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A New High Algebraic Order Efficient Finite Difference Method for the Solution of the Schrödinger Equation

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Abstract. The development of a new five-stages symmetric two-step method of fourteenth algebraic order with vanished phase–lag and its first, second, third and fourth derivatives is analyzed in this paper. More specifically: (1) we will present the development of the new method, (2) we will determine the local truncation error (LTE) of the new proposed method, (3) we will analyze the local truncation error based on the radial time independent Schrödinger equation, (4) we will study the stability and the interval of periodicity of the new proposed method based on a scalar test equation with frequency different than the frequency of the scalar test equation used for the phase–lag analysis, (5) we will test the efficiency of the new obtained method based on its application on the coupled differential equations arising from the Schrödinger equation.

1. Introduction and Definitions

In this paper we study the numerical solution of the close-coupled differential equations arising from the Schrödinger equation. The problem is described by the model:

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

where $1 \le i \le N$ and $m \ne i$ and the boundary conditions :

$$y_{ij} = 0 \; at \; x = 0 \tag{2}$$

$$y_{ij} \sim k_i\, x\, j_{l_i}(k_i x)\delta_{ij} + \left(\frac{k_i}{k_j}\right)^{1/2} K_{ij}\, k_i\, x\, n_{li}(k_i x) \tag{3}$$

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where $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions. We will examine the case in which all channels are open (see [1]).

If we define the matrix K' and the diagonal matrices M, N by (see for full details in [1]):

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

the new form of the asymptotic condition (27) is obtained:

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

The rotational excitation of a diatomic molecule by neutral particle impact can be found in several scientific areas (electronics, quantum chemistry, theoretical physics, material science, atomic physics, molecular physics etc). This problem is expressed by close–coupling differential equations of the Schrödinger type. Defining the entrance channel by the quantum numbers (j, l), the exit channels by (j', l'), and the total angular momentum by $J = j + l = j' + l'$, we find that (see for full details [1])

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

where

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

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

We will solve numerically the above mentioned problem using finite difference multistep methods of the general form:

$$\sum_{i=-m}^{m} c_i \, y_{n+i} = h^2 \sum_{i=-m}^{m} b_i \, f(x_{n+i}, y_{n+i}) . \tag{4}$$

where h is stepsize which is used in order to discretized the integration interval $[a, b]$, x_n denotes the n-th point of the discrete domain. The stepsize or the step length of integration is defined by $h = |x_{i+1} - x_i|$, $i = 1 - k(1)k - 1$. Finally, the quantity y_n is the approximated value of the function $y(x)$ at the point x_n. The approximate value is computed using the method (4).

Remark 1.1. *We call the method (4) symmetric multistep method or symmetric $2m$-step method if $c_{-i} = c_i$ and $b_{-i} = b_i$, $i = 0(1)m$.*

Applying the symmetric $2m$-step method to the scalar test equation

$$y'' = -\phi^2 \, y \tag{5}$$

the difference equation is obtained:

$$A_m(v) \, y_{n+m} + \cdots + A_1(v) \, y_{n+1} + A_0(v) \, y_n + A_1(v) \, y_{n-1} + \cdots + A_m(v) \, y_{n-m} = 0 \tag{6}$$

together with the corresponding characteristic equation which is given by:

$$A_m(v) \, \lambda^m + \cdots + A_1(v) \, \lambda + A_0(v) + A_1(v) \, \lambda^{-1} + \cdots + A_m(v) \, \lambda^{-m} = 0 . \tag{7}$$

where $v = \phi \, h$, h is the step length and $A_j(v)$ $j = 0(1)k$ are polynomials of v.

Definition 1.2. [22] *A symmetric 2m-step method with characteristic equation given by (7) has an interval of periodicity* $(0, v_0^2)$ *if, for all* $v \in (0, v_0^2)$, *the roots* $\lambda_i, i = 1(1)2\,m$ *of (7) satisfy:*

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

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

Definition 1.3. [22] *A multistep method is called P-stable if its interval of periodicity is equal to* $(0, \infty)$.

Definition 1.4. *A multistep method is called singularly P-stable if its interval of periodicity is equal to* $(0, \infty)\backslash S$ *with S a finite set of points.*

Definition 1.5. [50], [56] *For a symmetric 2m-step method, with the characteristic equation given by (7), its phase–lag is the leading term in the expansion of*

$$t = v - \theta(v)\,.$$

We call that for the above method the the phase–lag is of order q, if the quantity $t = O(v^{q+1})$ *as* $v \to \infty$ *holds.*

Definition 1.6. [41] *We call symmetric 2m-step method* **phase-fitted** *if its phase–lag is equal to zero.*

Theorem 1.7. [50] *The symmetric 2m-step method with characteristic equation given by (7) has phase–lag order q and phase–lag constant c given by*

$$-cv^{q+2} + O(v^{q+4}) = \frac{2\,A_m(v)\,\cos(m\,v) + \cdots + 2\,A_j(v)\,\cos(j\,v) + \cdots + A_0(v)}{2\,m^2\,A_m(v) + \cdots + 2\,j^2\,A_j(v) + \cdots + 2\,A_1(v)}\,. \tag{8}$$

2. The New Five-Stages Fourteenth Algebraic Order P–Stable Two–Step Method with Vanished Phase–Lag and its First, Second, Third and Fourth Derivatives

Let us consider the following family of five-stages symmetric two–step methods

$$\begin{aligned}
\widehat{y_n} &= y_n - a_0\,h^2\left(f_{n+1} - 2\,f_n + f_{n-1}\right)\\
\check{y}_n &= y_n - a_1\,h^2\left(f_{n+1} - 2\,\widehat{f_n} + f_{n-1}\right) - 2\,a_2\,h^2\,\widehat{f_n}\\
\widehat{y}_{n+\frac{1}{2}} &= \frac{1}{2}\left(y_n + y_{n+1}\right) - h^2\left[a_3\,\check{f_n} + \left(\frac{1}{8} - a_3\right)f_{n+1}\right]\\
\widehat{y}_{n-\frac{1}{2}} &= \frac{1}{2}\left(y_n + y_{n-1}\right) - h^2\left[a_3\,\check{f_n} + \left(\frac{1}{8} - a_3\right)f_{n-1}\right]\\
y_{n+1} + a_4\,y_n + y_{n-1} &= h^2\Bigg[b_1\,\left(f_{n+1} + f_{n-1}\right)\\
&\quad + b_0\,f_n + b_2\left(\widehat{f_{n+\frac{1}{2}}} + \widehat{f_{n-\frac{1}{2}}}\right)\Bigg]
\end{aligned} \tag{9}$$

where $a_0 = \frac{45469}{862066800}$, $a_2 = -\frac{86919}{13439282}$, $a_3 = \frac{6719641}{52720800}$, $f_{n+i} = y''\left(x_{n+i}, y_{n+i}\right), i = -1\left(\frac{1}{2}\right)1$, $\widehat{f_n} = y''\left(x_n, \widehat{y_n}\right)$, $\check{f_n} = y''\left(x_n, \check{y}_n\right)$ and a_i, $i = 1, 4\,b_j\,j = 0(1)2$ are free parameters.

The difference equation (6) and the characteristic equation (7) with $m = 1$ are produced by applying the above presented method (9) to the scalar test equation (5) leads. The polynomials $A_j(v)$, $j = 0, 1$ which are included in the formulae (6) and (7) are given by:

$$A_1(v) = 1 + \frac{1}{8}v^2\,(8\,b_1 + 4\,b_2) - \frac{1}{8}v^4\,b_2\,(8\,a_3 - 1) + 2\,v^6\,b_2\,a_1\,a_3 + 4\,v^8\,b_2 a_0\,a_3\,(a_2 - a_1)$$
$$A_0(v) = a_4 + v^2\,(b_0 + b_2) + 2\,v^4\,b_2\,a_3 + 4\,v^6\,b_2\,a_3\,(a_2 - a_1) + 8\,v^8\,b_2 a_0\,a_3\,(a_1 - a_2) \tag{10}$$

Requiring the above five-stages method (9) to have eliminated the phase-lag and its first, second, third and fourth derivatives with respect to v, we obtain the remaining coefficients b_0, b_1, b_2, a_1 and a_4 of the method (9), which are, in general, rational functions of v.

For the case of heavy cancelations for some values of $|v|$ in the above formulae for the coefficients a_i, $i = 1, 4$, b_j, $j = 0(1)2$ (for example when for some values of $|v|$ the denominators of the above mentioned formulae tends to zero), the following Taylor series expansions of the coefficients of the new proposed method are given :

$$\begin{aligned}
b_0 &= \frac{73205}{63882} - \frac{268231049\,v^{10}}{65515082994473112} - \frac{919415963248290307\,v^{12}}{153621188020681201106237952 0} \\
&- \frac{38351076781283114645648346 1\,v^{14}}{62905069835363814007460230376616960 00} \\
&- \frac{11299348929561333927546189563088930 7\,v^{16}}{91771091511420724576810859416671192748032 00000} \\
&- \frac{35749471886820681055614564261439791580134147 73\,v^{18}}{15375574855118094902606226647944345606813523295682560 00000} + \cdots
\end{aligned}$$

$$\begin{aligned}
b_1 &= \frac{51911}{383292} - \frac{268231049\,v^{10}}{393090497966838672} - \frac{7372668718000121\,v^{12}}{837933752840079278761297920} \\
&- \frac{13402462074996214041574451\,v^{14}}{75486083802436576808952276451940352 00} \\
&- \frac{17912278159753857466538125767254 11\,v^{16}}{28980344687817070918992902973685639815168000 00} \\
&- \frac{71236245323783632117323259820548586866076243\,v^{18}}{54266734782769746715080799933921219788753611631820800000 0} + \cdots
\end{aligned}$$

$$\begin{aligned}
b_2 &= -\frac{19970}{95823} + \frac{268231049\,v^{10}}{98272624491709668} + \frac{709836811410718063\,v^{12}}{230431782031021801659356928 0} \\
&+ \frac{97656730833408766110195611 9\,v^{14}}{18871520950609144202238069112985088000} \\
&+ \frac{95518844325726650959382894630347\,v^{16}}{10121811563759638740089433023897558023680000} \\
&+ \frac{71126707403604459863545762870680798756023011\,v^{18}}{41933385968503895188926072676211851654945972624588800000} + \cdots
\end{aligned}$$

$$
\begin{aligned}
a_1 &= -\frac{2793}{26878564} - \frac{7901\,v^8}{24613731926784} - \frac{2318230486344757\,v^{10}}{306609942157708473123840000} \\
&- \frac{4183375481971169560933 1\,v^{12}}{29541451658809034920096119398400000} \\
&- \frac{120687447714040670536331310419693\,v^{14}}{476227377868760475385058174299076666534400000} \\
&- \frac{3245293282551203463180274043267924530289 9\,v^{16}}{722067080598836680773653438655425481708730122240000000} \\
&- \frac{8419813153869698775909990314240348924870286575527\,v^{18}}{10581990978472080758991804050901542110136759645231775744000000 0} + \cdots
\end{aligned}
$$

$$
a_4 = -2 - \frac{134317\,v^{16}}{15752663892725760} - \frac{23669085961481\,v^{18}}{23085742540911986641305600} + \cdots \tag{11}
$$

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

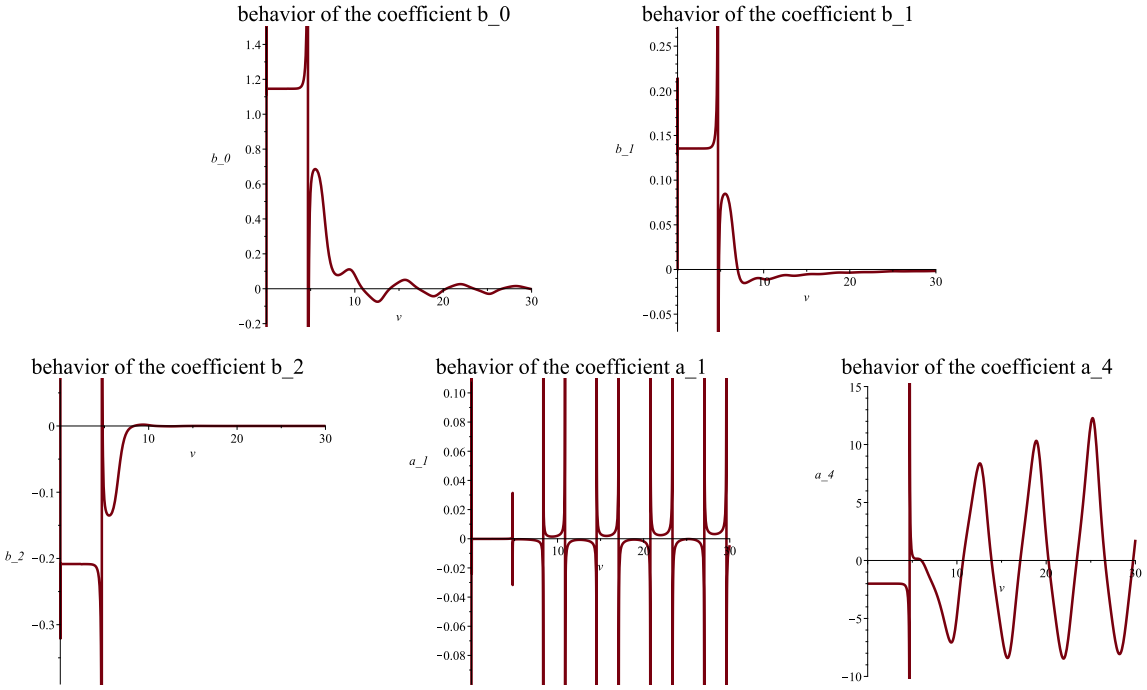

Figure 1: Behavior of the coefficients of the new proposed method for several values of $v = \phi h$.

Below we give the formula of the Local Truncation Error of the new proposed Five–Stages Two–Step Method (9), which is indicated as: *NM2S5S4DV* :

$$LTE_{NM2S5S4DV} = \frac{134317}{551343236245401600} h^{16} \left(y_n^{(16)} - 70\,\phi^8\, y_n^{(8)} - 224\,\phi^{10}\, y_n^{(6)} \right.$$
$$\left. -280\,\phi^{12}\, y_n^{(4)} - 160\,\phi^{14}\, y_n^{(2)} - 35\,\phi^{16}\, y_n \right) + O\left(h^{18}\right). \tag{12}$$

3. Analysis of the Method

3.1. Error Analysis

In order to study the local truncation error formula of the new proposed method, we use the following test equation :

$$y''(x) = (V(x) - V_c + G)\, y(x) \tag{13}$$

where

- $V(x)$ is a potential function,
- V_c a constant value approximation of the potential for the specific x,
- $G = V_c - E$ and E is the energy.

Remark 3.1. *The test equation (13) which is use for the local truncation error analysis is the radial time independent Schrödinger equation.*

The following methods will be studied :

3.1.1. Classical Method (i.e., Method (9) with Constant Coefficients)

$$LTE_{CL} = \frac{134317}{551343236245401600} h^{16}\, y_n^{(16)} + O\left(h^{18}\right). \tag{14}$$

3.1.2. The Five–Stages Two–Step Method with Vanished Phase–Lag and Its First, Second and Third Derivatives Developed in [61]

$$LTE_{NM2S5S3DV} = \frac{134317}{551343236245401600} h^{16} \left(y_n^{(16)} + 56\,\phi^{10}\, y_n^{(6)} + 140\,\phi^{12}\, y_n^{(4)} \right.$$
$$\left. +120\,\phi^{14}\, y_n^{(2)} + 35\,\phi^{16}\, y_n \right) + O\left(h^{18}\right). \tag{15}$$

3.1.3. The Five–Stages Two–Step Method with Vanished Phase–Lag and Its First, Second, Third and Fourth Derivatives Developed in Section 2.

$$LTE_{NM2S5S4DV} = \frac{134317}{551343236245401600} h^{16} \left(y_n^{(16)} - 70\,\phi^8\, y_n^{(8)} - 224\,\phi^{10}\, y_n^{(6)} \right.$$
$$\left. -280\,\phi^{12}\, y_n^{(4)} - 160\,\phi^{14}\, y_n^{(2)} - 35\,\phi^{16}\, y_n \right) + O\left(h^{18}\right). \tag{16}$$

In order to study the local truncation error formulae, we substitute the higher order derivatives, which are requested in the LTE formulae (14) - (16) given above, by the formulae produced using the test problem (13). Consequently , we obtain the new formulae of LTE with general form :

$$LTE = h^p \sum_{i=0}^{m} a_i G^i . \tag{17}$$

where a_i are constant numbers (classical methods) or formulae of ϕ (fitted methods) and p is the algebraic order of the specific method.

We investigate two cases for the parameter G :

- **The Energy and the Potential are closed each other.** Consequently, $G = V_c - E \approx 0 \Rightarrow G^i = 0$, $i = 1, 2, \ldots$.

  Consequently,

  - the local truncation error for the classical method (constant coefficients)
  - the local truncation error for the five–stages two–step method with eliminated phase–lag and its first, second and third derivatives developed in [61]
  - the local truncation error for the five–stages two–step method with eliminated phase–lag and its first, second, third and fourth derivatives developed in Section 2

  are the same since the formulae of the LTE are free from G (i.e. $LTE = h^p a_0$ in (14)) and the free from G terms in the local truncation errors are the same in the above mentioned three cases. Therefore, for these values of G, the above mentioned three methods are of comparable accuracy.

- **The Energy is much larger or much smaller then the Potential.** Therefore, $G = V_c - E >> 0$ or $G = V_c - E << 0$ and $|G| >> 0$. Consequently, the most accurate method is the method with the minimum power of G in the formula of LTE (i.e. the most accurate method is the method with minimum i in (17)).

In the following we present the asymptotic expansions of the Local Truncation Errors :

3.1.4. Classical Method

$$LTE_{CL} = \frac{134317}{5513432362454016 00} h^{16} \left(y(x)\ G^8 + \cdots \right) + O\left(h^{18}\right). \tag{18}$$

3.1.5. The Four–Stages Two–Step P–Stable Method with Vanished Phase–Lag and Its First, Second and Third Derivatives Developed in [61]

$$LTE_{NM2S5S3DV} = \frac{134317}{9845414932953600} h^{16} \left[\left(20\, g(x)\ y(x)\ \frac{\mathrm{d}^2}{\mathrm{d}x^2} g(x) + 15 \left(\frac{\mathrm{d}}{\mathrm{d}x} g(x) \right)^2 y(x) \right.\right.$$
$$\left.\left. +10 \left(\frac{\mathrm{d}^3}{\mathrm{d}x^3} g(x) \right) \frac{\mathrm{d}}{\mathrm{d}x} y(x) + 31 \left(\frac{\mathrm{d}^4}{\mathrm{d}x^4} g(x) \right) y(x) \right) G^5 + \cdots \right] + O\left(h^{18}\right). \tag{19}$$

3.1.6. The Five–Stages Two–Step Method with Vanished Phase–Lag and Its First, Second, Third and Fourth Derivatives Developed in Section 2.

$$LTE_{NM2S5S4DV} = \frac{134317}{615338433309600} h^{16} \left[\left(\left(\frac{\mathrm{d}^4}{\mathrm{d}x^4} g(x) \right) y(x) \right) G^5 + \cdots \right] + O\left(h^{18}\right). \tag{20}$$

The above analysis leads to the following theorem:

Theorem 3.2.

- *Classical Method (i.e., the method (9) with constant coefficients): For this method the error increases as the eighth power of G.*
- *Fourteenth Algebraic Order Five–Stages Two–Step Method with Vanished Phase–lag and its First, Second and Third Derivatives developed in [61]: For this method the error increases as the fifth power of G.*
- *Fourteenth Algebraic Order Five–Stages Two–Step Method with Vanished Phase–lag and its First, Second, Third and Fourth Derivatives developed in Section 2: For this method the error increases as the fifth power of G but with lower coefficient than the method developed in [61].*

Consequently, for large values of $|G| = |V_c - E|$, the new proposed fourteenth algebraic order five–stages two–step method with vanished phase–lag and its first, second, third and fourth derivatives developed in Section 2 is the most accurate method for the numerical solution of the radial Schrödinger equation .

3.2. Stability and Interval of Periodicity Analysis

The scalar test equation which will be used for the stability and interval of periodicity analysis is give by :

$$y'' = -\omega^2 y\,. \tag{21}$$

Remark 3.3. *The comparison of the test equations (5) and (21) leads to the conclusion that the frequency ϕ is not equal with the frequency ω, i.e., $\omega \neq \phi$.*

The application of the new method (9) to the scalar test equation (21) leads to the following difference equation :

$$A_1(s,v)\,(y_{n+1} + y_{n-1}) + A_0(s,v)\,y_n = 0$$

where

$$\begin{aligned} A_1(s,v) &= 1 + \frac{1}{8}\,(8\,b_1 + 4\,b_2)\,s^2 + \frac{1}{8}\,b_2\,(-8\,a_3 + 1)\,s^4 \\ &+ 4\,a_3\,b_2\left(v^2\,a_0\,a_2 + \frac{1}{2}\,a_1\right)s^6 - 4\,a_0\,a_1\,a_3\,b_2\,s^8 \\ A_0(s,v) &= a_4 + (b_0 + b_2)\,s^2 + 4\,a_3\,b_2\left(v^2\,a_2 + \frac{1}{2}\right)s^4 \\ &- 8\,a_3\,b_2\left(v^2\,a_0\,a_2 + \frac{1}{2}\,a_1\right)s^6 + 8\,a_0\,a_1\,a_3\,b_2\,s^8 \end{aligned} \tag{22}$$

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

Substituting the coefficients a_i, $i = 0, 1$ and b_i, $i = 0(1)2$ into the formulae (22), we obtain the new stability polynomials given by :

$$A_1(s,v) = \frac{T_{10}}{T_{denom4}} \quad , \quad A_0(s,v) = \frac{T_{11}}{T_{denom5}}$$

where the formulae T_k, $k = 10, 11$, T_{denom4} and T_{denom5} are given in the [24].

The $s - v$ plane of the new produced method is shown in Figure 2 .

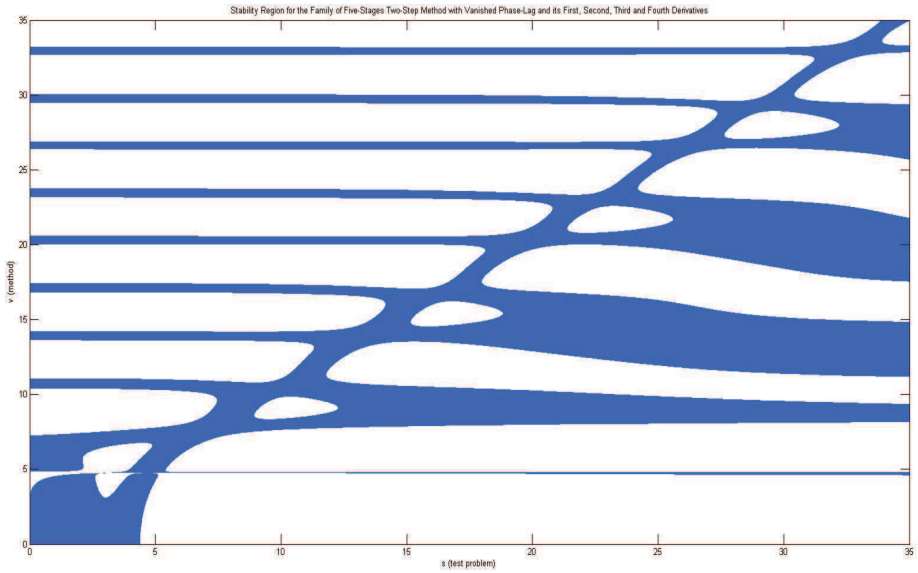

Figure 2: $s-v$ plane of the new obtained five–stages symmetric two–step fourteenth algebraic order method with vanished phase–lag and its first, second, third and fourth derivatives.

Remark 3.4. *The observation of the $s-v$ area leads to the following conclusion:*

- *The shadowed region of the $s-v$ area defines the space where the method is stable,*
- *The white region of the $s-v$ area defines the space where the method is unstable.*

The most of the real problems in sciences and engineering contain mathematical models which request the knowledge of one frequency per differential equation. In this category of problems belongs the coupled equations arising from the Schrödinger equation and the related problems in quantum chemistry, material science, theoretical physics, atomic physics, astronomy, astrophysics, physical chemistry and chemical physics. For these cases the critical region of the $s-v$ area is the surroundings of the first diagonal of the $s-v$ plane, where $s=v$. Investigating this region, we found that the interval of periodicity is equal to: $(0,\infty)$.

The intervals of periodicity of similar methods are presented in Table 1:

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 five–stages symmetric two–step fourteenth algebraic order method of the same form

Method	Interval of Periodicity
Method developed in [61]	$(0,24)$
Method developed in Section 2	$(0,\infty)$

The above analysis leads to the following theorem:

Theorem 3.5. *The five–stages symmetric two–step method developed in Section 2:*

- *is of fourteenth algebraic order,*

- *has vanished the phase–lag and its first, second, third and fourth derivatives*
- *has an interval of periodicity equals to:* $(0, \infty)$ *(when* $s = v$*)*

4. Numerical Results

The new proposed method will be tested on the numerical solution of coupled differential equations arising from the Schrödinger equation.

4.1. Error Estimation

The coupled differential equations of the Schrödinger type will be solved numerically using variable–step algorithms.

Definition 4.1. *We call a method of variable–step form if the basis of this method is the change of the step length.*

Remark 4.2. *In the above variable–step method, the change of the stepsize is based on the local truncation error estimation (LTEE) procedure in the case of our numerical experiments.*

In the last decades algorithms of constant or variable steps have been produced for the numerical solution of coupled differential equations arising from the Schrödinger equation (see for example [3]-[60]) .

For the purpose of our numerical experiments, an embedded pair is used.

Remark 4.3. *Symmetric multistep methods with the maximal possible algebraic order obtain highly accurate numerical solutions for oscillatory and/or periodical problems.*

Definition 4.4. *The local truncation error control in* y_{n+1}^L *is based on the formula:*

$$LTE = \mid y_{n+1}^H - y_{n+1}^L \mid \tag{23}$$

where y_{n+1}^L *gives the lower algebraic order solution which is obtained using the twelfth algebraic order method developed in [60] and* y_{n+1}^H *gives the higher order solution which is obtained using the five stages symmetric two–step method of fourteenth algebraic order with vanished phase-lag and its first, second, third and fourth derivatives obtained in Section 3.*

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 which is used for the n^{th} step of the integration and acc is the requested accuracy for the local error LTE. From the procedure used it is easy to see the changes of the step sizes are reduced on duplication or halving of them.
Additionally, we use also the technique of the local extrapolation which is defined as follows:

Definition 4.5. *Local extrapolation is the technique in which in every step of integration we use the approximation* y_{n+1}^H *although for the control of the LTE if it is less than acc the approximation* y_{n+1}^L *is used.*

4.2. Coupled differential equations

Problems which are expressed via coupled differential equations of the Schrödinger type can be observed in quantum chemistry, material science, theoretical physics, atomic physics, physical chemistry, theoretical chemistry, chemical physics, electronics etc.

The close-coupling differential equations arising from the Schrödinger equation are give by:

$$\mathbf{y}'' = -\mathbf{F}\,\mathbf{y} \tag{24}$$

where

$$F_{ij} = \frac{l_i(l_i+1)}{x^2}\,\delta_{ij} + V_{ij} \tag{25}$$

and $V_{ij} \to 0$ as $x \to \infty$.

Since we will investigate the open channels case, the following boundary conditions are hold (see for details [1]):

$$y_{ij} = 0 \; at \; x = 0 \tag{26}$$

$$y_{ij} \sim k_i x j_{l_i}(k_i x)\delta_{ij} + \left(\frac{k_i}{k_j}\right)^{1/2} K_{ij} k_i x n_{li}(k_i x) \tag{27}$$

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

In [1] detailed description of the problem is presented.

For our numerical experiments we use the following parameters:

$$\frac{2\mu}{\hbar^2} = 1000.0,\ \frac{\mu}{I} = 2.351,\ E = 1.1,$$
$$V_0(x) = \frac{1}{x^{12}} - 2\frac{1}{x^6},\ V_2(x) = 0.2283 V_0(x).$$

We follow the numerical procedure fully presented in [1]. Taken $J = 6$, we consider excitation of the rotator from the $j = 0$ state to levels up to $j' = 2, 4$ and 6 and consequently, we have sets of **four, nine and sixteen coupled differential equations**, respectively. Following the methodology obtained by Bernstein [7] and Allison [1], the potential is considered infinite for values of x less than some x_0.

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}. We 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	0.14	3.4×10^{-7}
	9	0.448	1.37	5.8×10^{-7}
	16	0.448	9.58	8.2×10^{-7}
Method VI	4	0.448	0.09	2.9×10^{-7}
	9	0.448	1.10	4.5×10^{-7}
	16	0.448	8.57	7.4×10^{-7}
Method VII	4	0.448	0.06	1.3×10^{-7}
	9	0.448	1.04	1.7×10^{-7}
	16	0.448	7.58	2.9×10^{-7}
Method VIII	4	0.448	0.04	9.7×10^{-8}
	9	0.448	1.01	1.2×10^{-7}
	16	0.448	7.15	2.3×10^{-7}
Method IX	4	0.448	0.04	8.8×10^{-8}
	9	0.448	1.02	9.2×10^{-8}
	16	0.448	7.48	8.9×10^{-8}
Method X	4	0.896	0.01	6.5×10^{-8}
	9	0.896	0.41	5.1×10^{-8}
	16	0.896	6.06	6.0×10^{-8}

The following variable step methods are used for comparison purposes:

- **Method I**: the Iterative Numerov method of Allison [1],
- **Method II**: the variable-step method of Raptis and Cash [42],
- **Method III**: the embedded Runge-Kutta Dormand and Prince method 5(4) [12],
- **Method IV**: the embedded Runge-Kutta method ERK4(2) developed in Simos [52],
- **Method V**: the embedded symmetric two-step method developed in [31],
- **Method VI**: the embedded symmetric two-step method developed in [26],
- **Method VII**: the embedded symmetric two-step method developed in [26],
- **Method VIII**: the embedded symmetric two-step method developed in [60],
- **Method IX**: the embedded symmetric two-step method developed in [62],
- **Method X**: the developed embedded symmetric two-step method developed in this paper.

In Table 2 we present the requested the methods mentioned above real time of computation for the calculation of the square of the modulus of the **S** matrix for sets of 4, 9 and 16 coupled differential equations. The maximum error in the computation of the square of the modulus of the **S** matrix is also presented in the same Table. We mention that N represents the number of equations of the set of coupled differential equations.

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

5. Conclusions

In the paper we developed a new five stages symmetric two-step of fourteenth algebraic order method with eliminated phase-lag and its first, second, third and fourth derivatives. We have also presented the analysis of the method (error analysis and stability analysis) as well as the application of the new developed method to coupled differential equations arising from the Schrödinger equation.

Based on the above, we concluded that the new obtained method is much more efficient than known ones for the numerical integration of the Schrödinger equation and related problems.

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References

[1] A. C. Allison, The numerical solution of coupled differential equations arising from the Schrödinger equation, *J. Comput. Phys.* **6 (3)** (1970) 378–391.
[2] A. C. Allison and A. Dalgarno, The rotational excitation of molecular hydrogen, *Proceedings of the Physical Society* **90 (3)** 609-614 (1967).
[3] 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 (16)** (2012) 3880–3889.
[4] Z. A. Anastassi, T. E. Simos, An optimized Runge–Kutta method for the solution of orbital problems, *J. Comput. Appl. Math.* **175 (1)** (2005) 1–9.
[5] P. Atkins, R. Friedman, *Molecular Quantum Mechanics*, Oxford Univ. Press, Oxford, 2011.
[6] R. B. Bernstein, A. Dalgarno, H. Massey , I. C. Percival, Thermal scattering of atoms by homonuclear diatomic molecules, *Proc. Roy. Soc. Ser. A* **274 (No. 1359)** (1963) 427–442.
[7] R. B. Bernstein, Quantum mechanical (phase shift) analysis of differential elastic scattering of molecular beams, *J. Chem. Phys.* **3 (3)** (1960) 795–804.
[8] 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 (3)** (1986) 329–337.
[9] 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 (3)** (1987) 363—368.
[10] C. J. Cramer, *Essentials of Computational Chemistry*, Wiley, Chichester, 2004.
[11] J. R. Dormand, M. E. A. El–Mikkawy, P. J. Prince, Families of Runge–Kutta–Nyström formulae, *IMA J. Numer. Anal.* **7 (2)** (1987) 235–250.
[12] J. R. Dormand, P. J. Prince, A family of embedded Runge–Kutta formulae, *J. Comput. Appl. Math.* **6 (1)** (1980) 19–26.
[13] J. M. Franco, M. Palacios, High–order *P*-stable multistep methods, *J. Comput. Appl. Math.* **30 (1)** (1990) 1–10.
[14] Fei Hui and Theodore E. Simos, Four Stages Symmetric Two-Step P-Stable Method With Vanished Phase-Lag And Its First, Second, Third and Fourth Derivatives, *Appl. Comput. Math.* **15 (2)** 220-238(2016)
[15] L. G. Ixaru, M. Rizea, Comparison of some four–step methods for the numerical solution of the Schrödinger equation, *Comput. Phys. Commun.* **38 (3)** (1985) 329–337.
[16] L. G. Ixaru, M. Micu, *Topics in Theoretical Physics*, Central Institute of Physics, 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 (1)** (1980) 23–27.
[18] F. Jensen, *Introduction to Computational Chemistry*, Wiley, Chichester, 2007.
[19] 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 (6)** (2010) 1639–1647.
[20] Z. Kalogiratou, Th. Monovasilis, Higinio 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.
[21] 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)** (2011) 3381–3390.
[22] J. D. Lambert, I. A. Watson, Symmetric multistep methods for periodic initial values problems, *J. Inst. Math. Appl.* **18 (2)** (1976) 189–202.
[23] J. D.Lambert, *Numerical Methods for Ordinary Differential Systems. The Initial Value Problem*, Wiley, New York, 1991, pp. 104–107.
[24] `http://www.icnaam.org/documents/Detailed_Computations_Filomat.pdf`
[25] A. R. Leach, *Molecular Modelling – Principles and Applications*, Pearson, Essex, 2001.
[26] Minjian Liang and T. E. Simos, A new four stages symmetric two-step method with vanished phase-lag and its first derivative for the numerical integration of the Schrödinger equation, *J. Math. Chem.* **54** 1187-1211 (2016).
[27] T. Lyche, Chebyshevian multistep methods for ordinary differential eqations, *Numer. Math.* **19 (1)** (1972) 65–75.
[28] T. Monovasilis, Z. Kalogiratou, T. E. Simos, A family of trigonometrically fitted partitioned Runge–Kutta symplectic methods, *Appl. Math. Comput.* **209(1)** (2009) 91–96.
[29] T. Monovasilis, Z. Kalogiratou, T. E. Simos, Exponentially fitted symplectic Runge–Kutta–Nyström methods, *Appl. Math. Inf. Sci.* **7 (1)** (2013) 81–85.
[30] T. Monovasilis, Z. Kalogiratou and T. E. Simos, Construction of Exponentially Fitted Symplectic RungeKuttaNyström Methods from Partitioned RungeKutta Methods, *Mediterr. J. Math.*, **13** (2016) 2271–2285.

[31] Kenan Mu and T. E. Simos, A Runge-Kutta type implicit high algebraic order two-step method with vanished phase-lag and its first, second, third and fourth derivatives for the numerical solution of coupled differential equations arising from the Schrödinger equation, *J Math. Chem.* **53 (5)** (2015) 1239–1256
[32] Hang Ning and T. E. Simos, A low computational cost eight algebraic order hybrid method with vanished phase-lag and its first, second, third and fourth derivatives for the approximate solution of the Schrödinger equation, *J. Math. Chem.* **53 (6)** (2015) 12951312
[33] G. A. Panopoulos and 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
[34] 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 (1)** (2013) 73–80.
[35] 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 (2)** (2014) 703–713.
[36] 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 (2)** (2013) 433–437.
[37] 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.
[38] G. D. Quinlan, S. Tremaine, Symmetric multistep methods for the numerical integration of planetary orbits, *Astronom. J.* **100 (5)** (1990) 1694–1700.
[39] Higinio Ramos, Z. Kalogiratou, Th. Monovasilis, T. E. Simos, An optimized two-step hybrid block method for solving general second order initial-value problems, *Numerical Algorithms*, **72** 1089-1102 (2016)
[40] A. D. Raptis, A. C. Allison, Exponential–fitting methods for the numerical solution of the Schrödinger equation, *Comput. Phys. Commun.* **14 (1-2)** (1978) 1–5.
[41] A. D. Raptis, T. E. Simos, A four–step phase–fitted method for the numerical integration of second order initial–value problem, *BIT* **31 (1)** (1991) 160–168.
[42] 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)** (1985) 113–119.
[43] 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)** (2005) 161–172.
[44] T. E. Simos, Dissipative trigonometrically–fitted methods for linear second-order IVPs with oscillating solution, *Appl. Math. Lett.* **17 (5)** (2004) 601–607.
[45] T. E. Simos, Closed Newton–Cotes trigonometrically–fitted formulae of high order for long–time integration of orbital problems, *Appl. Math. Lett.* **22 (10)** (2009) 1616–1621.
[46] T. E. Simos, Exponentially and trigonometrically fitted methods for the solution of the Schrödinger equation, *Acta Appl. Math.* **110 (3)** (2010) 1331–1352.
[47] T. E. Simos, New stable closed Newton–Cotes trigonometrically fitted formulae for long–time integration, *Abstract Appl. Anal.* (2012) #182536.
[48] 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.
[49] T. E. Simos, High order closed Newton–Cotes trigonometrically–fitted formulae for the numerical solution of the Schrödinger equation, *Appl. Math. Comput.* **209 (1)** (2009) 137–151.
[50] T. E. Simos, P. S. Williams, A finite–difference method for the numerical solution of the Schrödinger equation, *J. Comp. Appl. Math.* **79 (2)** (1997) 189–205.
[51] T. E. Simos, On the explicit four–step methods with vanished phase–lag and its first derivative, *Appl. Math. Inf. Sci.* **8 (2)** (2014) 447–458.
[52] T. E. Simos, Exponentially fitted Runge–Kutta methods for the numerical solution of the Schrödinger equation and related problems, *Comput. Mater. Sci.* **18 (3-4)** (2000) 315–332.
[53] Theodore E. Simos, Multistage Symmetric Two-Step P-Stable Method With Vanished Phase-Lag And Its First, Second And Third Derivatives, *Appl. Comput. Math.* **14 (3)** 296-315(2015)
[54] 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)** (2009) 2467–2474.
[55] E. Stiefel, D. G. Bettis, Stabilization of Cowell's method, *Numer. Math.* **13 (2)** (1969) 154–175.
[56] R. M. Thomas, Phase properties of high order almost *P*-stable formulae, *BIT* **24(2)** (1984) 225–238.
[57] 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)** (2005) 173–181.
[58] C. Tsitouras, I. T. Famelis, T. E. Simos, On modified Runge–Kutta trees and methods, *Comput. Math. Appl.* **62 (4)** (2011) 2101–2111.
[59] 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 (2)** (2010) 363–378.
[60] Xiaopeng Xi and T. E. Simos, A new high algebraic order four stages symmetric two-step method with vanished phase-lag and its first and second derivatives for the numerical solution of the Schrödinger equation and related problems, *J. Math. Chem.* **54 (7)** 1417-1439(2016).
[61] Licheng Zhang and Theodore E. Simos, An Efficient Numerical Method for the Solution of the Schrödinger Equation, *Advances in Mathematical Physics* in press
[62] Zhou Zhou and T. E. Simos, A new two stage symmetric two-step method with vanished phase-lag and its first, second, third and fourth derivatives for the numerical solution of the radial Schrödinger equation, *J. Math. Chem.* **54** 442-465 (2016).