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A New Four–Stages High Algebraic Order Two–Step Method with Vanished Phase–Lag and its First, Second and Third Derivatives for the Numerical Solution of the Schrödinger Equation

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Abstract

A new high algebraic order four–stages symmetric two–step method is developed, for the first time in the literature, in the present paper. Requesting the elimination of the phase–lag and its first, second and third derivatives and requiring also the highest possible algebraic order, we determine the coefficients of the method. We study also the affection of the elimination of the phase–lag and its derivatives on the efficiency of the new proposed method. More specifically we will investigate the following:

- the development of the method,
- the calculation of the local truncation error (LTE) of the new proposed method,
- the analysis of the method which consists of two stages: Stage 1: LTE analysis based on a test problem which is the radial Schrödinger equation. Stage 2: Stability and Interval

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of Periodicity Analysis based on a scalar test equation with frequency different than the frequency of the scalar test equation used for the phase–lag analysis,

- the introduction of two embedding techniques for the error control: one which is based on the algebraic order of the methods and the new one which is based on the highest possible order of the eliminated derivative of the phase–lag,
- the efficiency of the new proposed method based on the application of it to two problems: (i) the resonance problem of the Schrödinger equation and (ii) the coupled differential equations arising from the Schrödinger equation.

Based on the above study, it will be proved that the new proposed method is very effective for the numerical solution of the Schrödinger equation and related initial-value or boundary-value problems with periodical and /or oscillating solutions. We note here that the new developed method is an improvement of the recent developed methods in [1], [2], [3] and [4].

1. INTRODUCTION

A new four–stages symmetric two–step method of twelfth algebraic order for the effective approximate solution of the Schrödinger equation and related problems is proposed, for the first time in the literature, in this paper. The efficiency of the new propose method will be studied by applying it on the approximate solution of

- the radial time independent Schrödinger equation and
- the coupled differential equation of the Schrödinger equation type.

The above problems and their efficient solution are very important on Computational Chemistry (see [5] and references therein). A significant part of the quantum chemical calculations contains, as critical part, the Schrödinger equation. We mention that we can have only numerical solution of the Schrödinger's equation for more than one particle. The effective numerical solution of the Schrödinger equation can give us the following:

1. computation of important molecular properties (such as vibrational energy levels and wave functions of systems) and
2. provide us an essential presentation of the molecule's electronic structure (see for more details in [6–9]).

The method proposed in this paper will improve the methods developed for the first time in the literature in [1], [2] and [4]. In more details the methods obtained in [1] and [2] are of tenth algebraic order, while the new proposed method is of twelfth algebraic order. Additionally, while the method obtained in [4] is of twelfth algebraic order and has eliminated the phase–lag and its first and second derivatives, the new method, which is first introduced in the literature, is of twelfth algebraic order and has eliminated the phase–lag and its first, second and third derivatives. Additionally, we give a new error control which is based on high order vanishing of the derivatives of the phase–lag.

The above mentioned problems which will be studied in this paper belong to the category of the special second order initial value problems with periodical and/or oscillating solution of the form:

$$z''(x) = f(x, z), \;\; z(x_0) = z_0 \;\; and \;\; z'(x_0) = z'_0. \tag{1}$$

More specifically, we will investigate the numerical solution of systems of ordinary differential equations of second order in the model of which the first derivative z' does not appear explicitly and additionally their solutions have with periodical and/or oscillating behavior.

Below we give some bibliography on the subject of the paper. We give the bibliography based on the categories of methods which developed the last decades:

1. In [43], [46], [55], [58] – [61], [52] [69], exponentially, trigonometrically and phase fitted Runge–Kutta and Runge–Kutta Nyström methods was developed.
2. Multistep exponentially, trigonometrically and phase fitted methods and multistep methods with minimal phase–lag developed in [1]– [4], [14]– [17], [21]– [24], [30], [34], [40], [44]– [45], [49], [54], [56]– [57], [63]– [64], [70]– [71].
3. Symplectic integrators in [38]– [39], [47], [50], [53], [61]– [62], [67].
4. Nonlinear methods developed in [48].
5. General methods are developed in [10]– [13], [18]– [20], [31]– [33], [36]– [37].

2. ANALYSIS OF SYMMETRIC 2 m MULTISTEP METHODS

The analysis of symmetric multistep methods is based on the following algorithm:

1. Presentation of the general form of the $2\,m$–step finite difference method for the numerical solution of the initial value problem (1):

$$\sum_{i=-m}^{m} c_i \, z_{n+i} = h^2 \sum_{i=-m}^{m} b_i \, f(x_{n+i}, z_{n+i}). \tag{2}$$

2. Definitions: (1) Space of integration which is known as **integration interval** and (2) **stepsize (step length)** of integration

3. Procedure for the numerical solution of the initial value problem (1) using the above determined $2\,m$–step method:

   - Let us consider the space $[a, b]$ as the integration interval for the approximate integration of the initial value problem (1).
   - Using the points $\{x_i\}_{i=-m}^{m} \in [a, b]$ we divide the above determined integration interval $[a, b]$ into m equally spaced intervals.
   - Based on the above division of the integration area using the points x_i, $i = -m(1)m$, the quantity h by $h = |x_{i+1} - x_i|, \quad i = 1 - m(1)m - 1$ is determined. We call this quantity **the stepsize of integration** or **the step length of integration**.

4. Determination of a subclass of the general $2\,m$–step methods which is called symmetric $2\,m$–step methods.

   Definition 1. *A method (2) is called symmetric if and only if* $c_{-i} = c_i$ *and* $b_{-i} = b_i$, $i = 0(1)m$.

   Remark 1. *The linear operator*

$$L(x) = \sum_{i=-m}^{m} c_i\, z(x + ih) - h^2 \sum_{i=-m}^{m} b_i\, z''(x + ih) \tag{3}$$

   where $z \in C^2$, *is associated with the* $2\,m$*–step Method determined by (2).*

5. Definition of the algebraic order q of a $2\,m$–step Method presented by (2)

   Definition 2. [10] We call that a $2\,m$–step method given by (2) has algebraic of order q if the associated linear operator L given by (3) vanishes for any linear combination of the linearly independent functions $1,\, x,\, x^2,\, \ldots,\, x^{q+1}$.

6. Introduction and Definition of the terms for a symmetric $2\,m$–step method: scalar test equation, difference equation and characteristic equation

   Application of the symmetric $2\,m$–step method (2) to the scalar test equation

$$z'' = -\phi^2\, z \tag{4}$$

leads to the following difference equation:

$$A_m(v)\, z_{n+m} + \cdots + A_1(v)\, z_{n+1} + A_0(v)\, z_n + A_1(v)\, z_{n-1} + \cdots + A_m(v)\, z_{n-m} = 0 \quad (5)$$

and the associated characteristic equation

$$A_m(v)\, \lambda^m + \cdots + A_1(v)\, \lambda + A_0(v) + A_1(v)\, \lambda^{-1} + \cdots + A_m(v)\, \lambda^{-m} = 0. \quad (6)$$

where $v = \phi\, h$, h is the step length and $A_j(v)\, j = 0(1)k$ are polynomials of v which are called **stability polynomials** of the symmetric $2\,m$–step method (2).

7. Introduction and Definition of the terms for a symmetric $2\,m$–step method: interval of periodicity, phase–lag, phase-fitted method

Definition 3. [11] *We say that a symmetric* $2\,m$*–step method with characteristic equation given by (6) has a non–zero interval of periodicity* $(0, v_0^2)$ *when , for all* $v \in (0, v_0^2)$, *the roots* $\lambda_i, i = 1(1)2\,m$ *of characteristic equation Eq. (6) satisfy:*

$$\lambda_1 = e^{i\theta(v)} \quad , \quad \lambda_2 = e^{-i\theta(v)} \quad and \quad |\lambda_i| \leq 1\,,\, i = 3(1)2\,m \quad (7)$$

where $\theta(v)$ *is a real function of* v.

Definition 4. *(see* [11]*) A symmetric* $2\,m$*–step method is called* P*-stable method if its interval of periodicity is equal to* $(0, \infty)$.

Definition 5. *A symmetric* $2\,m$*–step method is called singularly almost* P*-stable method if its interval of periodicity is equal to* $(0, \infty) - S$ [2].

Definition 6. [12], [13] *For any symmetric* $2\,m$*–step method with a characteristic equation given by (6), the phase–lag is defined as the leading term in the expansion of*

$$t = v - \theta(v). \quad (8)$$

In the above mentioned case if the quantity $t = O(v^{s+1})$ *as* $v \to \infty$, *then the order of the phase–lag is equal to* s.

Definition 7. [14] *We call a symmetric* $2\,m$*–step method* **phase-fitted** *if its phase–lag is equal to zero.*

[2] where S is a set of distinct points

8. Direct formula for the computation of the phase–lag for a symmetric $2\,m$–step method

Theorem 1. [12] *A symmetric $2\,m$–step method with the characteristic equation given by (6) has phase–lag order s and phase–lag constant c given by*

$$-cv^{s+2}+O(v^{s+4})=\frac{2\,A_m(v)\,\cos(m\,v)+\cdots+2\,A_j(v)\,\cos(j\,v)+\cdots+A_0(v)}{2\,m^2\,A_m(v)+\cdots+2\,j^2\,A_j(v)+\cdots+2\,A_1(v)}. \quad (9)$$

Remark 2. *The above formula (9) is a direct one for the computation of the phase–lag of any symmetric $2\,m$–step method.*

Remark 3. *For the specific case of a symmetric two–step method and for the calculation of its phase–lag, we will apply the above mentioned direct formula (9) with $m=2$.*

3. THE NEW TWELFTH ALGEBRAIC ORDER FOUR–STAGES SYMMETRIC TWO–STEP METHOD WITH VANISHED PHASE–LAG AND ITS FIRST, SECOND AND THIRD DERIVATIVES

We consider the family of methods

$$\begin{aligned}
\widehat{z}_n &= z_n - a_0\,h^2\left(f_{n+1}-2\,f_n+f_{n-1}\right)-2\,a_1\,h^2\,f_n\\
\tilde{z}_n &= z_n - a_2\,h^2\left(f_{n+1}-2\,\widehat{f}_n+f_{n-1}\right)\\
\bar{z}_n &= z_n - a_3\,h^2\left(f_{n+1}-2\,\tilde{f}_n+f_{n-1}\right)\\
z_{n+1}+a_4\,z_n+z_{n-1} &= h^2\left[b_1\,\left(f_{n+1}+f_{n-1}\right)+b_0\,\bar{f}_n\right]
\end{aligned} \quad (10)$$

where $f_i=z''\left(x_i,z_i\right), i=-2(1)2$, $\widehat{f}_n=z''\left(x_n,\widehat{z}_n\right)$, $\tilde{f}_n=z''\left(x_n,\tilde{z}_n\right)$, $\bar{f}_n=z''\left(x_n,\bar{z}_n\right)$ and a_j, $j=0(1)4$ and b_i, $i=0,1$ are parameters.

We give attention to the following case of the above noted family of methods (10):

$$a_0=-\frac{27}{3200},\; a_1=\frac{3}{32},\; a_2=-\frac{10}{693}. \quad (11)$$

The requirement the above symmetric two-step method (10) with the newly defined free parameters (11) to have eliminated the phase–lag and its first, second and third derivatives leads to the following system of equations:

$$\mathrm{Phase-Lag(PL)}=\frac{T_0}{T_{denom}}=0 \quad (12)$$

$$\text{First Derivative of the Phase} - -\text{Lag} = \frac{T_1}{T_{denom}^2} = 0 \tag{13}$$

$$\text{Second Derivative of the Phase} - -\text{Lag} = \frac{T_2}{T_{denom}^3} = 0 \tag{14}$$

$$\text{Third Derivative of the Phase} - -\text{Lag} = \frac{T_3}{T_{denom}^4} = 0 \tag{15}$$

where T_j, $j = 0(1)3$ and T_{denom} are given in the Appendix A.

In order to obtain the free parameters of the new proposed method (10) we solve the system of equations (12)–(15):

$$a_4 = \frac{T_4}{T_{denom1}} \quad , \quad a_3 = 2310 \, \frac{T_5}{T_{denom2}}$$
$$b_0 = \frac{1}{81} \frac{T_6}{T_{denom3}} \quad , \quad b_1 = \frac{1}{81} \frac{T_7}{T_{denom3}} \tag{16}$$

where T_j, $j = 4(1)7$, T_{denom1}, T_{denom2} and T_{denom3} are given in the Appendix B.

We use the Taylor series expansions given in the Appendix C in the cases of heavy cancelations for some values of $|v|$ of the above mentioned formulae given by (16).

The behavior of the coefficients is given in the Figure 1.

We indicate the new proposed method (10) with the coefficients given by (11) and (16) and their Taylor series expansions given in Appendix C with the symbol: $NM4SH3DV$. For this method, the local truncation error is equal to:

$$LTE_{NM4SH3DV} = \frac{307}{186810624000} \, h^{14} \left(z_n^{(14)} - 35 \, \phi^8 \, z_n^{(6)} - 84 \, \phi^{10} \, z_n^{(4)} - 70 \phi^{12} \, z_n^{(2)} \right) + O\left(h^{16}\right). \tag{17}$$

4. ANALYSIS OF THE NEW OBTAINED METHOD

4.1. Comparative Local Truncation Error (LTE) Analysis

The following test problem is used for the local truncation error analysis:

$$z''(x) = \left(V(x) - V_c + G\right) \, z(x) \tag{18}$$

where

- $V(x)$ is a potential function,
- V_c a constant approximation of the potential on the specific point x,
- $G = V_c - E$ and

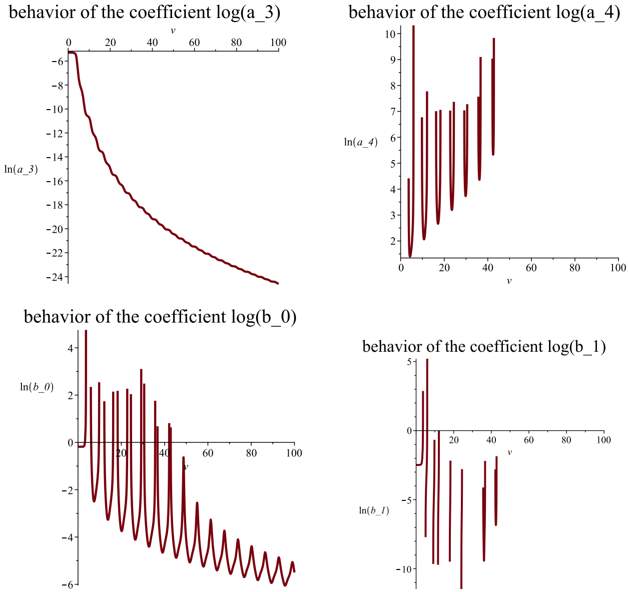

Figure 1. Behavior of the free parameters of the new proposed method (10) given by (16) for several values of $v = \phi\, h$.

- E is the energy.

Remark 4. *The Eq. (18) is the radial time independent Schrödinger equation with potential $V(x)$.*

We will investigate the following methods:

4.1.1. Classical Method (i.e., Method (10) with Constant Coefficients)

$$LTE_{CL} = \frac{307}{186810624000}\, h^{14}\, z_n^{(14)} + O\left(h^{16}\right). \tag{19}$$

4.1.2. Method with Vanished Phase–Lag and Its First and Second Derivatives Developed in [4]

$$
\begin{aligned}
LTE_{NM4SH2DV} &= \frac{307}{186810624000}\, h^{14} \left(z_n^{(14)} - 15\,\phi^8\, z_n^{(6)} \right. \\
&- \left. 24\,\phi^{10}\, z_n^{(4)} - 10\phi^{12}\, z_n^{(2)} \right) + O\left(h^{16}\right). \qquad (20)
\end{aligned}
$$

4.1.3. Method with Vanished Phase–Lag and Its First, Second and Third Derivatives Developed in Section 3.

$$
\begin{aligned}
LTE_{NM4SH3DV} &= \frac{307}{186810624000}\, h^{14} \left(z_n^{(14)} - 35\,\phi^8\, z_n^{(6)} \right. \\
&- \left. 84\,\phi^{10}\, z_n^{(4)} - 70\phi^{12}\, z_n^{(2)} \right) + O\left(h^{16}\right). \qquad (21)
\end{aligned}
$$

The following scheme is followed

- We calculate the new formulae of the Local Truncation Errors (LTEs) which are based on the test problem (18)
- In order to achieve the above we have to compute the derivatives of the function z which are included in the formulae of LTEs mentioned above (19), (20) and (21).
- In order to satisfy the above step we use expressions of the derivatives of the function z. Some of the requested expressions for the derivative of the function z are given in the Appendix D.
- Using the above achieved new formulae of the derivatives of the approximation of the function z to the point x_n and substitute them into the formulae of LTEs (19), (20) and (21), we obtain the new formulae of LTEs produced from the test equation (18).
- The new formulae of LTEs produced above are dependent from the quantity G and the energy E.
- We study two cases for the parameter G:

1. **The Potential and the Energy are closed each other.**

   Consequently we have

$$G = V_c - E \approx 0 \Rightarrow G^i = 0,\ i = 1, 2, \ldots. \tag{22}$$

   The general form of the LTEs is given by:

$$LTE = h^{14} \sum_{k=0}^{j} B_k\, G^k \tag{23}$$

   where B_k are constant numbers (classical case) or formulae of v and $G = V_c - E$ (frequency dependent cases).

   Remark 5. *In the case $G = V_c - E \approx 0$, we have:*

$$LTE_{G=0} = h^{14}\, B_0 \tag{24}$$

   where B_0 is equal for all the above formulae (19), (20) and (21).

   Therefore, for $G = V_c - E \approx 0$ we have that:

$$LTE_{CL} = LTE_{NM4SH2DV} = LTE_{NM4SH3DV} = h^{14}\, B_0 \tag{25}$$

   where B_0 is given in the Appendix E at every point $x = x_n$.

   Theorem 2. *From (22) it is easy to see that for $G = V_c - E \approx 0$ the local truncation error for the classical method (constant coefficients), the local truncation error for the method with eliminated phase–lag and its first and second derivatives and the local truncation error for the method with eliminated phase–lag and its first, second and third derivatives are the same and equal to $h^{14}\, B_0$, where B_0 is given in the Appendix E and consequently for $G = 0$ the methods are of comparable accuracy.*

2. **The Potential and the Energy are far from each other.** Therefore, $G >> 0$ or $G << 0$ and the value of $|G|$ is a large number. For these cases the most accurate method is the method with asymptotic form of LTE which has the minimum power of G.

- Finally we compute, based on the above, the asymptotic expressions of the LTEs.

4.1.4. Classical Method

$$LTE_{CL} = \frac{307}{186810624000} h^{14} \left(z(x)\, G^{7} + \cdots \right) + O\left(h^{16}\right). \tag{26}$$

4.1.5. Method with Vanished Phase–Lag and Its First and Second Derivatives Developed in [4]

$$LTE_{NM4SH2DV} = \frac{307}{2335132800} h^{14} \left(\left(\frac{d^2}{dx^2} g(x) \right) z(x)\, G^{5} + \cdots \right) + O\left(h^{16}\right). \tag{27}$$

4.1.6. Method with Vanished Phase–Lag and Its First, Second and Third Derivatives Developed in Section 3.

$$\begin{aligned} LTE_{NM4SH3DV} &= \frac{307}{6671808000} h^{14} \left[\left(15 \left(\frac{d}{dx} g(x) \right)^{2} z(x) \right.\right. \\ &+ 20\, g(x)\, z(x) \frac{d^2}{dx^2} g(x) + 27 \left(\frac{d^4}{dx^4} g(x) \right) z(x) \\ &+ \left.\left. 10 \left(\frac{d^3}{dx^3} g(x) \right) \frac{d}{dx} z(x) \right) G^{4} + \cdots \right] + O\left(h^{16}\right). \end{aligned} \tag{28}$$

From the above mentioned analysis we have the following theorem:

Theorem 3.

- *Classical Method (i.e., the method (10) with constant coefficients): For this method the error increases as the seventh power of G.*
- *High Algebraic Order Two–Step Method with Vanished Phase–lag and its First and Second Derivatives developed in [4]: For this method the error increases as the fifth power of G.*
- *Twelfth Algebraic Order Two–Step Method with Eliminated Phase–lag and its First, Second and Third Derivatives developed in Section 3: For this method the error increases as the fourth power of G.*

So, for the numerical solution of the time independent radial Schrödinger equation the New Proposed Twelfth Algebraic Order Method with vanished phase–lag and its first, second and third derivatives is the most accurate one , especially for large values of $|G| = |V_c - E|$.

4.2. Stability and Interval of Periodicity Analysis

The following test problem is used for the stability and interval of periodicity analysis of the new proposed method:

$$z'' = -\omega^2 \, z. \tag{29}$$

Remark 6. *If we compare the test equations (4) and (29) we arrive to the remark that the frequencies of these test problems are not equal, i.e.* $\omega \neq \phi$.

The application of the new proposed four–stages symmetric two–step method to the scalar test equation (29) leads to the difference equation:

$$A_1\,(s,v)\;\left(z_{n+1} + z_{n-1}\right) + A_0\,(s,v)\;z_n = 0 \tag{30}$$

which is associated to the characteristic equation:

$$A_1\,(s,v)\;\left(\lambda^2 + 1\right) + A_0\,(s,v)\;\lambda \,=\, 0 \tag{31}$$

where

$$\begin{aligned} A_1\,(s,v) &= 1 + b_1\,s^2 + a_3\,b_0\,s^4 - 2\,a_2\,a_3\,b_0\,s^6 + 4\,a_0\,a_2\,a_3\,b_0\,s^8 \\ A_0\,(s,v) &= a_4 + b_0\,s^2 - 2\,a_3\,b_0\,s^4 + 4\,a_2\,a_3\,b_0\,s^6 + 8\,a_2\,a_3\,b_0\;(a_1 - a_0)\;s^8 \end{aligned} \tag{32}$$

where $s = \omega\,h$ and $v = \phi\,h$.

Taken the coefficients a_j, $j = 0(1)2$ from (11) and the coefficients b_i, $j = 0,1$ and a_k, $k = 3,4$ from (16) and substituted them into the formulae (32) we have that:

$$A_1\,(s,v) = \frac{T_8}{T_{denom4}} \quad , \quad A_0\,(s,v) \,=\, 2\,\frac{T_9}{T_{denom4}} \tag{33}$$

where

$$\begin{aligned} T_8 &= 54\,s^8v^2 - 216\,s^2v^8 + 3200\,s^6v^2 \\ &- 7332\,s^2v^6 + 110880\,s^4v^2 - 149760\,s^2v^4 \\ &+ 997920\,s^2v^2 + 81\,\left(\cos\left(v\right)\right)^2 v^{10} \\ &+ 81\,\left(\cos\left(v\right)\right)^2 s^8 - 3037\,\left(\cos\left(v\right)\right)^2 v^8 \\ &+ 7848\,\sin\left(v\right)v^9 + 7848\,\cos\left(v\right)v^8 \\ &+ 4800\,\left(\cos\left(v\right)\right)^2 s^6 - 88560\,\left(\cos\left(v\right)\right)^2 v^6 \\ &+ 136920\,\sin\left(v\right)v^7 - 19200\,\cos\left(v\right)v^6 \end{aligned}$$

$$
\begin{aligned}
& + \quad 166320\,(\cos(v))^2\,s^4 - 1164240\,(\cos(v))^2\,v^4 \\
& + \quad 394560\,\sin(v)\,v^5 - 665280\,\cos(v)\,v^4 \\
& + \quad 665280\,\sin(v)\,v^3 + 274080\,v^6 + 1829520\,v^4 \\
& - \quad 1296\,\cos(v)\sin(v)\,s^2v^7 - 42936\,\cos(v)\sin(v)\,s^2v^5 \\
& - \quad 539520\,\cos(v)\sin(v)\,s^2v^3 \\
& - \quad 665280\,\cos(v)\sin(v)\,s^2v - 166320\,s^4 \\
& + \quad 27\,(\cos(v))^2\,s^8v^2 - 108\,(\cos(v))^2\,s^2v^8 \\
& + \quad 1296\,\cos(v)\sin(v)\,v^9 + 1600\,(\cos(v))^2\,s^6v^2 \\
& - \quad 2532\,(\cos(v))^2\,s^2v^6 \\
& - \quad 7848\,\sin(v)\,s^2v^7 + 28680\,\cos(v)\sin(v)\,v^7 \\
& - \quad 54936\,\cos(v)\,s^2v^6 + 55440\,(\cos(v))^2\,s^4v^2 \\
& - \quad 86880\,(\cos(v))^2\,s^2v^4 + 35736\,\sin(v)\,s^2v^5 \\
& + \quad 270720\,\cos(v)\sin(v)\,v^5 - 96000\,\cos(v)\,s^2v^4 \\
& - \quad 332640\,(\cos(v))^2\,s^2v^2 - 125760\,\sin(v)\,s^2v^3 \\
& - \quad 665280\,\cos(v)\sin(v)\,v^3 - 665280\,\cos(v)\,s^2v^2 \\
& + \quad 665280\,\sin(v)\,s^2v + 162\,v^{10} - 81\,s^8 + 11989\,v^8 - 4800\,s^6 \\
T_9 & = \quad 654\,s^8v^2 - 2616\,s^2v^8 + 3200\,s^6v^2 - 92004\,s^2v^6 \\
& + \quad 110880\,s^4v^2 - 341760\,s^2v^4 \\
& - \quad 332640\,s^2v^2 + 981\,(\cos(v))^2\,v^{10} \\
& + \quad 981\,(\cos(v))^2\,s^8 - 72337\,(\cos(v))^2\,v^8 \\
& + \quad 3888\,\sin(v)\,v^9 - 1296\,\cos(v)\,v^8 + 4800\,(\cos(v))^2\,s^6 \\
& - \quad 88560\,(\cos(v))^2\,v^6 \\
& + \quad 115200\,\sin(v)\,v^7 + 38400\,\cos(v)\,v^6 + 166320\,(\cos(v))^2\,s^4 \\
& - \quad 1164240\,(\cos(v))^2\,v^4 \\
& + \quad 1330560\,\sin(v)\,v^5 + 1330560\,\cos(v)\,v^4 + 235680\,v^6 + 498960\,v^4 \\
& + \quad 15696\,\cos(v)\sin(v)\,s^2v^7 + 93336\,\cos(v)\sin(v)\,s^2v^5 \\
& + \quad 539520\,\cos(v)\sin(v)\,s^2v^3 + 665280\,\cos(v)\sin(v)\,s^2v \\
& - \quad 166320\,s^4 + 327\,(\cos(v))^2\,s^8v^2 \\
& - \quad 1308\,(\cos(v))^2\,s^2v^8 - 15696\,\cos(v)\sin(v)\,v^9 \\
& + \quad 1600\,(\cos(v))^2\,s^6v^2 + 22668\,(\cos(v))^2\,s^2v^6
\end{aligned}
$$

$$
\begin{aligned}
& - && 3888\,\sin(v)\,s^2v^7 + 79320\,\cos(v)\sin(v)\,v^7 \\
& + && 9072\,\cos(v)\,s^2v^6 + 55440\,(\cos(v))^2\,s^4v^2 \\
& - && 86880\,(\cos(v))^2\,s^2v^4 - 115200\,\sin(v)\,s^2v^5 \\
& - && 270720\,\cos(v)\sin(v)\,v^5 + 192000\,\cos(v)\,s^2v^4 \\
& - && 332640\,(\cos(v))^2\,s^2v^2 - 1330560\,\sin(v)\,s^2v^3 \\
& + && 665280\,\cos(v)\sin(v)\,v^3 + 1330560\,\cos(v)\,s^2v^2 + 1962\,v^{10} \\
& - && 981\,s^8 + 89785\,v^8 - 4800\,s^6 - 648\,(\cos(v))^2\sin(v)\,v^9 \\
& - && 28920\,(\cos(v))^2\sin(v)\,v^7 \\
& - && 394560\,(\cos(v))^2\sin(v)\,v^5 \\
& - && 665280\,(\cos(v))^2\sin(v)\,v^3 \\
& + && 648\,(\cos(v))^2\sin(v)\,s^2v^7 \\
& + && 14664\,(\cos(v))^2\sin(v)\,s^2v^5 \\
& + && 125760\,(\cos(v))^2\sin(v)\,s^2v^3 \\
& - && 665280\,(\cos(v))^2\sin(v)\,s^2v \\
& - && 4536\,(\cos(v))^3\,s^2v^6 - 96000\,(\cos(v))^3\,s^2v^4 \\
& - && 665280\,(\cos(v))^3\,s^2v^2 + 648\,(\cos(v))^3\,v^8 \\
& - && 19200\,(\cos(v))^3\,v^6 - 665280\,(\cos(v))^3\,v^4 \\
T_{denom4} & = && v^3\Big(81\,(\cos(v))^2\,v^7 + 1296\,\cos(v)\sin(v)\,v^6 \\
& - && 3037\,(\cos(v))^2\,v^5 + 7848\,v^6\sin(v) \\
& + && 162\,v^7 + 28680\,\cos(v)\sin(v)\,v^4 + 7848\,\cos(v)\,v^5 \\
& - && 88560\,(\cos(v))^2\,v^3 + 136920\,v^4\sin(v) + 11989\,v^5 \\
& + && 270720\,\cos(v)\sin(v)\,v^2 - 19200\,\cos(v)\,v^3 \\
& - && 1164240\,(\cos(v))^2\,v + 394560\,v^2\sin(v) + 274080\,v^3 \\
& - && 665280\,\cos(v)\sin(v) - 665280\,\cos(v)\,v + 665280\,\sin(v) + 1829520\,v\Big).
\end{aligned}
$$

Remark 7. *The term $P-stable$ and singularly almost P-stable method are on the problems where we have the condition $\omega = \phi$.*

In Figure 2 we present the plot of the $s - v$ plane for the new proposed method.

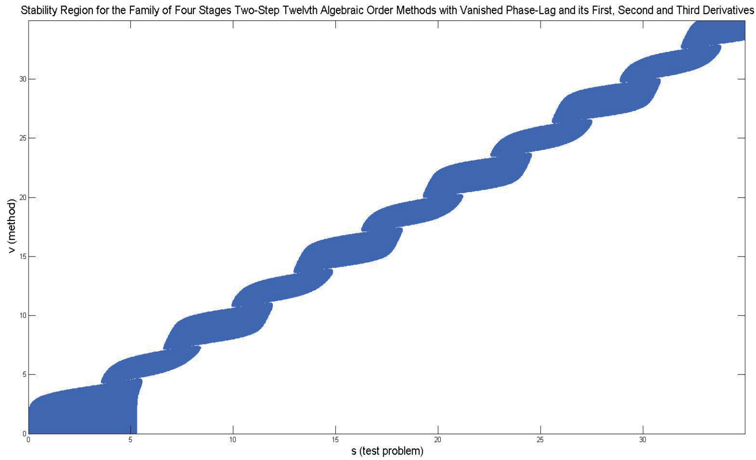

Figure 2. The plot of $s - v$ plane of the new proposed symmetric implicit twelfth algebraic order method with vanished phase–lag and its first, second and third derivatives.

Remark 8. *Observing the above mentioned plane we arrive to the following remarks :*

1. *the shadowed are is the stable space of the method ,*
2. *the white area is the unstable space of the method.*

Remark 9. *The conclusions from the observation of the $s - v$ plane of the method are depended on the problems on which the specific new proposed method will be applied:*

1. **Problems for which** $\phi \neq \omega$. *For the problems of this case, the study of the $s - v$ plane must be done in all the space* **excluding** *the area around the first diagonal.*
2. **Problems for which** $\phi = \omega$ *(as an example we refer the Schrödinger equation and related problems). For the problems of this case, the study of the $s - v$ plane must be done around the first diagonal of the $s - v$ plane.*

If we substitute on the stability polynomials, given by (33), $s = v$, then we will study the second case of the above mentioned problems in which the Schrödinger equation and related problems are belonged. Observing the space around the first diagonal of the plot $s - v$ we conclude that the interval of periodicity of the new proposed method is equal to $(0, \infty)$.

In Table 1 we present the interval of periodicity of similar methods:

Table in which the interval of periodicity of the new method is given together with the intervals of periodicity of similar methods.

Table 1. Comparative Intervals of Periodicity for symmetric two–step methods of the same form

Method	Interval of Periodicity
Method developed in [4]	$(0, 29)$
Method developed in Section 3	$(0, \infty)$

The above developments lead to the following theorem:

Theorem 4. *The method developed in section 3:*

- *is of four stages*
- *is of twelfth algebraic order,*
- *has eliminated the phase–lag and its first, second and third derivatives*
- *has an interval of periodicity equals to:* $(0, \infty)$.

5. NUMERICAL RESULTS

Our numerical experiments will be based on the application of the new obtained method on two problems:

- the approximate solution of the radial time–independent Schrödinger equation and
- the approximate solution of coupled differential equations arising from the Schrödinger equation

5.1. Radial Time–Independent Schrödinger Equation

We will study the numerical solution of the radial time independent Schrödinger equation which is given by:

$$z''(r) = \left[l(l+1)/r^2 + V(r) - k^2\right] z(r), \tag{34}$$

where

- we call *the effective potential* the function $W(r) = l(l+1)/r^2 + V(r)$. This function satisfies the relation: $W(x) \to 0$ as $x \to \infty$,

- we call *the energy* the quantity $k^2 \in \mathbb{R}$,
- we call *angular momentum* the quantity $l \in \mathbb{Z}$,
- we call *potential* the function V.

Since the problem (34)) is a boundary value one, we have to determine the boundary condition. The initial condition is defined from the value of the function z on the initial point of the integration area:

$$z(0) = 0$$

The final condition is defined at the end point of the integration space and is determined for large values of r from the physical conditions of the specific problem.

The numerical results from the numerical solution of the problem (34) are produced taking into account that the new developed method is a frequency dependent method. Consequently, the frequency ϕ (which is required from the coefficients of the new method) for the radial Schrödinger equation (for the case $l = 0$) is determined by:

$$\phi = \sqrt{|V(r) - k^2|} = \sqrt{|V(r) - E|}$$

where $V(r)$ is the potential and E is the energy.

5.1.1. Woods–Saxon Potential

Another quantity which is requested for the numerical integration of the radial Schrödinger equation by the new method is the potential $V(r)$. For our numerical experiments we use the Wood–Saxon potential:

$$V(r) = \frac{u_0}{1+q} - \frac{u_0\, q}{a\,(1+q)^2} \tag{35}$$

with $q = \exp\left[\frac{r - X_0}{a}\right]$, $u_0 = -50$, $a = 0.6$, and $X_0 = 7.0$.

The plot of the Woods–Saxon potential is given in Figure 3.

Using the methodology proposed by Ixaru et al. ([15] [17]), we use for the Woods–Saxon potential approximate values in some critical points (within the integration area). Based on these approximate values, the value of the parameter ϕ is defined.

Based on the above, the parameter ϕ is chosen as follows (see for details [16] and [17]):

$$\phi = \begin{cases} \sqrt{-50 + E} & \text{for} \quad r \in [0, 6.5 - 2h] \\ \sqrt{-37.5 + E} & \text{for} \quad r = 6.5 - h \\ \sqrt{-25 + E} & \text{for} \quad r = 6.5 \\ \sqrt{-12.5 + E} & \text{for} \quad r = 6.5 + h \\ \sqrt{E} & \text{for} \quad r \in [6.5 + 2h, 15]. \end{cases}$$

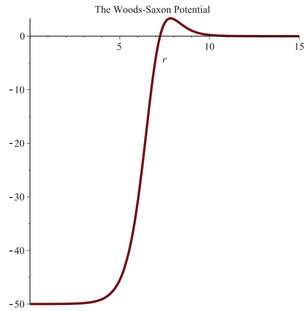

Figure 3. Plot of the Woods–Saxon potential.

From the above we observe that, for example, on the point of the integration area $r = 6.5 - h$, the value of ϕ is equal to: $\sqrt{-37.5 + E}$. Consequently, $v = \phi\, h = \sqrt{-37.5 + E}\, h$. On the point of the integration area $r = 6.5 - 3\, h$, the value of ϕ is equal to: $\sqrt{-50 + E}$, etc.

5.1.2. The Radial Schrödinger Equation and the Resonance Problem

We will solve numerically the radial time independent Schrödinger equation (34) using as potential the Woods-Saxon potential (35) and the new developed method.

The area of integration of the above mentioned problem is $(0, \infty\Big)$. Consequently, we have to approximate the infinite interval of integration with a finite one. This is necessary in order to be possible to apply a numerical methods for the solution of (34). For our experiments we will approximate the infinite space of integration by the finite space $r \in [0, 15]$. For our numerical example, we will apply the new propose method to a large domain of energies: $E \in [1, 1000]$.

We observe that for positive energies, $E = k^2$, the potential vanished for $x \to \infty$ faster than the term $\frac{l(l+1)}{x^2}$. Therefore and in this case the form of the radial Schrödinger equation is leaded to:

$$z''(r) + \left(k^2 - \frac{l(l+1)}{r^2} \right) z(r) = 0 \tag{36}$$

The mathematical model (36) of the Schrödinger equation has linearly independent solutions $k\, r\, j_l\,(k\, r\,)$ and $k\, r\, n_l\,(k\, r)$, where $j_l\,(k\, r)$ and $n_l\,(k\, r)$ are the spherical Bessel and Neumann functions respectively. Consequently, the asymptotic form of the solution of equation (34) (when $r \to \infty$) is given by:

$$z(r) \quad \approx \quad Akrj_l\,(kr) - Bkrn_l\,(kr)$$

$$\approx \quad AC \left[\sin\left(kr - \frac{l\pi}{2}\right) + \tan\delta_l \cos\left(kr - \frac{l\pi}{2}\right)\right]$$

where δ_l is the phase shift. The direct formula for the computation of the phase shift is given by:

$$\tan\delta_l = \frac{p\,(r_2)\,S\,(r_1) - p\,(r_1)\,S\,(r_2)}{p\,(r_1)\,C\,(r_1) - p\,(r_2)\,C\,(r_2)}$$

where r_1 and r_2 are distinct points in the asymptotic region (we selected as r_1 the right hand end point of the interval of integration (i.e. $r_1 = 15$) and $r_2 = r_1 - h$) with $S\,(r) = k\,r\,j_l\,(k\,r)$ and $C\,(r) = -k\,r\,n_l\,(k\,r)$. The problem is considered as an initial–value problem (as we have mentioned previously), and consequently we need the value of $z_j,\ j = 0, 1$ in order to apply a two–step method for the solution of the above described problem. The value z_0 is computed from the initial condition. The value z_1 is obtained by using high order Runge–Kutta–Nyström methods (see [18] and [19]). Based on the starting (initial) values $z_i,\ i = 0, 1$, we can compute at r_2 of the asymptotic region the phase shift δ_l.

We will solve the above described problem for positive energies. This problem has two types:

- we can find the phase-shift δ_l or
- we can find those E, for $E \in [1, 1000]$, at which $\delta_l = \frac{\pi}{2}$.

We selected to solve the latter problem, known as **the resonance problem**.

The boundary conditions are give by:

$$z(0) = 0 \quad , \quad z(r) = \cos\left(\sqrt{E}r\right) \quad \text{for large } r.$$

For comparison purposes we compute the positive eigenenergies of the resonance problem with the Woods-Saxon potential using the following methods:

- **Method QT8**: the eighth order multi–step method developed by Quinlan and Tremaine [20];
- **Method QT10**: the tenth order multi–step method developed by Quinlan and Tremaine [20];
- **Method QT12**: the twelfth order multi–step method developed by Quinlan and Tremaine [20];
- **Method MCR4**: the fourth algebraic order method of Chawla and Rao with minimal phase–lag [21];

- **Method RA**: the exponentially–fitted method of Raptis and Allison [22];
- **Method MCR6**: the hybrid sixth algebraic order method developed by Chawla and Rao with minimal phase–lag [23];
- **Method NMPF1**: the Phase-Fitted Method (Case 1) developed in [10];
- **Method NMPF2**: the Phase-Fitted Method (Case 2) developed in [10];
- **Method NMC2**: the Method developed in [24] (Case 2);
- **Method NMC1**: the method developed in [24] (Case 1);
- **Method NM2SH2DV**: the Two-Step Hybrid Method developed in [1];
- **Method NM4SH2DV**: the Four Stages Symmetric Two–Step method with eliminated phase-lag and its first and second derivatives developed in [4];
- **Method NM4SH3DV**: the Four Stages Symmetric Two–Step method with eliminated phase-lag and its first, second and third derivatives developed in Section 3.

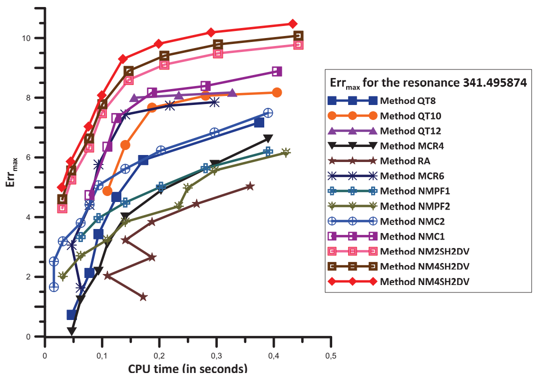

Figure 4. Accuracy (Digits) for several values of CPU Time (in Seconds) for the eigenvalue $E_2 = 341.495874$. The nonexistence of a value of Accuracy (Digits) indicates that for this value of CPU, Accuracy (Digits) is less than 0.

In Figures 4 and 5, we present the maximum absolute error $Err_{max} = |\log_{10}(Err)|$ where

$$Err = |E_{calculated} - E_{accurate}|$$

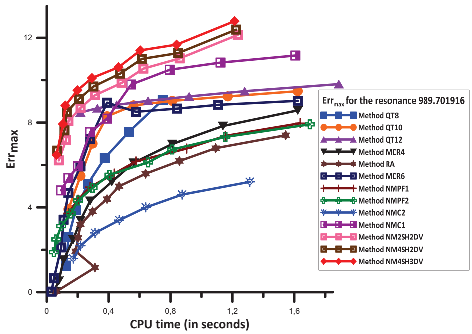

Figure 5. Accuracy (Digits) for several values of CPU Time (in Seconds) for the eigenvalue $E_3 = 989.701916$. The nonexistence of a value of Accuracy (Digits) indicates that for this value of CPU, Accuracy (Digits) is less than 0.

of the eigenenergies $E_2 = 341.495874$ and $E_3 = 989.701916$ respectively, for several values of CPU time (in seconds). The computational cost for each method is calculated via the CPU time (in seconds).

In order to compute the above mentioned absolute error we need references values which are mentioned as $E_{accurate}$. For our numerical experiments we use the well known two-step method of Chawla and Rao [23] with small step size of integration, in order to determine the reference values. Now the procedure for computation of the absolute errors mentioned above is the following: For each method we compute the eigenenergies, which are mentioned as $E_{calculated}$, and we compare the numerically computed eigenenergies with the reference values.

5.1.3 Remarks and Conclusions on the Numerical Results for the Radial Schrödinger Equation

The achieved numerical results lead us to the following conclusions:

1. **Method QT10** is more efficient than **Method MCR4** and **Method QT8**.

2. **Method QT10** is more efficient than **Method MCR6** for large CPU time and less efficient than **Method MCR6** for small CPU time.

3. **Method QT12** is more efficient than **Method QT10**

4. **Method NMPF1** is more efficient than **Method RA** and **Method NMPF2**

5. **Method NMC2** is more efficient than **Method RA**, **Method NMPF2** and **Method NMPF1**

6. **Method NMC1**, is more efficient than all the other methods mentioned above.

7. **Method NM2SH2DV**, is more efficient than all the other methods mentioned above.

8. **Method NM4SH2DV**, is more efficient than all the other methods mentioned above.

9. **Method NM4SH3DV**, is the most efficient one.

5.2. Error Estimation

For the numerical solution of the couple differential equations of the Schrödinger type variable–step methods will be applied. We call a method variable–step when during the integration procedure changes the stepsize of integration using a local truncation error estimation (LTEE) technique. Much research has been done the last decades on the development of numerical methods with constant or variable stepsize for the numerical solution of coupled differential equations arising from the Schrödinger equation and related problems (see for example [10]– [71]).

For our numerical experiments we will use an embedded pair and an error estimation procedure. Our methodology is based on the fact that for problems which have solutions with oscillatory and/or periodical behavior, the approximation is better using numerical methods with maximal algebraic order and/or with eliminated phase–lag and its derivatives of the highest possible order.

The local truncation error in y_{n+1}^{L} is estimated by

$$LTE = \mid z_{n+1}^{H} - z_{n+1}^{L} \mid \tag{37}$$

where z_{n+1}^{L} and z_{n+1}^{H} are determined with two methodologies

1. **Methodology based on algebraic order of the numerical methods**. In this methodology z_{n+1}^{L} defines the lower algebraic order solution and is achieved using the tenth algebraic order method developed in [2] and z_{n+1}^{H} defines the higher order solution which is achieved using the four–stages symmetric two–step method of twelfth algebraic order with vanished phase-lag and its first, second and third derivatives developed in Section 3.

2. **Methodology based on the higher order of the eliminated derivative of the phase–lag**. In this methodology z^L_{n+1} defines the solution which is achieved using the four–stages symmetric two–step method of twelfth algebraic order with eliminated phase-lag and its first and second derivatives developed in [4] and z^H_{n+1} defines the solution which is achieved using the four–stages symmetric two–step method of twelfth algebraic order with vanished phase-lag and its first, second and third derivatives developed in Section 3.

In our numerical experiments we reduce the changes of the step sizes on duplication of step sizes. We use the following procedure:

- if $LTE < acc$ then the step size is duplicated, i.e. $h_{n+1} = 2\,h_n$.
- if $acc \leq LTE \leq 100\,acc$ then the step size remains stable , i.e. $h_{n+1} = h_n$.
- if $100\,acc < LTE$ then the step size is halved and the step is repeated , i.e. $h_{n+1} = \frac{1}{2}\,h_n$.

where h_n is the step length used for the n^{th} step of the integration and acc is the requested accuracy of the local truncation error LTE.

Remark 10. *In our numerical test we use also the well known technique of* **the local extrapolation**. *Based on this technique we accept at each point of integration the higher order solution* z^H_{n+1} *while for the error estimation less than acc the lower order solution* z^L_{n+1} *is used.*

6.3. Coupled Differential Equations

Problems which are expressed via coupled differential equations arising from the Schrödinger equation can be observed in many areas of sciences like: quantum chemistry, material science, theoretical physics, quantum physics atomic physics, physical chemistry and chemical physics, quantum chemistry, etc.

The mathematical model of the close-coupling differential equations of the Schrödinger is given by:

$$\left[\frac{d^2}{dx^2} + k_i^2 - \frac{l_i(l_i+1)}{x^2} - V_{ii}\right] z_{ij} = \sum_{m=1}^{N} V_{im}\, z_{mj}$$

for $1 \leq i \leq N$ and $m \neq i$.

The following boundary conditions are hold, since we study the case in which all channels are open (see for details [25]):

$$z_{ij} = 0 \ at \ x = 0$$

$$z_{ij} \sim k_i \, x j_{l_i} \, (k_i x) \delta_{ij} + \left(\frac{k_i}{k_j} \right)^{1/2} K_{ij} \, k_i \, x \, n_{li} \, (k_i x) \tag{38}$$

where $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions, respectively.

Remark 11. *In the case of close channels the proposed method can be applied also efficiently.*

Based on the detailed analysis presented in [25] and defining a matrix K' and diagonal matrices M, N by:

$$\begin{aligned} K'_{ij} &= \left(\frac{k_i}{k_j} \right)^{1/2} K_{ij} \\ M_{ij} &= k_i x j_{l_i} (k_i x) \delta_{ij} \\ N_{ij} &= k_i x n_{l_i} (k_i x) \delta_{ij} \end{aligned}$$

we achieve that the asymptotic condition (38) is given now by:

$$\mathbf{z} \sim \mathbf{M} + \mathbf{N} \mathbf{K}'.$$

The rotational excitation of a diatomic molecule by neutral particle impact is a real problem which can be found in several scientific areas like quantum chemistry, theoretical chemistry, theoretical physics, quantum physics, material science, atomic physics, molecular physics etc. The model of this problem can be expressed via close–coupling differential equations of the Schrödinger type. In this model we have the following notations:

- the quantum numbers (j, l) present the entrance channel (see for details in [25]),
- the quantum numbers (j', l') present the exit channels and
- $J = j + l = j' + l'$ presents the total angular momentum.

The above lead to

$$\left[\frac{d^2}{dx^2} + k_{j'j}^2 - \frac{l'(l'+1)}{x^2} \right] z_{j'l'}^{Jjl}(x) = \frac{2\mu}{\hbar^2} \sum_{j''} \sum_{l''} < j'l'; J \mid V \mid j''l''; J > z_{j''l''}^{Jjl}(x)$$

where

$$k_{j'j} = \frac{2\mu}{\hbar^2} \left[E + \frac{\hbar^2}{2I} \{ j(j+1) - j'(j'+1) \} \right].$$

E denotes the kinetic energy of the incident particle in the center-of-mass system, I denotes the moment of inertia of the rotator, and μ denotes the reduced mass of the system.

The potential V is given by (see for details [25]):

$$V(x, \hat{\mathbf{k}}_{j'j}\hat{\mathbf{k}}_{jj}) = V_0(x)P_0(\hat{\mathbf{k}}_{j'j}\hat{\mathbf{k}}_{jj}) + V_2(x)P_2(\hat{\mathbf{k}}_{j'j}\hat{\mathbf{k}}_{jj})$$

and consequently , the element of the coupling matrix can be written as

$$< j'l'; J \mid V \mid j''l''; J >= \delta_{j'j''}\delta_{l'l''}V_0(x) + f_2(j'l', j''l''; J)V_2(x)$$

where the f_2 coefficients are determined from formulas given by Bernstein et al. [26] and $\hat{\mathbf{k}}_{j'j}$ is a unit vector parallel to the wave vector $\mathbf{k}_{j'j}$ and P_i, $i = 0, 2$ are Legendre polynomials (see for details [27]). The boundary conditions can be written as:

$$z_{j'l'}^{Jjl}(x) = 0 \text{ at } x = 0 \tag{39}$$

$$z_{j'l'}^{Jjl}(x) \sim \delta_{jj'}\delta_{ll'} \exp[-i(k_{jj}x - 1/2l\pi)] - \left(\frac{k_i}{k_j}\right)^{1/2} S^J(jl; j'l') \exp[i(k_{j'j}x - 1/2l'\pi)]$$

where S matrix and K matrix of (38) satisfy the relation:

$$\mathbf{S} = (\mathbf{I} + \mathbf{iK})(\mathbf{I} - \mathbf{iK})^{-1}.$$

For the numerical solution of the above mentioned problem and the computation of the cross sections for rotational excitation of molecular hydrogen by impact of various heavy particles, an algorithm is used. This algorithm contains a numerical method for the step-by-step integration from the initial value to matching points. For our numerical experiments an analogous algorithm with the algorithm developed for the numerical tests of [25] is used.

For our numerical tests we choose the **S** matrix with the following parameters

$$\frac{2\mu}{\hbar^2} = 1000.0 \quad ; \quad \frac{\mu}{I} = 2.351 \quad ; \quad E = 1.1$$

$$V_0(x) = \frac{1}{x^{12}} - 2\frac{1}{x^6} \quad ; \quad V_2(x) = 0.2283V_0(x).$$

Based on the description given in full details in [25], we take the value $J = 6$ and we consider excitation of the rotator from the $j = 0$ state to levels up to $j' = 2, 4$ and 6 which has as result sets of **four, nine and sixteen coupled differential equations**, respectively. Based on the methodology given by Bernstein [27] and Allison [25], we consider the potential infinite for values of x less than some x_0. Consequently, the wave functions tends to zero in this region and the boundary condition (39) effectively are given by as

$$z_{j'l'}^{Jjl}(x_0) = 0.$$

For the approximate solution of the above presented problem we have used the following methods:

- the Iterative Numerov method of Allison [25] which is indicated as **Method I**[3],
- the variable–step method of Raptis and Cash [28] which is indicated as **Method II**,
- the embedded Runge–Kutta Dormand and Prince method 5(4) [19] which is indicated as **Method III**,
- the embedded Runge–Kutta method ERK4(2) developed in Simos [29] which is indicated as **Method IV**,
- the embedded two–step method developed in [1] which is indicated as **Method V**,
- the embedded two–step method developed in [2] which is indicated as **Method VI**.
- the embedded two–step method developed in [3] which is indicated as **Method VII**.
- the new developed embedded two–step method developed in [4] which is indicated as **Method VIII**.
- the new developed embedded two–step method with error control based on the order of the eliminated derivative of the phase-lag of the method developed in this paper which is indicated as **Method IX**.
- the new developed embedded two–step method with error control based on the algebraic order of the method developed in this paper which is indicated as **Method X**.

In Table 2 we present the real time of computation requested by the numerical methods I-X mentioned above in order to calculate the square of the modulus of the **S** matrix for the sets of 4, 9 and 16 coupled differential equations respectively. In the same table we also present the maximum error in the calculation of the square of the modulus of the **S** matrix.

[3]We note here that Iterative Numerov method developed by Allison [25] is one of the most well-known methods for the numerical solution of the coupled differential equations arising from the Schrödinger equation

Table 2. Coupled Differential Equations. Real time of computation (in seconds) (RTC) and maximum absolute error (MErr) to calculate $|S|^2$ for the variable–step methods Method I - Method VII. acc=10^{-6}. Note that hmax is the maximum stepsize.N indicates the number of equations of the set of coupled differential equations

Method	N	hmax	RTC	MErr
Method I	4	0.014	3.25	1.2×10^{-3}
	9	0.014	23.51	5.7×10^{-2}
	16	0.014	99.15	6.8×10^{-1}
Method II	4	0.056	1.55	8.9×10^{-4}
	9	0.056	8.43	7.4×10^{-3}
	16	0.056	43.32	8.6×10^{-2}
Method III	4	0.007	45.15	9.0×10^{0}
	9			
	16			
Method IV	4	0.112	0.39	1.1×10^{-5}
	9	0.112	3.48	2.8×10^{-4}
	16	0.112	19.31	1.3×10^{-3}
Method V	4	0.448	0.20	1.1×10^{-6}
	9	0.448	2.07	5.7×10^{-6}
	16	0.448	11.18	8.7×10^{-6}
Method VI	4	0.448	0.15	3.2×10^{-7}
	9	0.448	1.40	4.3×10^{-7}
	16	0.448	10.13	5.6×10^{-7}
Method VII	4	0.448	0.10	2.5×10^{-7}
	9	0.448	1.10	3.9×10^{-7}
	16	0.448	9.43	4.2×10^{-7}
Method VIII	4	0.448	0.08	6.4×10^{-8}
	9	0.448	1.04	7.6×10^{-8}
	16	0.448	9.12	8.5×10^{-8}
Method IX	4	0.896	0.05	4.2×10^{-8}
	9	0.896	1.00	6.3×10^{-8}
	16	0.896	8.57	7.2×10^{-8}
Method X	4	0.896	0.04	4.0×10^{-8}
	9	0.896	0.58	5.9×10^{-8}
	16	0.896	8.55	7.0×10^{-8}

6. CONCLUSIONS

In this paper we develope, for the first time in the literature, a four–stages twelfth algebraic order symmetric two–step methods with eliminated phase–lag and its first, second and third derivatives. For this new proposed method we investigated:

- the development of the method ,
- the computation of the local truncation error and the comparison of the asymptotic form of the local truncation error (based on the radial Schrödinger equation) with the asymptotic forms of the local truncation error of similar methods,
- the stability and the interval of periodicity analysis and
- the computational effectiveness of the new proposed method. This analysis was based on the numerical experiments produced by the application of the new method, well known methods of the literature and recently obtained methods on the radial Schrödinger equation and on the coupled differential equations arising from the Schrödinger equation (which are of high importance for chemistry).

The theoretical developments and the numerical achievements obtained above, lead us to the conclusion that the new proposed method is much more efficient than the other methods of the literature for the numerical solution of the radial Schrödinger equation and of the coupled differential equations arising from the Schrödinger equation.

All computations were carried out on a IBM PC-AT compatible 80486 using double precision arithmetic with 16 significant digits accuracy (IEEE standard).

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Appendix A: Formulae for the T_i, $i = 0(1)3$ and T_{denom}

$$\begin{aligned}
T_0 &= \Big(27\,v^8 a_3 b_0 + 1600\,v^6 a_3 b_0 + 55440\,v^4 a_3 b_0 + 55440\,v^2 b_1 \\
&+ 55440\Big)\cos(v) - 327\,v^8 a_3 b_0 - 1600\,v^6 a_3 b_0 \\
&- 55440\,v^4 a_3 b_0 + 27720\,v^2 b_0 + 27720\,a_4 \\
T_1 &= -729\,\Big(v^8 a_3 b_0 + \frac{1600\,v^6 a_3 b_0}{27} + \frac{6160\,v^4 a_3 b_0}{3} + \frac{6160\,v^2 b_1}{3}
\end{aligned}$$

$$
\begin{aligned}
&+ \quad \frac{6160}{3}\Bigg)^2 \sin(v) - 960000\left(v^{12}{a_3}^2{b_0}^2 + \frac{693\, v^{10}{a_3}^2{b_0}^2}{10}\right.\\
&+ \quad \frac{18711\, v^8 a_3 b_0}{4000}\left(b_0 + \frac{218\, b_1}{9}\right)\\
&+ \quad \frac{924\, v^6 a_3 b_0}{5}\left(b_0 + \frac{27\, a_4}{800} + 2\, b_1 + \frac{327}{400}\right)\\
&+ \quad \frac{160083\, v^4 a_3 b_0}{50}\left(b_0 + \frac{20\, a_4}{231} + 2\, b_1 + \frac{40}{231}\right)\\
&+ \quad \left.\frac{160083\, b_0 a_3\,(a_4+2)\, v^2}{25} + \frac{160083\, a_4 b_1}{50} - \frac{160083\, b_0}{50}\right) v\\
T_2 &= -19683\left(v^8 a_3 b_0 + \frac{1600\, v^6 a_3 b_0}{27} + \frac{6160\, v^4 a_3 b_0}{3} + \frac{6160\, v^2 b_1}{3}\right.\\
&+ \quad \left.\frac{6160}{3}\right)^3 \cos(v) + 77760000\, v^{20}{a_3}^3{b_0}^3\\
&+ \quad 7445280000\, v^{18}{a_3}^3{b_0}^3 - 159667200000\,{b_0}^2{a_3}^2\left(\left(a_3 - \frac{1701}{320000}\right) b_0\right.\\
&- \quad \left.\frac{20601\, b_1}{160000}\right) v^{16} - 11064936960000\,{b_0}^2{a_3}^2\left(\left(a_3 - \frac{9}{1540}\right) b_0 - \frac{81\, a_4}{616000}\right.\\
&- \quad \left.\frac{9\, b_1}{770} - \frac{981}{308000}\right) v^{14} + 2083160217600\,{b_0}^2\left(b_0 + \frac{7155\, a_4}{117422}\right.\\
&- \quad \left.\frac{766153\, b_1}{58711} + \frac{17655}{58711}\right){a_3}^2 v^{12} + 44259747840000\, b_0 a_3\left({b_0}^2 a_3\right.\\
&+ \quad \left(\left(\frac{5873\, a_4}{47520} + 2\, b_1 - \frac{11947}{23760}\right) a_3 - \frac{9\, b_1}{320}\right) b_0\\
&- \quad \left.\frac{109\, {b_1}^2}{160}\right) v^{10} + 511200087552000\left({b_0}^2 a_3 + \left(\left(\frac{20\, a_4}{77} + 2\, b_1 + \frac{40}{77}\right) a_3\right.\right.\\
&- \quad \left.\left.\frac{40\, b_1}{693} - \frac{3}{440}\right) b_0 + \frac{3\, b_1}{6160}\left(a_4 - \frac{6400\, b_1}{27} - \frac{2834}{9}\right)\right) b_0 a_3 v^8\\
&+ \quad 1704000291840000\, b_0 a_3\left(\left((a_4+2)\, a_3 - 1/10\, b_1 - \frac{50}{693}\right) b_0 - \frac{1}{5}\,{b_1}^2\right.\\
&+ \quad \left.\left(\frac{16\, a_4}{693} - \frac{68}{693}\right) b_1 - \frac{3\, a_4}{2200} - \frac{109}{3300}\right) v^6\\
&- \quad 2044800350208000\, b_0 a_3\left(b_0 + (-3/4\, a_4 + 1/2)\, b_1 + \frac{25\, a_4}{693} + \frac{50}{693}\right) v^4\\
&+ \quad \left(\left((-1022400175104000\, a_4 - 2044800350208000)\, a_3\right.\right.\\
&- \quad \left.511200087552000\, b_1\right) b_0 + \left.511200087552000\, a_4 {b_1}^2\right) v^2\\
&- \quad 170400029184000\, a_4 b_1 + 170400029184000\, b_0\\
T_3 &= 531441\left(v^8 a_3 b_0 + \frac{1600\, v^6 a_3 b_0}{27} + \frac{6160\, v^4 a_3 b_0}{3} + \frac{6160\, v^2 b_1}{3}\right.\\
&+ \quad \left.\frac{6160}{3}\right)^4 \sin(v) - 8398080000\, v\left(v^{26}{a_3}^4{b_0}^4 + \frac{12311\, v^{24}{a_3}^4{b_0}^4}{108}\right.\\
&- \quad \frac{24640\,{b_0}^3{a_3}^3 v^{22}}{3}\left(\left(a_3 - \frac{1701}{640000}\right) b_0 - \frac{20601\, b_1}{320000}\right)
\end{aligned}
$$

$$- \quad 711480 \, ((a_3 - \frac{13}{3850}) \, b_0 - \frac{81 \, a_4}{1232000}$$

$$- \quad \frac{13 \, b_1}{1925} - \frac{981}{616000}) {b_0}^3 {a_3}^3 v^{20} - \frac{37945600 \, v^{18} {a_3}^3 {b_0}^3}{9} ((a_3$$

$$- \quad \frac{626711}{24640000}) b_0 - \frac{351 \, a_4}{246400} + \frac{54777001 \, b_1}{110880000} - \frac{1191}{123200})$$

$$+ \quad 146090560 \, {b_0}^2 {a_3}^2 (({a_3}^2 + \frac{34711 \, a_3}{1440747}) \, {b_0}^2 + ((\frac{724873 \, a_4}{284592000}$$

$$- \quad \frac{180058 \, b_1}{1440747} - \frac{6144947}{548856000}) a_3 - \frac{27 \, b_1}{35200}) b_0 - \frac{327 \, {b_1}^2}{17600}) v^{16}$$

$$+ \quad \frac{4218981536 \, {b_0}^2 {a_3}^2 v^{14}}{45} ({b_0}^2 a_3 + ((\frac{1068440 \, a_4}{6604389} + \frac{183074 \, b_1}{22237}$$

$$- \quad \frac{239120}{6604389}) a_3 - \frac{1620 \, b_1}{22237} - \frac{5103}{1778960}) b_0 - \frac{243 \, b_1}{355792} (a_4$$

$$+ \quad \frac{211840 \, b_1}{243} + \frac{5668}{45})) + \frac{4674897920 \, v^{12} {a_3}^2 {b_0}^2}{3} ({b_0}^2 a_3$$

$$+ \quad ((\frac{60311 \, a_4}{221760} + 2 \, b_1 + \frac{101891}{110880}) \, a_3 - \frac{58711 \, b_1}{554400}$$

$$- \quad \frac{39}{3080}) b_0 + \frac{48607 \, {b_1}^2}{138600} + (- \frac{9 \, a_4}{6160} - \frac{387}{3080}) \, b_1$$

$$- \quad \frac{243 \, a_4}{1408000} - \frac{2943}{704000}) + 13498767744 \, b_0 a_3 ({b_0}^3 {a_3}^2 + \frac{380 \, {b_0}^2 a_3}{693} ((a_4$$

$$+ \quad \frac{693 \, b_1}{190} + 2) a_3 - \frac{6 \, b_1}{19} - \frac{136133}{1504800}) + ((- \frac{80 \, {b_1}^2}{231}$$

$$+ \quad (\frac{72133 \, a_4}{19209960} + \frac{79351}{4802490}) \, b_1 - \frac{53 \, a_4}{35574}$$

$$- \quad \frac{2227}{160083}) a_3 + \frac{3 \, {b_1}^2}{1232}) b_0 + \frac{109 \, {b_1}^3}{1848}) v^{10}$$

$$+ \quad 67493838720 \, b_0 a_3 (a_3 \, ((a_4 + 2) \, a_3 - 1/5 \, b_1 - \frac{136}{693}) \, {b_0}^2 + ((-2/5 \, {b_1}^2$$

$$+ \quad (\frac{40 \, a_4}{693} - \frac{64}{231}) \, b_1 - \frac{839 \, a_4}{78408} - \frac{5279}{274428}) a_3 + \frac{4 \, {b_1}^2}{693}$$

$$+ \quad \frac{3 \, b_1}{2200}) b_0 + \frac{3 \, {b_1}^2}{6160} \, (a_4 + \frac{640 \, b_1}{27} + \frac{4142}{45})) v^8$$

$$- \quad 134987677440 \, ({b_0}^2 a_3 + (- \frac{9}{6160} + ((- \frac{3}{5} \, a_4$$

$$+ \quad \frac{4}{5}) b_1 + \frac{8 \, a_4}{77} + \frac{16}{77}) a_3) b_0$$

$$- \quad \frac{8 \, b_1}{693} \, ((a_4 + 2) \, b_1 - \frac{27 \, a_4}{1600} + \frac{4251}{1600})) b_0 a_3 v^6$$

$$- \quad 134987677440 \, b_0 a_3 (((a_4 + 2) \, a_3 + \frac{2}{5} \, b_1$$

$$- \quad \frac{4}{99}) b_0 - 2/5 \, a_4 {b_1}^2 + (\frac{16 \, a_4}{693}$$

$$- \quad \frac{8}{231}) b_1 - \frac{3 \, a_4}{4400} - \frac{109}{6600}) v^4 + (67493838720 \, {b_0}^2 a_3$$

$$
\begin{aligned}
&+ \quad \Bigg(\Big((-80992606464\,a_4 - 26997535488)\,b_1 \\
&+ \quad \frac{11687244800}{3} + \frac{5843622400\,a_4}{3}\Big)a_3 \\
&- \quad 13498767744\,{b_1}^2\Big)b_0 + 13498767744\,a_4{b_1}^3\Bigg)v^2 \\
&+ \quad \Big((13498767744\,a_4 + 26997535488)\,a_3 \\
&+ \quad 13498767744\,b_1\Big)b_0 - 13498767744\,a_4{b_1}^2\Big) \\
T_{denom} &= 27\,v^8 a_3 b_0 + 1600\,v^6 a_3 b_0 + 55440\,v^4 a_3 b_0 + 55440\,v^2 b_1 + 55440.
\end{aligned}
$$

Appendix B: Formulae for the T_j, $j = 4(1)7$, T_{denom1}, T_{denom2} and T_{denom3}

$$
\begin{aligned}
T_4 &= \Big(-1296\,v^5 + 38400\,v^3 + 1330560\,v\Big)\Big(\cos(v)\Big)^3 \\
&+ \quad \Big(\Big(1296\,v^6 + 57840\,v^4 + 789120\,v^2 + 1330560\Big)\sin(v) \\
&- \quad 1962\,v^7 + 144674\,v^5 + 177120\,v^3 \\
&+ \quad 2328480\,v\Big)\Big(\cos(v)\Big)^2 + \Big(\Big(31392\,v^6 - 158640\,v^4 \\
&+ \quad 541440\,v^2 - 1330560\Big)\sin(v) \\
&+ \quad 2592\,v^5 - 76800\,v^3 - 2661120\,v\Big)\cos(v) \\
&+ \quad \Big(-7776\,v^6 - 230400\,v^4 - 2661120\,v^2\Big)\sin(v) \\
&- \quad 3924\,v^7 - 179570\,v^5 - 471360\,v^3 - 997920\,v \\
T_{denom1} &= \Big(81\,v^7 - 3037\,v^5 - 88560\,v^3 - 1164240\,v\Big)\Big(\cos(v)\Big)^2 \\
&+ \quad \Big(\Big(1296\,v^6 + 28680\,v^4 \\
&+ \quad 270720\,v^2 - 665280\Big)\sin(v) + 7848\,v^5 \\
&- \quad 19200\,v^3 - 665280\,v\Big)\cos(v) \\
&+ \quad \Big(7848\,v^6 + 136920\,v^4 + 394560\,v^2 + 665280\Big)\sin(v) \\
&+ \quad 162\,v^7 + 11989\,v^5 + 274080\,v^3 + 1829520\,v \\
T_5 &= \Big(\cos(v)\Big)^2 v^2 + 3\Big(\cos(v)\Big)^2 + 2\,v^2 - 3 \\
T_{denom2} &= v\Big(27720\,v + 109\Big(\cos(v)\Big)^2 v^7 - 1889\Big(\cos(v)\Big)^2 v^5 \\
&- \quad 756\,\cos(v)\,v^5 + 7240\Big(\cos(v)\Big)^2 v^3 \\
&+ \quad 378\Big(\cos(v)\Big)^3 v^5 + 324\,v^6\sin(v) + 9600\,v^4\sin(v)
\end{aligned}
$$

$$
\begin{aligned}
&- && 16000\,\cos(v)\,v^3 + 110880\,v^2\sin(v)\\
&+ && 8000\left(\cos(v)\right)^3 v^3 + 55440\left(\cos(v)\right)^3 v\\
&+ && 55440\left(\cos(v)\right)^2\sin(v)\\
&+ && 27720\left(\cos(v)\right)^2 v - 55440\,\cos(v)\sin(v)\\
&- && 110880\,\cos(v)\,v + 7667\,v^5 + 28480\,v^3\\
&+ && 218\,v^7 - 10480\left(\cos(v)\right)^2\sin(v)\,v^2\\
&- && 1222\left(\cos(v)\right)^2\sin(v)\,v^4\\
&- && 1308\,\cos(v)\sin(v)\,v^6 - 7778\,\cos(v)\sin(v)\,v^4\\
&- && 44960\,\cos(v)\sin(v)\,v^2 - 54\left(\cos(v)\right)^2\sin(v)\,v^6\Big)\\
T_6 &= && \left(9072\,v^5 + 192000\,v^3 + 1330560\,v\right)\left(\cos(v)\right)^3\\
&+ && \Big(\Big(-1296\,v^6 - 29328\,v^4 - 251520\,v^2\\
&+ && 1330560\Big)\sin(v) + 2616\,v^7 - 45336\,v^5\\
&+ && 173760\,v^3 + 665280\,v\Big)\left(\cos(v)\right)^2\\
&+ && \Big(\Big(-31392\,v^6 - 186672\,v^4 - 1079040\,v^2 - 1330560\Big)\sin(v)\\
&- && 18144\,v^5 - 384000\,v^3 - 2661120\,v\Big)\cos(v)\\
&+ && \left(7776\,v^6 + 230400\,v^4 + 2661120\,v^2\right)\sin(v)\\
&+ && 5232\,v^7 + 184008\,v^5 + 683520\,v^3 + 665280\,v\\
T_7 &= && \left(-108\,v^7 - 2532\,v^5 - 86880\,v^3 - 332640\,v\right)\left(\cos(v)\right)^2\\
&+ && \Big(\Big(-1296\,v^6 - 42936\,v^4 - 539520\,v^2 - 665280\Big)\sin(v)\\
&- && 54936\,v^5 - 96000\,v^3 - 665280\,v\Big)\cos(v)\\
&+ && \left(-7848\,v^6 + 35736\,v^4 - 125760\,v^2 + 665280\right)\sin(v)\\
&- && 216\,v^7 - 7332\,v^5 - 149760\,v^3 + 997920\,v\\
T_{denom3} &= && v^2\Big(\Big(v^7 - \frac{3037\,v^5}{81} - \frac{3280\,v^3}{3} - \frac{43120\,v}{3}\Big)\left(\cos(v)\right)^2\\
&+ && \Big(\Big(16\,v^6 + \frac{9560\,v^4}{27} + \frac{30080\,v^2}{9} - \frac{24640}{3}\Big)\sin(v) + \frac{872\,v^5}{9}\\
&- && \frac{6400\,v^3}{27} - \frac{24640\,v}{3}\Big)\cos(v) + \Big(\frac{872\,v^6}{9} + \frac{45640\,v^4}{27} + \frac{43840\,v^2}{9}\\
&+ && \frac{24640}{3}\Big)\sin(v) + 2\,v^7 + \frac{11989\,v^5}{81} + \frac{91360\,v^3}{27} + \frac{67760\,v}{3}\Big).
\end{aligned}
$$

Appendix C: Taylor Series Expansion Formulae for the coefficients of the new obtained method given by (16)

$$a_4 = -2 - \frac{307\,v^{14}}{9340531200} - \frac{41\,v^{16}}{53801459712} - \frac{1552351\,v^{18}}{39614687304192000} + \cdots$$

$$\begin{aligned} a_3 &= \frac{1}{200} - \frac{307\,v^{8}}{4447872000} + \frac{237023\,v^{10}}{35026992000000} \\ &- \frac{7007173\,v^{12}}{33012239420160000} - \frac{1640860541\,v^{14}}{1580626023437260800000} \\ &+ \frac{1200862451441\,v^{16}}{1593271031624758886400000} \\ &- \frac{400971849577846457\,v^{18}}{2063355691561696341089280000000} + \cdots \end{aligned}$$

$$\begin{aligned} b_0 &= \frac{5}{6} - \frac{307\,v^{10}}{1111968000} + \frac{739\,v^{12}}{7472424960} + \frac{4424473\,v^{14}}{1320489576806400} \\ &+ \frac{16015614353\,v^{16}}{101160065499984691200} + \frac{175037669363\,v^{18}}{19915887895309486080000} + \cdots \end{aligned}$$

$$\begin{aligned} b_1 &= \frac{1}{12} + \frac{307\,v^{10}}{2223936000} + \frac{67\,v^{12}}{8302694400} + \frac{460087\,v^{14}}{1320489576806400} \\ &+ \frac{691168273\,v^{16}}{59505920882343936000} - \frac{33090811609\,v^{18}}{19915887895309486080000} + \cdots \end{aligned}$$

Appendix D: Expressions for the Derivatives of z_n

Expressions of the derivatives which are presented in the formulae of the Local Truncation Errors:

$$z^{(2)} = (V(x) - V_c + G)\ z(x)$$

$$z^{(3)} = \left(\frac{d}{dx} g(x)\right) z(x) + (g(x) + G) \frac{d}{dx} z(x)$$

$$z^{(4)} = \left(\frac{d^2}{dx^2} g(x)\right) z(x) + 2 \left(\frac{d}{dx} g(x)\right) \frac{d}{dx} z(x) + (g(x) + G)^2 z(x)$$

$$\begin{aligned} z^{(5)} &= \left(\frac{d^3}{dx^3} g(x)\right) z(x) + 3 \left(\frac{d^2}{dx^2} g(x)\right) \frac{d}{dx} z(x) \\ &+ 4 (g(x) + G) z(x) \frac{d}{dx} g(x) + (g(x) + G)^2 \frac{d}{dx} z(x) \end{aligned}$$

$$\begin{aligned}
z^{(6)} &= \left(\frac{d^4}{dx^4}g(x)\right)z(x)+4\left(\frac{d^3}{dx^3}g(x)\right)\frac{d}{dx}z(x)\\
&+ 7(g(x)+G)z(x)\frac{d^2}{dx^2}g(x)+4\left(\frac{d}{dx}g(x)\right)^2 z(x)\\
&+ 6(g(x)+G)\left(\frac{d}{dx}z(x)\right)\frac{d}{dx}g(x)+(g(x)+G)^3 z(x)\\
z^{(7)} &= \left(\frac{d^5}{dx^5}g(x)\right)z(x)+5\left(\frac{d^4}{dx^4}g(x)\right)\frac{d}{dx}z(x)\\
&+ 11(g(x)+G)z(x)\frac{d^3}{dx^3}g(x)+15\left(\frac{d}{dx}g(x)\right)z(x)\\
&+ \frac{d^2}{dx^2}g(x)+13\,(g(x)+G)\left(\frac{d}{dx}z(x)\right)\frac{d^2}{dx^2}g(x)\\
&+ 10\left(\frac{d}{dx}g(x)\right)^2\frac{d}{dx}z(x)+9\,(g(x)+G)^2 z(x)\\
&+ \frac{d}{dx}g(x)+(g(x)+G)^3\frac{d}{dx}z(x)\\
z^{(8)} &= \left(\frac{d^6}{dx^6}g(x)\right)z(x)+6\left(\frac{d^5}{dx^5}g(x)\right)\frac{d}{dx}z(x)\\
&+ 16(g(x)+G)z(x)\frac{d^4}{dx^4}g(x)+26\left(\frac{d}{dx}g(x)\right)z(x)\\
&+ \frac{d^3}{dx^3}g(x)+24\,(g(x)+G)\left(\frac{d}{dx}z(x)\right)\frac{d^3}{dx^3}g(x)\\
&+ 15\left(\frac{d^2}{dx^2}g(x)\right)^2 z(x)+48\left(\frac{d}{dx}g(x)\right)\\
&+ \left(\frac{d}{dx}z(x)\right)\frac{d^2}{dx^2}g(x)+22\,(g(x)+G)^2 z(x)\\
&+ \frac{d^2}{dx^2}g(x)+28\,(g(x)+G)z(x)\left(\frac{d}{dx}g(x)\right)^2\\
&+ 12(g(x)+G)^2\left(\frac{d}{dx}z(x)\right)\frac{d}{dx}g(x)+(g(x)+G)^4 z(x)
\end{aligned}$$

...

We compute the j-th derivative of the function z at the point x_n, i.e. $z_n^{(j)}$, substituting in the above formulae x with x_n.

Appendix E: Formula for the quantity B_0

$$
\begin{aligned}
B_0 = & \frac{107143\,(g(x))^2\left(\frac{d}{dx}y(x)\right)\left(\frac{d}{dx}g(x)\right)\frac{d^4}{dx^4}g(x)}{6671808000} \\
+ & \frac{307\,g(x)\,y(x)\left(\frac{d}{dx}g(x)\right)^2\frac{d^4}{dx^4}g(x)}{7983360} \\
+ & \frac{2149\,(g(x))^2\left(\frac{d}{dx}y(x)\right)\left(\frac{d^2}{dx^2}g(x)\right)\frac{d^3}{dx^3}g(x)}{83397600} \\
+ & \frac{221347\,g(x)\left(\frac{d}{dx}y(x)\right)\left(\frac{d}{dx}g(x)\right)\left(\frac{d^2}{dx^2}g(x)\right)^2}{4447872000} \\
+ & \frac{9517\,g(x)\left(\frac{d}{dx}y(x)\right)\left(\frac{d}{dx}g(x)\right)^2\frac{d^3}{dx^3}g(x)}{247104000} \\
+ & \frac{34691\,(g(x))^4\,y(x)\frac{d^4}{dx^4}g(x)}{26687232000} \\
+ & \frac{7061\,(g(x))^2\left(\frac{d}{dx}y(x)\right)\frac{d^7}{dx^7}g(x)}{4670265600} \\
+ & \frac{166087\,(g(x))^2\,y(x)\frac{d^8}{dx^8}g(x)}{186810624000} \\
+ & \frac{1068667\,g(x)\,y(x)\left(\frac{d^5}{dx^5}g(x)\right)\frac{d^3}{dx^3}g(x)}{46702656000} \\
+ & \frac{883853\,g(x)\,y(x)\left(\frac{d^6}{dx^6}g(x)\right)\frac{d^2}{dx^2}g(x)}{62270208000} \\
+ & \frac{574397\,g(x)\,y(x)\left(\frac{d^7}{dx^7}g(x)\right)\frac{d}{dx}g(x)}{93405312000} \\
+ & \frac{112669\,g(x)\left(\frac{d}{dx}y(x)\right)\left(\frac{d^5}{dx^5}g(x)\right)\frac{d^2}{dx^2}g(x)}{4447872000} \\
+ & \frac{24253\,g(x)\left(\frac{d}{dx}y(x)\right)\left(\frac{d^4}{dx^4}g(x)\right)\frac{d^3}{dx^3}g(x)}{667180800} \\
+ & \frac{156263\,g(x)\left(\frac{d}{dx}y(x)\right)\left(\frac{d^6}{dx^6}g(x)\right)\frac{d}{dx}g(x)}{13343616000} \\
+ & \frac{263099\,(g(x))^2\,y(x)\left(\frac{d^2}{dx^2}g(x)\right)\frac{d^4}{dx^4}g(x)}{8491392000}
\end{aligned}
$$

$$+\frac{782543\,(g(x))^2\,y(x)\left(\frac{d}{dx}g(x)\right)\frac{d^5}{dx^5}g(x)}{46702656000}$$
$$+\frac{7061\,g(x)\left(\frac{d}{dx}y(x)\right)\frac{d^9}{dx^9}g(x)}{18681062400}$$
$$+\frac{3626591\,g(x)\,y(x)\left(\frac{d}{dx}g(x)\right)\left(\frac{d^2}{dx^2}g(x)\right)\frac{d^3}{dx^3}g(x)}{31135104000}$$
$$+\frac{1494169\,g(x)\,y(x)\left(\frac{d^2}{dx^2}g(x)\right)^3}{62270208000}$$
$$+\frac{5219\left(\frac{d^3}{dx^3}g(x)\right)\left(\frac{d}{dx}y(x)\right)\frac{d^6}{dx^6}g(x)}{606528000}$$
$$+\frac{18727\left(\frac{d}{dx}g(x)\right)\left(\frac{d}{dx}y(x)\right)\frac{d^8}{dx^8}g(x)}{10378368000}$$
$$+\frac{598957\left(\frac{d}{dx}g(x)\right)^2 y(x)\left(\frac{d^2}{dx^2}g(x)\right)^2}{15567552000}$$
$$+\frac{2149\left(\frac{d^2}{dx^2}g(x)\right)^2\left(\frac{d}{dx}y(x)\right)\frac{d^3}{dx^3}g(x)}{40435200}$$
$$+\frac{129247\left(\frac{d^2}{dx^2}g(x)\right)^2 y(x)\frac{d^4}{dx^4}g(x)}{5660928000}$$
$$+\frac{307\left(\frac{d}{dx}g(x)\right)^3 y(x)\frac{d^3}{dx^3}g(x)}{14370048}$$
$$+\frac{5219\left(\frac{d^2}{dx^2}g(x)\right)y(x)\frac{d^8}{dx^8}g(x)}{5660928000}$$
$$+\frac{7061\left(\frac{d^3}{dx^3}g(x)\right)y(x)\frac{d^7}{dx^7}g(x)}{4245696000}$$
$$+\frac{307\,(g(x))^3\left(\frac{d}{dx}y(x)\right)\left(\frac{d}{dx}g(x)\right)\frac{d^2}{dx^2}g(x)}{55598400}$$
$$+\frac{152579\,(g(x))^3\,y(x)\left(\frac{d}{dx}g(x)\right)\frac{d^3}{dx^3}g(x)}{13343616000}$$
$$+\frac{193103\,(g(x))^2\,y(x)\left(\frac{d}{dx}g(x)\right)^2\frac{d^2}{dx^2}g(x)}{6671808000}$$
$$+\frac{2149\left(\frac{d}{dx}g(x)\right)\left(\frac{d}{dx}y(x)\right)\left(\frac{d^4}{dx^4}g(x)\right)\frac{d^2}{dx^2}g(x)}{30888000}$$
$$+\frac{14429\left(\frac{d}{dx}g(x)\right)y(x)\left(\frac{d^5}{dx^5}g(x)\right)\frac{d^2}{dx^2}g(x)}{486486000}$$
$$+\frac{252047\left(\frac{d}{dx}g(x)\right)y(x)\left(\frac{d^4}{dx^4}g(x)\right)\frac{d^3}{dx^3}g(x)}{6227020800}$$
$$+\frac{307\left(\frac{d^{11}}{dx^{11}}g(x)\right)\frac{d}{dx}y(x)}{15567552000}$$

$$+\frac{307\left(\frac{d^5}{dx^5}g(x)\right)^2 y(x)}{235872000}+\frac{307\left(\frac{d^{12}}{dx^{12}}g(x)\right)y(x)}{186810624000}$$
$$+\frac{3377\left(\frac{d^2}{dx^2}g(x)\right)\left(\frac{d}{dx}y(x)\right)\frac{d^7}{dx^7}g(x)}{707616000}$$
$$+\frac{307\left(\frac{d}{dx}g(x)\right)^3\left(\frac{d}{dx}y(x)\right)\frac{d^2}{dx^2}g(x)}{12636000}$$
$$+\frac{8903\left(\frac{d}{dx}g(x)\right)y(x)\frac{d^9}{dx^9}g(x)}{23351328000}$$
$$+\frac{140299\left(\frac{d}{dx}g(x)\right)\left(\frac{d}{dx}y(x)\right)\left(\frac{d^3}{dx^3}g(x)\right)^2}{3335904000}$$
$$+\frac{307\left(\frac{d^4}{dx^4}g(x)\right)\left(\frac{d}{dx}y(x)\right)\frac{d^5}{dx^5}g(x)}{26956800}$$
$$+\frac{20569\,g(x)\,y(x)\frac{d^{10}}{dx^{10}}g(x)}{186810624000}$$
$$+\frac{307\left(g(x)\right)^4\left(\frac{d}{dx}y(x)\right)\frac{d^3}{dx^3}g(x)}{444787200}$$
$$+\frac{123107\left(\frac{d}{dx}g(x)\right)^2 y(x)\frac{d^6}{dx^6}g(x)}{15567552000}$$
$$+\frac{307\left(\frac{d^2}{dx^2}g(x)\right)y(x)\left(\frac{d^3}{dx^3}g(x)\right)^2}{11664000}$$
$$+\frac{7061\left(\frac{d}{dx}g(x)\right)^2\left(\frac{d}{dx}y(x)\right)\frac{d^5}{dx^5}g(x)}{370656000}$$
$$+\frac{13201\left(\frac{d^4}{dx^4}g(x)\right)y(x)\frac{d^6}{dx^6}g(x)}{5660928000}$$
$$+\frac{7061\left(g(x)\right)^5 y(x)\frac{d^2}{dx^2}g(x)}{26687232000}$$
$$+\frac{357041\left(g(x)\right)^3 y(x)\frac{d^6}{dx^6}g(x)}{186810624000}$$
$$+\frac{147053\left(g(x)\right)^2 y(x)\left(\frac{d^3}{dx^3}g(x)\right)^2}{7783776000}$$
$$+\frac{83197\,g(x)\,y(x)\left(\frac{d^4}{dx^4}g(x)\right)^2}{6227020800}+\frac{197401\left(g(x)\right)^3 y(x)\left(\frac{d^2}{dx^2}g(x)\right)^2}{26687232000}$$
$$+\frac{307\left(g(x)\right)^5\left(\frac{d}{dx}y(x)\right)\frac{d}{dx}g(x)}{4447872000}+\frac{24253\left(g(x)\right)^3\left(\frac{d}{dx}y(x)\right)\frac{d^5}{dx^5}g(x)}{13343616000}$$
$$+\frac{307\left(g(x)\right)^7 y(x)}{186810624000}+\frac{307\left(g(x)\right)^4 y(x)\left(\frac{d}{dx}g(x)\right)^2}{333590400}$$
$$+\frac{307\,g(x)\,y(x)\left(\frac{d}{dx}g(x)\right)^4}{51321600}+\frac{307\left(g(x)\right)^2\left(\frac{d}{dx}y(x)\right)\left(\frac{d}{dx}g(x)\right)^3}{74131200}$$

at every point $x = x_n$.

References

[1] F. Hui, T. E. Simos, Hybrid high algebraic order two–step method with vanished phase–lag and its first and second derivatives, *MATCH Commun. Math. Comput. Chem.* **73** (2015) 619–648.

[2] J. Ma, T. E. Simos, Runge–Kutta type tenth algebraic order two–step method with vanished phase–lag and its first, second and third derivatives, *MATCH Commun. Math. Comput. Chem.* **74** (2015) 609–644.

[3] Zhou Zhou, Theodore E. Simos, Three–stages tenth algebraic order two–step method with vanished phase–lag and its first, second, third and fourth derivatives, *MATCH Commun. Math. Comput. Chem.* **75** (2015) 653–694.

[4] T. Lei, T. E. Simos, Four–stages twelfth algebraic order two–step method with vanished phase–lag and its first and second derivatives, for the numerical solution of the Schrödinger equation, *MATCH Commun. Math. Comput. Chem.* **76** (2016) 475–510.

[5] R. Vujasin, M. Senčanski, J. Radić–Perić, M. Perić, A comparison of various variational approaches for solving the one–dimensional vibrational Schrödinger equation, *MATCH Commun. Math. Comput. Chem.* **63** (2010) 363–378.

[6] C. J. Cramer, *Essentials of Computational Chemistry*, Wiley, Chichester, 2004.

[7] F. Jensen, *Introduction to Computational Chemistry*, Wiley, Chichester, 2007.

[8] A. R. Leach, *Molecular Modelling – Principles and Applications*, Pearson, Essex, 2001.

[9] P. Atkins, R. Friedman, *Molecular Quantum Mechanics*, Oxford Univ. Press, Oxford, 2011.

[10] 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. Comp. Appl. Math.* **236** (2012) 3880–3889.

[11] J. D. Lambert, I. A. Watson, Symmetric multistep methods for periodic initial values problems, *J. Inst. Math. Appl.* **18** (1976) 189–202.

[12] T. E. Simos, P. S. Williams, A finite–difference method for the numerical solution of the Schrödinger equation, *J. Comp. Appl. Math.* **79** (1997) 189–205.

[13] R. M. Thomas, Phase properties of high order almost P-stable formulae, *BIT* **24** (1984) 225–238.

[14] A. D. Raptis, T. E. Simos, A four–step phase–fitted method for the numerical integration of second order initial–value problem, *BIT* **31** (1991) 160–168.

[15] L. G. Ixaru, M. Rizea, Comparison of some four–step methods for the numerical solution of the Schrödinger equation, *Comput. Phys. Commun.* **38** (1985) 329–337.

[16] L. G. Ixaru, M. Micu, *Topics in Theoretical Physics*, Central Inst. Phys., Bucharest, 1978.

[17] L. G. 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** (1980) 23–27.

[18] J. R. Dormand, M. E. A. El–Mikkawy, P. J. Prince, Families of Runge–Kutta–Nyström formulae, *IMA J. Numer. Anal.* **7** (1987) 235–250.

[19] J. R. Dormand, P. J. Prince, A family of embedded Runge–Kutta formulae, *J. Comput. Appl. Math.* **6** (1980) 19–26.

[20] G. D. Quinlan, S. Tremaine, Symmetric multistep methods for the numerical integration of planetary orbits, *Astronom. J.* **100** (1990) 1694–1700.

[21] M. M. Chawla, P. S. Rao, An Noumerov–type method with minimal phase–lag for the integration of second order periodic initial–value problems. II. Explicit method, *J. Comput. Appl. Math.* **15** (1986) 329–337.

[22] A. D. Raptis, A. C. Allison, Exponential–fitting methods for the numerical solution of the Schrödinger equation, *Comput. Phys. Commun.* **14** (1978) 1–5.

[23] M. M. Chawla, P. S. Rao, An explicit sixth–order method with phase–lag of order eight for $y'' = f(t, y)$, *J. Comput. Appl. Math.* **17** (1987) 363—368.

[24] T. E. Simos, On the explicit four–step methods with vanished phase–lag and its first derivative, *Appl. Math. Inf. Sci.* **8** (2014) 447–458.

[25] A. C. Allison, The numerical solution of coupled differential equations arising from the Schrödinger equation, *J. Comput. Phys.* **6** (1970) 378–391.

[26] R. B. Bernstein, A. Dalgarno, H. Massey , I. C. Percival, Thermal scattering of atoms by homonuclear diatomic molecules, *Proc. Roy. Soc. Ser. A* **274** (1963) 427–442.

[27] R. B. Bernstein, Quantum mechanical (phase shift) analysis of differential elastic scattering of molecular beams, *J. Chem. Phys.* **33** (1960) 795–804.

[28] A. D. Raptis, J. R. Cash, A variable step method for the numerical integration of the one–dimensional Schrödinger equation, *Comput. Phys. Commun.* **36** (1985) 113–119.

[29] T. E. Simos, Exponentially fitted Runge–Kutta methods for the numerical solution of the Schrödinger equation and related problems, *Comput. Mater. Sci.* **18** (2000) 315–332.

[30] G. A. Panopoulos, T. E. Simos, A new optimized symmetric embedded predictor–corrector method (EPCM) for initial–value problems with oscillatory solutions, *Appl. Math. Inf. Sci.* **8** (2014) 703–713.

[31] J. M. Franco, M. Palacios, High–order P-stable multistep methods, *J. Comput. Appl. Math.* **30** (1990) 1–10.

[32] J. D. Lambert, *Numerical Methods for Ordinary Differential Systems. The Initial Value Problem*, Wiley, New York, 1991, pp. 104–107.

[33] E. Stiefel, D. G. Bettis, Stabilization of Cowell's method, *Numer. Math.* **13** (1969) 154–175.

[34] G. A. Panopoulos, Z. A. Anastassi, T. E. Simos, Two new optimized eight–step symmetric methods for the efficient solution of the Schrödinger equation and related problems, *MATCH Commun. Math. Comput. Chem.* **60** (2008) 773–785.

[35] T. E. Simos, G. Psihoyios, Preface, in: *Selected Papers of the International Conference on Computational Methods in Sciences and Engineering (ICCMSE 2003)*, *J. Comput. Appl. Math.* **175** (2005) IX–IX.

[36] T. Lyche, Chebyshevian multistep methods for ordinary differential eqations, *Numer. Math.* **19** (1972) 65–75.

[37] 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** (2003) 93–106.

[38] Z. Kalogiratou, T. Monovasilis, T. E. Simos, Symplectic integrators for the numerical solution of the Schrödinger equation, *J. Comput. Appl. Math.* **158** (2003) 83–92.

[39] Z. Kalogiratou, T. E. Simos, Newton–Cotes formulae for long–time integration, *J. Comput. Appl. Math.* **158** (2003) 75–82.

[40] G. Psihoyios, T. E. Simos, Trigonometrically fitted predictor–corrector methods for IVPs with oscillating solutions, *J. Comput. Appl. Math.* **158** (2003) 135–144.

[41] T. E. Simos, I. T. Famelis, C. Tsitouras, Zero dissipative, explicit Numerov–type methods for second order IVPs with oscillating solutions, *Numer. Algor.* **34** (2003) 27–40.

[42] T. E. Simos, Dissipative trigonometrically–fitted methods for linear second–order IVPs with oscillating solution, *Appl. Math. Lett.* **17** (2004) 601–607.

[43] K. Tselios, T. E. Simos, Runge–Kutta methods with minimal dispersion and dissipation for problems arising from computational acoustics, *J. Comput. Appl. Math.* **175** (2005) 173–181.

[44] 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** (2005) 161–172.

[45] G. Psihoyios, T. E. Simos, A fourth algebraic order trigonometrically fitted predictor–corrector scheme for IVPs with oscillating solutions, *J. Comput. Appl. Math.* **175** (2005) 137–147.

[46] Z. A. Anastassi, T. E. Simos, An optimized Runge–Kutta method for the solution of orbital problems, *J. Comput. Appl. Math.* **175** (2005) 1–9.

[47] T. E. Simos, Closed Newton–Cotes trigonometrically–fitted formulae of high order for long–time integration of orbital problems, *Appl. Math. Lett.* **22** (2009) 1616–1621.

[48] 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** (2009) 2467–2474.

[49] T. E. Simos, Exponentially and trigonometrically fitted methods for the solution of the Schrödinger equation, *Acta Appl. Math.* **110** (2010) 1331–1352.

[50] T. E. Simos, New stable closed Newton–Cotes trigonometrically fitted formulae for long–time integration, *Abstract Appl. Anal.* (2012) #182536.

[51] 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.

[52] D. 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. Inf. Sci.* **7** (2013) 433–437.

[53] T. Monovasilis, Z. Kalogiratou, T. E. Simos, Exponentially fitted symplectic Runge–Kutta–Nyström methods, *Appl. Math. Inf. Sci.* **7** (2013) 81–85.

[54] G. A. Panopoulos, T. E. Simos, An optimized symmetric 8-step semi–embedded predictor–corrector method for IVPs with oscillating solutions, *Appl. Math. Inf. Sci.* **7** (2013) 73–80.

[55] D. F. Papadopoulos, T. E Simos, The use of phase lag and amplification error derivatives for the construction of a modified Runge–Kutta–Nyström method, *Abstract Appl. Anal.* (2013) #910624.

[56] 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** (2012) 5370–5382.

[57] 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** (2011) 3756–3774.

[58] C. Tsitouras, I. T.. Famelis, T. E. Simos, On modified Runge–Kutta trees and methods, *Comput. Math. Appl.* **62** (2011) 2101–2111.

[59] 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** (2011) 3381–3390.

[60] Z. Kalogiratou, T. Monovasilis, T. E. Simos, New modified Runge–Kutta–Nyström methods for the numerical integration of the Schrödinger equation, *Comput. Math. Appl.* **60** (2010) 1639–1647.

[61] T. Monovasilis, Z. Kalogiratou, T. E. Simos, A family of trigonometrically fitted partitioned Runge–Kutta symplectic methods, *Appl. Math. Comput.* **209** (2009) 91–96.

[62] T. E. Simos, High order closed Newton–Cotes trigonometrically–fitted formulae for the numerical solution of the Schrödinger equation, *Appl. Math. Comput.* **209** (2009) 137–151.

[63] T. E. Simos, Multistage symmetric two–step P–stable method with vanished phase–lag and its first, second and third derivatives, *Appl. Comput. Math.* **14** (2015) 296–315.

[64] G. A. Panopoulos, T. E. Simos, An eight–step semi–embedded predictor–corrector method for orbital problems and related IVPs with oscillatory solutions for which the frequency is unknown, *J. Comp. Appl. Math.* **290** (2015) 1–15.

[65] H. Ramos, Z. Kalogiratou, T. Monovasilis, T. E. Simos, An optimized two–step hybrid block method for solving general second order initial–value problems, *Num. Algorithms* **72** (2016) 1089-1102.

[66] Z. Kalogiratou, T. Monovasilis, H. Ramos, T. E. Simos, A new approach on the construction of trigonometrically fitted two step hybrid methods, *J. Comp. Appl. Math.* **303** (2016) 146-155.

[67] T. Monovasilis, Z. Kalogiratou, T. E. Simos, Construction of exponentially fitted symplectic Runge–Kutta–Nyström methods from partitioned Runge–Kutta methods, *Mediterr. J. Math.* **13** (2016) 2271–2285.

[68] 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** (2003) 547–554.

[69] D. F. Papadopoulos, Z. A. Anastassi, T. E. Simos, An optimized Runge–Kutta–Nyström method for the numerical solution of the Schrödinger equation and related problems, *MATCH Commun. Math. Comput. Chem.* **64** (2010) 551–566.

[70] Z. A. Anastassi, T. E. Simos, Trigonometrically fitted six–step symmetric methods for the efficient solution of the Schrödinger equation, *MATCH Commun. Math. Comput. Chem.* **60** (2008) 733–752.

[71] T. E. Simos, A new Numerov–type method for the numerical solution of the Schrödinger equation, *J. Math. Chem.* **46** (2009) 981–1007.