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Trigonometrically-Fitted Multiderivative Methods for the Numerical Solution of the radial Schrödinger Equation

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Abstract

In this paper trigonometrically-fitted multiderivative methods are developed for the numerical solution of the radial Schrödinger equation. The methods are called multiderivative since uses derivatives of order two and four. A numerical illustration of the new developed method to the the resonance problem of the radial Schrödinger equation shows its efficiency compared with other similar well known methods of the literature.

1 Introduction

The radial Schrödinger equation has the form:

$$y''(r) = [l(l+1)/r^2 + V(r) - k^2]y(r). \tag{1}$$

Differential equations of this type, which represent a boundary value problem, occur frequently in theoretical physics and chemistry, material sciences, quantum mechanics and quantum chemistry, electronics etc. (see for example [1] - [4]).

In the following we give some definitions for (1):

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- The function $W(r) = l(l+1)/r^2 + V(r)$ is called *the effective potential.* This satisfies $W(r) \to 0$ as $r \to \infty$
- k^2 is a real number denoting *the energy*
- l is a given integer representing *angular momentum*
- V is a given function which denotes the potential.
- The boundary conditions are:

$$y(0) = 0 \tag{2}$$

and a second boundary condition, for large values of r, determined by physical considerations.

From the literature is known that the last decades many numerical methods have been developed for the numerical solution of the Schrödinger equation (see [5] - [9] and [10] - [24]). The result of the above activity was the development of fast and reliable methods. The numerical methods for the numerical solution of the Schrödinger equation can be divided into two main categories:

1. Methods with constant coefficients
2. Methods with coefficients dependent on the frequency of the problem [1].

In this paper we will investigate methods of the second category.

In this paper we introduce an explicit trigonometrically-fitted multiderivative method for the numerical solution of the radial Schrödinger equation. The method is called multiderivative since it includes second and fourth derivative of the function. We apply the new obtained method to the resonance problem of the Schrödinger equation. In this illustration we use, for comparison purposes, the Numerov's method and the exponentially-fitted Numerov-type method of Raptis and Allison [25]. The above application shows the efficiency of the new developed method.

[1] In the case of the radial Schrödinger equation the frequency of the problem is equal to: $\sqrt{|l(l+1)/r^2 + V(r) - k^2|}$

2 A New Family Of Multiderivative Methods

We introduce the following family of methods to integrate $y'' = f(x)\,y(x)$:

$$\bar{y}_{n+1} = 2\,y_n - y_{n-1} + a_0\,h^2\,y''_n + a_1\,h^4\,y^{(4)}_n \tag{3}$$

$$y_{n+1} = 2\,y_n - y_{n-1} + h^2\left[c_0\,y''_n + c_1\left(\bar{y}''_{n+1} + y''_{n-1}\right)\right] + h^4\left[c_2\,y^{(4)}_n + c_3\left(\bar{y}^{(4)}_{n+1} + y^{(4)}_{n-1}\right)\right] \tag{4}$$

where $y''_{n\pm i} = f_{n\pm i}\,y_{n\pm i}$, $y^{(4)}_{n\pm i} = \left(f''_{n\pm i} + f^2_{n\pm i}\right)\,y_{n\pm i} + 2\,f'_{n\pm i}\,y'_{n\pm i}$ and $i = -1(1)1$. We note also that $\bar{y}''_{n+1} = f_{n+1}\,\bar{y}_{n+1}$ where $\bar{y}_{n+1}$ is calculated from the relation (3). It is easy to see that in order the above method (3)-(4) to be applicable, then approximate schemes for the first derivatives of y are needed.

2.1 Construction of the Trigonometrically-Fitted scheme for (3)

In order the stage (3) of the above method to integrate exactly any linear combination of the functions:

$$\{\ \cos(\pm v\,x),\ \sin(\pm v\,x),\ x\,\cos(\pm v\,x),\ x\,\sin(\pm v\,x)\ \} \tag{5}$$

the appropriate parameters of the new method are the solution of a system of equations, which is produced in the following way:

We calculate $y_{n\pm i}$, $i = -1(1)1$, and $y''_n = f_n\,y_n$, $y^{(4)}_n = (f''_n + f^2_n)\,y_n + 2\,f'_n\,y'_n$ for $y(x) = \cos(v\,x)$, $y(x) = \sin(v\,x)$ and $y(x) = x\,\cos(v\,x)$, $y(x) = x\,\sin(v\,x)$. So, the following system of equations is hold:

$$2\cos(w) - 2 = w^2\left(-a_0 + a_1\,w^2\right) \tag{6}$$

$$2\sin(w) = 2\,w\,a_0 - 4\,w^3\,a_1 \tag{7}$$

where $w = v\,h$.

Solving the system in the previous section eqs. (6)-(7), we obtain the parameters of the first layer of the new method, which are:

$$a_0 = \frac{-w\sin(w) - 4\cos(w) + 4}{w^2},$$
$$a_1 = \frac{-2\cos(w) + 2 - w\sin(w)}{w^4} \tag{8}$$

The above parameters a_i, $i = 0, 1$ converted into its Taylor series expansions which are given below.

$$a_0 = 1 - \frac{1}{360}w^4 + \frac{1}{10080}w^6 - \frac{1}{604800}w^8 + \frac{1}{59875200}w^{10} - \frac{1}{8717829120}w^{12} + \ldots$$
$$a_1 = \frac{1}{12} - \frac{1}{180}w^2 + \frac{1}{6720}w^4 - \frac{1}{453600}w^6 + \frac{1}{47900160}w^8 - \frac{1}{7264857600}w^{10} + \frac{1}{1494484992000}w^{12} + \ldots \tag{9}$$

In Figure 1 we present the behavior of the quantities a[0] = a_0 and a[1] = a_1, where a_i, $i = 0\,1$ are given by (8).

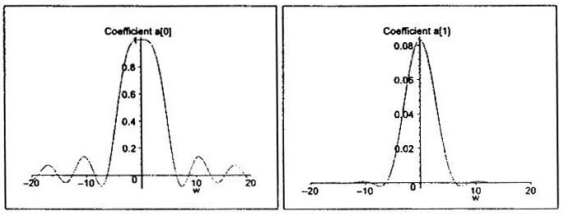

Figure 1: Behavior of the coefficients a_i, $i = 0, 1$ given by (8)

2.2 Construction of the Trigonometrically-Fitted scheme for (4)

In order the stage (4) of the above method to integrate exactly any linear combination of the functions:

$$\{\ 1,\ x,\ x^2,\ x^3,\ x^4,\ x^5,\ \cos(\pm v\,x), \sin(\pm v\,x),\ x\cos(\pm v\,x),\ x\sin(\pm v\,x)\ \} \tag{10}$$

the appropriate parameters of the new method are the solution of a system of equations, which is produced in the following way:

We calculate $y_{n\pm i}$, and $y''_{n\pm i} = f_{n\pm i}\, y_{n\pm i}$, $y^{(4)}_{n\pm i} = \left(f''_{n\pm i} + f^2_{n\pm i}\right) y_{n\pm i} + 2\, f'_{n\pm i}\, y'_{n\pm i}$, $i = -1(1)1$ for $y(x) = x^n$, $n = 0(1)5$, for $y(x) = \cos(v\,x)$, $y(x) = \sin(v\,x)$ and for $y(x) = x\cos(v\,x)$, $y(x) = x\sin(v\,x)$. So, the following system of equations is hold:

$$2 = 2\,c_0 + 4\,c_1, \tag{11}$$

$$2 = 24\,c_1 + 24\,c_2 + 48\,c_3, \tag{12}$$

$$2\cos(w) - 2 = w^2\left(-2\cos(w)\,c_1 + 2\cos(w)\,c_3\,w^2 - c_0 + c_2\,w^2\right), \tag{13}$$

$$\begin{aligned} 2\sin(w) = -2\,w\big(&4\cos(w\,h)\,c_3\,w^2 - 2\cos(w)\,c_1 + c_1\,w\sin(w) - c_0 \\ &+2\,c_2\,w^2 - c_3\,w^3\sin(w)\big) \end{aligned} \tag{14}$$

where $w = v\,h$.

The solution of eqs. (11)-(12) gives us the parameters c_i, $i = 0(1)2$ as function of c_0:

$$\begin{aligned} c_2 &= -\frac{5}{12} - 2\,c_3 + \frac{1}{2}\,c_0 \\ c_1 &= \frac{1}{2} - \frac{1}{2}\,c_0 \end{aligned} \tag{15}$$

Based on (15) and eq. (13)-(14) we have the parameters c_0 and c_3:

$$\begin{aligned} c_0 &= \frac{Q_a}{Q_b} \\ c_0 &= \frac{Q_c}{Q_d} \end{aligned} \tag{16}$$

$$\begin{aligned} Q_a = &-12\,w^3 + 96\sin(w) - 5\,w^5 - 12\,w^3\cos(w) \\ &-48\sin(2\,w) - 12\,w^2\sin(2\,w) - 5\cos(w)\,w^5 \end{aligned}$$

$$Q_b = -6\,w^5 + 24\,w^2\sin(w) - 6\cos(w)\,w^5 - 12\,w^2\sin(2\,w)$$

$$\begin{aligned} Q_c = &\,24\,w^4\cos(w) + 22\,w^4 + w^5\sin(2\,w) \\ &+2\,w^5\sin(w) - 24\cos(w) + 24\cos(3\,w) + 48 \end{aligned}$$

$$-48\cos(2w) - 48w^2 + 48w^2\cos(2w) + 2w^4\cos(2w)$$

$$Q_d = 24\sin(w)w^7 - 48w^4 + 48w^4\cos(2w)$$

$$+12w^7\sin(2w) + 24w^4\cos(w) - 24w^4\cos(3w)$$

The above parameters c_i, $i = 0, 3$ converted into its Taylor series expansions which are given below.

$$c_0 = \frac{115}{126} - \frac{59}{79380}w^2 - \frac{25}{22004136}w^4 + \frac{114643}{3604277476800}w^6 + \frac{1597}{6986753262720}w^8 - \frac{65050859}{1070042222445356160000}w^{10} - \frac{740921261}{5123362161068365294080 0}w^{12} + \ldots$$

$$c_3 = -\frac{13}{15120} - \frac{59}{1905120}w^2 - \frac{43387}{52809926400}w^4 - \frac{163057}{7863878131200}w^6 - \frac{57265111}{108993350898432000}w^8 - \frac{2636607443}{197546256451450368000}w^{10} - \frac{16655985752267}{491842767462563068231680 00}w^{12} + \ldots \quad (17)$$

In Figure 2 we present the behavior of the quantities c[0] = c_0 and c[3] = c_3 where c_i, $i = 0, 3$ are given by (16).

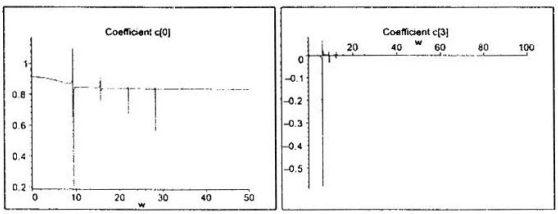

Figure 2: Behavior of the coefficient c_i, $i = 0, 3$ given by (16)

Based on the above coefficients we can find that the local truncation error of the above scheme (3)-(4) is given by:

$$L.T.E(h) = -\frac{11}{90720}h^8\left(y_n^{(6)} + 2w^2y_n^{(4)} + w^4y_n^{(2)}\right) \quad (18)$$

3 Computational Implementation

As we have mentioned previously, in order the above methods (3)-(4) to be applicable we need approximate schemes for the first derivatives of y. This is due to the following formula:

$$y^{(4)}_{n\pm i} = \left(f''_{n\pm i} + f^2_{n\pm i}\right) y_{n\pm i} + 2\, f'_{n\pm i}\, y'_{n\pm i} \text{and} i = -1(1)1. \tag{19}$$

The general formulae of the first derivatives on the points x_i, $i = n-1(1)n+1$ are given by:

$$\begin{aligned} h\, y'_{n+1} &= a_{2,n+1}\, y_{n+1} + a_{1,n+1}\, y_n + a_{0,n+1}\, y_{n-1} \\ &+h^2 \left(b_{2,n+1}\, y''_{n+1} + b_{1,n+1}\, y''_n + b_{0,n+1}\, y''_{n-1}\right) \end{aligned} \tag{20}$$

$$\begin{aligned} h\, y'_n &= a_{2,n}\, y_{n+1} + a_{1,n}\, y_n + a_{0,n}\, y_{n-1} \\ &+h^2 \left(b_{2,n}\, y''_{n+1} + b_{1,n}\, y''_n + b_{0,n}\, y''_{n-1}\right) \end{aligned} \tag{21}$$

$$\begin{aligned} h\, y'_{n-1} &= a_{2,n-1}\, y_{n+1} + a_{1,n-1}\, y_n + a_{0,n-1}\, y_{n-1} \\ &+h^2 \left(b_{2,n-1}\, y''_{n+1} + b_{1,n-1}\, y''_n + b_{0,n-1}\, y''_{n-1}\right) \end{aligned} \tag{22}$$

In order the formulae (20)-(22) to integrate exactly any linear combination of the functions:

$$\{\ 1,\ x,\ \cos(\pm v\, x), \sin(\pm v\, x),\ x\, \cos(\pm v\, x), x\, \sin(\pm v\, x)\ \} \tag{23}$$

the appropriate parameters of the above formulae are the solution of systems of equations, which is produced in the following way:

We calculate $y_{n\pm i}$, and $y''_{n\pm i} = f_{n\pm i}\, y_{n\pm i}$, $y'_{n\pm i}$ $i = -1(1)1$ for $y(x) = x^n$, $n = 0, 1$, for $y(x) = \cos(v\, x)$, $y(x) = \sin(v\, x)$ and for $y(x) = x\, \cos(v\, x)$, $y(x) = x\, \sin(v\, x)$. So, the following systems of equations are hold:

$$0 = a_{2,\,n+1} + a_{1,\,n+1} + a_{0,\,n+1} \tag{24}$$

$$h\,v\cos(h\,v) = \sin(h\,v)\left(a_{2,n+1} - a_{0,n+1} - h^2\,b_{2,n+1}\,v^2 + h^2\,b_{0,n+1}\,v^2\right) \tag{25}$$

$$-h\,v\sin(h\,v) = a_{2,n+1}\cos(h\,v) + a_{1,n+1}$$

$$+a_{0,n+1}\cos(h\,v) - h^2\,b_{2,n+1}\,v^2\cos(h\,v)$$

$$-h^2\,b_{1,n+1}\,v^2 - h^2\,b_{0,n+1}\,v^2\cos(h\,v) \tag{26}$$

$$h\,(\cos(h\,v)\,v\,x + h\,v\cos(h\,v) + \sin(h\,v))$$

$$= a_{2,n+1}\sin(h\,v)\,x + a_{2,n+1}\sin(h\,v)\,h$$

$$-a_{0,n+1}\sin(h\,v)\,x + a_{0,n+1}\sin(h\,v)\,h + 2\,h^2\,b_{2,n+1}\,v\cos(h\,v)$$

$$-h^2\,b_{2,n+1}\,v^2\sin(h\,v)\,x - h^3\,b_{2,n+1}\,v^2\sin(h\,v) + 2\,h^2\,b_{1,n+1}\,v$$

$$+2\,h^2\,b_{0,n+1}\,v\cos(h\,v) + h^2\,b_{0,n+1}\,v^2\sin(h\,v)\,x - h^3\,b_{0,n+1}\,v^2\sin(h\,v) \tag{27}$$

$$-h\,(-\cos(h\,v) + \sin(h\,v)\,v\,x + h\,v\sin(h\,v))$$

$$= a_{2,n+1}\cos(h\,v)\,x + a_{2,n+1}\cos(h\,v)\,h$$

$$+a_{1,n+1}\,x + a_{0,n+1}\cos(h\,v)\,x - a_{0,n+1}\cos(h\,v)\,h - 2\,h^2\,b_{2,n+1}\,v\sin(h\,v)$$

$$-h^2\,b_{2,n+1}\,v^2\cos(h\,v)\,x - h^3\,b_{2,n+1}\,v^2\cos(h\,v) - h^2\,b_{1,n+1}\,x\,v^2$$

$$+2\,h^2\,b_{0,n+1}\,v\sin(h\,v) - h^2\,b_{0,n+1}\,v^2\cos(h\,v)\,x + h^3\,b_{0,n+1}\,v^2\cos(h\,v) \tag{28}$$

$$0 = a_{2,n} + a_{1,n} + a_{0,n} \tag{29}$$

$$h\,v = \sin(h\,v)\left(a_{2,n} - a_{0,n} - h^2\,b_{2,n}\,v^2 + h^2\,b_{0,n}\,v^2\right) \tag{30}$$

$$0 = a_{2,n}\cos(h\,v) + a_{1,n} + a_{0,n}\cos(h\,v) - h^2\,b_{2,n}\,v^2\cos(h\,v)$$

$$-h^2\,b_{1,n}\,v^2 - h^2\,b_{0,n}\,v^2\cos(h\,v) \tag{31}$$

$$h\,v\,x = a_{2,n}\sin(h\,v)\,x + a_{2,n}\sin(h\,v)\,h$$

$$-a_{0,n}\sin(h\,v)\,x + a_{0,n}\sin(h\,v)\,h$$

$$+2\,h^2\,b_{2,n}\,v\cos(h\,v) - h^2\,b_{2,n}\,v^2\sin(h\,v)\,x - h^3\,b_{2,n}\,v^2\sin(h\,v)$$

$$+2\,h^2\,b_{1,n}\,v + 2\,h^2\,b_{0,n}\,v\cos(h\,v) + h^2\,b_{0,n}\,v^2\sin(h\,v)\,x$$

$$-h^3\,b_{0,n}\,v^2\sin(h\,v) \tag{32}$$

$$h = a_{2,n}\cos(h\,v)\,x + a_{2,n}\cos(h\,v)\,h + a_{1,n}\,x$$

$$+a_{0,n}\cos(h\,v)\,x - a_{0,n}\cos(h\,v)\,h$$

$$-2\,h^2\,b_{2,n}\,v\sin(h\,v) - h^2\,b_{2,n}\,v^2\cos(h\,v)\,x - h^3\,b_{2,n}\,v^2\cos(h\,v)$$

$$-h^2\,b_{1,n}\,x\,v^2 + 2\,h^2\,b_{0,n}\,v\sin(h\,v) - h^2\,b_{0,n}\,v^2\cos(h\,v)\,x$$

$$+h^3\,b_{0,n}\,v^2\cos(h\,v) \tag{33}$$

$$0 = a_{2,n-1} + a_{1,n-1} + a_{0,n-1} \tag{34}$$

$$h\,v\cos(h\,v) = -\sin(h\,v)\left(a_{0,n-1} - h^2\,b_{0,n-1}\,v^2 + h^2\,b_{2,n-1}\,v^2 - a_{2,n-1}\right) \tag{35}$$

$$h\,v\sin(h\,v) = a_{2,n-1}\cos(h\,v) + a_{1,n-1}$$

$$+a_{0,n-1}\cos(h\,v) - h^2\,b_{2,n-1}\,v^2\cos(h\,v)$$

$$-h^2\,b_{1,n-1}\,v^2 - h^2\,b_{0,n-1}\,v^2\cos(h\,v) \tag{36}$$

$$h\left(\cos(h\,v)\,v\,x - h\,v\cos(h\,v) - \sin(h\,v)\right)$$

$$= a_{2,n-1}\sin(h\,v)\,x + a_{2,n-1}\sin(h\,v)\,h$$

$$-a_{0,n-1}\sin(h\,v)\,x + a_{0,n-1}\sin(h\,v)\,h + 2\,h^2\,b_{2,n-1}\,v\cos(h\,v)$$

$$-h^2\,b_{2,n-1}\,v^2\sin(h\,v)\,x - h^3\,b_{2,n-1}\,v^2\sin(h\,v) + 2\,h^2\,b_{1,n-1}\,v$$

$$+2\,h^2\,b_{0,n-1}\,v\cos(h\,v) + h^2\,b_{0,n-1}\,v^2\sin(h\,v)\,x - h^3\,b_{0,n-1}\,v^2\sin(h\,v) \tag{37}$$

$$h\left(\cos(h\,v) + \sin(h\,v)\,v\,x - h\,v\sin(h\,v)\right)$$

$$= a_{2,n-1}\cos(h\,v)\,x + a_{2,n-1}\cos(h\,v)\,h$$

$$+a_{1,n-1}\,x + a_{0,n-1}\cos(h\,v)\,x - a_{0,n-1}\cos(h\,v)\,h - 2\,h^2\,b_{2,n-1}\,v\sin(h\,v)$$

$$-h^2\,b_{2,n-1}\,v^2\cos(h\,v)\,x - h^3\,b_{2,n-1}\,v^2\cos(h\,v) - h^2\,b_{1,n-1}\,x\,v^2$$

$$+2\,h^2\,b_{0,n-1}\,v\sin(h\,v) - h^2\,b_{0,n-1}\,v^2\cos(h\,v)\,x + h^3\,b_{0,n-1}\,v^2\cos(h\,v) \tag{38}$$

Considering that:

$$b_{1,n+1} = b_{1,n} = b_{1,n-1} = 1, \tag{39}$$

the solution of the above system of equations is given by:

$$a_{0,n+1} = -a_{2,n+1} - a_{1,n+1}$$

$$a_{1,n+1} = \frac{-w\sin(2\,w) - 2\,w^3\sin(w) + 2\,w^2}{4\cos(w) - 2\,w\sin(w) - 2 - 2\cos(2\,w)}$$

$$a_{2,n+1} = (2w\sin(w) + 2w\sin(3w) + 7w^2\cos(w) +$$
$$w^2\cos(3w) - 2w\sin(4w)$$
$$-2w^3\sin(3w) + 2w^3\sin(w) - 8w^2)/$$
$$\left(8\cos(w) - 12w\sin(w) - 4 - 8\cos(3w) + 4w\sin(3w) + 4\cos(4w)\right)$$
$$b_{2,n+1} = \left(-2w^2\sin(3w) + 2w^2\sin(w) + 15w\cos(w)\right.$$
$$-7w\cos(3w) - 16w$$
$$\left.+8w\cos(2w) - 4\sin(3w) + 4\sin(w) + 2\sin(4w)\right)/$$
$$\left(8w\cos(w) - 12w^2\sin(w) - 4w\right.$$
$$\left.-8w\cos(3w) + 4w^2\sin(3w) + 4w\cos(4w)\right)$$
$$b_{0,n+1} = \left(-3w\cos(w) - 5w\cos(3w) - 2w^2\sin(3w)\right.$$
$$+10w^2\sin(w) + 8\sin(w) - 8w$$
$$\left.-4\sin(2w) + 16w\cos(2w)\right)/$$
$$\left(8w\cos(w) - 12w^2\sin(w) - 4w\right.$$
$$\left.-8w\cos(3w) + 4w^2\sin(3w) + 4w\cos(4w)\right)$$
$$a_{0,n} = -a_{2,n} - a_{1,n}$$
$$a_{1,n} = \frac{w^3\sin(w)}{-2\cos(w) + w\sin(w) + 2\cos(w)^2}$$
$$a_{2,n} = -\frac{1}{4}\left(4w\cos(w)^4 + 4w^2\cos(w)^3\sin(w) +\right.$$
$$2w^3\cos(w)^3 + 4\cos(w)^3\sin(w)$$
$$-4w\cos(w)^3 + 3w^3\cos(w)^2 - 4\sin(w)\cos(w)^2$$
$$-3w^2\cos(w)\sin(w) - w^3\cos(w)$$
$$\left.-2w^3 + w^2\sin(w)\right)w/\left(4\cos(w)^5 - 4\cos(w)^4 - 4\cos(w)^3 + w^2\cos(w)^3\right.$$
$$\left.+4\cos(w)^2 + w^2\cos(w)^2 - w^2\cos(w) - w^2\right)$$
$$b_{0,n} = \left(\sin(w) - 5w\cos(w) + 7w - 3w\cos(2w)\right.$$
$$+\sin(3w) - w^2\sin(2w) + w\cos(3w)$$
$$\left.-2\sin(2w) + w^2\sin(3w) - 3w^2\sin(w)\right)/$$

$$
\begin{aligned}
&\left(-4\,w\cos(w)+6\,w^2\sin(w)+2\,w\right.\\
&\left.+4\,w\cos(3\,w)-2\,w^2\sin(3\,w)-2\,w\cos(4\,w)\right)\\
b_{2,\,n}=&\left(-w\cos(w)-w+5\,w\cos(2\,w)-w^2\sin(3\,w)+3\,w^2\sin(w)\right.\\
&\left.+\sin(3\,w)+\sin(w)\right.\\
&\left.-3\,w\cos(3\,w)-w^2\sin(2\,w)-2\sin(2\,w)\right)/\\
&\left(4\,w\cos(w)-4\,w\cos(3\,w)-6\,w^2\sin(w)\right.\\
&\left.+2\,w^2\sin(3\,w)-2\,w+2\,w\cos(4\,w)\right)\\
a_{0,\,n-1}=&-a_{2,\,n-1}-a_{1,\,n-1}\\
a_{2,\,n-1}=&\left(-2\,w\sin(w)-2\,w\sin(3\,w)-7\,w^2\cos(w)\right.\\
&\left.-w^2\cos(3\,w)+4\,w\sin(2\,w)\right.\\
&\left.+2\,w^3\sin(3\,w)-2\,w^3\sin(w)+8\,w^2\cos(2\,w)\right)/\\
&\left(-8\cos(w)+12\,w\sin(w)+4+8\cos(3\,w)-4\,w\sin(3\,w)-4\cos(4\,w)\right)\\
a_{1,\,n-1}=&\frac{-w\sin(2\,w)+2\,w^3\sin(w)+2\,w^2}{-4\cos(w)+2\,w\sin(w)+2+2\cos(2\,w)}\\
b_{2,\,n-1}=&\frac{R_0}{R_1}\\
b_{0,\,n-1}=&\left(7\,w\cos(w)-10\,w^2\sin(w)+2\sin(4\,w)\right.\\
&\left.+2\,w^2\sin(3\,w)+4\sin(w)-4\sin(3\,w)\right.\\
&\left.-8\,w\cos(2\,w)+w\cos(3\,w)\right)/\\
&\left(-8\,w\cos(w)+12\,w^2\sin(w)+4\,w\right.\\
&\left.+8\,w\cos(3\,w)-4\,w^2\sin(3\,w)-4\,w\cos(4\,w)\right) \qquad (40)\\
R_0=&\,2\,w^2\sin(3\,w)-2\,w^2\sin(w)-11\,w\cos(w)\\
&+3\,w\cos(3\,w)+8\,w+8\sin(w)-4\sin(2\,w)\\
R_1=&-8\,w\cos(w)+12\,w^2\sin(w)+4\,w+8\,w\cos(3\,w)\\
&-4\,w^2\sin(3\,w)-4\,w\cos(4\,w)
\end{aligned}
$$

where $w = v\,h$.

The above parameters converted into its Taylor series expansion which are given below.

$$a_{1,n+1} = \frac{4}{5} + \frac{26}{375}w^2 - \frac{7283}{787500}w^4 - \frac{116849}{118125000}w^6 - \frac{134870117}{1819125000000}w^8 - \frac{54101039939}{10641881250000000}w^{10} - \frac{7614770209313}{22347950625000000000}w^{12} + \dots$$

$$a_{2,n+1} = \frac{1}{10} - \frac{13}{375}w^2 + \frac{8261}{525000}w^4 + \frac{616849}{236250000}w^6 + \frac{1289870117}{3638250000000}w^8 + \frac{107122337771}{2364862500000000}w^{10} + \frac{249464770209313}{446959012500000000000}w^{12} + \dots$$

$$b_{2,n+1} = \frac{11}{30} + \frac{89}{2250}w^2 + \frac{3523}{787500}w^4 + \frac{60569}{118125000}w^6 + \frac{973272893}{16372125000000}w^8 + \frac{6668999669}{967443750000000}w^{10} + \frac{17745770178953}{22347950625000000000}w^{12} + \dots$$

$$b_{0,n+1} = \frac{1}{30} - \frac{11}{2250}w^2 - \frac{211}{112500}w^4 - \frac{5633}{16875000}w^6 - \frac{776727107}{16372125000000}w^8 - \frac{64841003641}{10641881250000000}w^{10} - \frac{16554229821047}{22347950625000000000}w^{12} + \dots$$

$$a_{2,n} = -\frac{7}{10} - \frac{3}{125}w^2 - \frac{20887}{3150000}w^4 - \frac{199259}{118125000}w^6 - \frac{696693821}{2425500000000}w^8 - \frac{867643786523}{21283762500000000}w^{10} - \frac{47205043981 1057}{893918025000000000}w^{12} + \dots$$

$$a_{1,n} = \frac{12}{5} + \frac{6}{125}w^2 - \frac{541}{87500}w^4 - \frac{28619}{39375000}w^6 - \frac{33645277}{606375000000}w^8 - \frac{136629191}{35831250000000}w^{10} - \frac{1902229758053}{744931687500000000}w^{12} + \dots$$

$$b_{2,n} = \frac{1}{60} - \frac{67}{9000}w^2 - \frac{1909}{900000}w^4 - \frac{333839}{945000000}w^6 - \frac{6398289833}{130977000000000}w^8 - \frac{527032460329}{851350500000000000}w^{10} - \frac{133616478778193}{1787836050000000000000}w^{12} + \dots$$

$$b_{0,n} = \frac{11}{60} + \frac{283}{9000}w^2 + \frac{25387}{6300000}w^4 + \frac{459911}{945000000}w^6 + \frac{7574366417}{130977000000000}w^8 + \frac{44463668917}{6548850000000000}w^{10} + \frac{140750025128057}{1787836050000000000000}w^{12} + \dots$$

$$
\begin{aligned}
a_{2,n-1} &= -\frac{3}{2} - \frac{1}{75}\,w^2 + \frac{3991}{315000}\,w^4 + \frac{36991}{15750000}\,w^6 \\
&\quad + \frac{244400309}{727650000000}\,w^8 + \frac{187411339903}{4256752500000000}\,w^{10} \\
&\quad + \frac{5458857963089}{993242250000000000}\,w^{12} + \ldots \\
a_{1,n-1} &= 4 + \frac{2}{75}\,w^2 - \frac{491}{157500}\,w^4 - \frac{10973}{23625000}\,w^6 \\
&\quad - \frac{13400309}{363825000000}\,w^8 - \frac{5411339903}{2128376250000000}\,w^{10} \\
&\quad - \frac{759721667801}{4469590125000000000}\,w^{12} + \ldots \\
b_{2,n-1} &= \frac{1}{6} + \frac{13}{450}\,w^2 + \frac{149}{39375}\,w^4 + \frac{5519}{11812500}\,w^6 \\
&\quad + \frac{23093417}{409303125000}\,w^8 + \frac{7121540809}{1064188125000000}\,w^{10} \\
&\quad + \frac{872296155739}{1117397531250000000}\,w^{12} + \ldots \\
b_{0,n-1} &= -\frac{1}{6} - \frac{7}{450}\,w^2 - \frac{101}{39375}\,w^4 - \frac{4481}{11812500}\,w^6 \\
&\quad - \frac{20656583}{409303125000}\,w^8 - \frac{6698459191}{1064188125000000}\,w^{10} \\
&\quad - \frac{842703844261}{1117397531250000000}\,w^{12} + \ldots
\end{aligned}
\tag{41}
$$

Based on the above coefficients we can find that the local truncation error of the formulae (20)-(22) are given by:

$$
\begin{aligned}
L.T.E._{n+1} &= h^5\Big(-\frac{1}{45}\,y_n^{(5)} - \frac{2}{45}\,w^2\,y_n^{(3)} - \frac{1}{45}\,w^4\,y_n^{(1)}\Big) \\
L.T.E._{n} &= h^5\Big(\frac{7}{360}\,y_n^{(5)} + \frac{7}{180}\,w^2\,y_n^{(3)} + \frac{7}{360}\,w^4\,y_n^{(1)}\Big) \\
L.T.E._{n-1} &= h^5\Big(-\frac{2}{45}\,w^2\,y_n^{(3)} - \frac{1}{45}\,y_n^{(5)} - \frac{1}{45}\,w^4\,y_n^{(1)}\Big)
\end{aligned}
\tag{42}
$$

For the application of the first layer (3) of the method (3)-(4) the following formula is also needed:

$$
h\,y'_n = aa_{1,n}\,y_n + aa_{0,n}\,y_{n-1} + h^2\left(bb_{1,n}\,y''_n + bb_{0,n}\,y''_{n-1}\right) \tag{43}
$$

In order the formula (43) to integrate exactly any linear combination of the functions:

$$
\{\ \cos(\pm v\,x),\ \sin(\pm v\,x),\ x\,\cos(\pm v\,x),\ x\,\sin(\pm v\,x)\ \} \tag{44}
$$

the appropriate parameters of the above formula are the solution of a system of equations, which is produced in the following way:

We calculate $y_{n\pm i}$, and $y''_{n\pm i} = f_{n\pm i}\, y_{n\pm i}$, $y'_{n\pm i}$ $i = -1, 0$ for $y(x) = \cos(v\,x)$, $y(x) = \sin(v\,x)$ and $y(x) = x\cos(v\,x)$, $y(x) = x\sin(v\,x)$. So, the following system of equations is hold:

$$h\,v = \sin(h\,v)\,(-aa_{0,n} + h^2\,bb_{0,n}\,v^2) \tag{45}$$

$$0 = aa_{1,n} + aa_{0,n}\cos(h\,v) - h^2\,bb_{1,n}\,v^2 - h^2\,bb_{0,n}\,v^2\cos(h\,v) \tag{46}$$

$$\begin{aligned} h\,v\,x = {} & -aa_{0,n}\sin(h\,v)\,x + aa_{0,n}\sin(h\,v)\,h \\ & +2\,h^2\,bb_{1,n}\,v + 2\,h^2\,bb_{0,n}\,v\cos(h\,v) \\ & +h^2\,bb_{0,n}\,v^2\sin(h\,v)\,x - h^3\,bb_{0,n}\,v^2\sin(h\,v) \end{aligned} \tag{47}$$

$$\begin{aligned} h = {} & aa_{1,n}\,x + aa_{0,n}\cos(h\,v)\,x - aa_{0,n}\cos(h\,v)\,h - h^2\,bb_{1,n}\,x\,v^2 \\ & +2\,h^2\,bb_{0,n}\,v\sin(h\,v) - h^2\,bb_{0,n}\,v^2\cos(h\,v)\,x + h^3\,bb_{0,n}\,v^2\cos(h\,v). \end{aligned} \tag{48}$$

Considering that:

$$bb_{1,n-1} = 1, \tag{49}$$

the solution of the above system of equations is given by:

$$\begin{aligned} aa_{0,n} &= \frac{w\sin(w) + w^2\cos(w)}{-1 + \cos(2\,w)} \\ aa_{1,n} &= \frac{-w\sin(2\,w) - 2\,w^2}{-2 + 2\cos(2\,w)} \\ bb_{1,n} &= \frac{-2\,w + \sin(2\,w)}{-2\,w + 2\,w\cos(2\,w)} \\ bb_{0,n} &= \frac{w\cos(w) - \sin(w)}{-w + w\cos(2\,w)} \end{aligned} \tag{50}$$

where $w = v\,h$.

The above parameters converted into its Taylor series expansion which are given below.

$$
\begin{aligned}
aa_{0,n} &= -1 + \frac{7}{360}\,w^4 + \frac{31}{7560}\,w^6 + \frac{127}{201600}\,w^8 \\
&\quad + \frac{73}{855360}\,w^{10} + \frac{1414477}{130767436800}\,w^{12} + \ldots \\
aa_{1,n} &= 1 + \frac{1}{45}\,w^4 + \frac{4}{945}\,w^6 + \frac{1}{1575}\,w^8 \\
&\quad + \frac{8}{93555}\,w^{10} + \frac{1382}{127702575}\,w^{12} + \ldots \\
bb_{0,n} &= \frac{1}{6} + \frac{7}{180}\,w^2 + \frac{31}{5040}\,w^4 + \frac{127}{151200}\,w^6 \\
&\quad + \frac{73}{684288}\,w^8 + \frac{1414477}{108972864000}\,w^{10} \\
&\quad + \frac{8191}{5337446400}\,w^{12} + \ldots \\
bb_{1,n} &= \frac{1}{3} + \frac{2}{45}\,w^2 + \frac{2}{315}\,w^4 + \frac{4}{4725}\,w^6 \\
&\quad + \frac{2}{18711}\,w^8 + \frac{2764}{212837625}\,w^{10} \\
&\quad + \frac{4}{2606175}\,w^{12} + \ldots
\end{aligned}
\tag{51}
$$

Based on the above coefficients we can find that the local truncation error of the formula (43) is given by:

$$
L.T.E._n = -\frac{1}{24}\,h^4\left(y_n^{(4)} + 2\,w^2\,y_n^{(2)} + w^4\,y_n\right) \tag{52}
$$

Remark 1 *We note here that the exponentially-fitted versions of the above formulae can be constructed with similar procedures i.e. with substitution of* $\cos(x)$ *and* $\sin(x)$ *by* $\exp(x)$.

4 Numerical Illustrations

In this section we present some numerical results to illustrate the performance of our new methods. Consider the numerical integration of the Schrödinger equation (1) using the well-known Woods-Saxon potential (see [1], [4-6], [8]) which is given by

$$
V(r) = V_w(r) = \frac{u_0}{(1+z)} - \frac{u_0 z}{[a(1+z)^2]} \tag{53}
$$

with $z = \exp[(r - R_0)/a]$, $u_0 = -50$, $a = 0.6$ and $R_0 = 7.0$.. In Figure 3 we give a graph of this potential. In the case of negative eigenenergies (i.e. when $E \in [-50, 0]$) we have

the well-known **bound-states problem** while in the case of positive eigenenergies (i.e. when $E \in (0, 1000]$) we have the well-known **resonance problem** (see [5], [6] and [28]).

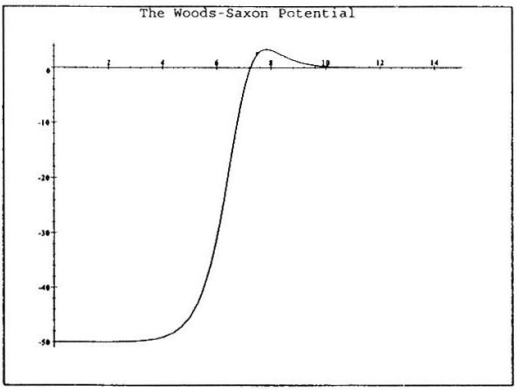

Figure 3: The Woods-Saxon potential.

4.1 Resonance Problem

In the asymptotic region the equation (1) effectively reduces to

$$y''(x) + (k^2 - \frac{l(l+1)}{x^2})y(x) = 0, \tag{54}$$

for x greater than some value X.

The above equation has linearly independent solutions $kxj_l(kx)$ and $kxn_l(kx)$, where $j_l(kx), n_l(kx)$ are the **spherical Bessel and Neumann functions** respectively. Thus the solution of equation (1) has the asymptotic form (when $x \to \infty$)

$$\begin{aligned} y(x) &\simeq Akxj_l(kx) - Bn_l(kx) \\ &\simeq D[\sin(kx - \pi l/2) + \tan\delta_l \cos(kx - \pi l/2)] \end{aligned} \tag{55}$$

where δ_l is the **phase shift** which may be calculated from the formula

$$\tan\delta_l = \frac{y(x_2)S(x_1) - y(x_1)S(x_2)}{y(x_1)C(x_2) - y(x_2)C(x_1)} \tag{56}$$

for x_1 and x_2 distinct points on the asymptotic region (for which we have that x_1 is the right hand end point of the interval of integration and $x_2 = x_1 - h$, h is the stepsize) with $S(x) = kxj_l(kx)$ and $C(x) = kxn_l(kx)$.

Since the problem is treated as an initial-value problem, one needs y_0 and y_1 before starting a two-step method. From the initial condition, $y_0 = 0$. The value y_1 is computed using the Runge-Kutta-Nyström 12(10) method of Dormand et. al. [36]-[37]. With these starting values we evaluate at x_1 of the asymptotic region the phase shift δ_l from the above relation.

4.1.1 The Woods-Saxon Potential

As a test for the accuracy of our methods we consider the numerical integration of the Schrödinger equation (1) with $l = 0$ in the well-known case where the potential $V(r)$ is the Woods-Saxon one (53).

One can investigate the problem considered here, following two procedures. The first procedure consists of finding the **phase shift** $\delta(E) = \delta_l$ for $E \in [1, 1000]$. The second procedure consists of finding those E, for $E \in [1, 1000]$, at which δ equals $\pi/2$. In our case we follow the first procedure i.e. we try to find the phase shifts for given energies. The obtained phase shift is then compared to the analytic value of $\pi/2$.

The above problem is the so-called **resonance problem** when *the positive eigenenergies lie under the potential barrier*. We solve this problem, using the technique fully described in [5].

The boundary conditions for this problem are:

$$\begin{aligned} y(0) &= 0, \\ y(x) &\sim \cos[\sqrt{E}x] \text{ for large } x. \end{aligned}$$

The domain of numerical integration is [0, 15].

For comparison purposes in our numerical illustration we use the well known Numerov's method (which is indicated as Method [a]), the explicit Numerov-type method of Chawla [32] (which is indicated as Method [b]), the multiderivative method developed by Simos

[39] (which is indicated as Method [c]), the multiderivative method with minimal phase-lag developed by Simos [39] (which is indicated as Method [d]), the method of Raptis and Allison [25] (which is indicated as Method [e]) and the new trigonometrically-fitted method (3) - (4) developed in this paper (which is indicated as Method [f]).

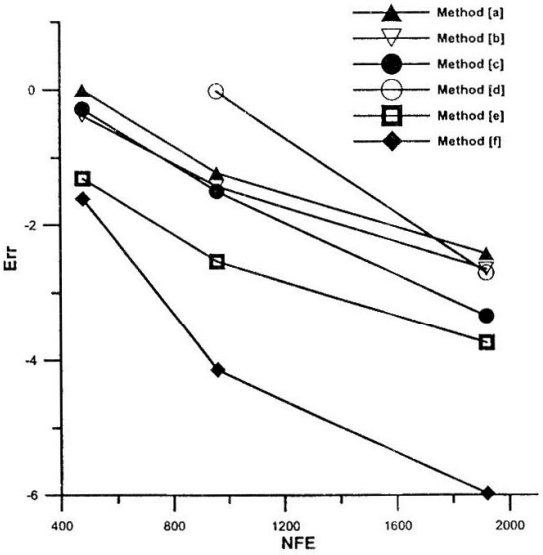

Figure 4: Error Err for several values of NFE for the eigenvalue $E_3 = 989.701916$.

The numerical results obtained for the four methods, for several number of function evaluations (NFE), were compared with the analytic solution of the Woods-Saxon potential resonance problem, rounded to six decimal places. Figure 2 show the errors $Err = -log_{10}|E_{calculated} - E_{analytical}|$ of the highest eigenenergy $E_3 = 989.701916$ for several values of NFE.

5 Conclusions

In this paper a new approach for constructing efficient methods for the numerical solution of the Schrödinger type equations is introduced. Using this new approach we have developed two multiderivative methods.

From the numerical results we have the following remarks:

- The Numerov's method and the explicit Numerov-type method of Chawla [32] have approximately the same behavior.
- The multiderivative method with minimal phase-lag developed by Simos [39] (Method [d]) has much better behavior than the multiderivative method developed by Simos [39] (Method [c]).
- The method of Raptis and Allison [25] has better behavior than the Numerov's methods, the explicit Numerov-type method of Chawla [32], the multiderivative method developed by Simos [39] (Method [c]) and the multiderivative method with minimal phase-lag developed by Simos [39] (Method [d]).
- Finally the new developed method is more efficient than all the other methods.

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

References

[1] L.Gr. Ixaru and M. Micu, *Topics in Theoretical Physics*. Central Institute of Physics, Bucharest, 1978.

[2] L.D. Landau and F.M. Lifshitz: *Quantum Mechanics*. Pergamon, New York, 1965.

[3] I. Prigogine, Stuart Rice (Eds): Advances in Chemical Physics Vol. 93: New Methods in Computational Quantum Mechanics, John Wiley & Sons, 1997.

[4] G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand, Toronto, 1950.

[5] T.E. Simos, Atomic Structure Computations in Chemical Modelling: Applications and Theory (Editor: A. Hinchliffe, UMIST), *The Royal Society of Chemistry* 38-142(2000).

[6] T.E. Simos, Numerical methods for 1D, 2D and 3D differential equations arising in chemical problems, *Chemical Modelling: Application and Theory*, The Royal Society of Chemistry, 2(2002),170-270.

[7] T.E. Simos and P.S. Williams, On finite difference methods for the solution of the Schrödinger equation, *Computers & Chemistry* **23** 513-554(1999).

[8] T.E. Simos: *Numerical Solution of Ordinary Differential Equations with Periodical Solution.* Doctoral Dissertation, National Technical University of Athens, Greece, 1990 (in Greek).

[9] A. Konguetsof and T.E. Simos, On the Construction of exponentially-fitted methods for the numerical solution of the Schrödinger Equation, *Journal of Computational Methods in Scinces and Engineering* **1** 143-165(2001).

[10] T.E. Simos, Eighth order methods with minimal phase-lag for accurate computations for the elastic scattering phase-shift problem, *Journal of Mathematical Chemistry* **21** 359-372(1997).

[11] T.E. Simos, Some embedded modified Runge-Kutta methods for the numerical solution of some specific Schrodinger equations, *Journal of Mathematical Chemistry* **24** 23-37(1998).

[12] T.E. Simos, A family of P-stable exponentially-fitted methods for the numerical solution of the Schrodinger equation, *Journal of Mathematical Chemistry* **25** 65-84(1999).

[13] G. Avdelas and T. E. Simos, Embedded eighth order methods for the numerical solution of the Schrodinger equation, *Journal of Mathematical Chemistry* **26** 327-341(1999).

[14] T.E. Simos, A new explicit Bessel and Neumann fitted eighth algebraic order method for the numerical solution of the Schrodinger equation, *Journal of Mathematical Chemistry* **27** 343-356(2000).

[15] Jesus Vigo-Aguiar and T.E. Simos, A family of P-stable eighth algebraic order methods with exponential fitting facilities, *Journal of Mathematical Chemistry* **29** 177-189(2001).

[16] G. Avdelas, A. Konguetsof and T.E. Simos, A generator and an optimized generator of high-order hybrid explicit methods for the numerical solution of the Schrodinger equation. Part 1. Development of the basic method, *Journal of Mathematical Chemistry* **29** 281-291(2001).

[17] G. Avdelas, A. Konguetsof and T.E. Simos, A generator and an optimized generator of high-order hybrid explicit methods for the numerical solution of the Schrodinger equation. Part 2. Development of the generator, optimized generator and numerical results, *Journal of Mathematical Chemistry* **29** 293-305(2001).

[18] T.E. Simos and J. Vigo-Aguiar, A modified phase-fitted Runge-Kutta method for the numerical solution of the Schrodinger equation, *Journal of Mathematical Chemistry* **30** 121-131(2001).

[19] T.E. Simos and J. Vigo-Aguiar, Symmetric eighth algebraic order methods with minimal phase-lag for the numerical solution of the Schrodinger equation, *Journal of Mathematical Chemistry* **31** 135-144(2002).

[20] Z. Kalogiratou and T.E. Simos, Construction of trigonometrically and exponentially fotted Runge-Kutta-Nystrom methods for the numerical solution of the Schrodinger equation and related problems, *Journal of Mathematical Chemistry* **31** 211-232(2002).

[21] J. Vigo-Aguiar and T.E. Simos, Family of twelve steps exponentially fitting symmetric multistep methods for the numerical solution of the Schrodinger equation, *Journal of Mathematical Chemistry* **32** 257-270(2002).

[22] G. Avdelas, E. Kefalidis and T.E. Simos, New P-stable eighth algebraic order exponentially-fitted methods for the numerical integration of the Schrodinger equation, *Journal of Mathematical Chemistry* **31** 371-404(2002).

[23] T.E. Simos, A Family of Trigonometrically-Fitted Symmetric Methods for the Efficient Solution of the Schrodinger Equation and Related Problems *Journal of Mathematical Chemistry* **34** 39-58(2003).

[24] Kostas Tselios and T.E. Simos, Symplectic Methods for the Numerical Solution of the Radial Shrodinger equation *Journal of Mathematical Chemistry* **34** 83-94(2003).

[25] A.D. Raptis and A.C. Allison: Exponential - fitting methods for the numerical solution of the Schrödinger equation, *Computer Physics Communications*, **14** 1-5(1978).

[26] A.D. Raptis, Exponential multistep methods for ordinary differential equations, *Bull. Greek Math. Soc.* **25** 113-126(1984).

[27] L.Gr. Ixaru, Numerical Methods for Differential Equations and Applications, Reidel, Dordrecht - Boston - Lancaster, 1984.

[28] L.Gr. Ixaru and 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** 23-27(1980).

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

[30] J.P. Coleman, Numerical methods for $y'' = f(x,y)$ in *Proc. of the First Intern. Colloq. on Numerical Analysis* (Bulgaria 1992), Edit. D. Bainov and V. Civachev, 27-38(1992).

[31] J.P. Coleman, Numerical methods for $y'' = f(x,y)$ via rational approximation for the cosine. *IMA J. Numer. Anal.* **9** 145-165(1989).

[32] M.M. Chawla, Numerov made explicit has better stability, *BIT* **24** 117-118(1984).

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

[34] J.M. Blatt: Practical points concerning the solution of the Schrödinger equation, *Journal of Computational Physics*, **1** 382-396 (1967).

[35] J.W. Cooley, An improved eigenvalue corrector formula for solving Schrödinger's equation for central fields. *Math. Comp.* **15** 363-374 (1961).

[36] J.R. Dormand, M.E. El-Mikkawy and P.J. Prince, Families of Runge-Kutta-Nyström formulae, *IMA Journal of Numerical Analysis* **7** 423-430(1987).

[37] J.R. Dormand, M.E.A. El-Mikkawy and P.J. Prince, High-Order Embedded Runge-Kutta-Nyström Formulae, *IMA J. Numer. Anal.* **7** 595-617.

[38] T. E. Simos, P. S. Williams: A New Runge-Kutta-Nystrom Method with Phase-Lag of Order Infinity for the Numerical Solution of the Schrödinger Equation, *MATCH Commun. Math. Comput. Chem.* **45** 123-137(2002).

[39] T. E. Simos, Multiderivative Methods for the Numerical Solution of the Schrödinger Equation, *MATCH Commun. Math. Comput. Chem.* **45** 7-26(2004).