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Multiderivative Methods for the Numerical Solution of the Schrödinger Equation

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Abstract

In this paper multiderivative methods are developed for the numerical integration of the one-dimensional Schrödinger equation. The method is called multiderivative since uses derivatives of order two and four. An application to the the resonance problem of the radial Schrödinger equation indicates that the new method is more efficient than the Numerov method and other well known methods of the literature.

1 Introduction

The one-dimensional Schrödinger equation has the form:

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

Models of this type, which represent a boundary value problem, occur frequently in theoretical physics and chemistry, (see for example [1] - [4]).

In the following we present some notations for (1):

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- The function $W(r) = l(l+1)/r^2 + V(r)$ denotes *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.

It is known from the literature that the last decades many numerical methods have been constructed for the approximate solution of the Schrödinger equation (see [5] - [25]). The aim and the scope of the above activity was the development of fast and reliable methods.

The developed methods can be divided into two main categories:

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

In this paper we introduce an explicit multiderivative method for the numerical solution of the Schrödinger equation. The method is called multiderivative since it has second and forth derivative of the function. We also produce an explicit multiderivative method with minimal phase-lag. The application of the new developed methods to the resonance problem of the Schrödinger equation shows the efficiency of the new developed methods. For comparison purposes we use the well known Numerov method and the Numerov-type methods with minimal phase-lag developed by Chawla [31]-[32].

[1] In the case of the 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

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

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

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

where $y_{n\pm i}'' = f_{n\pm i}\,y_{n\pm i}$, $y_{n\pm i}^{(4)} = \left(f_{n\pm i}'' + f_{n\pm i}^2\right)\,y_{n\pm i} + 2\,f_{n\pm i}'\,y_{n\pm i}'$ 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 mentioned that $y_{n\pm i} = y\left[x_0 + \left(n \pm i\right)h\right]$, $i = 0, 1$ and x_0 is the initial point of integration. It is noted that h is the integration step. 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.

In order the above method (3)-(4) to be of algebraic order six, then the following system of equations must hold:

$$\begin{aligned} 1 - a_0 &= 0 \\ \frac{1}{12} - a_1 &= 0 \\ 1 - c_0 - 2\,c_1 &= 0 \\ -c_1 + \frac{1}{12} - c_2 - 2\,c_3 &= 0 \\ -\frac{1}{12}\,c_1 + \frac{1}{360} - c_3 &= 0 \\ \frac{1}{20160} - \frac{1}{360}\,c_1 - \frac{1}{12}\,c_3 &= 0 \end{aligned} \tag{5}$$

We note that the above system of equations is obtained if we substitute Taylor series expansions of $y_{n\pm j}$, $y_{n\pm j}''$ and $y_{n\pm j}^{(4)}$, $j = -1, 1$ into the new method (3)-(4). After computation of the local truncation error and demanding to have the maximum algebraic order we arrive to the above system of equations.

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

$$a_0 = 1,\ a_1 = \frac{1}{12},\ c_0 = \frac{115}{126},$$
$$c_1 = \frac{11}{252},\ c_2 = \frac{313}{7560}\ \text{and} c_3 = -\frac{13}{15120} \tag{6}$$

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

$$L.T.E(h) = -\frac{11}{90720}\, h^8\, y_n^{(6)} \tag{7}$$

In order to investigate the periodic stability properties of the numerical methods for problems of Schrödinger type, Lambert and Watson [26] have introduced the scalar test equation

$$y'' = -q^2\, y \tag{8}$$

and the **interval of periodicity**, where q is a constant.

Based on their theory when the symmetric two-step multiderivative method is applied to the scalar test equation (8), we obtain the difference equation:

$$y_{n+1} - 2\, B(H)\, y_n + y_{n-1} = 0 \tag{9}$$

and the associate characteristic equation:

$$z^2 - 2\, B(H)\, z + 1 = 0 \tag{10}$$

where $H = q\, h$.

For our method (3)-(4) we have

$$B(H) = 1 - \frac{1}{2} H^2 \left(1 - \frac{11}{252} H^2 + \frac{11}{3024} H^4\right)$$
$$+\frac{1}{2} H^4 \left(\frac{5}{126} + \frac{13}{15120} H^2 - \frac{13}{181440} H^4\right) \tag{11}$$

Definition 1 *(see [26]) A symmetric two-step method with the characteristic equation given by (10) is said to have an interval of periodicity* $\left(0, H_0^2\right)$ *if, for*

all $H \in \left(0, H_0^2\right)$, *the roots* z_i, $i = 1, 2$ *satisfy*

$$z_1 = e^{i\,\theta(H)}, \text{ and} z_2 = e^{-i\,\theta(H)} \tag{12}$$

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

Based on the above definition it is easy for one to see that the following theorem is hold:

Theorem 1 *A method that has a characteristic equation given by (10) has a non-empty interval of periodicity* $(0, H_0^2)$, *if for all* $H^2 \in (0, H_0^2)$, $|B(H)| < 1$.

So we have that in order the above method (3)-(4) to have a non-empty interval of periodicity the following conditions must hold:

$$1 \pm B(H) > 0 \tag{13}$$

for all $H^2 \in (0, H_0^2)$.

Substituting $B(H)$ from (11) we obtain that (13) is hold for every $H^2 \in (0, 6.88)$ i.e. larger than the corresponding interval of periodicity of Numerov's method (which is equal to $(0, 6)$).

3 A New Family Of Multiderivative Methods with Minimal Phase-Lag

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

$$\tilde{y}_{n+1} = 2\,y_n - y_{n-1} + h^2\,y_n'' \tag{14}$$

$$\hat{y}_n = y_n - b_c\,h^2\left(\tilde{y}_{n+1}'' - 2\,y_n'' + y_{n-1}''\right) \tag{15}$$

$$\bar{y}_{n+1} = 2\,y_n - y_{n-1} + a_0\,h^2\,\tilde{y}_n'' + a_1\,h^4\,\hat{y}_n^{(4)} \tag{16}$$

$$\begin{aligned} y_{n+1} = 2\,y_n - y_{n-1} + h^2\left[c_0\,y_n'' + c_1\left(\bar{y}_{n+1}'' + y_{n-1}''\right)\right] \\ + h^4\left[c_2\,y_n^{(4)} + c_3\left(\bar{y}_{n+1}^{(4)} + y_{n-1}^{(4)}\right)\right] \end{aligned} \tag{17}$$

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 $i = -1(1)1$ and b_c is a constant. We note also that $\tilde{y}''_{n+1} = f_{n+1}\, \tilde{y}_{n+1}$ where $\tilde{y}_{n+1}$ is calculated from the relation (14) and $\hat{y}''_{n+1} = f_{n+1}\, \hat{y}_{n+1}$ where $\hat{y}_{n+1}$ is calculated from the relation (15). It is easy to see that in order the above method (14)-(17) to be applicable, then approximate schemes for the first derivatives of y are needed.

Following the procedure described in the previous paragraph we can find that the local truncation error of the above scheme (14)-(17) is given by:

$$L.T.E(h) = -\frac{11}{90720}\, h^8 \left(y^{(6)}_n - 360\, b_c y^{(4)}_n\right) \tag{18}$$

Theorem 2 *For all H in the interval of periodicity, we can write:*

$$cos\left[\theta\left(H\right)\right] = B(H), \tag{19}$$

where $H^2 \in (0, H_0^2)$.

Definition 2 *For any symmetric two-step method with the characteristic equation given by (10) the phase-lag* [2] *is equal to (see [27] and [28]):*

$$t = H - \theta(H) = H - cos^{-1}\left(B(H)\right) = c\, H^{p+1} + O\left(H^{p+3}\right) \tag{20}$$

where c is the phase-lag constant *and p is* phase-lag order.

Based on the above Coleman [29] has found the following remark:

Remark 1

$$t = c\, H^{p+1} + O\left(H^{p+3}\right) \Rightarrow cos(H) - B(H) =$$
$$cos(H) - cos(H - t) = c\, H^{p+2} + O\left(H^{p+4}\right) \tag{21}$$

[2] Phase-lag physically means how well the numerical method approximates the solution of the scalar test equation $y'' = -q^2\, y$. If we have a method of phase-lag order p this means that |Solution Approximate − Solution Analytical| = $O\left(h^p\right)$.

where t is the phase-lag of the method.

When we apply the above method (14)-(17) to the scalar test equation (8), the difference equation (9) and the associate characteristic equation (10) is obtained, where:

$$B(H) = 1 - \frac{1}{2} H^2 (1 - \frac{11}{252} H^2 (1 - b_c H^4) + \frac{11}{3024} H^4 (1 - b_c H^4)) \\ + \frac{1}{2} H^4 (\frac{5}{126} + \frac{13}{15120} H^2 (1 - b_c H^4) - \frac{13}{181440} H^4 (1 - b_c H^4)) \quad (22)$$

Based on Definition 2 and Remark 1 we have that:

$$cos(H) - B(H) = -\frac{1}{2} H^2 + \frac{1}{24} H^4 - \frac{1}{720} H^6 + \frac{1}{40320} H^8 \\ + \frac{1}{2} H^2 (1 - \frac{11}{252} H^2 (1 - b_c H^4) + \frac{11}{3024} H^4 (1 - b_c H^4)) \\ - \frac{1}{2} H^4 (\frac{5}{126} + \frac{13}{15120} H^2 (1 - b_c H^4) - \frac{13}{181440} H^4 (1 - b_c H^4)) \quad (23)$$

It is easy to see that in order to have minimal phase-lag, the following equation must hold:

$$\frac{11}{181440} + \frac{11}{504} b_c = 0 \quad (24)$$

The solution of the above equation is given by:

$$b_c = \frac{-1}{360} \quad (25)$$

Substituting the above value of b_c into the above formula (23) we find that:

$$cos(H) - B(H) = \frac{1}{259200} H^{10} + \frac{13}{130636800} H^{12}. \quad (26)$$

Based on the Remark 1, we say that the above method is of phase-lag order eight.

Substituting $B(H)$ from (22), b_c from (25) we obtain that (13) is hold for every $H^2 \in (0, 7.34)$ i.e. larger than the corresponding interval of periodicity of the method developed in previous section.

4 Computational Implementation

As we have mentioned previously, in order the above methods (3)-(4) and (14)-(17)to be applicable we need approximate schemes for the first derivatives of y. This is due to the following formula:

$$y^{(4)}_{n\pm i} = \left(f''_{n\pm i} + f^2_{n\pm i}\right) y_{n\pm i} + 2\, f'_{n\pm i}\, y'_{n\pm i} \text{andi} = -1(1)1. \tag{27}$$

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

$$\begin{aligned} h\, y'_{n+1} &= a_{2,n+1}\, y_{n+1} + a_{1,n+1}\, y_n + a_{0,n+1}\, y_{n-1} \\ &+h^2 \left(b_{2,n+1}\, y''_{n+1} + b_{1,n+1}\, y''_n + b_{0,n+1}\, y''_{n-1}\right) \\ h\, y'_n &= a_{2,n}\, y_{n+1} + a_{1,n}\, y_n + a_{0,n}\, y_{n-1} \\ &+h^2 \left(b_{2,n}\, y''_{n+1} + b_{1,n}\, y''_n + b_{0,n}\, y''_{n-1}\right) \\ h\, y'_{n-1} &= a_{2,n-1}\, y_{n+1} + a_{1,n-1}\, y_n + a_{0,n-1}\, y_{n-1} \\ &+h^2 \left(b_{2,n-1}\, y''_{n+1} + b_{1,n-1}\, y''_n + b_{0,n-1}\, y''_{n-1}\right) \end{aligned} \tag{28}$$

In order the above methods to have maximal algebraic order the following system of equations must hold:

$$\begin{aligned} -a_{2,n+1} - a_{0,n+1} - a_{1,n+1} &= 0 \\ a_{0,n+1} + 1 - a_{2,n+1} &= 0 \\ -b_{2,n+1} - b_{0,n+1} - b_{1,n+1} - \frac{1}{2}\, a_{2,n+1} - \frac{1}{2}\, a_{0,n+1} + 1 &= 0 \\ b_{0,n+1} - \frac{1}{6}\, a_{2,n+1} + \frac{1}{6}\, a_{0,n+1} - b_{2,n+1} + \frac{1}{2} &= 0 \\ -\frac{1}{2}\, b_{0,n+1} - \frac{1}{24}\, a_{2,n+1} - \frac{1}{24}\, a_{0,n+1} - \frac{1}{2}\, b_{2,n+1} + \frac{1}{6} &= 0 \end{aligned} \tag{29}$$

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

$$
\begin{aligned}
a_{0,n} - a_{2,n} + 1 &= 0 \\
-\frac{1}{2}a_{2,n} - b_{1,n} - b_{0,n} - \frac{1}{2}a_{0,n} - b_{2,n} &= 0 \\
-\frac{1}{6}a_{2,n} + b_{0,n} + \frac{1}{6}a_{0,n} - b_{2,n} &= 0 \\
-\frac{1}{2}b_{0,n} - \frac{1}{24}a_{2,n} - \frac{1}{24}a_{0,n} - \frac{1}{2}b_{2,n} &= 0
\end{aligned} \tag{30}
$$

$$
\begin{aligned}
-a_{1,n-1} - a_{2,n-1} - a_{0,n-1} &= 0 \\
1 - a_{2,n-1} + a_{0,n-1} &= 0 \\
-1 - \frac{1}{2}a_{2,n-1} - \frac{1}{2}a_{0,n-1} - b_{2,n-1} - b_{1,n-1} - b_{0,n-1} &= 0 \\
\frac{1}{2} + \frac{1}{6}a_{0,n-1} - \frac{1}{6}a_{2,n-1} - b_{2,n-1} + b_{0,n-1} &= 0 \\
-\frac{1}{6} - \frac{1}{24}a_{0,n-1} - \frac{1}{24}a_{2,n-1} - \frac{1}{2}b_{2,n-1} - \frac{1}{2}b_{0,n-1} &= 0
\end{aligned} \tag{31}
$$

The solution of the above system of equations for the case: $b_{1,n+1} = b_{1,n} = b_{1,n-1} = 1$ is given by:

$$
\begin{aligned}
a_{2,n+1} = \frac{1}{10},\ a_{1,n+1} &= \frac{4}{5},\ a_{0,n+1} = \frac{-9}{10} \\
b_{2,n+1} = \frac{11}{30},\ b_{0,n+1} &= \frac{1}{30} \\
a_{2,n} = \frac{-7}{10},\ a_{1,n} &= \frac{12}{5},\ a_{0,n} = \frac{-17}{10} \\
b_{2,n} = \frac{1}{60},\ b_{0,n} &= \frac{11}{60} \\
a_{2,n-1} = \frac{-3}{2},\ a_{1,n-1} &= 4,\ a_{0,n-1} = \frac{-5}{2} \\
b_{2,n-1} = \frac{1}{6},\ b_{0,n-1} &\frac{-1}{6}
\end{aligned} \tag{32}
$$

The local truncation error of the above formulae is given by:

$$
L.T.E._{n+1} = L.T.E._n = L.T.E._{n-1} = -\frac{1}{45}h^5 y_n^{(5)} \tag{33}
$$

For the application of the first layer (3) of the method (3)-(4) and for the application of the first and second layer (14)-(15) of the methods (14)-(17) the following formula is also needed:

$$h\,y'_n = aa_{1,n}\,y_n + aa_{0,n}\,y_{n-1} + h^2\left(bb_{1,n}\,y''_n + bb_{0,n}\,y''_{n-1}\right) \tag{34}$$

$$\begin{aligned} -aa_{1,n} - aa_{0,n} &= 0 \\ aa_{0,n} + 1 &= 0 \\ -bb_{1,n} - bb_{0,n} - \frac{1}{2}\,aa_{0,n} &= 0 \\ bb_{0,n} + \frac{1}{6}\,aa_{0,n} &= 0 \end{aligned} \tag{35}$$

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

$$bb_{0,n} = \frac{1}{6},\ aa_{0,n} = -1,\ bb_{1,n} = \frac{1}{3},\ aa_{1,n} = 1 \tag{36}$$

The local truncation error of the above formula is given by:

$$L.T.E._n = -\frac{1}{24}\,h^4\,y_n^{(4)} \tag{37}$$

5 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

$$V(r) = V_w(r) = \frac{u_0}{(1+z)} - \frac{u_0 z}{[a(1+z)^2]} \tag{38}$$

with $z = \exp[(r - R_0)/a]$, $u_0 = -50$, $a = 0.6$ and $R_0 = 7.0$.. In Figure 1 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 [15]).

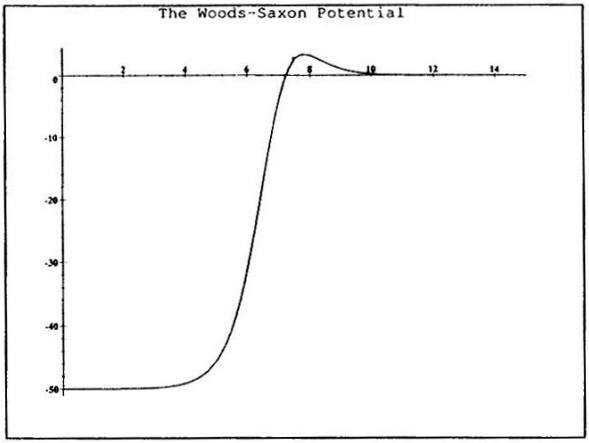

Figure 1: The Woods-Saxon potential.

5.1 Resonance Problem

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

$$y''(x) + (k^2 - \frac{l(l+1)}{x^2})y(x) = 0, \tag{39}$$

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 $x \to \infty$)

$$\begin{aligned} y(x) &\simeq Akxj_l(kx) - Bn_l(kx) \\ &\simeq D[\sin(kx - \pi l/2) + \tan\delta_l \cos(kx - \pi l/2)] \end{aligned} \tag{40}$$

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

$$\tan\delta_l = \frac{y(x_2)S(x_1) - y(x_1)S(x_2)}{y(x_1)C(x_2) - y(x_2)C(x_1)} \tag{41}$$

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. [35]-[36]. With these starting values we evaluate at x_1 of the asymptotic region the phase shift δ_l from the above relation.

5.1.1 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 (38).

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 [31] (which is indicated as method [b]), the explicit Numerov-type method with minimal phase-lag of Chawla et. al. [32] (which is indicated as method [c]), the multiderivative method (3)-(4) developed in this paper (which is indicated as method [d]) and the multiderivative method (14)-(17) developed in this paper (which is indicated as method [e]).

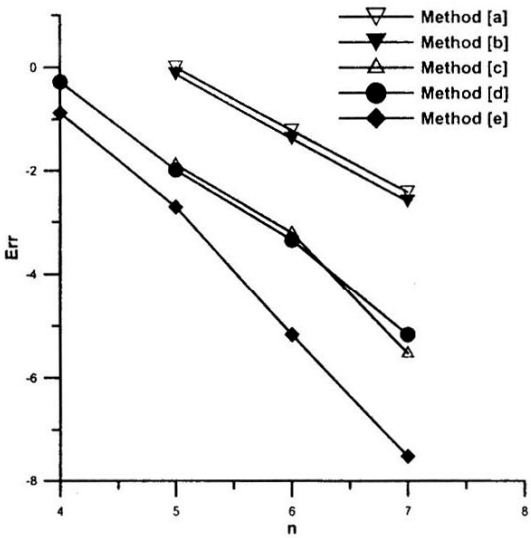

Figure 2: Error Err for several values of n for the eigenvalue $E_3 = 989.701916$. The nonexistence of a value of Err indicates that for this value of n, Err is positive.

The numerical results obtained for the four methods, with stepsizes equal to $h = \frac{1}{2^n}$, 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 n.

5.2 The Bound-States Problem

For negative energies we solve the so-called bound-states problem, i.e. the equation (1) with $l = 0$ and boundary conditions given by

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

In order to solve this problem numerically we use a strategy which has been proposed by Cooley [34] and has been improved by Blatt [33]. This strategy involves integrating forward from the point $x = 0$, backward from the point $x_b = 15$ and matching up the solution at some internal point in the range of integration. As initial conditions for the backward integration we take:

$$y(x_b) = \exp(-\sqrt{-E}x_b) \text{ and } y(x_b - h) = \exp[-\sqrt{-E}(x_b - h)] \,, \qquad (42)$$

where h is the steplength of integration of the numerical method.

The true solutions to the Woods-Saxon bound-states problem were obtained correct to nine decimal places using the analytic solution and the numerical results obtained for the six methods mentioned above were compared to this true solution. In Figure 3 some results for $Err = -log_{10}|E_{calculated} - E_{analytical}|$ of the eigenenergy $E_{13} = -3.9082324810$ using stepsizes equal to $h = \frac{1}{2^n}$ for several values of n are shown.

6 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 [31] have approximately the same behavior.

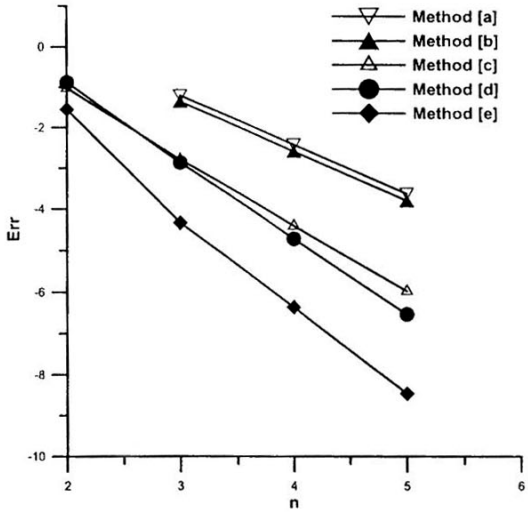

Figure 3: Error Err for several values of n for the eigenvalue $E_{13} = -3.9082324810$. The nonexistence of a value of Err indicates that for this value of n, Err is positive.

- The explicit Numerov-type method with minimal phase-lag of Chawla et. al. [32] and the new multiderivative method (3)-(4) have approximately the same behavior.
- The multiderivative method (14)-(17) is the most accurate method.

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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