J Math Chem (2015) 53:1470–1487
DOI 10.1007/s10910-015-0500-z

ORIGINAL PAPER

Exponentially fitted TDRK pairs for the Schrödinger equation

Yanping Yang[1] · **Ke Wu**[1] · **Yonglei Fang**[1]

Received: 12 January 2015 / Accepted: 27 March 2015 / Published online: 11 April 2015

Abstract Two exponentially fitted two-derivative Runge–Kutta pairs for the numerical integration of the Schrödinger equation are presented in this paper. The asymptotic expressions of the local errors for large energies are given. The numerical results in the integration of the radial Schrödinger equation with the Woods–Saxon potential and the Lennard-Jones potential show the high efficiency of our new methods when compared with some famous optimized codes in the literature.

Keywords Two-derivative Runge–Kutta method · Schrödinger equation · Error analysis

1 Introduction

In this paper we are interested in effective integration of the one-dimensional Schrödinger equation

$$\varphi''(x) = \left(\frac{l(l+1)}{x^2} + V(x) - E\right)\varphi(x), \tag{1}$$

✉ Yonglei Fang
ylfangmath@gmail.com

Yanping Yang
ypyang0703@163.com

Ke Wu
wukehi@126.com

[1] School of Mathematics and Statistics, Zaozhuang University, Zaozhuang 277160, People's Republic of China

in which $\frac{l(l+1)}{x^2}$ is called the *centrifugal potential* and the function $V(x)$ is the *potential* satisfying $V(x) \to 0$ as $x \to \infty$. E is a real number which is called the *energy* and the function $W(x) = \frac{l(l+1)}{x^2} + V(x)$ is denoted as the *effective potential,* for which $W(x) \to 0$ if $x \to 0$. Two boundary conditions are associated with this equation: one is $\varphi(0) = 0$ and the other imposed at large x is determined by physical considerations. This type of equations often appear in scientific fields such as nuclear physics, quantum chemistry, molecular physics and so forth. There have been a large number of numerical methods for the solution of the Schrödinger equation (1) (see Refs. [1–42]), most of which belong to the class of multi-step and hybrid methods. Compared with multi-step methods whose implementation requires a series of starting values, Runge-Kutta (-Nyström)-type methods are favorable because the initial values that are available are sufficient for them to run. Recently, Chan et al. [43] investigated the two-derivative Runge–Kutta (TDRK) methods which incorporate the second-order derivative in the scheme and promise a higher efficiency. On the other hand, regarding the oscillatory character of the solution to the Schrödinger equation (1), there have appeared a lot of numerical integrators of adapted type, a pronounced class of which is based on important properties such as exponentially/trigometrically fitted or phase optimized properties (see Ref. [44–84]).

The purpose of this paper is to construct practical optimized two-derivative Runge–Kutta (TDRK) pairs for the numerical integration of the radial Schrödinger equation (1). Section 2 presents the basic elements of TDRK methods and the idea of exponential fitting methods. In Sect. 3, we construct two exponentially fitted TDRK pairs for the numerical integration of the Schrödinger equations. In Sect. 4 we analyze the asymptotic expressions errors for the new methods. Numerical results are reported in Sect. 5 to show the effectiveness and competence of our new methods when they are applied to the resonant-state problem of the Woods–Saxon potential with fixed step-size and the Lennard-Jones potential with variable step-size. Section 6 is devoted to conclusions.

2 Basic theory

2.1 Two-derivative Runge–Kutta methods

For the numerical solution of first-order differential equation

$$y'(x) = f(x, y), \quad y(x_0) = y_0, \tag{2}$$

we consider a special form of *two-derivative Runge–Kutta (TDRK)* methods studied by Chan et al. [43]

$$\begin{cases} Y_i = y_n + c_i h f(x_n, y_n) + h^2 \sum_{j=1}^{s} a_{ij} g(x_n + c_j h, Y_j), \ i = 1, \ldots, s, \\ y_{n+1} = y_n + h f(x_n, y_n) + h^2 \sum_{i=1}^{s} b_i g(x_n + c_i h, Y_i), \end{cases} \tag{3}$$

where $g(x, y) = y''(x) := \frac{\partial f(x,y)}{\partial x} + \frac{\partial f(x,y)}{\partial y} f(x, y)$.

The coefficients of the TDRK method can be expressed by the Butcher tableau

$$\begin{array}{c|c} c & A \\ \hline & b^T \end{array} = \begin{array}{c|ccc} c_1 & a_{11} & \cdots & a_{1s} \\ \vdots & \vdots & \ddots & \vdots \\ c_s & a_{s1} & \cdots & a_{ss} \\ \hline & b_1 & \cdots & b_s \end{array}$$

or can be denoted simply by (c, A, b). This special type of TDRK methods involve only one evaluation of function f and s evaluations of function g per step. The order conditions are obtained by Chan et al. [43].

It should be noted that the embedded $q(p)$ pair of TDRK method is based on the TDRK method (c, A, b) of order q and another TDRK method $(c, A, \bar{b})$ of order p $(p < q)$. An embedded pair can be characterized by Butcher tableau

$$\begin{array}{c|c} c & A \\ \hline & b^T \\ \hline & \bar{b}^T \end{array}$$

Embedded pairs of explicit TDRK methods are widely used in variable step-size algorithms for their cheap error estimations. For embedded methods, an estimate in the integration point $x_{n+1} = x_n + h$ has the following expression

$$EST_{n+1} = \|y_{n+1} - \bar{y}_{n+1}\|,$$

which can be used to control the step-size for the numerical integration of the Schrödinger equation by the well known control procedure [45]

- if $EST_{n+1} < \frac{Tol}{100}$, $h_{n+1} = 2h_n$,
- if $\frac{Tol}{100} \leq EST_{n+1} < Tol$, $h_{n+1} = h_n$,
- if $EST_{n+1} \geq Tol$, $h_{n+1} = \frac{h_n}{2}$ and repeat the step,

in which Tol is the maximum allowable local error.

In order to apply the scheme (3) to the problem (1), one has to transform the second-order ODE (1) into a form of first-order system (2) with $y = (\varphi, \psi)^T$, $\psi = \varphi'$, and

$$f(x, y) = \begin{pmatrix} \psi(x) \\ (W(x) - E)\,\varphi(x) \end{pmatrix}. \tag{4}$$

Therefore, for the scheme (3), we have

$$g(x, y) = \begin{pmatrix} (W(x) - E)\varphi(x) \\ (W(x) - E)\psi(x) + \varphi(x)W'(x) \end{pmatrix}. \tag{5}$$

2.2 Exponentially fitted TDRK methods

The method (3) is related to the operator

$$L[u](x) = u(x+h) - u(x) - hu'(x) - \sum_{i=1}^{s} b_i u''(x + c_i h, u_i),$$
$$u_i = u(x) + c_i h u'(x) + \sum_{j=1}^{i-1} a_{ij} u''(x + c_j h, u_j), \tag{6}$$

in which u is a continuously differentiable function.

Definition 2.1 [40–42] The method (6) is called exponential of order p if the related linear operator L vanishes for any linear combination of the linearly independent functions

$$\left\{\exp(\omega_0 x), \exp(\omega_1 x), \ldots, \exp(\omega_p x)\right\},$$

where $\omega_i, i = 0, \ldots, p$ are real or complex numbers.

Remark 2.1 [40–42] If $\omega_i = \omega$ for $i = 0, 1, \ldots, n, n \leq p$, then the operator L vanishes for any linear combination of

$$\{\exp(\omega x), x\exp(\omega x), x^2\exp(\omega x), \ldots, x^n \exp(\omega x), \exp(\omega_{n+1} x), \ldots, \exp(\omega_p x)\}.$$

For the construction of the new methods, we give the following theorem.

Theorem 2.1 *Method (3) is of exponential order p if*

$$\cos(v) = 1 + \sum_{k=1}^{s} (-1)^k v^{2k} b^T A^{k-1} e,$$
$$\sin(v) = v + \sum_{k=1}^{s} (-1)^k v^{2k+1} b^T A^{k-1} c, \tag{7}$$

in which $v = \omega_l h$ *for* $l = 0, 1, \ldots, p$.

Remark 2.2 If $\omega_r = \omega_q = \omega$, for $q, r \in 0, 1, \ldots, p$ then the following conditions should be added

$$-\sin(v) = \sum_{k=1}^{s} (-1)^k 2k v^{2k-1} b^T A^{k-1} e,$$
$$\cos(v) = 1 + \sum_{k=1}^{s} (-1)^k (2k+1) v^{2k} b^T A^{k-1} c. \tag{8}$$

Based on the above results, we shall construct two six-order exponentially fitted TDRK methods as well as two exponentially fitted TDRK pairs for the numerical integration of the Schrödinger equation.

3 Construction of the new methods

In this section, we consider the following embedded pair of TDRK 6(5) methods with the following tableau:

$$
\begin{array}{c|ccccc}
0 & & & & & \\
\frac{1}{3} & \frac{1}{18} & & & & \\
\frac{1}{3} & \frac{1}{8} & & & & \\
\frac{2}{3} & \frac{1}{9} & \frac{1}{9} & & & \\
\frac{4}{5} & \frac{-2}{125} & \frac{42}{125} & & & \\
\hline
 & \frac{11}{120} & \frac{9}{20} & \frac{-4}{15} & \frac{9}{40} & 0 \\
\hline
 & \frac{5}{48} & \frac{9}{28} & 0 & 0 & \frac{25}{336}
\end{array}
\tag{9}
$$

Based on this TDRK pair, we shall construct two kinds of EFTDRK pairs with exponential order one and two.

3.1 Two sixth order EFTDRK methods

In this section, we present two sixth-order EFTDRK methods based on the classical sixth-order TDRK method given in (9).

3.1.1 First six-order EFTDRK method

First we set free b_1 and b_2 while keeping the rest of the coefficients. Then we require the first method to integrate exactly the linear combination of the functions

$$\{\cos(\omega x), \sin(\omega x)\}.$$

To achieve this goal, we demand the new method to integrate exactly $\exp(i\omega x)$ for real and imaginary part. From (7) and (9), we have

$$
\begin{aligned}
\cos(v) &= 1 - v^2 b^T e + v^4 b^T A e - v^6 b^T A^2 e, \\
\sin(v) &= v - v^3 b^T c + v^5 b^T A c - v^7 b^T A^2 c.
\end{aligned}
$$

Solving these two equations, we have

$$
\begin{aligned}
b_1 &= -\left(720v - 93v^3 + 4v^5 + 360v\cos(v) + 60\sin(v)(v^2 - 18)\right) \Big/ \left(360v^3\right), \\
b_2 &= \left(-2v^3 + 120v + v^5 - 120\sin(v)\right) \Big/ \left(40v^3\right), \quad v = \omega h.
\end{aligned}
$$

For small values of $|v|$, the Taylor series of b_1 and b_2 are given by

$$b_1 = \frac{11}{120} - \frac{v^4}{1680} + \frac{v^6}{60480} - \frac{31v^8}{119750400} + \frac{v^{10}}{389188800} - \frac{23v^{12}}{130767438000} + \cdots,$$
$$b_2 = \frac{9}{20} + \frac{v^4}{160} - \frac{v^6}{120960} + \frac{v^8}{13305600} - \frac{v^{10}}{2075673600} + \frac{v^{12}}{435891456000} + \cdots.$$

It can be verified straightly that previous coefficients satisfy all the sixth order conditions given by Chan et al. [43]. We denote this method as EFTDRK6I.

3.1.2 Second six-order EFTDRK method

We require the second method to integrate exactly the linear combination of the functions

$$\{\cos(\omega x), \sin(\omega x), x\cos(\omega x), x\sin(\omega x)\}.$$

To achieve this goal, we set free b_1, b_2, b_3 and b_4 while keeping the rest of the coefficients. Then we demand the new method to integrate exactly

$$\{\exp(i\omega x), x\exp(i\omega x)\}$$

for real and imaginary part. From (7–9), we have

$$\begin{aligned}
\cos(v) &= 1 - v^2 b^T e + v^4 b^T A e - v^6 b^T A^2 e,\\
\sin(v) &= v - v^3 b^T c + v^5 b^T A c - v^7 b^T A^2 c,\\
-\sin(v) &= -2v b^T e + 4v^3 b^T A e - 6v^5 b^T A^2 e,\\
\cos(v) &= 1 - 3v^2 b^T c + 5v^4 b^T A c - 7v^6 b^T A^2 c.
\end{aligned}$$

From these four equations we obtain

$$\begin{aligned}
b_1 &= \left(2v\left(18 - 24v^2 + v^4\right) + v\left(-198 - 30v^2 + v^4\right)\cos(v)\right.\\
&\quad \left. + \left(162 + 6v^2 - 9v^4\right)\sin(v)\right) \Big/ 12v^5,\\
b_2 &= -3\left(-4v(3 + v^2) + v^2(v^2 - 42)\cos(v) - 9(v^2 - 6)\sin(v)\right) \Big/ 2v^2,\\
b_3 &= 2\left(-24v + v(v^2 - 30)\cos(v) + (54 - 7v^2)\sin(v)\right) \Big/ v^5,\\
b_4 &= 27(2v + v\cos(v) - 3\sin(v)) \Big/ 2v^5.
\end{aligned} \tag{10}$$

For small values of $|v|$, their Taylor series are given by

$$b_1 = \frac{11}{120} + \frac{\nu^2}{280} + \frac{\nu^4}{4480} - \frac{233\nu^6}{9979200} + \frac{191\nu^8}{296524800} - \frac{1813\nu^{10}}{19813248000}, \cdots,$$
$$b_2 = \frac{9}{20} - \frac{3\nu^4}{140} + \frac{\nu^4}{1344} - \frac{17\nu^6}{1108800} + \frac{67\nu^8}{345945600} - \frac{59\nu^{10}}{36324288000} + \cdots,$$
$$b_3 = -\frac{4}{15} + \frac{\nu^2}{35} - \frac{\nu^4}{840} + \frac{31\nu^6}{1247400} - \frac{\nu^8}{3243240} + \frac{23\nu^{10}}{9081072000} + \cdots,$$
$$b_4 = \frac{9}{40} - \frac{3\nu^2}{280} + \frac{\nu^4}{4480} - \frac{\nu^6}{369600} + \frac{\nu^8}{46126080} - \frac{\nu^{10}}{8072064000} + \cdots.$$

It can be checked straightly that previous coefficients satisfy all the sixth order conditions given by Chan et al. [43]. We denote this method as EFTDRK6II.

3.2 Two EFTDRK 6(5) pairs

3.2.1 The first EFTDRK 6(5) pair

Based on the sixth order exponentially fitted TDRK method EFTDRK6I, in this section, we shall give the first EFTDRK 6(5) method. we require the lower order method to integrate exactly the linear combination of the functions

$$\{\cos(\omega x), \sin(\omega x)\},$$

and we obtain

$$b_1^* = \frac{-1440\nu + 195\nu^3 - 8\nu^5 - 720\nu\cos(\nu) + 2160\sin(\nu) - 120\nu^2\sin(\nu)}{720\nu^3},$$
$$b_2^* = \frac{840\nu + 50\nu^3 + 7\nu^5 - 840\sin(\nu)}{280\nu^3}.$$

For small values of $|\nu|$, their Taylor series are given by

$$b_1^* = \frac{5}{48} - \frac{\nu^4}{1680} + \frac{\nu^6}{60480} - \frac{31\nu^8}{119750400} + \frac{\nu^{10}}{389188800} - \frac{23\nu^{12}}{130767438000}, \cdots,$$
$$b_2^* = \frac{9}{28} + \frac{\nu^4}{160} - \frac{\nu^6}{120960} + \frac{\nu^8}{13305600} - \frac{\nu^{10}}{2075673600} + \frac{\nu^{12}}{435891456000} + \cdots.$$

It can be verified straightly that the coefficients satisfy all the fifth order conditions given by Chan et al. [43]. We denote this new EFTDRK pair as EFTDRK6(5)I.

3.2.2 The second EFTDRK 6(5) pair

In this section, we shall present the first EFTDRK 6(5) method based on the sixth order EFTDRK method EFTDRK6II. we require the lower order method to integrate exactly the linear combination of the functions

$$\{\cos(\omega x), \sin(\omega x), x\cos(\omega x), x\sin(\omega x)\}.$$

We set free b_1, b_2, b_3 and b_4 while keeping the rest of the coefficients. Then we demand the new method to integrate exactly $\{\exp(i\omega x), x\exp(i\omega x)\}$ for real and imaginary part. From these four equations we obtain

$$\begin{aligned}
b_1^* &= \left(\nu\left(720 - 960\nu^2 + 43\nu^4\right) + 20\nu\left(\nu^4 - 30\nu^2 - 198\right)\cos(\nu)\right.\\
&\quad \left. -60\left(3\nu^4 - 2\nu^2 - 54\right)\sin(\nu)\right)\Big/240\nu^5,\\
b_2^* &= \left(1260\nu + 420\nu^3 - 9\nu^5 - 105(\nu^2-42)\cos(\nu) + 945\left(\nu^2-6\right)\sin(\nu)\right)\Big/240\nu^5,\\
b_3^* &= \left(4\nu\left(\nu^4 - 180\right) + 30\nu\left(\nu^2 - 30\right)\cos(\nu) - 30\left(7\nu^2 - 54\right)\sin(\nu)\right)\Big/15\nu^2,\\
b_4^* &= -9\left(-120\nu + \nu^5 - 60\nu\cos(\nu) + 180\sin(\nu)\right)\Big/(40\nu^5).
\end{aligned}$$

For small values of $|\nu|$, their Taylor series are given by

$$\begin{aligned}
b_1^* &= \frac{5}{48} + \frac{\nu^2}{280} + \frac{\nu^4}{4480} - \frac{233\nu^6}{9979200} + \frac{191\nu^8}{296524800} + \frac{28837\nu^{10}}{355687428096000} + \cdots,\\
b_2^* &= \frac{9}{28} - \frac{3\nu^2}{140} + \frac{\nu^4}{1344} - \frac{17\nu^6}{1108800} + \frac{67\nu^8}{345945600} - \frac{59\nu^{10}}{36324288000} + \cdots,\\
b_3^* &= 0 + \frac{\nu^2}{35} - \frac{\nu^4}{840} + \frac{31\nu^6}{1247400} - \frac{\nu^8}{3243240} + \frac{23\nu^{10}}{9081072000} + \cdots,\\
b_4^* &= 0 - \frac{3\nu^2}{280} + \frac{\nu^4}{4480} - \frac{\nu^6}{369600} + \frac{\nu^8}{46126060} - \frac{\nu^{10}}{8072064000} + \cdots.
\end{aligned}$$

It can be verified straightly that the coefficients satisfy all the fifth order conditions given by Chan et al. [43]. We denote this new pair as EFTDRK6(5)II.

4 Error analysis

In this section, we carry out the error analysis of the new methods derived in Sect. 3 based on the approach of Anastassi and Simos [41,42]. It is not necessary to investigate the error of the fifth order method since it is not responsible for the propagation of the error. We only consider the error analysis of the sixth order methods. Our interest lies mainly in solving the Schrödinger equation. So we will follow the approach of Ixaru and Rizea [39] which was put forward for exponentially fitted Numerov method to find the asymptotic expressions for large energy solving Schrödinger equation. The numerical performance of the method is crucially influenced by the fitted frequency ν. We make a reasonable choice of "local" estimate of frequency in the following way: Divide $[0, \infty]$ into some subinterval $[x_i, x_{i+1}]$, so that the $W(x)$ is considered to be a constant which is approximated by $\bar{W}$. Then the problem (1) reduces to the approximation $\varphi_i'' = (\bar{W} - E)\varphi_i$ whose general solution is given by

$$\varphi_i(x) = C_1 \exp\left(\mathrm{i}\sqrt{E-\bar{W}}x\right) + C_2 \exp\left(-\mathrm{i}\sqrt{E-\bar{W}}x\right), \quad C_1, C_2 \in C.$$

Hence, a proper fitting frequency ω in each interval $[x_i, x_{i+1}]$ is chosen as $\omega = \sqrt{E-\bar{W}}$. The error vectors (one component for $\varphi(x)$ and the other for $\psi(x)$) for the classical TDRK methods and the two new methods EFTDRK6I and EFTDRK6II have the following expressions for large values of $|E|$:

$$\begin{aligned}
\text{LTE(CLASSICAL)} &\approx \frac{h^7}{5040}\begin{pmatrix} -\psi(x)E^3 \\ \varphi(x)E^4 \end{pmatrix}, \\
\text{LTE(EFTDRK6I)} &\approx \frac{h^7}{5040}\begin{pmatrix} \big(-8\varphi(x)W'(x) + 2\psi(x)\Delta W\big)E^2 \\ -2\varphi(x)\Delta W E^3 \end{pmatrix}, \\
\text{LTE(EFTDRK6II)} &\approx \frac{h^7}{5040}\begin{pmatrix} 2\varphi(x)W'(x)E^2 \\ \big(9\varphi(x)W''(x) + 2W'(x)\psi(x) + \Delta W^2\varphi(x)\big)E^2 \end{pmatrix}.
\end{aligned}$$

where $\Delta W = W(x) - \bar{W}$.

For the purpose of error comparison, we observe that the global error on φ and ψ produced by the classical TDRK method is in proportional with E^3 and E^4, respectively. The global error on φ and ψ produced by the EFTDRK6I method is increased with E^2 and E^3, respectively. While the increase of the global error on φ and ψ produced by the EFTDRK6II method is in proportion with E^2 and E^2, respectively. We can conclude that the method EFTDRK6II is the most efficient method for the Schrödinger equation with large $|E|$ since the increase of the global error is the smallest.

5 Numerical experiments

5.1 Comparisons with fixed step-size

For comparison we select the following Runge-Kutta type methods:

- EFTDRK6I: the first higher order exponentially fitted two-derivative RK method of the new pairs derived in Sect. 3.1.1.
- EFTDRK6II: the second higher order exponentially fitted two-derivative RK method of the new pairs derived in Sect. 3.1.2.
- PHRK5S: the higher order method of the phase-fitted RK pair of Simos [4].
- MPHRK5V: the higher order method of the phase-fitted RK pair of Van de Vyver [34].
- MORK5V: the higher order method of the optimized RK pair of Van de Vyver [37].
- RK5EXP2MCM: the exponentially fitted fifth order RK method with exponential order two derived by Simos [41].
- RK5EXP2JMC: the exponentially fitted fifth order RK method with exponential order two derived by Simos [42].

We consider the numerical integration of the Schrödinger equation (1) with the well-known Woods–Saxon potential

$$V(x) = c_0 z\big(1 - a(1 - z)\big),$$

where $z = \Big(\exp\big(a(x-b)+1\big)\Big)^{-1}$, $c_0 = -50$, $a = 5/3$, $b = 7$. We put $l = 0$ in (1). The problem is solved in the interval [0,15].

The so-called resonance problem is to find those energies $E \in [0, 1000]$ for which the phase shift is equal to $\pi/2$. The boundary conditions for this problem are given by

$$y(0) = 0 \quad \text{and} \quad y(x) = \cos\left(\sqrt{E}x\right) \quad \text{for large } x.$$

In order to determine the eigenvalues E we use the shooting strategy which involves an iteration process. In short, this strategy consists of integrating forwards from the point $x = 0$, backwards from the point $x = x_{\text{end}}$ and then matching up the solution at some intermediate point $x = x_c$. Here the matching point is taken as $x_c = 6.5$. Following Van de Vyver [34] and Ixaru et al. [39], we choose the fitting frequency as

$$\omega = \begin{cases} \sqrt{50+E}, & x \in [0, 6.5], \\ \sqrt{E}, & x \in [6.5, 15]. \end{cases}$$

For technical details, the reader is referred to Blatt [5].

The numerical results obtained by the RK-type methods are compared with the analytic solution of the Woods–Saxon potential. In Figs. 1, 2, 3 and 4, we plot the error $\log_{10}|E_{\text{analytical}} - E_{\text{calculated}}|$ versus the computational effort by the number of function evaluations (FUNCTION EVALUATIONS) and the cpu times (CPU SECONDS) required by each method for $E_{\text{analytical}} = 53.588872, 163.215341, 341.495874, 989.701916$, respectively.

In view of the Figs. 1, 2, 3 and 4, we observe that EFTDRK6II is superior to all the other methods, especially for larger energy E.

5.2 Comparison with some embedded pairs

In this experiment we compare the following five embedded Runge–Kutta-type pairs:

- PHARK5(4)S: the phase-fitted embedded RK 5(4) pair derived by Simos in [4].
- MODPHARK5(4)V: the modified phase-fitted embedded RK 5(4) pair given by Van de Vyver in [34].
- MORK5(4)V: the optimized embedded RK 5(4) pair derived by Van de Vyver in [37].
- EFTDRK6(5)I: the new pair derived in Sect. 3.2.1.
- EFTDRK6(5)II: the new pair derived in Sect. 3.2.2.

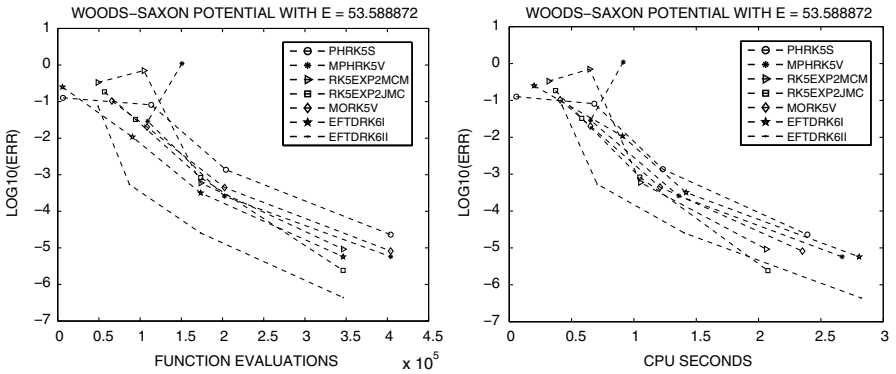

Fig. 1 Efficiency curves for $E = 53.588872$

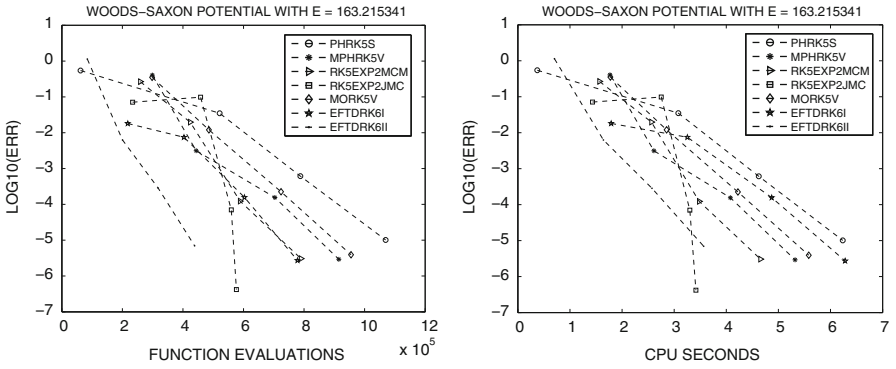

Fig. 2 Efficiency curves for $E = 163.215341$

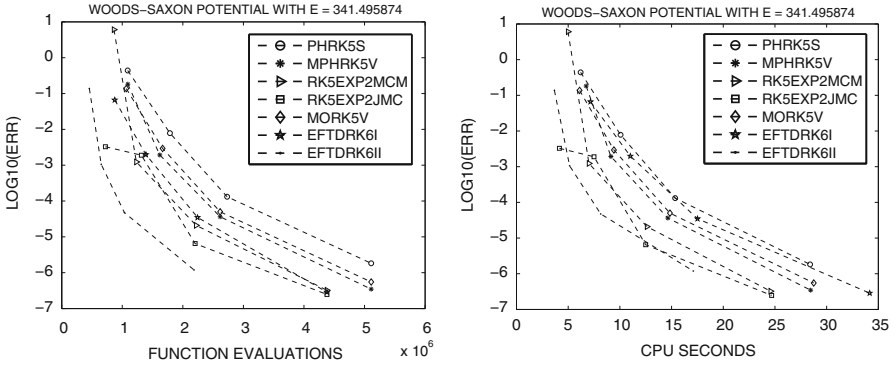

Fig. 3 Efficiency curves for $E = 341.495874$

Here we consider the numerical integration of the Schrödinger equation (1) with the Lennard-Jones potential of wide interest (see [34])

$$v(x) = \frac{l(l+1)}{x^2} + 500\left(\frac{1}{x^{12}} - \frac{1}{x^6}\right).$$

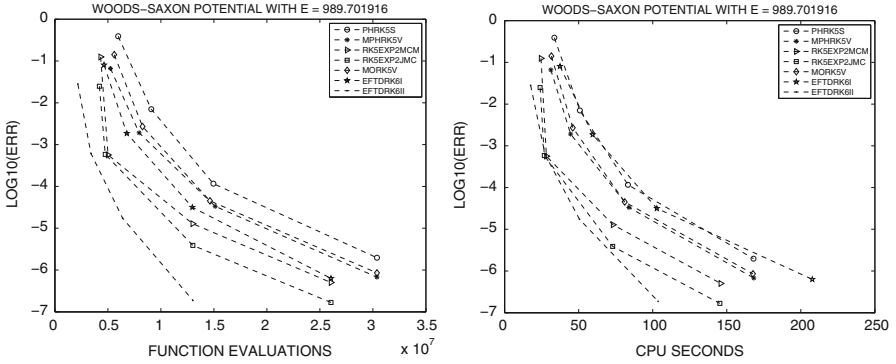

Fig. 4 Efficiency curves for $E = 989.701916$

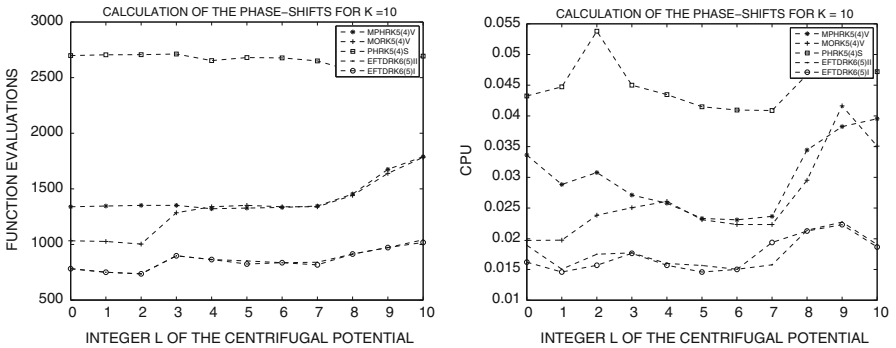

Fig. 5 Efficiency curves for $k = 10$

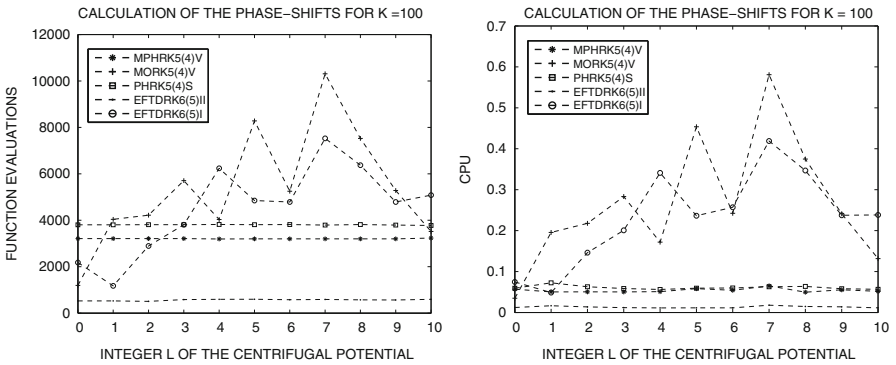

Fig. 6 Efficiency curves for $k = 100$

We compute the phase-shifts correct to four decimal places for the energies $k^2 = 100$ and $k^2 = 10000$, respectively. The fitting frequency is taken as $\omega = k$. For the calculation of the phase-shifts, we plot the number of function evaluations and the cpu times as a function of $l = 0, \ldots, 10$ in Fig. 5 ($k^2 = 100$) and in Fig. 6 ($k^2 = 10000$).

Form Figs. 5 and 6, we conclude that our new EFTDRK pair EFTDRK6(5)II is the most efficient.

5.3 The choice of frequency for oscillatory problems

In this section, we address the question of evaluating the fitting frequency for trigonometrically/exponentially fitted integrators solving oscillatory problems. Generally speaking, if the principal frequency or an estimate of the principal frequency of the problem is available, it is reasonable to take it as the fitting frequency. However, in most cases, the principal frequency is not easy to obtain or estimate and the topic of how to choose the most suitable fitting frequency for the trigonometrically fitted methods has been a challenge.Some interesting strategies can be found in the recent literature [75–77].

Here we try to propose a new method-dependent approach. The fitting frequency is calculated by vanishing the leading term of the local error of the method. To be specific, take the method EFTDRK6I derived in Sect. 3.1.1 for an example (the method EFTDRK6II can be considered in a similar way). The local truncation errors of the method EFTDRK6I is

$$\text{LTE(EFTDRK6I)} = \frac{y^{(7)}(x) - \omega^4 y^{(3)}(x)}{5040} h^7 + \mathcal{O}(h^8). \tag{11}$$

Therefore, at every step a suitable choice for ω can be chosen as

$$\omega_n^4 = \frac{y^{(7)}(x_n)}{y^{(3)}(x_n)}. \tag{12}$$

Problem 5.1 We consider the inhomogeneous problem in [75]

$$y'' + y = \epsilon y^3, \qquad y(0) = 1, \quad y'(0) = 0, \tag{13}$$

to be solved in the interval $[0, 20\pi]$. When ϵ is very small, the solution of the problem (13) is close to that of the problem

$$y'' + y = 0, \qquad y(0) = 1, \quad y'(0) = 0, \tag{14}$$

Therefore the principal frequency of the problem (13) is (approximately) $\omega = 1$. Usually this frequency $\omega = 1$ is taken as a fitting frequency. In Fig. 7, we show the growth of the error $y(x_n) - y_n$ produced by the method EFTDRK6I solving the problem (13) for $\epsilon = 10^{-3}$ with $\omega = 1$ (on the left) and ω_n determined by (12) (on the right), respectively, with the step-size $h = 0.01$. We can see that the method EFTDRK6I gives almost the same global error for both the two versions of fitting frequency. However, the following example shows the advantages of our new policy.

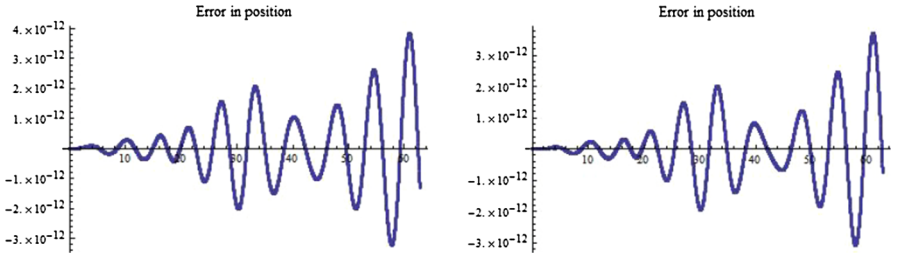

Fig. 7 Errors shown using the frequency $\omega = 1$ (*left*) and ω obtained by (12) (*right*)

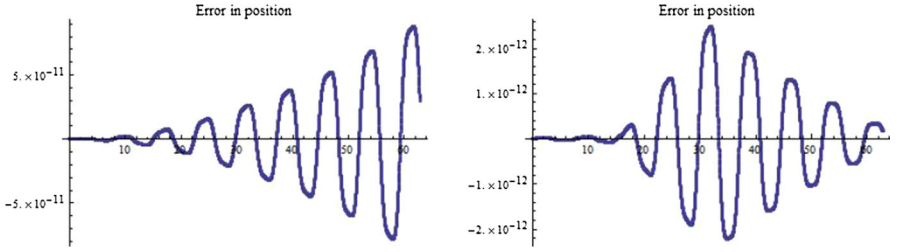

Fig. 8 Errors shown using the frequency $\omega = 0.847213085$ (*left*) and ω obtained by (12) (*right*)

Problem 5.2 Consider the nonlinear cubic oscillators given in [76]

$$y'' = -y^3, \qquad y(0) = 1, \quad y'(0) = 0, \tag{15}$$

with exact solution $y(x) = \mathrm{cn}(x, 1/2)$, in which cn is the Jacobi elliptic function and the exact frequency of the solution is

$$\omega = \frac{1}{4}K(1/2) = 0.847213085$$

where K is the complete elliptical integral of the first kind. In Fig. 7, we plot the error of $y(x_n) - y_n$ in the interval $[0, 20\pi]$ obtained by the EFTDRK6I method for problem (15) with $\omega = 0.847213085$ (on the left) and ω chosen by (12) (on the right) with the step-size $h = 0.01$.

From Fig. 8, we observe that the method EFTDRK6I is more accurate with the fitting frequency determined by (12) than with the usual choice of the frequency $\omega = 0.847213085$.

Another adopted strategy can be based on the optimization of the error of the total energy by the golden section search technique.

6 Conclusions

In this paper, two exponentially fitted two-derivative Runge–Kutta (EFTDRK) methods as well as EFTDRK paris for the numerical integration of the Schrödinger equation

are presented in this paper. The asymptotic expressions of the local errors for large energies are obtained. We have compared our new methods with some optimized (exponentially fitted or phase-fitted) RK methods for the numerical solution of the Schrödinger equation. The analysis of the asymptotic expressions of the local errors for large energies suggest theoretical advantages of the newly constructed TDRK methods. And when applied to the radial time-independent Schrödinger equation with the Woods–Saxon potential and the Lennard-Jones potential, they are shown to outperform some highly effective codes in the literature, especially in the case of higher resonance. The special structure involving the second-order derivative and the optimized exponential fitting property are responsible to the excellent behavior of the new methods. Finally, we discuss the choice of the frequency for the method EFTDRK6I solving oscillatory problems. A reasonable frequency is obtained by vanishing the local truncation error. Another possible way of determining the fitting frequency is by minimizing the error of the total energy. We will continue this research in the future.

Acknowledgments The authors are deeply grateful to the anonymous referees, for their valuable comments and suggestions. This research is partially supported by NSFC (No. 11101357) and the foundation of Scientific Research Project of Shandong Universities (No. J14LI04).

References

1. J. Vigo-Aguiar, T.E. Simos, Family of twelve steps exponentially fitting symmetric multistep methods for the numerical solution of the Schrödinger equation. J. Math. Chem. **32**(3), 257–270 (2002)
2. J. Vigo-Aguiar, T.E. Simos, Review of multistep methods for the numerical solution of the radial Schrödinger equation. Int. J. Quantum Chem. **103**(3), 278–290 (2005)
3. T.E. Simos, J. Vigo Aguiar, A modified Runge–Kutta method with phase-lag of order infinity for the numerical solution of the Schrödinger equation and related problems. Comput. Chem. **25**(3), 275–281 (2001)
4. T.E. Simos, An embedded Runge–Kutta method with phase-lag of order infinity for the numerical solution of the Schrödinger equation. Int. J. Mod. Phys. C **11**(6), 1115–1133 (2000)
5. J.M. Blatt, Practical points concerning the solution of the Schrödinger equation. J. Comput. Phys. **1**, 378–391 (1967)
6. Z.A. Anastassi, D.S. Vlachos, T.E. Simos, A family of Runge–Kutta methods with zero phase-lag and derivatives for the numerical solution of the Schrödinger equation and related problems. J. Math. Chem. **46**(4), 1158–1171 (2009)
7. G. Avdelas, T.E. Simos, J. Vigo-Aguiar, An embedded exponentially-fitted Runge–Kutta method for the numerical solution of the Schrödinger equation and related periodic initial-value problems. Comput. Phys. Commun. **131**(1–2), 52–67 (2000)
8. T.E. Simos, J. Vigo-Aguiar, Exponentially fitted symplectic integrator. Phys. Rev. E. **67**(1), 016701 (2003)
9. J. Vigo-Aguiar, S. Natesan, A parallel boundary value technique for singularly perturbed two-point boundary value problems. J. Supercomput. **27**(2), 195–206 (2004)
10. J. Vigo-Aguiar, H. Ramos, Dissipative Chebyshev exponential-fitted methods for numerical solution of second-order differential equations. J. Comput. Appl. Math. **158**(1), 187–211 (2003)
11. T.E. Simos, J. Vigo-Aguiar, On the construction of efficient methods for second order IVPS with oscillating solution. Int. J. Mod. Phys. C **12**(10), 1453–1476 (2001)
12. J. Vigo-Aguiar, J. Martin-Vaquero, R. Criado, On the stability of exponential fitting BDF algorithms. J. Comput. Appl. Math. **175**(1), 183–194 (2005)
13. J. Vigo-Aguiar, T.E. Simos, J.M. Ferrandiz, Controlling the error growth in long-term numerical integration of perturbed oscillations in one or several frequencies. Proc. R. Soc. Lond. Seri. A Math. Phys. Eng. Sci. **460**(2042), 561–567 (2004)

14. J. Vigo-Aguiar, J.C. Reboredo, H. Ramos, Topics of contemporary computational mathematics. Int. J. Comput. Math. **89**(8), 265–267 (2012)
15. J. Vigo-Aguiar, J.A. López-Ramos, Applications of computational mathematics in science and engineering. Int. J. Comput. Math. **88**(9), 1805–1807 (2011)
16. J. Vigo-Aguiar, G.V. Berghe, Advances in computational and mathematical methods in science and engineering. J. Comput. Appl. Math. **235**(7), 17–45 (2011)
17. J. Vigo-Aguiar, H. Ramos, A numerical ODE solver that preserves the fixed points and their stability. J. Comput. Appl. Math. **235**(7), 1856–1867 (2011)
18. J. Ranilla, E.S. Quintana-Ori, J. Vigo-Aguiar, High performance computing tools in science and engineering. J. Supercomput. **58**(2), 143–144 (2011)
19. F.G. Alonso, J. Reyes, J.M. Ferrándiz, J. Vigo-Aguiar, Multistep numerical methods for the integration of oscillatory problems in several frequencies. Adv. Eng. Softw **40**(8), 543–553 (2009)
20. J.M. Vaquero, J. Vigo-Aguiar, Exponential fitted Gauss, Radau and Lobatto methods of low order. Numer. Algorithm **48**(4), 327–346 (2008)
21. J.A. Reyes, F.G. Alonso, J.M. Ferrándiz, J. Vigo-Aguiar, Numeric multistep variable methods for perturbed linear system integration. Appl. Math. Comput. **190**(1), 63–79 (2007)
22. J. Vigo-Aguiar, J.M. Vaquero, Exponential fitting BDF algorithms and their properties. Appl. Math. Comput. **190**(1), 80–110 (2007)
23. J.M. Vaquero, J. Vigo-Aguiar, Adapted BDF algorithms: higher-order methods and their stability. J. Sci. Comput. **32**(2), 287–313 (2007)
24. G. Avdelas, A. Konguetsof, T.E. Simos, A generator and an optimized generator of highorder hybrid explicit methods for the numerical solution of the Schrödinger equation. Part 2: Development of the generator, optimized generator and numerical results. J. Math. Chem. **29**(4), 305–393 (2001)
25. G. Avdelas, E. Kefalidis, T.E. Simos, New P-stable eighth algebraic order exponentiallyfitted methods for the numerical integration of the Schrödinger equation. J. Math. Chem. **31**(4), 371–404 (2002)
26. Z. Kalogiratou, T.E. Simos, Construction of trigonometrically and exponentially fitted Runge–Kutta–Nyström methods for the numerical solution of the Schrödinger equation and related problems. J. Math. Chem. **31**(2), 211–232 (2002)
27. A. Konguetsof, A new two-step hybrid method for the numerical solution of the Schrödinger equation. J. Math. Chem. **47**(2), 871–890 (2010)
28. Th Monovasilis, Z. Kalogiratou, Th Monovasilis, T.E. Simos, Trigonometrically fitted and exponentially fitted symplectic methods for the numerical integration of the Schrödinger equation. J. Math. Chem. **40**(3), 257–267 (2006)
29. G. Psihoyios, T.E. Simos, Sixth algebraic order trigonometrically fitted predictor-corrector methods for the numerical solution of the radial Schrödinger equation. J. Math. Chem. **37**(3), 295–316 (2005)
30. D.P. Sakas, T.E. Simos, A family of multiderivative methods for the numerical solution of the Schrödinger equation. J. Math. Chem. **37**(3), 317–331 (2005)
31. T.E. Simos, Stabilization of a four-step exponentially fitted method and its application to the Schrödinger equation. Int. J. Mod. Phys. C **18**(3), 315–328 (2007)
32. T. Monovasilis, T.E. Simos, Symplectic methods for the numerical integration of the Schrödinger equation. Comput. Mater. Sci. **38**(3), 526–532 (2007)
33. K. Tselios, T.E. Simos, Symplectic methods for the numerical solution of the radial Shrödinger equation. J. Math. Chem. **34**(1–2), 83–94 (2003)
34. H. Van de Vyver, An embedded phase-fitted modified Runge–Kutta method for the numerical integration of the radial Schrödinger equation. Phys. Lett. A **352**, 278–285 (2006)
35. H. Van de Vyver, Comparison of some special optimized fourth-order Runge–Kutta methods for the numerical solution of the Schrödinger equation. Comput. Phys. Commun. **166**(2), 109–122 (2005)
36. H. Van de Vyver, Modified explicit Runge–Kutta methods for the numerical solution of the Schrödinger equation. Comput. Phys. Commun. **171**(2), 1025–1036 (2005)
37. H. Van de Vyver, An embedded 5(4) pair of modified explicit Runge–Kutta methods for the numerical solution of the Schrödinger equation. Int. J. Mod. Phys. C **16**(6), 879–894 (2005)
38. S.W. Liu, J. Zheng, Y.L. Fang, A new modified embedded 5(4) pair of explicit Runge–Kutta methods for the numerical solution of the Schr*d*inger equation. J. Math. Chem. **51**(3), 937–953 (2013)
39. LGr Ixaru, M. Rizea, A Numerov-like scheme for the numerical solution of the Schrödinger equation in the deep continuum spectrum of energies. Comput. Phys. Commun. **19**(1), 23–27 (1980)
40. T.E. Simos, An exponentially-fitted Runge–Kutta method for the numerical integration of initial-value problems with periodic or oscillating solutions. Comput. Phys. Commun. **115**(1), 1–8 (1998)

41. Z.A. Anastassi, T.E. Simos, Trigonometrically fitted fifth-order Runge–Kutta methods for the numerical solution of the Schrödinger equation. Math. Comput. Model. **42**, 877–886 (2005)
42. Z. Anastassi, T.E. Simos, Trigonometrically fitted Runge–Kutta methods for the numerical solution of the Schrödinger equation. J. Math. Chem. **37**(3), 281–293 (2005)
43. R.P.K. Chan, A.Y.J. Tasi, On explicit two-derivative Runge–Kutta methods. Numer. Algorithm **53**(2–3), 171–194 (2010)
44. L.G. Ixaru, G. Vanden Berghe (eds.), *Exponential fitting* (Kluwer Academic Publishers, Dordrecht, 2004)
45. A.D. Raptis, J.R. Cash, A variable step method for the numerical integration of the one-dimensional Schrödinger equation. Comput. Phys. Commun. **36**(2), 113–119 (1985)
46. D.F. Papadopoulos, T.E. Simos, The use of phase lag and amplification error derivatives for the construction of a modified Runge–Kutta–Nystrom method. Abstr. Appl. Anal. **2013**, Article ID 910624, 11 (2013). doi:10.1155/2013/910624
47. Z.A. Anastassi, T.E. Simos, A parametric symmetric linear four-step method for the efficient integration of the Schrödinger equation and related oscillatory problems. J. Comput. Appl. Math. **236**(16), 3880–3889 (2012)
48. I. Alolyan, Z.A. Anastassi, T.E. Simos, A new family of symmetric linear four-step methods for the efficient integration of the Schrödinger equation and related oscillatory problems. Appl. Math. Comput. **218**(9), 5370–5382 (2012)
49. I. Alolyan, T.E. Simos, A family of high-order multistep methods with vanished phase-lag and its derivatives for the numerical solution of the Schrödinger equation. Comput. Math. Appl. **62**(10), 3756–3774 (2011)
50. Ch. Tsitouras, ITh Famelis, T.E. Simos, On modified Runge–Kutta trees and methods. Comput. Math. Appl. **62**(4), 2101–2111 (2011)
51. A.A. Kosti, Z.A. Anastassi, T.E. Simos, Construction of an optimized explicit Runge–Kutta–Nyström method for the numerical solution of oscillatory initial value problems. Comput. Math. Appl. **61**(11), 3381–3390 (2011)
52. Z. Kalogiratou, Th Monovasilis, T.E. Simos, New modified Runge–Kutta–Nystrom methods for the numerical integration of the Schrödinger equation. Comput. Math. Appl. **60**(6), 1639–1647 (2010)
53. Th Monovasilis, Z. Kalogiratou, T.E. Simos, A family of trigonometrically fitted partitioned Runge–Kutta symplectic methods. Appl. Math. Comput. **209**(1), 91–96 (2009)
54. T.E. Simos, High order closed Newton–Cotes trigonometrically-fitted formulae for the numerical solution of the Schrödinger equation. Appl. Math. Comput. **209**(1), 137–151 (2009)
55. Z.A. Anastassi, T.E. Simos, An optimized Runge–Kutta method for the solution of orbital problems. J. Comput. Appl. Math. **175**(1), 1–9 (2005)
56. G. Psihoyios, T.E. Simos, A fourth algebraic order trigonometrically fitted predictor–corrector scheme for IVPs with oscillating solutions. J. Comput. Appl. Math. **175**(1), 137–147 (2005)
57. D.P. Sakas, T.E. Simos, Multiderivative methods of eighth algrebraic order with minimal phase-lag for the numerical solution of the radial Schrödinger equation. J. Comput. Appl. Math. **175**(1), 161–172 (2005)
58. K. Tselios, T.E. Simos, Runge–Kutta methods with minimal dispersion and dissipation for problems arising from computational acoustics. J. Comput. Appl. Math. **175**(1), 173–181 (2005)
59. T.E. Simos, Dissipative trigonometrically-fitted methods for linear second-order IVPs with oscillating solution. Appl. Math. Lett. **17**(5), 601–607 (2004)
60. Z. Kalogiratou, T.E. Simos, Newton–Cotes formulae for long-time integration. J. Comput. Appl. Math. **158**(1), 75–82 (2003)
61. Z. Kalogiratou, T. Monovasilis, T.E. Simos, Symplectic integrators for the numerical solution of the Schrödinger equation. J. Comput. Appl. Math. **158**(1), 83–92 (2003)
62. A. Konguetsof, T.E. Simos, A generator of hybrid symmetric four-step methods for the numerical solution of the Schrödinger equation. J. Comput. Appl. Math. **158**(1), 93–106 (2003)
63. G. Psihoyios, T.E. Simos, Trigonometrically fitted predictor–corrector methods for IVPs with oscillating solutions. J. Comput. Appl. Math. **158**(1), 135–144 (2003)
64. A. Konguetsof, T.E. Simos, An exponentially-fitted and trigonometrically-fitted method for the numerical solution of periodic initial-value problems. Comput. Math. Appl. **45**(1–3), 547–554 (2003)
65. Dimitris F. Papadopoulos, T.E. Simos, A modified Runge–Kutta–Nyström method by using phase lag properties for the numerical solution of orbital problems. Appl. Math. Info. Sci **7**(2), 433–437 (2013)

66. Th Monovasilis, Z. Kalogiratou, T.E. Simos, Exponentially fitted symplectic runge–Kutta–Nyström methods. Appl. Math. Info. Sci. **7**(1), 81–85 (2013)
67. G.A. Panopoulos, T.E. Simos, An optimized symmetric 8-step semi-embedded predictor–corrector method for IVPs with oscillating solutions. Appl. Math. Info. Sci. **7**(1), 73–80 (2013)
68. T.E. Simos, On the explicit four-step methods with vanished phase-lag and its first derivative. Appl. Math. Info. Sci. **8**(2), 447–458 (2014)
69. G.A. Panopoulos, T.E. Simos, A new optimized symmetric embedded predictor–corrector method (EPCM) for initial-value problems with oscillatory solutions. Appl. Math. Info. Sci. **8**(2), 703–713 (2014)
70. T.E. Simos, Closed Newton–Cotes trigonometrically-fitted formulae of high order for long-time integration of orbital problems. Appl. Math. Lett. **22**(10), 1616–1621 (2009)
71. T.E. Simos, Exponentially and trigonometrically fitted methods for the solution of the Schrödinger equation. Acta Appl. Math. **110**(3), 1331–1352 (2009)
72. S. Stavroyiannis, T.E. Simos, Optimization as a function of the phase-lag order of nonlinear explicit two-step P-stable method for linear periodic IVPs. Appl. Numer. Math. **59**(10), 2467–2474 (2009)
73. T.E. Simos, Optimizing a hybrid two-step method for the numerical solution of the Schrödinger equation and related problems with respect to phase-lag. J. Appl. Math **2012**(420387), 17 (2012)
74. T.E. Simos, New stable closed Newton–Cotes trigonometrically fitted formulae for long-time integration. Abstr. Appl. Anal **2012**(182536), 15 (2012)
75. J. Vigo-Aguiar, H. Ramos, On the choice of the frequency in trigonometrically-fitted methods for periodic problems. J. Comput. Appl. Math. **277**, 94–105 (2015)
76. H. Ramos, J. Vigo-Aguiar, On the frequency choice in trigonometrically fitted methods. Appl. Math. Lett. **23**(11), 1378–1381 (2010)
77. H. Van de Vyver, Frequency evaluation for exponentially fitted Runge–Kutta methods. J. Comput. Appl. Math. **184**(2), 442–463 (2005)
78. J. Martin-Vaquero, J. Vigo-Aguiar, Exponential fitting BDF algorithms: explicit and implicit 0-stable methods. J. Comput. Appl. Math. **192**(1), 100–113 (2015)
79. T.E. Simos, J. Vigo-Aguiar, An exponentially-fitted high order method for long-term integration of periodic initial-value problems. Comput. Phys. Commun. **140**(3), 358–365 (2001)
80. J. Vigo-Aguiar, H. Ramos, Variable stepsize implementation of multistep methods for $y'' = f(x, y, y')$. J. Comput. Appl. Math. **192**(1), 114–131 (2006)
81. T.E. Simos, J. Vigo-Aguiar, A symmetric high order method with minimal phase-lag for the numerical solution of the Schrödinger equation. Int. J. Mod. Phys. C **12**(7), 1035–1042 (2001)
82. B.A. Wade, A.Q.M. Khaliq, M. Yousuf, J. Vigo-Aguiar, R. Deininger, On smoothing of the Crank–Nicolson and higher order schemes for pricing barrier options. J. Comput. Appl. Math. **204**(1), 144–158 (2007)
83. J. Vigo-Aguiar, S. Natesan, An efficient numerical method for singular perturbation problems. J. Comput. Appl. Math. **192**(1), 132–141 (2006)
84. J. Vigo-Aguiar, J. Martin-Vaquero, H. Ramos, Exponential fitting BDF–Runge–Kutta algorithms. Comput. Phys. Commun. **178**(1), 15–34 (2008)