

A family of multiderivative methods for the numerical solution of the Schrödinger equation

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Received 20 February 2004; revised 25 April 2004

A family of multiderivative methods with minimal phase-lag are introduced in this paper, for the numerical solution of the Schrödinger equation. The methods are called multiderivative since uses derivatives of order two, four or six. Numerical application of the new obtained methods to the Schrödinger equation shows their efficiency compared with other similar well known methods of the literature.

KEY WORDS: dispersion, methods, phase-lag, stability

AMS subject classification: PACS: 0.260, 95.10.E

1. Introduction

The radial Schrödinger equation has the form:

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

The above boundary value problem occurs frequently in theoretical physics and chemistry, material sciences, quantum mechanics and quantum chemistry, electronics etc. (see for example [1–4]).

We give some definitions for (1):

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

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- 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.

The last decades a lot of research has been done on the development of numerical methods for the numerical solution of the Schrödinger equation (see for example [5–9] and [10–24]). The above research gave us fast and reliable methods.

The 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 first category. More specifically we introduce a family of explicit multiderivative methods of eighth algebraic order with phase-lag of order twelve, fourteen, sixteen and eighteen for the numerical solution of the radial Schrödinger equation. The methods are called multiderivative since they include second, fourth and sixth derivative of the function. Based on the above methods a variable step method is developed. We apply the new obtained method to the coupled differential equations of the Schrödinger type. The above application shows the efficiency of the new developed methods.

2. A new family of multiderivative methods

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

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

$$\bar{y}_{n,i} = y_n - b_i h^2 (\bar{y}''_{n+1} - 2 y''_n + y''_{n-1}) \quad \text{and} \quad i = 1(1)3, \tag{4}$$

$$\hat{y}_{n+1} = 2 y_n - y_{n-1} + a_0 h^2 \bar{y}''_{n,3} + a_1 h^4 \bar{y}_{n,3}^{(4)}, \tag{5}$$

$$\bar{y}_{n,4} = y_n - b_4 h^2 (\hat{y}''_{n+1} - 2 y''_n + y''_{n-1}), \tag{6}$$

$$\hat{y}_n = y_n + b_5 h^4 (\hat{y}_{n+1}^{(4)} - 2 \bar{y}_{n,4}^{(4)} + y_{n-1}^{(4)}), \tag{7}$$

$$\hat{\hat{y}}_{n+1} = 2 y_n - y_{n-1} + a_0 h^2 \hat{y}''_n + a_1 h^4 \hat{y}_n^{(4)} + a_2 h^6 \hat{y}_n^{(6)}, \tag{8}$$

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

$$y_{n+1} = 2 y_n - y_{n-1} + h^2 \left[c_0 y_n'' + c_1 \left(\hat{y}_{n+1}'' + y_{n-1}'' \right) \right] + h^4 \left[c_2 y_n^{(4)} + c_3 \left(\hat{y}_{n+1}^{(4)} + y_{n-1}^{(4)} \right) \right], \tag{9}$$

where

$$\begin{aligned} y_{n\pm i}'' &= f_{n\pm i} y_{n\pm i}, \\ y_{n\pm i}^{(4)} &= \left(f_{n\pm i}'' + f_{n\pm i}^2 \right) y_{n\pm i} + 2 f_{n\pm i}' y_{n\pm i}', \\ y_{n\pm i}^{(6)} &= \left(f_{n\pm i}^{(4)} + 4 f_{n\pm i}'' + 7 f_{n\pm i} f_{n\pm i}^{(2)} + f_{n\pm i}^3 \right) y_{n\pm i} \\ &\quad + \left(4 f^{(3)} + 6 f_{n\pm i} f_{n\pm i}' \right) y_{n\pm i}' \quad \text{and} \quad i = -1(1)1. \end{aligned}$$

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)
- $\bar{y}_{n,i}'' = f_n \bar{y}_{n,i}$ where $\bar{y}_{n,i}$ is calculated from the relation (4)
- $\hat{y}_{n+1}'' = f_{n+1} \hat{y}_{n+1}$ where \hat{y}_{n+1} is calculated from the relation (5)
- $\hat{y}_n'' = f_n \hat{y}_n$ where \hat{y}_n is calculated from the relation (7)
- $\hat{\hat{y}}_{n+1}'' = f_{n+1} \hat{\hat{y}}_{n+1}$ where $\hat{\hat{y}}_{n+1}$ is calculated from the relation (8)

It is easy to see that in order the above method (3)–(9) to be applicable, then approximate schemes for the first derivatives of y are needed.

In order the above method (3)–(9) to be of algebraic order eight, then the following system of equations must hold:

$$\begin{aligned} 1 - a_0 &= 0 \\ \frac{1}{12} - a_1 &= 0 \\ -a_2 + \frac{1}{360} &= 0 \\ 1 - c_0 - 2 c_1 &= 0 \\ -c_1 + \frac{1}{12} - c_2 - 2 c_3 &= 0 \\ -\frac{1}{12} c_1 + \frac{1}{360} - c_3 &= 0 \\ \frac{1}{20160} - \frac{1}{360} c_1 - \frac{1}{12} c_3 &= 0. \end{aligned} \tag{10}$$

We note that the above system of equations is obtained if we substitute Taylor series expansions of $y_{n\pm j}$, $y_{n\pm j}''$, $y_{n\pm j}^{(4)}$, $j = -1, 1$ and $y_n^{(6)}$, into the new method (3)–(9). 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

$$\begin{aligned} a_0 = 1, \quad a_1 = \frac{1}{12}, \quad a_2 = \frac{1}{360}, \quad c_0 = \frac{115}{126}, \\ c_1 = \frac{11}{252}, \quad c_2 = \frac{313}{7560}, \quad \text{and} \quad c_3 = -\frac{13}{15120}. \end{aligned} \quad (11)$$

Based on the above coefficients we can find that the local truncation error of the above schemes (3)–(9) is given by

$$\text{L.T.E}(h) = -\frac{h^{10}}{76204800} \left(59 y_n^{(10)} + 3326400 b_5 y_n^{(6)} - 165 y_n^{(8)} \right). \quad (12)$$

In order to investigate the periodic stability properties of the numerical methods for problems of Schrödinger type, Lambert and Watson [25] have introduced the scalar test equation

$$y'' = -q^2 y \quad (13)$$

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 (13), we obtain the difference equation:

$$y_{n+1} - 2 B(H) y_n + y_{n-1} = 0 \quad (14)$$

and the associate characteristic equation:

$$z^2 - 2 B(H) z + 1 = 0, \quad (15)$$

where $H = q h$.

For our method (3)–(9) we have

$$\begin{aligned} B(H) := & 1 - \frac{19}{21772800} H^{20} b_5 b_3 - \frac{19}{10886400} H^{18} b_5 b_4 \\ & + \frac{17}{60480} H^{16} b_5 b_4 + \frac{17}{120960} H^{18} b_5 b_3 \\ & - \frac{97}{15120} H^{14} b_5 b_4 - \frac{97}{30240} H^{16} b_5 b_3 \\ & + \frac{11}{252} H^{12} b_5 b_4 + \frac{11}{504} H^{14} b_5 b_3 - \frac{13}{130636800} H^{22} b_5 b_3 \\ & - \frac{13}{65318400} H^{20} b_5 b_4 - \frac{H^6}{720} - \frac{H^2}{2} + \frac{H^4}{24} \\ & - \frac{13}{32659200} H^{26} b_5 b_3 b_2 b_1 - \frac{13}{32659200} H^{26} b_5 b_4 b_3 b_2 \\ & + \frac{13}{16329600} H^{28} b_5 b_4 b_3 b_2 b_1 - \frac{19}{5443200} H^{24} b_5 b_3 b_2 b_1 \\ & - \frac{19}{5443200} H^{24} b_5 b_4 b_3 b_2 + \frac{19}{2721600} H^{26} b_5 b_4 b_3 b_2 b_1 \end{aligned}$$

$$\begin{aligned}
 & + \frac{19}{10886400} H^{22} b_5 b_4 b_3 + \frac{13}{65318400} H^{24} b_5 b_3 b_2 \\
 & + \frac{13}{65318400} H^{24} b_5 b_4 b_3 - \frac{97}{7560} H^{20} b_5 b_4 b_3 b_2 \\
 & + \frac{97}{3780} H^{22} b_5 b_4 b_3 b_2 b_1 + \frac{17}{30240} H^{22} b_5 b_3 b_2 b_1 \\
 & + \frac{17}{30240} H^{22} b_5 b_4 b_3 b_2 - \frac{17}{15120} H^{24} b_5 b_4 b_3 b_2 b_1 \\
 & + \frac{11}{126} H^{18} b_5 b_3 b_2 b_1 + \frac{11}{126} H^{18} b_5 b_4 b_3 b_2 \\
 & - \frac{11}{63} H^{20} b_5 b_4 b_3 b_2 b_1 - \frac{97}{7560} H^{20} b_5 b_3 b_2 b_1 + \frac{H^8}{40320} \\
 & + \frac{13 H^{10}}{10886400} - \frac{11}{504} H^{10} b_5 + \frac{97}{30240} H^{12} b_5 \\
 & - \frac{17}{120960} H^{14} b_5 + \frac{19}{21772800} H^{16} b_5 + \frac{13}{130636800} H^{18} b_5 \\
 & - \frac{11}{252} H^{16} b_5 b_3 b_2 - \frac{11}{252} H^{16} b_5 b_4 b_3 + \frac{97}{15120} H^{18} b_5 b_3 b_2 \\
 & + \frac{97}{15120} H^{18} b_5 b_4 b_3 - \frac{17}{60480} H^{20} b_5 b_3 b_2 - \frac{17}{60480} H^{20} b_5 b_4 b_3 \\
 & + \frac{19}{10886400} H^{22} b_5 b_3 b_2. \tag{16}
 \end{aligned}$$

Definition 1. (see [25]) A symmetric two-step method with the characteristic equation given by (15) is said to have an interval of periodicity $(0, H_0^2)$ if, for all $H \in (0, H_0^2)$, the roots $z_i, i = 1, 2$ satisfy

$$z_1 = e^{i\theta(H)} \quad \text{and} \quad z_2 = e^{-i\theta(H)}, \tag{17}$$

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 (15) 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)–(9) to have a non-empty interval of periodicity the following conditions must hold:

$$1 \pm B(H) > 0 \tag{18}$$

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

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

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

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

Definition 2. For any symmetric two-step method with the characteristic equation given by (15) the phase-lag² is equal to (see [26]):

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

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

Based on the above Coleman [27] has found the following remark:

Remark 1

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

where t is the phase-lag of the method.

Based on Definition 2 and Remark 1 we have that:

$$\begin{aligned} \cos(H) - B(H) = & -\frac{19}{21772800} H^{20} b_5 b_3 - \frac{19}{10886400} H^{18} b_5 b_4 \\ & + \frac{17}{60480} H^{16} b_5 b_4 + \frac{17}{120960} H^{18} b_5 b_3 \\ & - \frac{97}{15120} H^{14} b_5 b_4 - \frac{97}{30240} H^{16} b_5 b_3 \\ & + \frac{11}{252} H^{12} b_5 b_4 + \frac{11}{504} H^{14} b_5 b_3 \\ & - \frac{13}{130636800} H^{22} b_5 b_3 - \frac{13}{65318400} H^{20} b_5 b_4 \\ & - \frac{H^{12}}{479001600} + \frac{H^{14}}{87178291200} \\ & - \frac{H^{16}}{20922789888000} + \frac{H^{18}}{6402373705728000} \\ & - \frac{H^{20}}{2432902008176640000} + \frac{H^{22}}{112400072777607680000} \end{aligned}$$

²Phase-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 $|\text{Solution Approximate} - \text{Solution Analytical}| = O(h^p)$.

$$\begin{aligned}
& -\frac{13}{32659200} H^{26} b_5 b_3 b_2 b_1 - \frac{13}{32659200} H^{26} b_5 b_4 b_3 b_2 \\
& + \frac{13}{16329600} H^{28} b_5 b_4 b_3 b_2 b_1 - \frac{19}{5443200} H^{24} b_5 b_3 b_2 b_1 \\
& - \frac{19}{5443200} H^{24} b_5 b_4 b_3 b_2 + \frac{19}{2721600} H^{26} b_5 b_4 b_3 b_2 b_1 \\
& + \frac{19}{10886400} H^{22} b_5 b_4 b_3 + \frac{13}{65318400} H^{24} b_5 b_3 b_2 \\
& + \frac{13}{65318400} H^{24} b_5 b_4 b_3 - \frac{97}{7560} H^{20} b_5 b_4 b_3 b_2 \\
& + \frac{97}{3780} H^{22} b_5 b_4 b_3 b_2 b_1 + \frac{17}{30240} H^{22} b_5 b_3 b_2 b_1 \\
& + \frac{17}{30240} H^{22} b_5 b_4 b_3 b_2 - \frac{17}{15120} H^{24} b_5 b_4 b_3 b_2 b_1 \\
& + \frac{11}{126} H^{18} b_5 b_3 b_2 b_1 + \frac{11}{126} H^{18} b_5 b_4 b_3 b_2 \\
& - \frac{11}{63} H^{20} b_5 b_4 b_3 b_2 b_1 - \frac{97}{7560} H^{20} b_5 b_3 b_2 b_1 + \frac{H^{10}}{680400} \\
& - \frac{11}{504} H^{10} b_5 + \frac{97}{30240} H^{12} b_5 - \frac{17}{120960} H^{14} b_5 \\
& + \frac{19}{21772800} H^{16} b_5 + \frac{13}{130636800} H^{18} b_5 - \frac{11}{252} H^{16} b_5 b_3 b_2 \\
& - \frac{11}{252} H^{16} b_5 b_4 b_3 + \frac{97}{15120} H^{18} b_5 b_3 b_2 + \frac{97}{15120} H^{18} b_5 b_4 b_3 \\
& - \frac{17}{60480} H^{20} b_5 b_3 b_2 - \frac{17}{60480} H^{20} b_5 b_4 b_3 \\
& + \frac{19}{10886400} H^{22} b_5 b_3 b_2. \tag{22}
\end{aligned}$$

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

$$\frac{1}{680400} - \frac{11}{504} b_5 = 0. \tag{23}$$

$$\frac{11}{252} b_5 b_4 - \frac{1}{479001600} + \frac{97}{30240} b_5 = 0, \tag{24}$$

$$-\frac{97}{15120} b_5 b_4 + \frac{11}{504} b_5 b_3 + \frac{1}{87178291200} - \frac{17}{120960} b_5 = 0, \tag{25}$$

$$\frac{17}{60480} b_5 b_4 - \frac{97}{30240} b_5 b_3 - \frac{1}{20922789888000} + \frac{19}{21772800} b_5 - \frac{11}{252} b_5 b_3 b_2 - \frac{11}{252} b_5 b_4 b_3 = 0, \tag{26}$$

$$-\frac{19}{10886400} b_5 b_4 + \frac{17}{120960} b_5 b_3 + \frac{1}{6402373705728000} + \frac{11}{126} b_5 b_3 b_2 b_1 + \frac{11}{126} b_5 b_4 b_3 b_2 + \frac{13}{130636800} b_5 + \frac{97}{15120} b_5 b_3 b_2 + \frac{97}{15120} b_5 b_4 b_3 = 0. \tag{27}$$

For the solution of the above system of equations table 1
 Substituting the above values of $b_i, i = 1(1)5$ into the above formula (22) we find the orders of the phase-lag give in the table 1.

Substituting $B(H)$ from (16) and $b_i, i = 1(1)5$ from table 1 we obtain that (18) is hold for every H^2 which belongs into the interval presented in table 1.

3. Computational implementation

As we have mentioned previously, in order the above method (3)–(9) to be applicable we need approximate schemes for the first derivatives of y . This is due to the following formula:

$$y_{n\pm i}^{(4)} = (f''_{n\pm i} + f_{n\pm i}^2) y_{n\pm i} + 2 f'_{n\pm i} y'_{n\pm i} \quad \text{and} \quad i = -1(1)1. \tag{28}$$

$$y_{n\pm i}^{(6)} = \left(f_{n\pm i}^{(4)} + 4 f''_{n\pm i} + 7 f_{n\pm i} f_{n\pm i}^{(2)} + f_{n\pm i}^3 \right) y_{n\pm i} \tag{29}$$

$$+ (4 f^{(3)} + 6 f_{n\pm i} f'_{n\pm i}) y'_{n\pm i} \quad \text{and} \quad i = -1(1)1. \tag{30}$$

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

Table 1
 Solution of the system of equations (23)–(27). Phase-lag (PL) and interval of periodicity (IP) of the produced methods.

b_1	b_2	b_3	b_4	b_5	PL	IP
0	0	0	$\frac{1}{14850}$	$-\frac{1537}{21120}$	$O(H^{12})$	(0, 15.27)
0	0	$-\frac{9487969}{634233600}$	$\frac{1}{14850}$	$-\frac{1537}{21120}$	$O(H^{14})$	(0, 14.24)
0	$\frac{1173468341}{40077181056}$	$-\frac{9487969}{634233600}$	$\frac{1}{14850}$	$-\frac{1537}{21120}$	$O(H^{16})$	(0, 15.05)
0	$\frac{1173468341}{40077181056}$	$-\frac{9487969}{634233600}$	$\frac{1}{14850}$	$-\frac{1537}{21120}$	$O(H^{18})$	(0, 15.05)
$\frac{279918048241817}{2106610365763200}$	$\frac{1173468341}{40077181056}$	$-\frac{9487969}{634233600}$	$\frac{1}{14850}$	$-\frac{1537}{21120}$	$O(H^{20})$	(0, 13.57)

$$\begin{aligned}
 h y'_{n+1} &= a_{2,n+1} y_{n+1} + a_{1,n+1} y_n + a_{0,n+1} y_{n-1} \\
 &\quad + h^2 (b_{2,n+1} y''_{n+1} + b_{1,n+1} y''_n + b_{0,n+1} y''_{n-1}) \\
 h y'_n &= a_{2,n} y_{n+1} + a_{1,n} y_n + a_{0,n} y_{n-1} \\
 &\quad + h^2 (b_{2,n} y''_{n+1} + b_{1,n} y''_n + b_{0,n} y''_{n-1}) \\
 h y'_{n-1} &= a_{2,n-1} y_{n+1} + a_{1,n-1} y_n + a_{0,n-1} y_{n-1} \\
 &\quad + h^2 (b_{2,n-1} y''_{n+1} + b_{1,n-1} y''_n + b_{0,n-1} y''_{n-1}).
 \end{aligned} \tag{31}$$

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

$$\begin{aligned}
 -a_{2,n+1} - a_{0,n+1} - a_{1,n+1} &= 0 \\
 a_{0,n+1} + 1 - a_{2,n+1} &= 0 \\
 -b_{2,n+1} - b_{0,n+1} - b_{1,n+1} - \frac{1}{2} a_{2,n+1} - \frac{1}{2} a_{0,n+1} + 1 &= 0 \\
 b_{0,n+1} - \frac{1}{6} a_{2,n+1} + \frac{1}{6} a_{0,n+1} - b_{2,n+1} + \frac{1}{2} &= 0 \\
 -\frac{1}{2} b_{0,n+1} - \frac{1}{24} a_{2,n+1} - \frac{1}{24} a_{0,n+1} - \frac{1}{2} b_{2,n+1} + \frac{1}{6} &= 0,
 \end{aligned} \tag{32}$$

$$\begin{aligned}
 -a_{0,n} - a_{2,n} - a_{1,n} &= 0 \\
 a_{0,n} - a_{2,n} + 1 &= 0 \\
 -\frac{1}{2} a_{2,n} - b_{1,n} - b_{0,n} - \frac{1}{2} a_{0,n} - b_{2,n} &= 0 \\
 -\frac{1}{6} a_{2,n} + b_{0,n} + \frac{1}{6} a_{0,n} - b_{2,n} &= 0 \\
 -\frac{1}{2} b_{0,n} - \frac{1}{24} a_{2,n} - \frac{1}{24} a_{0,n} - \frac{1}{2} b_{2,n} &= 0,
 \end{aligned} \tag{33}$$

$$\begin{aligned}
 -a_{1,n-1} - a_{2,n-1} - a_{0,n-1} &= 0 \\
 1 - a_{2,n-1} + a_{0,n-1} &= 0 \\
 -1 - \frac{1}{2} a_{2,n-1} - \frac{1}{2} a_{0,n-1} - b_{2,n-1} - b_{1,n-1} - b_{0,n-1} &= 0 \\
 \frac{1}{2} + \frac{1}{6} a_{0,n-1} - \frac{1}{6} a_{2,n-1} - b_{2,n-1} + b_{0,n-1} &= 0 \\
 -\frac{1}{6} - \frac{1}{24} a_{0,n-1} - \frac{1}{24} a_{2,n-1} - \frac{1}{2} b_{2,n-1} - \frac{1}{2} b_{0,n-1} &= 0.
 \end{aligned} \tag{34}$$

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

$$\begin{aligned}
 a_{2,n+1} = \frac{1}{10}, \quad a_{1,n+1} = \frac{4}{5}, \quad a_{0,n+1} = \frac{-9}{10} \\
 b_{2,n+1} = \frac{11}{30}, \quad b_{0,n+1} = \frac{1}{30}
 \end{aligned}$$

$$\begin{aligned}
 a_{2,n} &= \frac{-7}{10}, & a_{1,n} &= \frac{12}{5}, & a_{0,n} &= \frac{-17}{10} \\
 & & b_{2,n} &= \frac{1}{60}, & b_{0,n} &= \frac{11}{60} \\
 a_{2,n-1} &= \frac{-3}{2}, & a_{1,n-1} &= 4, & a_{0,n-1} &= \frac{-5}{2} \\
 & & b_{2,n-1} &= \frac{1}{6}, & b_{0,n-1} &= \frac{-1}{6}.
 \end{aligned} \tag{35}$$

The local truncation error of the above formulae is given by

$$\text{L.T.E.}_{n+1} = \text{L.T.E.}_n = \text{L.T.E.}_{n-1} = -\frac{1}{45} h^5 y_n^{(5)}. \tag{36}$$

For the application of the first and second layer (3) and (4) of the methods (3)–(9) the following formula is also needed:

$$\begin{aligned}
 h y'_n &= aa_{1,n} y_n + aa_{0,n} y_{n-1} + h^2 (bb_{1,n} y''_n + bb_{0,n} y''_{n-1}) \\
 & -aa_{1,n} - aa_{0,n} = 0, \\
 & aa_{0,n} + 1 = 0, \\
 & -bb_{1,n} - bb_{0,n} - \frac{1}{2} aa_{0,n} = 0, \\
 & bb_{0,n} + \frac{1}{6} aa_{0,n} = 0.
 \end{aligned} \tag{37}$$

The solution of the above system of equations is given by

$$bb_{0,n} = \frac{1}{6}, \quad aa_{0,n} = -1, \quad bb_{1,n} = \frac{1}{3}, \quad aa_{1,n} = 1. \tag{38}$$

The local truncation error of the above formula is given by

$$\text{L.T.E.}_n = -\frac{1}{24} h^4 y_n^{(4)}. \tag{39}$$

3.1. Local error estimation

In the literature there are many methods for the estimation of the local truncation error (LTE) for the integration of systems of initial-value problems (see for example [28] and [29] and references therein).

In this paper the local error estimation technique is based on an embedded pair of integration methods and on the fact that when the phase-lag order is maximal then the approximation of the solution for the problems with an oscillatory or periodic solution is better.

We have the following definition

Definition 3. We define the local phase-lag error estimate in the lower order solution y_{n+1}^L by the quantity

$$\text{L.P.L.E} = |y_{n+1}^{\text{PLH}} - y_{n+1}^{\text{PLL}}|, \quad (40)$$

where y_{n+1}^{PLH} is the solution obtained with higher phase-lag order method and y_{n+1}^{PLL} is the solution obtained with lower phase-lag order method. In the present case y_{n+1}^{PLH} is the solution obtained using the multiderivative method of phase-lag order $2M$ obtained in this paper while y_{n+1}^{PLL} is the solution obtained using the multiderivative method of phase-lag order $2M - 2$ obtained in this paper, where $M = 7(1)10$. Under the assumption that h is sufficiently small, the **local phase-lag error** in y_{n+1}^{PLH} can be neglected compared with that in y_{n+1}^{PLL} .

If a local error of acc is requested and the n th step of the integration procedure is obtained using a step size equal to h_n , the estimated step size for the $(n + 1)$ st step, which would give a local phase-lag error of acc , must be

$$h_{n+1} = h_n \left(\frac{\text{acc}}{\text{L.P.L.E}} \right)^{1/q}, \quad (41)$$

where q is the phase-lag order of the method.

However, for ease of programming we have restricted all step changes to halving and doubling. Thus, based on the procedure developed in Ref. [30], the step control procedure which we have actually used is

$$\begin{aligned} \text{If } \text{L.P.L.E} < \text{acc}/100, \quad h_{n+1} &= 2h_n \\ \text{If } \text{acc} > \text{L.P.L.E} \geq \text{acc}/100, \quad h_{n+1} &= h_n \\ \text{If } \text{L.P.L.E} \geq \text{acc}, \quad h_{n+1} &= \frac{h_n}{2} \text{ and repeat the step.} \end{aligned} \quad (42)$$

We note, here, that the local phase-lag error estimate is in the lower order solution y_{n+1}^{PLL} . However, if this error estimate is acceptable, i.e., less than acc , we adopt the widely used procedure of performing local extrapolation. Thus, although we are actually controlling an estimate of the local phase-lag error in lower order solution y_{n+1}^{PLL} , it is the higher phase-lag order solution y_{n+1}^{PLH} which we actually accept at each point.

3.2. Coupled differential equations of the Schrödinger type

There are many problems in theoretical physics and chemistry, which can be transformed to the solution of coupled differential equations of the Schrödinger type.

The close-coupling differential equations of the Schrödinger type may be written in the form

$$\left[\frac{d^2}{dx^2} + k_i^2 - \frac{l_i(l_i + 1)}{x^2} - V_{ii} \right] y_{ij} = \sum_{m=1}^N V_{im} y_{mj} \quad (43)$$

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

We have investigated the case in which all channels are open. So we have the following boundary conditions (see for details [31]):

$$y_{ij} = 0 \text{ at } x = 0 \quad (44)$$

$$y_{ij} \sim k_i x j_{l_i}(k_i x) \delta_{ij} + \left(\frac{k_i}{k_j} \right)^{1/2} K_{ij} k_i x n_{l_i}(k_i x), \quad (45)$$

where $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions, respectively. We can use the present methods to problems involving close channels.

Based on the detailed analysis developed in [31] and defining a matrix K' and diagonal matrices M , N by

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

we find that the asymptotic condition (45) may be written as

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

One of the most popular methods for the approximate solution of the coupled differential equations arising from the Schrödinger equation is the Iterative Numerov method of Allison [31].

An important problem which can be transformed to close-coupling differential equations of the Schrödinger type is the rotational excitation of a diatomic molecule by neutral particle impact. Denoting, as in Ref. [31], 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

$$\begin{aligned} & \left[\frac{d^2}{dx^2} + k_{j'j}^2 - \frac{l'(l' + 1)}{x^2} \right] y_{j'l'}^{Jjl}(x) \\ &= \frac{2\mu}{\hbar^2} \sum_{j''} \sum_{l''} \langle j'l'; J | V | j''l''; J \rangle y_{j''l''}^{Jjl}(x), \end{aligned} \quad (46)$$

where

$$k_{j'j} = \frac{2\mu}{\hbar^2} \left[E + \frac{\hbar^2}{2I} \{j(j+1) - j'(j'+1)\} \right]. \quad (47)$$

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.

Following the analysis of [31], the potential V may be written as

$$V(x, \hat{\mathbf{k}}_{j'j} \hat{\mathbf{k}}_{jj}) = V_0(x) P_0(\hat{\mathbf{k}}_{j'j} \hat{\mathbf{k}}_{jj}) + V_2(x) P_2(\hat{\mathbf{k}}_{j'j} \hat{\mathbf{k}}_{jj}), \quad (48)$$

and the coupling matrix element is given by

$$\langle j'l'; J | V | j''l''; J \rangle = \delta_{j'j''} \delta_{l'l''} V_0(x) + f_2(j'l', j''l''; J) V_2(x), \quad (49)$$

where the f_2 coefficients can be obtained from formulas given by Bernstein et al. [32] and $\hat{\mathbf{k}}_{j'j}$ is a unit vector parallel to the wave vector $\mathbf{k}_{j'j}$ and P_i , $i = 0, 2$ are Legendre polynomials (see for details [32] and [33]). The boundary conditions may then be written as (see [31])

$$y_{j'l'}^{Jj}(x) = 0 \text{ at } x = 0 \quad (50)$$

$$y_{j'l'}^{Jj}(x) \sim \delta_{jj'} \delta_{ll'} \exp[-i(k_{jj}x - 1/2l\pi)] - \left(\frac{k_i}{k_j}\right)^{1/2} \times S^J(jl; j'l') \exp[i(k_{j'j}x - 1/2l'\pi)], \quad (51)$$

where the scattering \mathbf{S} matrix is related to the \mathbf{K} matrix of (45) by the relation

$$\mathbf{S} = (\mathbf{I} + i\mathbf{K})(\mathbf{I} - i\mathbf{K})^{-1}. \quad (52)$$

The calculation of the cross sections for rotational excitation of molecular hydrogen by impact of various heavy particles requires the existence of the numerical method for the integration from the initial value to matching points.

In our numerical test we choose the \mathbf{S} matrix which is calculated using the following parameters

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

As is described in [31], we take $J = 6$ and consider excitation of the rotator from the $j=0$ state to levels up to $j'=2, 4$ and 6 giving sets of **four, nine and sixteen coupled differential equations**, respectively. Following Bernstein [33] and Allison [31] the reduction of the interval $[0, \infty)$ to $[0, x_0]$ is obtained. The

Table 2
 RTC (real time of computation (in seconds)) and MErr (maximum absolute error) in the calculation of $|S|^2$ for the variable-step methods (1)–(3). $acc = 10^{-6}$.
 h_{\max} is the maximum stepsize.

Method	N	h_{\max}	RTC	MErr
Iterative numerov [31]	4	0.014	3.25	1.210^{-3}
	9	0.014	23.51	5.710^{-2}
	16	0.014	99.15	6.810^{-1}
Variable-step method of Raptis and Cash [30]	4	0.056	1.65	8.910^{-4}
	9	0.056	8.68	7.410^{-3}
	16	0.056	45.21	8.610^{-2}
New variable-step method	4	0.056	1.40	1.510^{-5}
	9	0.056	7.35	8.010^{-4}
	16	0.056	28.15	6.310^{-3}

wavefunctions are then vanished in this region and consequently the boundary condition (50) may be written as

$$y_{j'l}^{Jj'l}(x_0) = 0. \quad (53)$$

For the numerical solution of this problem we have used (1) the well known Iterative Numerov method of Allison [31], (2) the variable-step method of Raptis and Cash [30] and (3) the new variable-step method. In table 2 we present the real time of computation required by the methods mentioned above to calculate the square of the modulus of the S matrix for sets of 4, 9 and 16 coupled differential equations. In table 2 we also present the maximum absolute error produced in the above computations. In table 2 N indicates the number of equations of the set of coupled differential equations.

4. Conclusions

In this paper a new family of efficient multiderivative methods for the numerical solution of the Schrödinger type equations is introduced.

From the numerical results we have the following remarks:

- The Variable-step Method of Raptis and Cash [30] gives better results than the Iterative Numerov Method of Allison [31].
- The new developed method is more efficient than all 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).

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