Journal of Mathematical Chemistry 26 (1999) 327–341

Embedded eighth order methods for the numerical solution of the Schrödinger equation

G. Avdelas [a] and T.E. Simos [b]

[a] *Laboratory of Applied Mathematics and Computers, Department of Sciences, Technical University of Crete, Kounoupidiana, 73 100 Chania, Crete, Greece*
[b] *Section of Mathematics, School of Engineering, Department of Civil Engineering, University of Thrace, GR-67 100 Xanthi, Greece*
E-mail: tsimos@mail.ariadne-t.gr

Received 22 April 1999; revised 2 November 1999

A new method for the approximate numerical integration of the radial Schrödinger equation is developed in this paper. Phase-lag and stability analysis of the new method is included. The new method is called the embedded method because of a simple natural error control mechanism. Numerical results obtained for the phase-shift problem of the radial Schrödinger equation show the validity of the developed theory.

1. Introduction

There has been a great activity in the last decade for the numerical solution of the radial Schrödinger equation (see [1] and references therein). The aim of this activity is the construction of an efficient and reliable algorithm that approximates the solution.

The radial Schrödinger equation can be written as

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

Differential equations of the above type occur very frequently in many problems in theoretical physics and chemistry, in chemical physics, in physical chemistry, in astrophysics, in electronics and elsewere (see, for example, [9]). For the above reason the construction of an efficient and reliable numerical method is needed. In (1) the function $W(r) = l(l+1)/r^2 + V(r)$ denotes *the effective potential*, which satisfies $W(r) \to 0$ as $r \to \infty$, k^2 is a real number denoting *the energy*, l is a given integer and 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.

In [2,14] an explanation about the inefficiency of boundary and initial value methods is given.

One of the most popular and well known methods for the numerical solution of (1) is *Numerov's method*. The reason is that while the Numerov's method is of order four, it has a phase-lag of order four (i.e., of the same order as the linear symmetric four-step sixth algebraic order methods) and much more larger interval of periodicity than the linear symmetric four-step methods. High-order numerical methods for the eigenvalue problem of the radial Schrödinger equation have been developed for some special potentials $V(x)$ which are even functions (see, for example, [6,7]).

The Runge–Kutta type or hybrid methods is an alternative approach for deriving higher-order methods. This type of methods has been proposed by Cash and Raptis [4].

Another approach for developing efficient methods for the numerical solution of (1) is exponential fitting (see [17] and references therein). This approach is appropriate because for large values of r and positive k^2 the solution of (1) is *periodic*.

In [1] Avdelas and Simos have proposed a new approach for solving the Schrödinger type equations via simple fourth and sixth algebraic embedded pairs with a simple error control mechanism.

In section 2 the theory of the phase-lag analysis of symmetric two-step methods is developed. A family of eight algebraic order explicit methods is proposed in section 3 and their complete phase-lag and stability analysis is developed. In section 4 a simple error control mechanism, based on the phase-lag error, is described. An application of the proposed methods to the radial Schrödinger equation is presented in section 5, to show the efficiency of the new methods.

2. Phase-lag analysis

In the last decade there has been a great interest in the numerical solution of special second order periodic initial-value problems (see [5] and references therein):

$$y'' = f(x, y), \qquad y(x_0) = y_0, \qquad y'(x_0) = y'_0. \tag{3}$$

In order to investigate the periodic stability properties of numerical methods for solving the initial-value problem (3) Lambert and Watson [8] introduce the scalar test equation

$$y'' = -w^2 y \tag{4}$$

and the *interval of periodicity*.

Based on the theory developed in [8], when a symmetric two-step method is applied to the scalar test equation (4), a difference equation of the form

$$y_{n+1} - 2C(H)y_n + y_{n-1} = 0 \tag{5}$$

is obtained, where $H = wh$, h is the step length, $C(H) = B(H)/A(H)$, $A(H)$ and $B(H)$ are polynomials in H and y_n is the computed approximation to $y(nh)$, $n = 0, 1, 2, \ldots$.

The characteristic equation associated with (5) is

$$s^2 - 2C(H)s + 1 = 0. \tag{6}$$

A very important insight for the construction of the numerical methods for the above described problems has been developed by Brusa and Nigro [3], where they introduced the property of the frequency distortion as an important characteristic of a method for solving special second order initial-value problems. For frequency distortion other authors (see [5] and references therein) use the terms *phase-lag, phase error or dispersion*. From now on we use the term *phase-lag*.

A significant number of methods with minimal phase-lag have been developed in the last decade (see [1] and references therein).

Based on Coleman [5] when a symmetric two-step method is applied to the scalar test equation $y'' = -w^2 y$, a difference equation (5) is obtained. The characteristic equation associated with (5) is given by (6). The roots of the characteristic equation (6) are denoted as s_1 and s_2.

We have the following definitions.

Definition 1 [16,18]. The method (5) is defined as unconditionally stable if $|s_1| \leqslant 1$ and $|s_2| \leqslant 1$ for all values of wh.

Definition 2. Following Lambert and Watson [8] we say that the numerical method (5) has an interval of periodicity $(0, H_0^2)$, if, for all $H^2 \in (0, H_0^2)$, s_1 and s_2 satisfy

$$s_1 = \mathrm{e}^{\mathrm{i}\theta(H)} \quad \text{and} \quad s_2 = \mathrm{e}^{-\mathrm{i}\theta(H)}, \tag{7}$$

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

Definition 3. For any method corresponding to the characteristic equation (6) the phase-lag is defined as the leading term in the expansion of

$$t = H - \theta(H) = H - \cos^{-1}\bigl[C(H)\bigr]. \tag{8}$$

If the quantity $t = \mathrm{O}(H^{q+1})$ as $H \to 0$, the order of phase-lag is q.

Definition 4 [8]. The method (5) is *P-stable* if its *interval of periodicity* is $(0, \infty)$.

And we have the following theorems:

Theorem 1. A method which has the characteristic equation (6), has an interval of periodicity $(0, H_0^2)$, if for all $H^2 \in (0, H_0^2)$ $|C(H)| < 1$.

For the proof, see [15].

Theorem 2. About the method which has an interval of periodicity $(0, H_0^2)$ we can write

$$\cos\left[\theta(H)\right] = C(H), \quad \text{where } H^2 \in \left(0, H_0^2\right). \tag{9}$$

For the proof, see [15].

Based on the above Coleman [5] has arrived at the following remark.

Remark 1. If the phase-lag order is $q = 2r$ then we have

$$\begin{aligned} &t = cH^{2r+1} + \mathrm{O}\left(H^{2r+3}\right) \\ &\quad \Rightarrow \cos(H) - C(H) = \cos(H) - \cos(H-t) = cH^{2r+2} + \mathrm{O}\left(H^{2r+4}\right). \end{aligned} \tag{10}$$

3. The new embedded methods

In this section we will develop a group of families of methods of algebraic order eight with minimal phase-lag. We note that these methods have a natural error-control mechanism. In order to explain the term "embedded" we mention the following. We denote the family of this group with phase-lag of order p as family b and the next family with phase-lag of order $p+2$ as family $b+1$. So we can use, as in embedded Runge–Kutta methods, the family $b+1$ to estimate the error of the phase-lag of the family b; for this reason these methods can be called *embedded*.

3.1. The new embedded eighth algebraic order method

We consider the following family of explicit methods:

$$\overline{y}_{n+1} = 2y_n - y_{n-1} + h^2 y_n'', \tag{11}$$

$$\overline{y}_{n,k,b} = y_n - a_{b-k} h^2 \left[\overline{y}_{n+1}'' - 2\overline{y}_{n,k-1,b}'' + y_{n-1}''\right], \quad k = 1(1)b, \tag{12}$$

$$\overline{\overline{y}}_{n+1} = 2y_n - y_{n-1} + \frac{h^2}{12}\left[\overline{y}_{n+1}'' + 10\overline{y}_{n,b,b}'' + y_{n-1}''\right], \tag{13}$$

$$\begin{aligned} \overline{y}_{n+1/2} = {} & \frac{1}{104}\left[5\overline{\overline{y}}_{n+1} + 146y_n - 47y_{n-1}\right] \\ & + \frac{h^2}{4992}\left[-59\overline{\overline{y}}_{n+1}'' + 1438y_n'' + 253y_{n-1}''\right], \end{aligned} \tag{14}$$

$$\overline{y}_{n-1/2} = \frac{1}{52}\left[3\overline{\overline{y}}_{n+1} + 20y_n + 29y_{n-1}\right] + \frac{h^2}{4992}\left[41\overline{\overline{y}}_{n+1}'' - 682y_n'' - 271y_{n-1}''\right], \tag{15}$$

$$\widehat{y}_{n+1} = 2y_n - y_{n-1} + \frac{h^2}{60}\left[\overline{\overline{y}}_{n+1}'' + 26y_n'' + y_{n-1}'' + 16\left(\overline{y}_{n+1/2}'' + \overline{y}_{n-1/2}''\right)\right], \tag{16}$$

$$\begin{aligned} \widehat{y}_{n+1/2} = {} & \frac{1}{128}\left[-25\widehat{y}_{n+1} + 205y_n - 15y_{n-1} - 37y_{n-2}\right] \\ & + \frac{h^2}{1536}\left[23\widehat{y}_{n+1}'' + 761y_n'' + 509y_{n-1}'' + 27y_{n-2}''\right], \end{aligned} \tag{17}$$

$$\widehat{y}_{n-1/2} = \frac{1}{128}\big[37\widehat{y}_{n+1} + 27y_n + 27y_{n-1} + 37y_{n-2}\big] + \frac{h^2}{512}\big[-9\widehat{y}''_{n+1} - 171y''_n - 171y''_{n-1} - 9y''_{n-2}\big], \tag{18}$$

$$\widehat{y}_{n+1/4} = \frac{1}{4096}\big[605\widehat{y}_{n+1} + 4070y_n - 579y_{n-1} - 160\big(\widehat{y}_{n+1/2} - \widehat{y}_{n-1/2}\big)\big] - \frac{h^2}{49152}\big[113\widehat{y}''_{n+1} - 1390y''_n - 103y''_{n-1} + 1944\big(\widehat{y}''_{n+1/2} - \widehat{y}''_{n-1/2}\big)\big], \tag{19}$$

$$\widehat{y}_{n-1/4} = -\frac{1}{4096}\big[579\widehat{y}_{n+1} - 4070y_n - 605y_{n-1} - 160\big(\widehat{y}_{n+1/2} - \widehat{y}_{n-1/2}\big)\big] + \frac{h^2}{49152}\big[103\widehat{y}''_{n+1} + 1390y''_n - 113y''_{n-1} + 1944\big(\widehat{y}''_{n+1/2} - \widehat{y}''_{n-1/2}\big)\big], \tag{20}$$

$$y_{n+1} - 2y_n + y_{n-1} = \frac{h^2}{3780}\big[47\big(\widehat{y}''_{n+1} + y''_{n-1}\big) + 1328\big(\widehat{y}''_{n+1/2} + \widehat{y}''_{n-1/2}\big) - 1024\big(\widehat{y}''_{n+1/4} + \widehat{y}''_{n-1/4}\big) + 3078y''_n\big], \tag{21}$$

where

$$y''_n = f(x_n, y_n), \qquad \overline{y}''_{n+1} = f\big(x_{n+1}, \overline{y}_{n+1}\big),$$
$$\overline{y}''_{n\pm1/2} = f\big(x_{n+1/2}, \overline{y}_{n\pm1/2}\big), \qquad \overline{y}''_{n,k-1,b} = f\big(x_n, \overline{y}_{n,k-1,b}\big),$$
$$\overline{\overline{y}}''_{n+1} = f\big(x_{n+1}, \overline{\overline{y}}_{n+1}\big), \qquad \widehat{y}''_{n+1} = f\big(x_{n+1}, \widehat{y}_{n+1}\big),$$
$$\widehat{y}''_{n\pm1/2} = f\big(x_{n+1}, \widehat{y}_{n\pm1/2}\big), \qquad \widehat{y}''_{n\pm1/4} = f\big(x_{n+1}, \widehat{y}_{n\pm1/4}\big),$$

k is the number of the layer, b is the number of the family and $\overline{y}_{n,0,b} = y_n$. We note that a_{b-k}, $k = 1(1)b$, are free parameters of the group of families which can be chosen in order that some critical properties of a numerical method are satisfied. If we follow the definition of a stage given by Coleman in [5], then we observe that in (11)–(21) each of the couples of formulas (14)–(15), (17)–(18), (19)–(20) corresponds to a stage. Also the formulae (12)–(13) correspond to a stage. Then one can easily see that in each family, say b, the total number of stages N is given by

$$N = b + 6. \tag{22}$$

Applying the Taylor series expansions of y_{n+1}, y_n and y_{n-1} about x_n in (11)–(21) we have the following result for the local truncation error (L.T.E.) of the families (11)–(21):

$$\text{L.T.E.} = h^{10}\bigg[-\frac{71}{47174400}\,y_n^{(4)}F'_n - \frac{15553}{14631321600}\,y_n^{(8)}F_n - \frac{31}{232243200}\,y_n^{(10)} - \frac{1633}{1415232000}\,y_n^{(6)}F_n^2 - \frac{71}{393120}\,a_b y_n^{(4)}F'_n\bigg], \tag{23}$$

where $F_n = \partial f/\partial x$, $F'_n = \mathrm{d}F/\mathrm{d}x$.

We apply this group of families to the scalar test equation (4). Setting $H = wh$ we get a difference equation of the form (5).

Theorem 3. For the method given by (11)–(21) the polynomial $C(H)$ in (5) is given by

$$C(H) = 1 - \frac{H^2}{2} + \frac{H^4}{24} - \frac{H^6}{720} + \frac{H^8}{40320} + \frac{119H^{10}}{40435200} + \frac{H^{12}}{29030400} + \left(\frac{H^{14}}{2903040} + \frac{95H^{12}}{2830464} + \frac{55H^{10}}{67392}\right)\Delta_b, \tag{24}$$

where

$$\Delta_b = \sum_{i=0}^{b-1} \left(-2H^2\right)^i \prod_{j=0}^{i} a_j \tag{25}$$

with a_k, $k = 0(1)b-1$, $b = 1, 2, \ldots,$ real numbers.

For the proof, see appendix A.

The characteristic equation associated with (5) is (6).

With the help of theorems 1 and 2, and remarks 1 and 2 of section 2 we have the following theorem.

Theorem 4. For all explicit methods defined by (11)–(21) and for proper a_k, $k = 0(1)b-1$, $b = 1, 2, \ldots,$ the phase-lag is $\mathrm{O}(H^{2N}) = \mathrm{O}(H^{2b+12})$.

Proof. From definition 2 and remark 1 of the previous section we can conclude that the phase-lag of the family of methods (11)–(21) is given as the leading term in the expansion of

$$S = \frac{\cos(H) - C(H)}{H^2}. \tag{26}$$

If we substitute the series expansion of $C(H)$ given by (24) and the Taylor series expansion of $\cos(H)$ into (26) we have

$$\begin{aligned} S &= \frac{\sum_{N=5}^{\infty}\left[(-1)^N \frac{H^{2N}}{(2N)!}\right] - \left[\left(\frac{55}{67392} + \frac{95H^2}{2830464} + \frac{H^4}{2903040}\right)\Delta_b - \frac{119}{40435200} - \frac{H^2}{29030400}\right]H^{10}}{H^2} \\ &= -\left[\frac{911}{283046400} + \frac{31H^2}{958003200} + \frac{H^4}{87178291200} \right. \\ &\quad \left. + \left(\frac{55}{67392} + \frac{95H^2}{2830464} + \frac{H^4}{2903040}\right)\Delta_b\right]H^8 + \mathrm{O}\left(H^{2b+12}\right). \end{aligned} \tag{27}$$

Then it is easy to find the values of coefficients a_k, $k = 1(1)b$, $b = 1, 2, \ldots$, from the indentity

$$\left(\frac{55}{67392} + \frac{95H^2}{2830464} + \frac{H^4}{2903040}\right)\Delta_b \equiv -\frac{911}{283046400} - \frac{31H^2}{958003200} - \frac{H^4}{87178291200}, \tag{28}$$

or from

$$\Delta_b \equiv -\frac{911}{231000} + \frac{5231H^2}{42688800} - \frac{16709351H^4}{4930556400000} + \cdots, \tag{29}$$

or from

$$\sum_{i=0}^{b-1}\left(-2H^2\right)^i \prod_{j=0}^{i} a_j \equiv s_0 + s_1 H^2 + s_2 H^4 + \cdots, \tag{30}$$

where s_i, $i = 0, 1, 2, \ldots$, are known coefficients of the polynomial of H of the second part of (29).

Using (30) sequentially for $b = 1, 2, \ldots$ we can have the following algorithm to find the coefficients of the method:

$$\begin{aligned} a_0 &= s_0, \\ a_1 &= \frac{s_1}{-2a_0} = -\frac{s_1}{2s_0}, \\ a_2 &= \frac{s_2}{(-2)^2 a_0 a_1} = \frac{s_2}{(-2)^2 s_0}\,\frac{-2s_0}{s_1} = \frac{s_2}{-2s_1}, \end{aligned}$$

and generally

$$a_b = \frac{s_b}{(-2)^b a_0 a_1 \cdots a_{b-1}} = \frac{s_b}{(-2)^b s_0}\,\frac{-2s_0}{s_1}\,\frac{-2s_1}{s_2}\cdots\frac{-2s_{b-2}}{s_{b-1}} = \frac{s_b}{-2s_{b-1}}. \tag{31}$$

Then, it is easy that for a specific value of $b = 1, 2, \ldots$ and for the corresponding a_k, $k = 0(1)b - 1$, which are given from relationships (31), the phase-lag of the method (11)–(21) is $\mathrm{O}(H^{2N}) = \mathrm{O}(H^{2b+12})$, where $N = b + 6$. $\square$

In order to find the intervals of periodicity of the family of methods (11)–(21) under the condition to have minimal phase-lag of order $\mathrm{O}(H^{2N})$ (i.e., for the coefficients a_i, $i = 0(1)b$, given by (31)) we can see from the theorem 1 that it must be $[1 + C(H)][1 - C(H)] > 0$. By applying the polynomial $C(H)$ given by (24) to the above formula and following the proof of the theorem 2 and corollary of [5] (see [5, pp. 149–150]), it can be seen that the intervals of periodicity for each family of methods are given by table 1.

Table 1
Interval of periodicity for the embedded eighth order method. b is the number of the family.

b	$H_{0,b}^2$	b	$H_{0,b}^2$
1	8.26	2	17.17
3	9.28	4	20.03
5	9.70	6	22.35
7	9.83	8	24.26
9	9.86	10	25.85
11	9.87	12	27.21
13	9.87	14	28.37
...	...	...	...
29	9.87	30	33.91
...	...	...	...
49	9.87	50	36.94
...	...	...	...

4. Error estimation – local phase-lag error

The local truncation error (L.T.E.) for the integration of systems of initial-value problems is estimated using several methods (see, for example, [12]).

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

We have the following definition:

Definition 5. We define the *local phase-lag error* estimate in the lower order solution y_{n+1}^{PLL} by the quantity

$$\mathrm{L.PL.E.} = \left|y_{n+1}^{\mathrm{PLH}} - y_{n+1}^{\mathrm{PLL}}\right|, \tag{32}$$

where y_{n+1}^{PLH} is the solution obtained with higher phase-lag order method using the family $b+1$ and y_{n+1}^{PLL} is the solution obtained with lower phase-lag order method using the family b.

Remark 2. 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 the local phase-lag error of acc is requested and the step size of the integration used for the nth step length is h_n the estimated step size for the $(n+1)$st step, which would give a local phase-lag error of acc, must be

$$h_{n+1} = h_n \left(\frac{\mathrm{acc}}{\mathrm{L.PL.E.}}\right)^{1/q}, \tag{33}$$

where q is the order of the phase-lag.

However, for ease of programming we have restricted all step changes to halving and doubling. Thus, based on the procedure developed in [10] for the local truncation error, the step control procedure which we have actually used is:

$$\begin{array}{ll} \text{If L.PL.E.} < \text{acc}, & h_{n+1} = 2h_n. \\ \text{If 100 acc} > \text{L.PL.E.} \geqslant \text{acc}, & h_{n+1} = h_n. \\ \text{If L.PL.E.} \geqslant \text{100 acc}, & h_{n+1} = \dfrac{h_n}{2} \quad \text{and repeat the step.} \end{array} \tag{34}$$

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 error in the lower phase-lag order solution y_{n+1}^{PLL}, it is the higher order solution y_{n+1}^{PLH} which we actually accept at each point.

Now our procedure to estimate the local phase-lag error in y_{n+1}^{PLL} using the phase-lag of y_{n+1}^{PLH} is clear. At every step we start with $k = 1$ and go on increasing k and checking the local phase-lag error (L.PL.E.) until L.PL.E. is less than the bound acc ($1 \leqslant k \leqslant b$). If there is a k for which L.PL.E. $<$ acc then the step size is doubled, otherwise we carry out the integration. Moreover, when we applied our method to our computer (i586 PC) we observed that, if the value of b was greater than 5, then (because of the round off errors) the phase-lag became of higher order than the precision of the computer used.

5. Numerical illustrations

In the present section we will illustrate the efficiency of the new proposed embedded technique by applying it to a well known problem. We consider the numerical integration of the radial Schrödinger equation (1) with one boundary condition $y(0) = 0$, and a second boundary condition for large values of r determined by physical considerations. The form of the second boundary condition depends crucially on the sign of k^2. In the case where $k^2 > 0$, then, in general, the potential function $V(r)$ dies away faster than the term $l(l+1)/r^2$, and equation (1) effectively reduces to $y''(r) + (k^2 - l(l+1)/r^2)y(r) = 0$, for large r. The reduced equation has linearly independent solutions $krj_l(kr)$ and $krn_l(kr)$, where $j_l(kr)$ and $n_l(kr)$ are the spherical Bessel and Neumann functions, respectively. Thus, the solution of equation (1) has the asymptotic form

$$\begin{aligned} y(r) &\cong_{r\to\infty} Akrj_l(kr) - Bkrn_l(kr) \\ &\cong_{r\to\infty} A\left[\sin\left(kr - \frac{l\pi}{2}\right) + \tan\delta_l \cos\left(kr - \frac{l\pi}{2}\right)\right], \end{aligned}$$

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

$$\tan\delta_l = \frac{y(r_2)S(r_1) - y(r_1)S(r_2)}{y(r_1)C(r_2) - y(r_2)C(r_1)} \tag{35}$$

for r_1 and r_2 distinct points in the asymptotic region with $S(r) = krj_l(kr)$ and $C(r) = -krn_l(kr)$.

We illustrate the performance of the new method derived in section 3 by applying it to the solution of (1), where $V(r)$ is the *Lennard-Jones potential* which has been widely discussed in the literature. For this problem the potential $V(r)$ is given by

$$V(r) = m\left(\frac{1}{r^{12}} - \frac{1}{r^6}\right), \quad \text{where } m = 500. \tag{36}$$

We solve this problem as an initial value one and, in order to be able to use a two-step method, we need an extra initial condition to be specified, e.g., y_1 ($=y(h)$). It is well known that, for values of r close to the origin, the solution of (1) behaves like

$$y(r) \simeq Cr^{l+1} \quad \text{as } r \to 0. \tag{37}$$

In view of this we use $y_1 = h^{l+1}$ as our extra initial condition.

The problem we consider is the computation of the relevant phase shifts correct to 6 decimal places. We will consider five approaches:

(1) based on the sixth algebraic order embedded method of Avdelas and Simos [1],

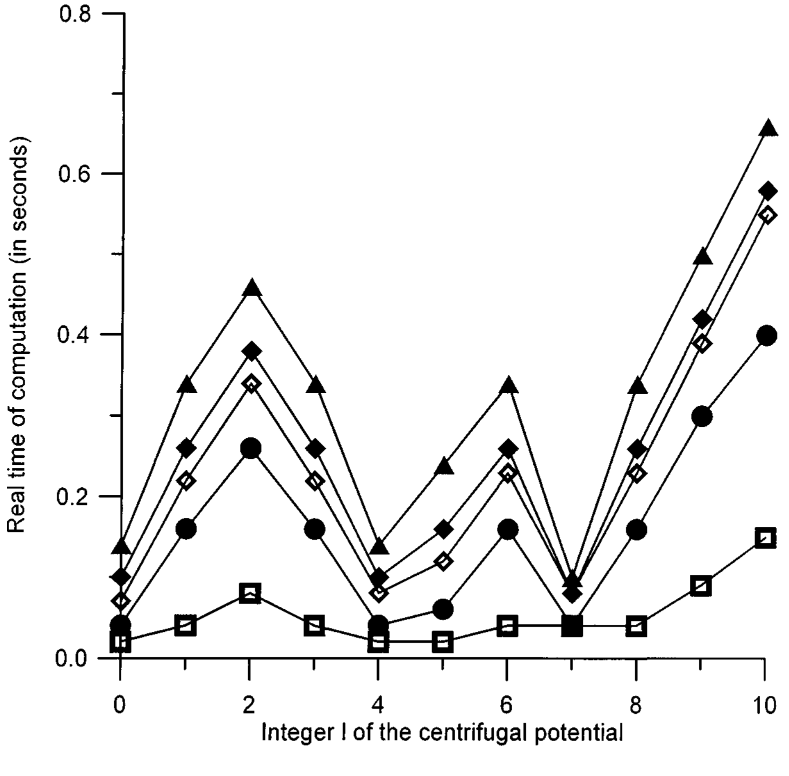

Figure 1. —▲— Method (1). —◆— Method (2). —◇— Method (3). —●— Method (4). —□— Method (5).

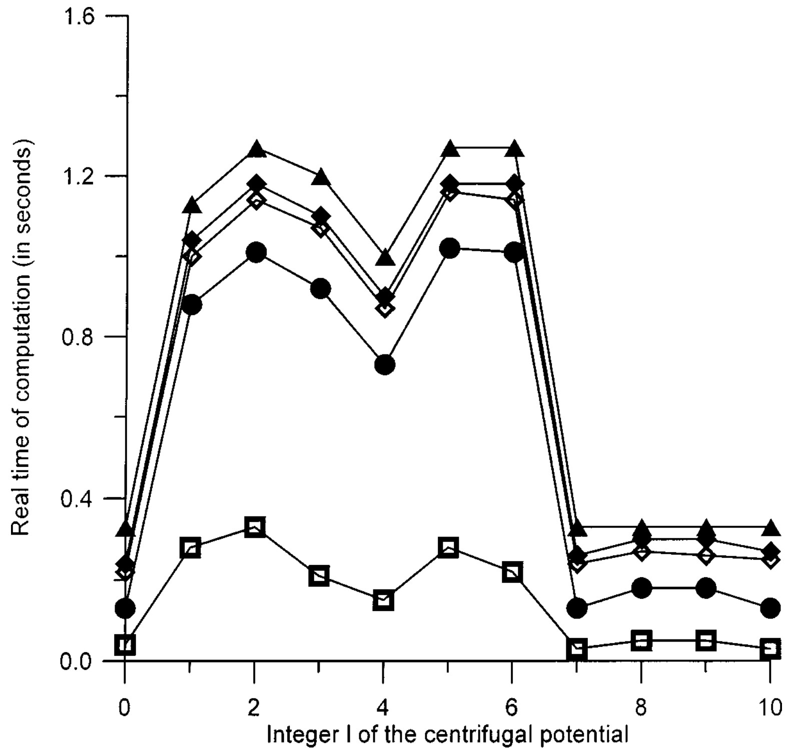

Figure 2. Method (1). Method (2). Method (3). Method (4). Method (5).

(2) based on the variable step method of Simos [14],

(3) based on the variable step method of Simos and Mousadis [15],

(4) based on the generator of P-stable methods of Avdelas and Simos [2],

(5) based on the family of methods developed in section 3.

The procedures (1)–(4) are described in [1,14,15,2], respectively, and are used without modification.

The method used in (5) is developed in section 3 and the error control procedure is described in section 4.

In figures 1–3 we present the real time of computation of the phase shifts correct to 6 decimal places. We note that, based on [10], the acc we take for the application of the new methods is equal to 10^{-2M}, where M is the number of required correct decimal digits.

6. Conclusions

We have constructed a new family of methods with an embedded automatic error control procedure. We note that for this family of methods we have proposed proce-

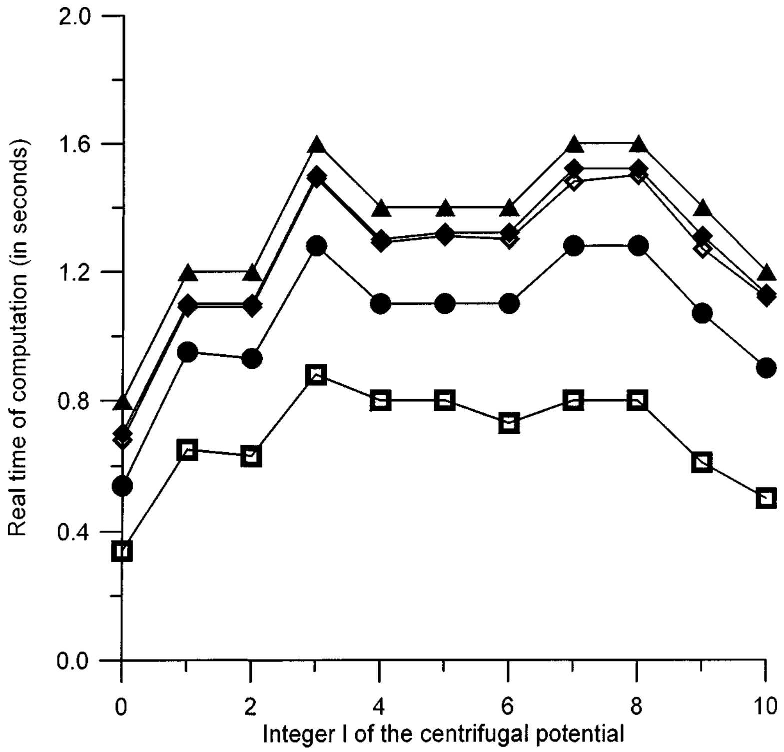

Figure 3. —▲— Method (1). —◆— Method (2). —◇— Method (3). —●— Method (4). —□— Method (5).

dures to define the parameters of the methods of the families such that the phase-lag of the methods be minimal (until the phase-lag became of the order of the precision of the computer used). We also note that this family of embedded methods has intervals of periodicity greater than the well known methods of Numerov and Cash and Raptis [4]. It can be seen from the theoretical and numerical results that the new methods are considerably more efficient than the other numerical methods which we have considered for the numerical solution of the Schrödinger equation.

All computations were carried out on a PC i586 using double precision arithmetics (16 significant digits accuracy).

Appendix A. Proof of the theorem 3

To calculate the coefficients a_k of the family b of the group of methods (11)–(21) we have applied the above mentioned algorithm to the test equation (4). So, we have the following formulae:

$$\begin{aligned} \overline{y}_{n+1} &= \left(2 - H^2\right) y_n - y_{n-1}, \\ \overline{y}_{n,k,b} &= y_n - a_{b-k} H^2 \left[\left(2 - H^2\right) y_n - 2\overline{y}_{n,k-1,b}\right], \quad k = 1(1)b, \qquad \overline{y}_{n,0,b} = y_n. \end{aligned} \tag{38}$$

The above relationships give

$$\overline{y}_{n,b,b} = \left[1 - H^4 \sum_{i=0}^{b-1} \left(-2H^2\right)^i \prod_{j=0}^{i} a_j\right] y_n, \tag{39}$$

or if we use the relationship (25)

$$\begin{aligned}
\overline{y}_{n,b,b} &= \left[1 - \Delta_b H^4\right] y_n, \qquad (40)\\
\overline{\overline{y}}_{n+1} &= \left[2 - H^2 + \frac{H^4}{12} + \frac{5H^6}{6}\Delta_b\right] y_n - y_{n-1},\\
\overline{y}_{n+1/2} &= \left[\frac{3}{2} - \frac{5H^2}{16} - \frac{H^4}{128} + \frac{59H^6}{59904} + \left(\frac{25H^6}{624} + \frac{295H^8}{29952}\right)\Delta_b\right] y_n\\
&\quad - \left(\frac{1}{2} + \frac{H^6}{16}\right) y_{n-1},\\
\overline{y}_{n-1/2} &= \left[\frac{1}{2} + \frac{H^2}{16} + \frac{5H^4}{384} - \frac{41H^6}{59904} + \left(\frac{5H^6}{104} - \frac{205H^8}{29952}\right)\Delta_b\right] y_n\\
&\quad + \left(\frac{1}{2} + \frac{H^6}{16}\right) y_{n-1},\\
\widehat{y}_{n+1} &= \left[2 - H^2 + \frac{H^4}{12} - \frac{H^6}{360} - \frac{H^8}{12480} - \left(\frac{35H^8}{936} + \frac{H^{10}}{1248}\right)\Delta_b\right] y_n - y_{n-1},\\
\widehat{y}_{n+1/2} &= \left[\frac{155}{128} - \frac{169H^2}{512} - \frac{H^4}{768} - \frac{13H^6}{18432} + \frac{823H^8}{14376960} + \frac{23H^{10}}{19169280}\right.\\
&\quad \left. + \left(\frac{875H^8}{119808} + \frac{515H^{10}}{718848} + \frac{23H^{12}}{1916928}\right)\Delta_b\right] y_n + \left(\frac{5}{64} - \frac{81H^2}{256}\right) y_{n-1}\\
&\quad - \left(\frac{37}{128} + \frac{9H^2}{512}\right) y_{n-2},\\
\widehat{y}_{n-1/2} &= \left[\frac{101}{128} + \frac{41H^2}{512} + \frac{5H^4}{768} + \frac{61H^6}{92160} - \frac{23H^8}{319488} - \frac{3H^{10}}{2129920}\right.\\
&\quad \left. - \left(\frac{1295H^8}{119808} + \frac{71H^{10}}{79872} + \frac{3H^{12}}{212992}\right)\Delta_b\right] y_n - \left(\frac{5}{64} - \frac{81H^2}{256}\right) y_{n-1}\\
&\quad + \left(\frac{37}{128} + \frac{9H^2}{512}\right) y_{n-2},\\
\widehat{y}_{n+1/4} &= \left[\frac{10425}{8192} - \frac{18177H^2}{131072} - \frac{3097H^4}{524288} - \frac{373H^6}{786432}\right.\\
&\quad - \frac{811H^8}{10485760} + \frac{2631H^{10}}{545259520} + \frac{45H^{12}}{436207616}\\
&\quad \left. + \left(-\frac{1225}{196608} + \frac{6125H^2}{13631488} + \frac{1653H^4}{27262976} + \frac{225H^6}{218103808}\right) H^8 \Delta_b\right] y_n
\end{aligned}$$

$$+\left(-\frac{1209}{4096}+\frac{1737H^2}{65536}-\frac{6561H^4}{262144}\right)y_{n-1}$$
$$+\left(\frac{185}{8192}-\frac{28179H^2}{131072}-\frac{729H^4}{524288}\right)y_{n-2},$$

$$\widehat{y}_{n-1/4}=\left[\frac{5959}{8192}+\frac{9985H^2}{131072}+\frac{9803H^4}{1572864}+\frac{5587H^6}{11796480}\right.$$
$$+\frac{21593H^8}{283115520}-\frac{23759H^{10}}{4907335680}-\frac{45H^{12}}{436207616}$$
$$\left.+\left(\frac{3535}{589824}-\frac{170047H^2}{368050176}-\frac{14917H^4}{245366784}-\frac{225H^6}{218103808}\right)H^8\Delta_b\right]y_n$$
$$-\left(-\frac{1209}{4096}+\frac{1737H^2}{65536}-\frac{6561H^4}{262144}\right)y_{n-1}$$
$$-\left(\frac{185}{8192}-\frac{2817H^2}{131072}-\frac{729H^4}{524288}\right)y_{n-2}.$$

Using the above relationships (21) becomes:

$$y_{n+1}+2\left[-1+\frac{H^2}{2}-\frac{H^4}{24}+\frac{H^6}{720}-\frac{H^8}{40320}-\frac{119H^{10}}{40435200}-\frac{H^{12}}{29030400}\right.$$
$$\left.-\left(\frac{55H^{10}}{67392}+\frac{95H^{12}}{2830464}+\frac{H^{14}}{2903040}\right)\Delta_b\right]y_n+y_{n-1}. \tag{41}$$

Therefore, (5) and (41) give the formula (24) of $C(H)$.

Acknowledgements

The authors wish to thank the anonymous referees for their careful reading of the manuscript and their fruitful comments and suggestions.

References

[1] G. Avdelas and T.E. Simos, Embedded methods for the numerical solution of the Schrödinger equation, Comput. Math. Appl. 31 (1996) 85–102.

[2] G. Avdelas and T.E. Simos, A generator of high-order embedded P-stable method for the numerical solution of the Schrödinger equation, J. Comput. Appl. Math. 72 (1996) 345–358.

[3] L. Brusa and L. Nigro, A one-step method for direct integration of structural dynamic equations, Int. J. Numer. Methods Engrg. 15 (1980) 685–699.

[4] J.R. Cash and A.D. Raptis, A high order method for the numerical solution of the one-dimensional Schrödinger equation, Comput. Phys. Commun. 33 (1984) 299–304.

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

[6] V. Fack and G. Vanden Berghe, A finite difference approach for the calculation of perturbed oscillator energies, J. Phys. A: Math. Gen. 18 (1985) 3355–3363.

[7] V. Fack and G. Vanden Berghe, (Extended) Numerov method for computing eigenvalues of specific Schrödinger equations, J. Phys. A: Math. Gen. 20 (1987) 4153–4160.

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

[9] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics* (Pergamon, New York, 1965).

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

[11] A.D. Raptis and J.R. Cash, Exponential and Bessel fitting methods for the numerical solution of the Schrödinger equation, Comput. Phys. Commun. 44 (1987) 95–103.

[12] L.F. Shampine, H.A. Watts and S.M. Davenport, Solving nonstiff ordinary differential equations – The state of the art, SIAM Rev. 18 (1976) 376–411.

[13] T.E. Simos, New variable-step procedure for the numerical integration of the one-dimensional Schrödinger equation, J. Comput. Phys. 108 (1993) 175–179.

[14] T.E. Simos, Eighth-order method for accurate computations for the elastic scattering phase-shift problem, Internat. J. Quant. Chem. 68 (1998) 191–200.

[15] T.E. Simos and G. Mousadis, A two-step method for the numerical solution of the radial Schrödinger equation, Comput. Math. Appl. 29 (1995) 31–37.

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

[17] R.M. Thomas and T.E. Simos, A family of hybrid exponentially fitted predictor–corrector methods for the numerical integration of the radial Schrödinger equation, J. Comput. Appl. Math. 87 (1997) 215–226.

[18] P.J. van der Houwen and B.P. Sommeijer, Explicit Runge–Kutta (–Nyström) methods with reduced phase errors for computing oscillating solutions, SIAM J. Numer. Anal. 24 (1987) 595–617.