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A family of P-stable eighth algebraic order methods with exponential fitting facilities

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A P-stable exponentially-fitted method of algebraic order eight for the approximate numerical integration of the Schrödinger equation is developed in this paper. Since the method is P-stable (i.e., its interval of periodicity is equal to $(0, \infty)$), large stepsizes for the numerical integration can be used. Based on this new method and on a sixth algebraic order exponentially-fitted P-stable method developed by Simos and Williams [1], a new variable step method is obtained. Numerical results presented for the coupled differential equations arising from the Schrödinger equation show the efficiency of the developed method.

KEY WORDS: Schrödinger equation, P-stability, error control, variable-step, phase-shift problem, scattering problems

1. Introduction

Much research has been done on the numerical solution of the radial Schrödinger equation (see [2–9] and references therein). The scope of this work is the development of an accurate and computationally efficient method that approximate the solution.

The radial Schrödinger equation can be written as

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

A lot of problems in theoretical physics and chemistry, in chemical physics, in physical chemistry, in astrophysics, in electronics and elsewere, are expressed with equations of the above type (see, e.g., [10,11]). For the approximate solution of the problems of the

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previously mentioned type the development of suitable numerical methods is needed. In (1) the function $W(x) = l(l+1)/x^2 + V(x)$ denotes *the effective potential*, which satisfies $W(x) \to 0$ as $x \to \infty$, 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 x, determined by physical considerations.

One of the most popular and well known methods for the numerical solution of (1) is *Numerov's method*. This is explained by the fact that Numerov's method is of order four, has a phase-lag of order four (i.e., of the same order with 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 produced for some special potentials $V(x)$ which are even functions (see, e.g., [12,13]). We note here that due to the fact that the Schrödinger type equations have oscillating solutions it would be of much interest to investigate the construction of high algebraic order P-stable numerical methods for their efficient solution. This is because when we have a P-stable method, large step sizes can be used without lost of accuracy.

The Runge–Kutta type or hybrid methods is an alternative approach for deriving higher order methods. These type of methods has been proposed by Cash and Raptis [14].

In [6] Simos has contructed low algebraic order (fourth algebraic order) P-stable exponentially-fitted methods.

The purpose of this paper is the development of P-stable exponentially-fitted eighth algebraic order hybrid method for the solution of (1). In section 2 the stability analysis of two-step methods is presented. In section 3 an one-parameter family of eighth algebraic order methods is presented and the development of eighth algebraic order exponentially-fitted method is described. In section 4 an error control mechanism is described. An application of the proposed variable step method to the coupled differential equations arising from the Schrödinger equation is presented in section 5, to show the efficiency of the new methods.

2. Stability analysis

Great interest has been noticed the past years in the numerical solution of special second order periodic initial-value problems (see [15] and references therein)

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

In order to investigate the periodic stability properties of numerical methods for solving the initial-value problem (3) Lambert and Watson [16] introduce the scalar test equation

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

and the *interval of periodicity*.

Based on the theory developed in [15], 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

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

Based on Coleman [15] 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 [17,18].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 [16] 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. [16]. The method (5) is *P-stable* if its *interval of periodicity* is $(0, \infty)$.

And 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 [19].

3. The new family of eighth algebraic order P-stable methods

We consider the following family of implicit methods:

$$\bar{y}_{n+1/2} = \frac{1}{2}(y_n + y_{n+1}) - h^2\left(ay''_n + \left(\frac{1}{8} - a\right)y''_{n+1}\right) + \mathrm{O}(h^3), \tag{8}$$

$$\bar{y}_{n-1/2} = \frac{1}{2}(y_n + y_{n-1}) - h^2\left(ay''_n + \left(\frac{1}{8} - a\right)y''_{n-1}\right) + \mathrm{O}(h^3), \tag{9}$$

$$\tilde{y}_{n+1/2} = \frac{1}{2}(y_n + y_{n+1}) - \frac{h^2}{96}\left(y''_{n+1} + 10\bar{y}''_{n+1/2} + y_n\right) + \mathrm{O}(h^5), \tag{10}$$

$$\tilde{y}_{n-1/2} = \frac{1}{2}(y_n + y_{n-1}) - \frac{h^2}{96}\left(y''_{n-1} + 10\bar{y}''_{n-1/2} + y_n\right) + \mathrm{O}(h^5), \tag{11}$$

$$\check{y}_{n+1/2} = \frac{1}{2}(y_n + y_{n+1}) - \frac{h^2}{1920}\left(19y''_{n+1} + 204\tilde{y}''_{n+1/2} + 14y_n + 4\tilde{y}''_{n-1/2} - y''_{n-1}\right) + \mathrm{O}(h^7), \tag{12}$$

$$\check{y}_{n-1/2} = g_0(y_n + y_{n-1}) - \frac{h^2}{1920}\left(-y''_{n+1} + 4\tilde{y}''_{n+1/2} + 14y''_n + 204\tilde{y}''_{n-1/2} + 19y''_{n-1}\right) + \mathrm{O}(h^7), \tag{13}$$

$$\bar{y}_{n+1/4} = \frac{1}{4}(3y_n + y_{n+1}) - \frac{h^2}{61440}\left(241y''_{n+1} + 4176\tilde{y}''_{n+1/2} + 1506y''_n - 184\tilde{y}''_{n-1/2} + 21y''_{n-1}\right) + \mathrm{O}(h^7), \tag{14}$$

$$\bar{y}_{n-1/4} = \frac{1}{4}(3y_n + y_{n-1}) - \frac{h^2}{61440}\left(21y''_{n+1} - 184\tilde{y}''_{n+1/2} + 1506y''_n + 4176\tilde{y}''_{n-1/2} + 241y''_{n-1}\right) + \mathrm{O}(h^7), \tag{15}$$

$$y_{n+1} = 2y_n - y_{n-1} - h^2\left(q_0y''_{n+1} + q_1y''_n + q_0y''_{n-1} + q_2\left(\check{y}''_{n+1/2} + \check{y}''_{n-1/2}\right) + q_3\left(\bar{y}''_{n+1/4} + \bar{y}''_{n-1/4}\right)\right), \tag{16}$$

where $y''_n = f(x_n, y_n)$, $\bar{y}''_{n\pm1/2} = f(x_{n\pm1/2}, \bar{y}''_{n\pm1/2})$, $\bar{y}''_{n\pm1/4} = f(x_{n\pm1/4}, \bar{y}''_{n\pm1/4})$, $\tilde{y}''_{n\pm1/2} = f(x_{n\pm1/2}, \tilde{y}''_{n\pm1/2})$, $\check{y}''_{n\pm1/2} = f(x_{n\pm1/2}, \check{y}''_{n\pm1/2})$. In order the above method to integrate exactly any linear combination of the functions:

$$\left\{1, x, x^2, x^3, x^4, x^5, x^6, x^7, \exp(\pm vx)\right\} \tag{17}$$

we obtain the following system of equations:

$$\begin{aligned} 2q_0 + q_1 + 2q_2 + 2q_3 &= 1,\\ 48q_0 + 12q_2 + 3q_3 &= 4,\\ 3840q_0 + 240q_2 + 15q_3 &= 128,\\ w^2\left[2q_3\cosh\left(\frac{w}{4}\right) + 2q_0\cosh(w) + 2q_2\cosh\left(\frac{w}{2}\right) + q_1\right] &= 2\cosh(w) - 2, \end{aligned} \tag{18}$$

where $w = vh$.

Solving the above system of equations for q_i, $i = 0, 1, 2, 3$, we obtain:

$$
\begin{aligned}
q_0 &= \frac{1}{30}\,\frac{-30\cosh(w) + 30 - 32\,w^2\cosh(\frac{1}{4}\,w) + 18\,w^2\cosh(\frac{1}{2}\,w) + 29\,w^2}{w^2\,(-64\cosh(\frac{1}{4}\,w) - \cosh(w) + 20\cosh(\frac{1}{2}\,w) + 45)},\\
q_1 &= -\frac{1}{15}\,\frac{416\,w^2\cosh(\frac{1}{4}\,w) + 29\,w^2\cosh(w) + 230\,w^2\cosh(\frac{1}{2}\,w)}{w^2\,(-64\cosh(\frac{1}{4}\,w) - \cosh(w) + 20\cosh(\frac{1}{2}\,w) + 45)}\\
&\quad - \frac{1350\cosh(w) + 1350}{w^2\,(-64\cosh(\frac{1}{4}\,w) - \cosh(w) + 20\cosh l(\frac{1}{2}\,w) + 45)} \qquad (19)\\
q_2 &= -\frac{1}{15}\,\frac{256\,w^2\cosh(\frac{1}{4}\,w) + 9\,w^2\cosh(w) - 115\,w^2 - 300\cosh(w) + 300}{w^2\,(-64\cosh(\frac{1}{4}\,w) - \cosh(w) + 20\cosh(\frac{1}{2}\,w) + 45)},\\
q_3 &= \frac{16}{15}\,\frac{w^2\cosh(w) + 16\,w^2\cosh(\frac{1}{2}\,w) + 13\,w^2 - 60\cosh(w) + 60}{w^2\,(-64\cosh(\frac{1}{4}\,w) - \cosh(w) + 20\cosh(\frac{1}{2}\,w) + 45)}.
\end{aligned}
$$

In order to avoid cancelations for small values of w, the following Taylor series expansions can be used:

$$
\begin{aligned}
q_0 = {} & \tfrac{47}{3780} - \tfrac{31}{453600}\,w^2 + \tfrac{257}{1916006400}\,w^4 + \tfrac{16691}{22317642547200}\,w^6\\
& - \tfrac{121447}{18364231581696000}\,w^8 + \tfrac{65572457}{41958596317859020800000}\,w^{10}\\
& + \tfrac{213452429}{2857212574860927880396800}\,w^{12} - \tfrac{100897105901}{1371462035933245382590464000000}\,w^{14} + \cdots, \qquad (20)\\
q_1 = {} & \tfrac{57}{70} + \tfrac{31}{5040}\,w^2 - \tfrac{257}{21288960}\,w^4 - \tfrac{16691}{247973806080}\,w^6 + \tfrac{121447}{204047017574400}\,w^8\\
& - \tfrac{65572457}{466206625753989120000}\,w^{10} - \tfrac{213452429}{31746806387343643115520}\,w^{12}\\
& + \tfrac{100897105901}{15238467065924948695449600000}\,w^{14} + \cdots, \qquad (21)\\
q_2 = {} & \tfrac{332}{945} + \tfrac{31}{22680}\,w^2 - \tfrac{257}{95800320}\,w^4 - \tfrac{16691}{1115882127360}\,w^6 + \tfrac{121447}{918211579084800}\,w^8\\
& - \tfrac{65572457}{2097929815892951040000}\,w^{10} - \tfrac{213452429}{142860628743046394019840}\,w^{12}\\
& + \tfrac{100897105901}{68573101796662269129523200000}\,w^{14} + \cdots, \qquad (22)\\
q_3 = {} & -\tfrac{256}{945} - \tfrac{62}{14175}\,w^2 + \tfrac{257}{29937600}\,w^4 + \tfrac{16691}{348713164800}\,w^6 - \tfrac{121447}{286941118464000}\,w^8\\
& + \tfrac{65572457}{655603067466547200000}\,w^{10} + \tfrac{213452429}{44643946482201998131200}\,w^{12}\\
& - \tfrac{100897105901}{21429094311456959102976000000}\,w^{14} + \cdots. \qquad (23)
\end{aligned}
$$

It is easy for one to see that when $w = \mathrm{i}\phi$, where $\mathrm{i} = \sqrt{-1}$, then the method integrates exactly any linear combination of the functions:

$$\left\{1, x, x^2, x^3, x^4, x^5, x^6, x^7, \cos(\phi x), \sin(\phi x)\right\}. \qquad (24)$$

Now we must calculate the free parameter a in order to obtain a P-stable method. If we apply the new method (with coefficients obtained for the trigonometrically-fitted method) to the scalar test equation (4) we get a difference equation of the form (5) and a characteristic equation (6) with $A(H)$ and $B(H)$ given as follows.

$$\begin{aligned} A(H) = {} & \tfrac{61}{960}\, q_2\, H^4 + \tfrac{13}{1920}\, q_2\, H^6 + \tfrac{1129}{30720}\, q_3\, H^4 + \tfrac{499}{589824}\, H^8\, q_3 + H^2\, q_0 \\ & + \tfrac{13}{9216}\, H^8\, q_2 + 1 + q_2\, H^2 - \tfrac{499}{73728}\, H^8\, q_3\, a - \tfrac{13}{1152}\, H^8\, q_2\, a + \frac{1}{2}\, q_3\, H^2 \\ & + \tfrac{499}{122880}\, q_3\, H^6, \qquad (25) \\ B(H) = {} & -\tfrac{3}{4}\, q_3\, H^2 - \tfrac{1}{2}\, q_2\, H^2 - \tfrac{1}{2}\, H^2\, q_1 - \tfrac{13}{1920}\, q_2\, H^6 - \tfrac{499}{122880}\, q_3\, H^6 - \tfrac{1751}{30720}\, q_3\, H^4 \\ & + 1 - \tfrac{59}{960}\, q_2\, H^4 - \tfrac{499}{73728}\, H^8\, q_3\, a - \tfrac{13}{1152}\, H^8\, q_2\, a, \end{aligned}$$

where $H = sh$.

So, we have

$$\begin{aligned} A(H) + B(H) = {} & \tfrac{1}{480}\, q_2\, H^4 - \tfrac{311}{15360}\, q_3\, H^4 + \tfrac{499}{589824}\, H^8\, q_3 + H^2\, q_0 + \tfrac{13}{9216}\, H^8\, q_2 + 2 \\ & + \tfrac{1}{2}\, q_2\, H^2 - \tfrac{499}{36864}\, H^8\, q_3\, a - \tfrac{13}{576}\, H^8\, q_2\, a - \tfrac{1}{4}\, q_3\, H^2 - \tfrac{1}{2}\, H^2\, q_1, \qquad (26) \\ A(H) - B(H) = {} & \tfrac{1}{8}\, q_2\, H^4 + \tfrac{13}{960}\, q_2\, H^6 + \tfrac{3}{32}\, q_3\, H^4 + \tfrac{499}{589824}\, H^8\, q_3 + H^2\, q_0 + \tfrac{13}{9216}\, H^8\, q_2 \\ & + \tfrac{3}{2}\, q_2\, H^2 + \tfrac{5}{4}\, q_3\, H^2 + \tfrac{499}{61440}\, q_3\, H^6 + \tfrac{1}{2}\, H^2\, q_1. \qquad (27) \end{aligned}$$

Substituting the coefficients of the method obtained above to the stability polynomials (26) and (27) we observe that the polynomial $A(H) - B(H) \geqslant 0$ for all $H \in (0, \infty)$. About polynomial $A(H) + B(H)$ we observe that if we require that the coefficient of H^8 to be greater or equal to [100 − the coefficient of H^4], then $A(H)+B(H) \geqslant 0$ for all $H \in (0, \infty)$. Based on the above remark we find the following value of a:

$$\begin{aligned} a = {} & -\tfrac{1}{80}\Big(-6635297537\, w^2 + 155\, w^2 \cos(w) + 39920\, w^2 \cos\big(\tfrac{1}{2}\, w\big) \\ & + 17694555136\, w^2 \cos\big(\tfrac{1}{4}\, w\big) - 71700 + 71700 \cos(w) \\ & + 2211334656\, w^2 \cos\big(\tfrac{1}{4}\, w\big)^4 - 13272445440\, w^2 \cos\big(\tfrac{1}{4}\, w\big)^2 \\ & - 29583360 \cos\big(\tfrac{1}{4}\, w\big)^4 + 29583360 \cos\big(\tfrac{1}{4}\, w\big)^2\Big) \\ & \Big/ \Big(14340 - 14340 \cos(w) - 12467\, w^2 + 13312\, w^2 \cos\big(\tfrac{1}{4}\, w\big) \\ & - 7984\, w^2 \cos\big(\tfrac{1}{2}\, w\big) - 31\, w^2 \cos(w)\Big). \qquad (28) \end{aligned}$$

The appropriate Taylor series expansion for the above coefficient is given by:

$$\begin{aligned} a = {} & -\tfrac{54428471}{2320} + \tfrac{16800258699}{107648000}\, w^2 - \tfrac{321764515985367}{439548313600000}\, w^4 \\ & + \tfrac{2385315279219883013}{2121084342108160000000}\, w^6 - \tfrac{1439684326453099160 1529}{866081158569603891200000000}\, w^8 \\ & + \tfrac{4299091967801448925370 35079}{5465318543037628395028480000000000000}\, w^{10} \\ & - \tfrac{178602403760251287965375739954 07783}{14882532847311646798714795091558400000000000000}\, w^{12} \end{aligned}$$

$$+\frac{440206650532414700666363592653318541 43}{386707733504545830417805235659053465600000000000000000}\,w^{14}+\cdots. \tag{29}$$

Applying the Taylor series expansions of y_{n+1}, y_n and y_{n-1} about x_n in (8)–(16) we have the following result for the local truncation error (LTE) of the family of exponentially-fitted methods (8)–(16):

$$\mathrm{LTE}=-\frac{31\,h^{10}}{232243200}\big(y_n^{(10)}-w^2\,y_n^{(8)}\big). \tag{30}$$

For comparison purposes in table 1 we list the properties of two-step hybrid exponentially-fitted method developed in this paper, together with the corresponding properties of some similar two-step exponentially-fitted methods presented previously in the literature. We present the properties of the methods: MI: Numerov's method, MII: derived by Raptis and Allison, MIII: derived by Raptis and Cash, MIV: method of Thomas, Mitsou and Simos – case I, MV: method of Simos and Williams, MVI: method of Simos and Williams [1] and MVII: the new developed method. We note that all the methods presented in the table are implicit.

4. Error estimation – local error estimation

There are several methods in the literature for the estimation of the local truncation error (LTE) for the integration of systems of initial-value problems (see, e.g., [20]).

The local error estimation technique in this work is based on an embedded pair of integration methods and on the fact that when the algebraic order 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 4. We define the *local error* estimate in the lower order solution y_{n+1}^L by the quantity

$$\mathrm{LEE}=\big|y_{n+1}^H-y_{n+1}^L\big|, \tag{31}$$

Table 1

Properties of some two-step exponentially-fitted methods. $S=\{H^2\colon H=q\pi,\ q=1,2,\ldots\}$, A.O. is the algebraic order of the method, inter. period is the interval of periodicity of the method.

Method	A.O.	Inter. period	Integrated exponential functions
MI	4	(0,6)	$1,\ x,\ x^2,\ x^3,\ x^4,\ x^5$
MII	4	$(0,\infty)-S$	$1,\ x,\ x^2,\ x^3,\ \exp(\pm wx)$
MIII	6	$(0,\infty)-S$	$1,\ x,\ x^2,\ x^3,\ x^4,\ x^5,\ \exp(\pm wx)$
MIV	4	$(0,\infty)-S$	$1,\ x,\ x^2,\ x^3,\ x^4,\ x^5,\ x^6,\ x^7,\ \exp(\pm wx)$
MV	4	$(0,\infty)-S$	$1,\ x,\ x^2,\ x^3,\ x^4,\ x^5,\ x^6,\ x^7,\ x^8,\ x^9,\ \exp(\pm wx)$
MVI	6	$(0,\infty)$	$1,\ x,\ x^2,\ x^3,\ x^4,\ x^5,\ \exp(\pm wx)$
MVII	8	$(0,\infty)$	$1,\ x,\ x^2,\ x^3,\ x^4,\ x^5,\ x^6,\ x^7,\ \exp(\pm wx)$

where y_{n+1}^H is the solution obtained with P-stable method of algebraic order eight developed in this paper and y_{n+1}^L is the solution obtained with P-stable exponentially-fitted method of sixth algebraic order developed by Simos and Williams [1].

Remark 1. Under the assumption that h is sufficiently small, the *local error* in y_{n+1}^H can be neglected compared with that in y_{n+1}^L.

If the local 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 error of acc, must be

$$h_{n+1} = h_n \left(\frac{acc}{\mathrm{LEE}} \right)^{1/q}, \tag{32}$$

where q is the algebraic order.

However, for ease of programming we have restricted all step changes to halving and doubling. Thus, based on the procedure developed in [21], the step control procedure which we have actually used is

$$\begin{array}{ll} \text{If LEE} < acc, & h_{n+1} = 2h_n; \\ \text{If } 100\, acc > \text{LEE} \geqslant acc, & h_{n+1} = h_n; \\ \text{If LEE} \geqslant 100\, acc, & h_{n+1} = \dfrac{h_n}{2} \text{ and repeat the step.} \end{array} \tag{33}$$

We note, here, that the local error estimate is in the lower order solution y_{n+1}^L. 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 lower order solution y_{n+1}^L, it is the higher order solution y_{n+1}^H which we actually accept at each point.

5. Numerical illustrations

In the present section we will illustrate the efficiency of the described in section 4 variable-step technique by applying it to the numerical solution of coupled differential equations arising from the Schrödinger equation.

5.1. *Coupled differential equations*

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

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2} + k_i^2 - \frac{l_i(l_i+1)}{x^2} - V_{ii} \right] y_{ij} = \sum_{m=1}^{N} V_{im} y_{mj} \tag{34}$$

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

We have investigated the case in which all channels are open. So, the boundary conditions are (see for details [21]):

$$y_{ij} = 0 \quad \text{at } x = 0, \tag{35}$$

$$y_{ij} \sim k_i x j_{l_i}(k_i x)\delta_{ij} + \left(\frac{k_i}{k_j}\right)^{1/2} K_{ij} k_i x n_{li}(k_i x), \tag{36}$$

where $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions, respectively. The methods here have much larger intervals of periodicity than Numerov's method (and many other traditional difference methods). This property is essential to avoid numerical instabilities. Such methods are thus very suitable for problems involving closed channels.

Using the detailed analysis developed in [21] and defining a matrix K' and diagonal matrices M, N by:

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

we find that the asymptotic condition (36) may be written:

$$y \sim M + NK'. \tag{37}$$

The iterative Numerov method of Allison [21] is well known for problems of this type.

An example of a problem that can be transformed to a set of close-coupled differential equations of the Schrödinger type is the rotational excitation of a diatomic molecule by neutral particle impact. Denoting, as in [21], the entrance channel by the quantum numbers by (j, l), the exit channels by (j', l'), and the total angular momentum by $J = j + l = j' + l'$, we find that

$$\left[\frac{d^2}{dx^2} + k^2_{j'j} - \frac{l'(l+1)}{x^2}\right] y^{Jjl}_{j'l'}(x) = \frac{2\mu}{\hbar^2} \sum_{j''} \sum_{l''} \langle j'l';\ J \big| V \big| j''l'';\ J\rangle y^{Jjl}_{j''l''}(x), \tag{38}$$

where

$$k_{j'j} = \frac{2\mu}{\hbar^2}\left[E + \frac{\hbar^2}{2I}\left\{j(j+1) - j'(j'+1)\right\}\right], \tag{39}$$

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 [21], the potential V may be written

$$V(x, \hat{\mathbf{k}}_{j'j} \cdot \hat{\mathbf{k}}_{jj}) = V_0(x) P_0(\hat{\mathbf{k}}_{j'j} \cdot \hat{\mathbf{k}}_{jj}) + V_2(x) P_2(\hat{\mathbf{k}}_{j'j} \cdot \hat{\mathbf{k}}_{jj}), \tag{40}$$

and the coupling matrix element is

$$\langle j'l'; J \big| V \big| j''l''; J\rangle = \delta_{j'j''}\delta_{l'l''} V_0(x) - f_2(j'l', j''l''; J) V_2(x), \tag{41}$$

where the f_2 coefficients can be obtained from formulae given by Berstein et al. [22], $\hat{\mathbf{k}}_{j'j}$ 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 [22]). The boundary conditions may then be written (see [21])

$$y_{j'l'}^{Jjl}(x) = 0 \quad \text{at } x = 0, \tag{42}$$

$$y_{j'l'}^{Jjl}(x) \sim \delta_{jj'}\delta_{ll'} \exp\left[-\mathrm{i}\left(k_{jj}x - \frac{l\pi}{2}\right)\right] - \left(\frac{k_i}{k_j}\right)^{1/2} S^J\big(jl;\, j'l'\big) \times \exp\left[\mathrm{i}\left(k_{j'j}x - \frac{l'\pi}{2}\right)\right], \quad \text{as } x \to \infty, \tag{43}$$

where the scattering matrix S is related to the K matrix of (36) by the relation

$$S = (I + \mathrm{i}K)(I - \mathrm{i}K)^{-1}. \tag{44}$$

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

In our numerical test, we choose the S matrix given by the following parameters

$$\frac{2\mu}{\hbar^2} = 1000.0, \qquad \frac{\mu}{I} = 2.351, \qquad E = 1.1,$$

$$V_0(x) = \frac{1}{x^{12}} - \frac{2}{x^6}, \qquad V_2(x) = 0.2283 V_0(x).$$

Following [21], 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 Berstein [23] and Allison [21] a reduction of the interval $[0, \infty)$ to $[x_0, \infty]$ is made. The wave functions are then zero in this region and, consequently, the boundary condition (42) may be written

$$y_{j'l'}^{Jjl}(x_0) = 0. \tag{45}$$

For the numerical solution we have used

(i) the Iterative Numerov method of Allison [21],

(ii) the variable-step method of Raptis and Cash [24],

(iii) the variable-step method of Simos [25],

(iv) the variable-step exponentially-fitted method of Simos and Williams [26],

(v) the explicit variable-step method developed in [27],

(vi) the variable-step Bessel and Neumann fitted method developed in [28],

(vii) the variable-step fourth algebraic order method developed in [3],

(viii) the variable-step sixth algebraic order method developed in [3],

(ix) the method RKN12 described in [29, p. 298]. This method is based on the Runge–Kutta–Nyström method of order 12(10) developed by Dormand et al. [30], and

(x) the new variable-step P-stable exponentially-fitted method developed in this paper.

In table 2, we present the real computation time required by these methods to calculate the square of the modulus of the S matrix for sets of 4, 9 and 16 coupled differential

Table 2
RTC (real time of computation (in seconds)) to calculate $|S|^2$ for the variable-step methods (i)–(x). $acc = 10^{-6}$, hmax is the maximum step size, MErr is the maximum absolute error.

Method	N	hmax	RTC	MErr
Iterative Numerov [21]	4	0.014	3.25	$1.2 \cdot 10^{-3}$
	9	0.014	23.51	$5.7 \cdot 10^{-2}$
	16	0.014	99.15	$6.8 \cdot 10^{-1}$
Variable-step method of Raptis and Cash [24]	4	0.056	1.55	$8.9 \cdot 10^{-4}$
	9	0.056	8.43	$7.4 \cdot 10^{-3}$
	16	0.056	43.32	$8.6 \cdot 10^{-2}$
Variable-step method of Simos [25]	4	0.056	1.05	$8.0 \cdot 10^{-4}$
	9	0.056	5.25	$6.7 \cdot 10^{-3}$
	16	0.056	27.15	$8.1 \cdot 10^{-2}$
Variable-step method of Simos and Williams [26]	4	0.448	0.24	$5.2 \cdot 10^{-4}$
	9	0.448	0.96	$4.4 \cdot 10^{-3}$
	16	0.448	5.04	$6.4 \cdot 10^{-2}$
Variable-step method of Simos [27]	4	0.448	0.27	$5.3 \cdot 10^{-4}$
	9	0.448	1.48	$4.5 \cdot 10^{-3}$
	16	0.448	6.31	$6.5 \cdot 10^{-2}$
Variable-step method of Simos and Williams [28]	4	0.448	0.18	$4.5 \cdot 10^{-4}$
	9	0.448	0.92	$3.8 \cdot 10^{-3}$
	16	0.224	5.32	$4.2 \cdot 10^{-2}$
Variable-step methods of order four of Avdelas and Simos [3]	4	0.112	1.37	$8.4 \cdot 10^{-4}$
	9	0.112	7.72	$7.0 \cdot 10^{-3}$
	16	0.112	33.11	$8.4 \cdot 10^{-2}$
Variable-step methods of order six of Avdelas and Simos [3]	4	0.224	1.03	$8.1 \cdot 10^{-4}$
	9	0.224	6.91	$6.7 \cdot 10^{-3}$
	16	0.224	14.05	$7.1 \cdot 10^{-2}$
RKN12	4	0.224	0.78	$9.6 \cdot 10^{-5}$
	9	0.224	4.93	$9.8 \cdot 10^{-4}$
	16	0.224	13.25	$9.5 \cdot 10^{-3}$
Variable-step P-stable exponentially-fitted method developed in this paper	4	0.896	0.03	$2.1 \cdot 10^{-8}$
	9	0.896	0.21	$9.2 \cdot 10^{-8}$
	16	0.896	1.72	$3.4 \cdot 10^{-7}$

equations. In the same table the maximum absolute error is also presented. In table 2, N indicates the number of equations of the set of coupled differential equations.

6. Remarks and conclusion

In this paper a variable-step technique for the numerical solution of the Schrödinger equation and related problems is described.

From the results presented above we arrive to the following conclusions.

1. The variable-step fourth and sixth algebraic order methods of Avdelas and Simos [3] are more efficient (more accurate and more rapid) than the Iterative Numerov of Allison [21], the variable-step method of Raptis and Cash [24] and the variable-step method of Simos [25].
2. The method of Simos and Williams [26] and the method of Simos [27] are more efficient than the Iterative Numerov of Allison [21], the variable-step method of Raptis and Cash [24], the variable-step method of Simos [25], the variable-step fourth and sixth algebraic order methods of Avdelas and Simos [3]. The method of Simos and Williams [28] is more efficient than the method of Simos [27].
3. Finally, the new variable-step P-stable exponentially-fitted technique is the most efficient one.

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