $[0, 500]$ using a stepsize $h = 1/2^j$, $4, 5, 6, 7$. Both the modified Runge-Kutta presented in this study and the traditional Runge-Kutta methods are employed for numerical integration. For the modified methods, the "best fitting frequency" is determined and applied.

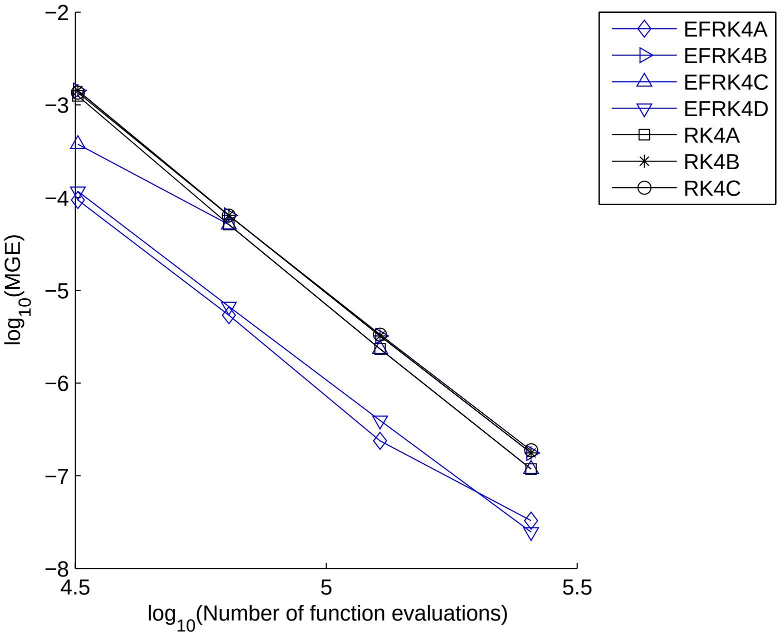

FIGURE 1. Accuracy plots of the methods

Fig. 1 displays the maximum global error for each method, plotted on a decimal logarithmic scale against the stepsize. From the figure, it is evident that the modified methods provide superior accuracy compared to their classical counterparts. Among these, the Runge-Kutta-Gill method yields the most accurate result.

Furthermore, the time evolution of the species concentrations and the phase plot diagram are presented in Fig. 2. The phase plot vividly illustrates the periodic trajectories, confirming the oscillatory nature of the Lotka-Volterra system and the enhanced accuracy achieved with the modified Runge-Kutta methods.

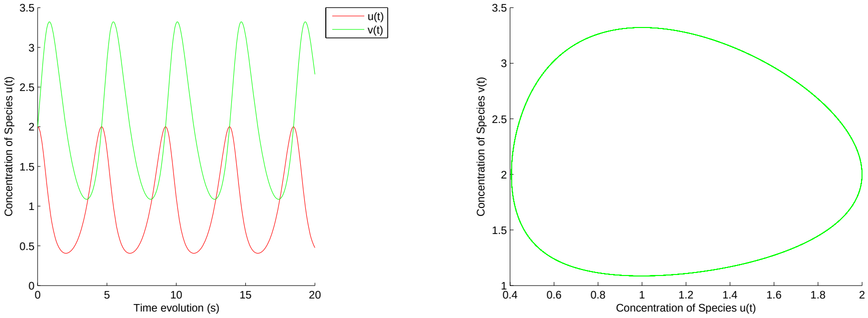

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Figure 2. Time evolution and phase plots

Finally, we simulate the Brusselator system for positive constants A and B, comparing the phase plots generated for $A = 1$ and $B = 1.7$ over the interval $[0, 100]$. The simulation are conducted using all the modified Runge-Kutta methods and their classical counterparts, with initial values $y_1^0 = 1$ and $y_2^0 = 1$ for stepsizes $h = 1/2^j$, $4, 5, 6, 7$. The maximum global error are presented in Fig. 3 to illustrate the comparative performance of the methods.

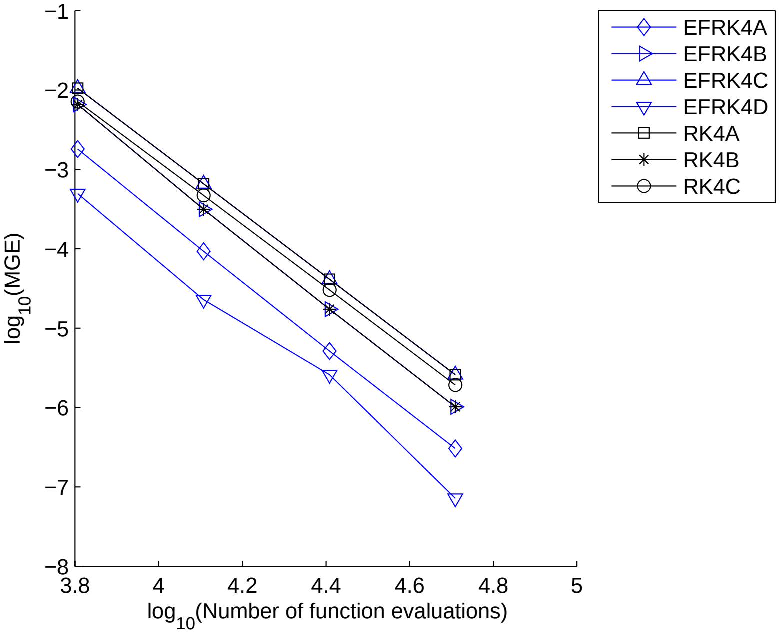

Figure 3. Accuracy plots of the methods

Nicholis and Prigogine [27], in their bifurcation analysis of the Brusselator system, established conditions that determine the system's stability. According to their findings, the system becomes unstable when $B > A^2 + 1$ and remain stable solution when $B < A^2 + 1$. To validate these propositions, simulations were performed using the modified Runge-Kutta-Gills method for both unstable and stable scenarios: $A = 1$, $B = 3$ (unstable) and $A = 1$, $B = 1.7$ (stable). The results obtained with the modified Runge-Kutta methods effectively demonstrate the system's behaviour under these conditions.

The phase plot and time evolution of the unstable solution ($A = 1$, $B = 3$) is shown in Fig. 4, revealing chaotic behaviours characterised by irregular oscillations, indicative of instability. Conversely, the phase plot for the stable solution ($A = 1$, $B = 1.7$) presented in Fig. 5 illustrates an attractor or fixed point at (A,B)=(1,1.7), demonstrating a stable interaction between the system components for the parameters. These findings confirm the theoretical propositions and highlights the accuracy of the modified Runge-Kutta-Gill methods in capturing the dynamics of the Brusselator system.

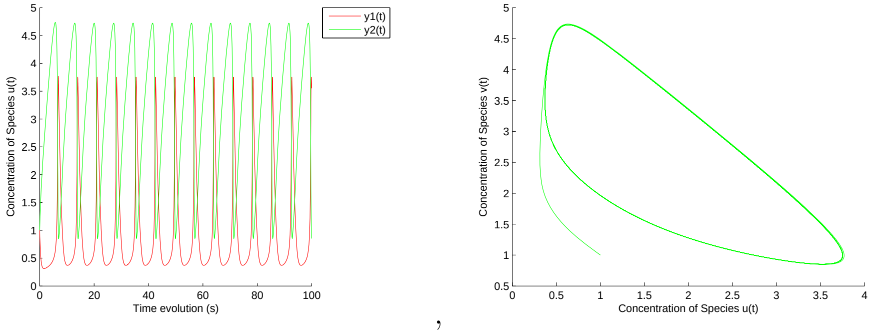

FIGURE 4. Time evolution and phase plots for the unstable parameters ($A = 1$, $B = 3$)

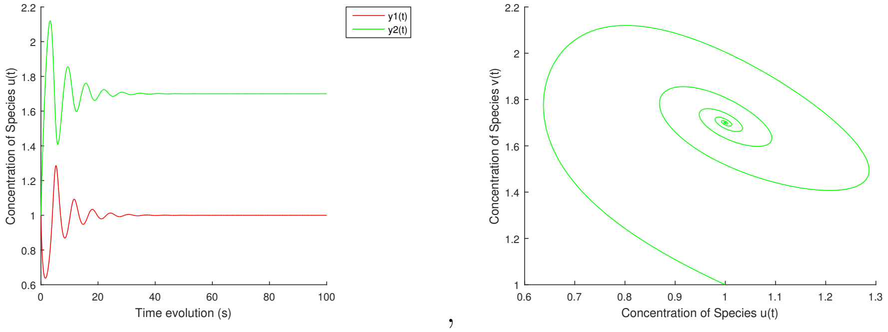

FIGURE 5. Time evolution and phase plots for the unstable parameters ($A = 1$, $B = 1.7$)

Summarily, the Runge-Kutta-Gill methods is the most accurate of all the modified Runge-Kutta methods presented in subsection 3.2.

6. CONCLUSION

This paper investigates the effective simulation of two practical oscillatory chemical reaction processes. The oscillatory properties of the systems are addressed through the development of modified exponentially fitted Runge-Kutta methods, in contrast to classical methods with constant coefficients. Two classical Runge-Kutta methods and a Runge-Kutta-Gill method of order four have been modified using the concept of exponential fitting, with the fitting conditions of these methods presented in detail.

The proposed exponentially fitted methods reduce to classical methods when $z \to 0$. A key advantage of these new methods lies in their ability to estimate the frequency of oscillation. While many researchers determine frequency using the principal frequency derived from the truncation error, this approach may not always be appropriate. Vigo-Aguiar and Ramos [34] emphasised that the choice of frequency may depend on factors such as the differential equation, initial conditions, and the integration interval. In this study, we have adopted the frequency selection approach outlined by Vigo-Aguiar and Ramos [34].

As future work, the exponential fitting conditions could be extended to diagonal implicit methods, which are well-suited for implementation within the class of implicit methods for stiff-oscillatory systems.

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