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EXPONENTIAL FITTED METHODS FOR THE NUMERICAL SOLUTION OF THE SCHRÖDINGER EQUATION*

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Abstract

A new sixth-order Runge-Kutta type method is developed for the numerical integration of the radial Schrödinger equation and of the coupled differential equations of the Schrödinger type. The formula developed contains certain free parameters which allows it to be fitted automatically to exponential functions. We give a comparative error analysis with other sixth order exponentially fitted methods. The theoretical and numerical results indicate that the new method is more accurate than the other exponentially fitted methods.

1. Introduction

In recent years the Schrödinger equation has been the subject of great activity, the aim is to achieve a fast and reliable algorithm that generates a numerical solution.

1.1. Radial Schrödinger equation

The one dimensional or radial Schrödinger equation has the form:

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

where one boundary condition is $y(0) = 0$ with the other boundary condition being specified at $x = \infty$. Equations of this type occur very frequently in theoretical physics[5], and there is a real need to be able to solve them both efficiently and reliably by numerical methods. In (**??**) the function $W(x) = l(l+1)/x^2 + V(x)$ is denoted as *the effective potential*, for which $W(x) \to 0$ as $x \to \infty$, and k^2 is a real number denoting *the energy*. The boundary conditions are:

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

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

Boundary value methods based on either collocation or finite differences are not very popular for the solution of (**??**) due to the fact that the problem is posed on an infinite interval. Initial value methods, such as shooting, need to take into account the fact that $\mid y'(x) \mid$ is very large near $x = 0$. So, it is very inappropriate to use

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standard library packages for the numerical solution of (**??**). Also Runge-Kutta and Runge-Kutta-Nyström methods have been proved inefficient for the numerical solution of the Schrödinger equation (see [9] for details).

One of the most popular method for the solution of (**??**) is the **Numerov's method.** This method is only of order four, but in practice it has been found to have a superior performance to higher order four-step method. The reason for this, as proved in [9], is that the Numerov method has the same phase-lag order with the four-step methods but it has a larger interval of periodicity. So, the investigation of linear multistep methods is not a fruitful way to deriving efficient high order methods.

An alternative approach to deriving higher order methods for (**??**) was given by Cash and Raptis[1]. In [1] *a* sixth order Runge-Kutta type method with a large interval of periodicity was derived. This method has a phase-lag of order six (while the Numerov's method has phase-lag of order four) and an interval of periodicity much more larger than the method of Numerov.

Another alternative approach for developing efficient methods for the solution of (**??**) is to use exponential fitting. This approach is appropriate because for large x the solution of (**??**) is *periodic*. Raptis and Allison[6] have derived a Numerov type exponentially fitted method. Numerical results presented in [6] indicate that these fitted methods are much more efficient than Numerov's method for the solution of (**??**). Many authors have investigated the idea of exponential fitting, since Raptis and Allison. Perhaps the most significant work in this general area was that of Ixaru and Rizea[3]. They showed that for the resonance problem defined by (**??**) it is generally more efficient to derive methods which exactly integrate functions of the form:

$$\{1, x, x^2, \ldots, x^p, \exp(\pm wx), x\exp(\pm wx), \ldots, x^m \exp(\pm wx)\} \tag{3}$$

than to use classical exponential fitting methods. A powerful low order method of this type was developed by Raptis[7]. Also Simos[10] has derived a four-step method of this type which gives much more accurate results compared with other four-step methods. Simos[11] has derive a family of four-step methods which gives more efficient results than other four-step methods. Also Raptis and Cash[8] have derived an exponential fitted method and Cash, Raptis and Simos[2] have derived a method fitted to (**??**) with $m = 1$ and $p = 3$.

The purpose of this paper is to derive Runge-Kutta type methods fitted to (**??**) and in particular to derive a method with $m = 3$. We give a comparative error analysis with other sixth order exponentially fitted methods. The theoretical and numerical results indicate that the new method is more accurate than the other exponentially fitted methods.

1.2. Coupled differential equations

The close-coupled equations may be written

$$[\frac{d^2}{dR^2} + k_i^2 - \frac{l_i(l_i+1)}{R^2} - V_{ii}]y_{ij} = \sum_{k=1}^{N}{}_{k\neq i} V_{ik} y_{kj} \tag{4}$$

for $1 \leq i \leq N,\ 1 \leq j \leq N$ and where $\mathbf{V}$ and $\mathbf{Y}$ are matrices.

We restrict our attention to the case in which all channels are open so that the boundary conditions are

$$y_{ij} = 0 \text{ at } R = 0 \tag{5}$$

$$y_{ij} \sim k_i R j_{l_i}(k_i R)\delta_{ij} + \left(\frac{k_i}{k_j}\right)^{1/2} R_{ij} k_i R n_{l_i}(k_i R) \tag{6}$$

where $j_l(x)$ and $n_l(x)$ are the **spherical Bessel and Neumann functions** respectively. For boundary condition (**??**) and its derivation see [16].

If the matrix elements V_{ij} have no singularities of order two or higher at the origin, then for small R the solutions of (**??**) that satisfy (**??**) are given by

$$w_{ij} = a_{ij} R^{l_q+1} \tag{7}$$

where a is a matrix of constants. The solutions thus obtained will not, in general, satisfy the asymptotic boundary condition (**??**). Thus N linearly independent solutions of (**??**) must be found and a suitable linear combination of them matched to the correct asymptotic form.

The criterion for linearly independent solutions of this equation is that the phase shifts must themselves be markedly different and independent as noted by Buckingham[14]. We make the assumption that if the rows of a are linearly independent then the respective asymptotic forms will also be linearly independent. Thus the solutions y_{ij} may be expanded as

$$y_{ij} = \sum_{k=1}^{N} w_{ik} c_{kj} \tag{8}$$

or in the matrix form

$$\mathbf{y} = \mathbf{w}.\mathbf{c} \tag{9}$$

The solutions $\mathbf{y}$ may be matched to the boundary conditions at two values of r large enough so that the terms V_{ij} are negligible. Then, defining a matrix $\mathbf{R'}$ and diagonal matrices $\mathbf{M}^R, \mathbf{N}^R$ by

$$\begin{aligned} R'_{ij} &= \left(\frac{k_i}{k_j}\right)^{1/2} R_{ij} \\ M^R_{ij} &= \delta_{ij} k_i R j_{l_i}(k_i R) \\ N^R_{ij} &= \delta_{ij} k_i R n_{l_i}(k_i R) \end{aligned} \tag{10}$$

the asymptotic condition (**??**) may be written

$$\mathbf{y} \sim \mathbf{M} + \mathbf{N}.\mathbf{R'} \ . \tag{11}$$

Following Barnes et. al.[15], and writing

$$\mathbf{w} = \mathbf{M}.\mathbf{A} + \mathbf{N}.\mathbf{B}, \tag{12}$$

where the matrices **A** and **B** are found by matching the numerical solution of (**??**) to (**??**) for two values of r, say r_1 and r_2, large enough so that in equation (**??**) the term of the centrifugal potential to be neglected, we obtain the relations

$$\begin{aligned} \mathbf{c} &= \mathbf{A}^{-1} \\ \mathbf{R}' &= \mathbf{B}.\mathbf{A}^{-1} \end{aligned} \tag{13}$$

which lead directly to the formation of the R matrix.

2. The New Method

Consider the method:

$$y_{n+1} - ay_n + y_{n-1} = h^2[b_0(y''_{n+1} + y''_{n-1}) + b_1(y''_{n+1/2} + y''_{n-1/2}) + \gamma y''_n] \tag{14}$$

where, for example, $y''_{n+1} = f(x_{n+1})y_{n+1}$ with $x_{n+1} = x_n + h$ and $f(x_{n+1}) = [l(l+1)/x^2_{n+1} + V(x_{n+1}) - k^2]$.

We require that the method (**??**) should be exact for any linear combination of the functions:

$$\{\exp(\pm vx), x\exp(\pm vx), x^2\exp(\pm vx), x^3\exp(\pm vx)\} \tag{15}$$

In this case the method which will be obtained will integrates the exponential functions (**??**) with the maximum value of $m = 3$ compared with the previous exponential fitted methods (for which the maximum value of m was 2). To construct a method of the form (**??**) which integrates exactly the functions (**??**), we require that the method (**??**) integrates exactly:

$$\{\exp(\pm v_0 x), \exp(\pm v_1 x), \exp(\pm v_2 x), \exp(\pm v_3 x) \tag{16}$$

and then put $v_0 = v_1 = v_2 = v_3 = v$. In this case equations (**??**) and (**??**) are equivalent (see [9] for details).

Demanding that (**??**) integrates exactly (**??**), we obtain the system of equations for b_0, b_1 and γ :

$$a + 2w_j^2 b_0 \cosh(w_j) + 2w_j^2 b_1 \cosh(w_j/2) + \gamma w_j^2 = 2\cosh(w_j), \tag{17}$$

where $w_j = v_j h, j = 0, 1, 2$.

Solving for a, b_0, b_1 and γ and then setting $v_0 = v_1 = v_2 = v_3 = v$ we obtain:

$$\begin{aligned} a &= (24w^3 Z_1 - 9w^4 Z_2 + w^5 Z_6)/D \\ b_0 &= \{12wZ_3 - w^2[\cosh(3/2w) - 25\cosh(w/2)] - w^3 Z_4 - 24Z_5\}/D \\ b_1 &= \{-8w^2[\cosh(2w) + 5] - 24[1 - \cosh(2w)]\}/D \\ \gamma &= \{wZ_1 + w^2[45\cosh(3/2w) - \cosh(5/2w) + 100\cosh(w/2)] - w^3 Z_6 - 24wZ_7/D \end{aligned} \tag{18}$$

where $D = -24w^3 Z_3 - 9w^4 Z_5 - w^5 Z_4$, $Z_1 = [3\sinh(3/2w) - \sinh(5/2w) - 4\sinh(w/2)]$, $Z_2 = 5\cosh(3/2w) - \cosh(5/2w) - 4\cosh(w/2)$, $Z_3 = \sinh(3/2w) - 3\sinh(w/2)$, $Z_4 = \sinh(3/2w) + 3\sinh(w/2)$, $Z_5 = \cosh(3/2w) - \cosh(w/2)$, $Z_6 = 9\sinh(3/2w) -$

$\sinh(5/2w)$
$-34\sinh(w/2)$, $Z_7 = \cosh(5/2w) + 3\cosh(3/2w) - 4\cosh(w/2)$ and $w = v$ h.

In order to use method (**??**) in practice we need to find computable approximations to the terms $y''_{n+1/2}$, $y''_{n-1/2}$, where we still require the method to be exact for any linear combination of the functions (**??**). Following the approach of Cash and Raptis we look for approximations of the form:

$$\begin{aligned} y_{n+1/2} + y_{n-1/2} &= A_1(y_{n+1} + y_{n-1}) + A_2 y_n + h^2[A_3(y''_{n+1} + y''_{n-1}) + A_4 y''_n] \\ y_{n-1/2} &= B_1(y_{n+1} + y_{n-2}) + B_2(y_n + y_{n-1}) + h^2[B_3(y''_{n+1} + y''_{n-2}) + \\ &\quad B_4(y''_n + y''_{n-1})] \end{aligned} \tag{19}$$

where the constants $A_1, A_2, A_3, A_4, B_1, B_2, B_3$ and B_4 are to be determined. In order for these approximations to be exact for (**??**) we obtain the following systems of equations:

$$\begin{aligned} 2\cosh(w_j/2) &= 2A_1\cosh(w_j) + A_2 + 2w_j^2 A_3\cosh(w_j) + w_j^2 A_4 \\ 1/2 &= B_1\cosh(3w_j/2) + B_2\cosh(w_j/2) + w_j^2 B_3\cosh(3w_j/2) + \\ &\quad w_j^2 B_4\cosh(w_j/2) \end{aligned} \tag{20}$$

Solving for $A_1, A_2, A_3, A_4, B_1, B_2, B_3$ and B_4, and then setting $v_0 = 0$ and $v_1 = v_2 = v_3 = v$ we obtain:

$$\begin{aligned} A_1 = &\ \{12wZ_3 - w^2[5\cosh(3/2w) + 19\cosh(w/2)] - w^3 Z_4 + 24Z_5\}/(2X) \\ A_2 = &\ \{12wZ_1 - w^2[15\cosh(3/2w) + 5\cosh(5/2w) + 124\cosh(w/2)] - \\ &\ w^3 Z_6 + 24Z_7)/(2X) \\ A_3 = &\ (wZ_4 - 3Z_5)/(2X) \\ A_4 = &\ \{wZ_6 + 3[5\cosh(3/2w) - \cosh(5/2w) - 4\cosh(w/2)]\}/(2X) \end{aligned} \tag{21}$$

with Z_1, Z_3, Z_4, Z_5, Z_6 and Z_7 are given by (**??**) and $X = -8w^2[\cosh(2w) + 5] - 24[1 - \cosh(2w)]$,

$$\begin{aligned} B_1 = &\ \{72w[\sinh(3/2w) - \sinh(5/2w) - 2\sinh(w/2)] + 2w^2[125\cosh(3/2 \\ &\ w) - 19\cosh(5/2w) - 10\cosh(w/2)] + 6w^3[11\sinh(3/2w) - \sinh(5/2w) \\ &\ -4\sinh(w/2)] - 48[\cosh(3/2w) + \cosh(5/2w) - 2\cosh(w/2)]\}/(2Y) \\ B_2 = &\ \{72w[\sinh(7/2w) - 2\sinh(5/2w) + 3\sinh(w/2)] - 6w^2[58\cosh(5/2w) \\ &\ +5\cosh(7/2w) + 225\cosh(w/2)] + 18w^3[4\sinh(5/2w) - \sinh(7/2w) \\ &\ -21\sinh(w/2)] + 144[2\cosh(5/2w) + \cosh(7/2w) - 3\cosh(w/2)]\}/(2Y) \\ B_3 = &\ \{-6w[11\sinh(3/2w) - \sinh(5/2w) - 4\sinh(w/2)] + 6[9\cosh(3/2w) \\ &\ + \cosh(5/2w) - 10\cosh(w/2)]\}/(2Y) \\ B_4 = &\ \{-18w[4\sinh(5/2w) - \sinh(7/2w) - 21\sinh(w/2)] - 6[14\cosh(5/2w) - \\ &\ 5\cosh(7/2w) - 9\cosh(w/2)]\}/(2Y) \end{aligned} \tag{22}$$

where $Y = -72w[\sinh(3w/2) - 3\sinh(5w/2) + \sinh(7w/2) + 5\sinh(w/2)] - 2w^2 - 6w^3[11\sinh(3w/2) + 11\sinh(5w/2) - 3\sinh(7w/2) - 67\sinh(w/2)] + 48[\cosh(3w/2) - 5\cosh(5w/2) - 3\cosh(7w/2) + 7\cosh(w/2)]$.

The above formulae are subject to heavy cancellations for small values of $w = v$ h. In this case it is much more convenient to use the below mentioned series expansions for the coefficients of the method.

$$
\begin{aligned}
a = \;& 2 + w_8/120960 \\
b_0 = \;& 1/60 - w_2/1890 + w_4/51840 - 113w_6/159667200 + 8419w_8/348713164800 \\
b_1 = \;& 4/15 + 2w_2/945 + 11w_4/90720 - w_6/246400 + 61601w_8/348713164800 \\
\gamma = \;& 13/30 - w_2/315 - 17w_4/60480 - 1879w_6/79833600 + 2339w_8/11623772160 \\
A_1 = \;& 3/32 - 43w_2/16128 - 895w_4/16257024 + 4532287w_6/450644705280 \\
& -8052029677w_8/11810496435978240 \\
A_2 = \;& 29/16 + 43w_2/8064 + 895w_4/8128512 - 4532287w_6/225322352640 \\
& -1669677271w_8/11810496435978240 \\
A_3 = \;& -1/384 + 43w_2/193536 - 11779w_4/975421440 + 552169w_6/1081547292672 \\
& -11922163069w_8/708629786158694400 \\
A_4 = \;& 31/192 + 215w_2/96768 + 38629w_4/487710720 + 16565w_6/540773646336 \\
& -18994511981w_8/354314893079347200 \qquad (23) \\
B_1 = \;& 37/128 - 699w_2/7168 + 46825w_4/2408448 - 198006703w_6/66762178560 \\
& +658552202023w_8/1749703175700480 \\
B_2 = \;& 27/128 + 699w_2/7168 - 46825w_4/2408448 + 198006703w_6/66762178560 \\
& -836286943207w_8/1749703175700480 \\
B_3 = \;& -9/512 + 233w_2/28672 - 322199w_4/144506880 + 76153487w_6/160229228544 \\
& -9147016782389w_8/104982190542028800 \\
B_4 = \;& -171/512 + 2563w_2/28672 - 2487301w_4/144506880 \\
& +42196991w_6/14566293504 - 47396848578511w_8/104982190542028800
\end{aligned}
$$

So the final scheme is:

$$y_{n+1} - ay_n + y_{n-1} = h^2[b_0(y''_{n+1} + y''_{n-1}) + b_1(\overline{y}''_{n+1/2} + \overline{y}''_{n-1/2}) + \gamma y''_n] \qquad (24)$$

with $\overline{y}_{n+1/2}$ and $\overline{y}_{n-1/2}$ given by:

$$
\begin{aligned}
& \overline{y}_{n+1/2} + \overline{y}_{n-1/2} = A_1(y_{n+1} + y_{n-1}) + A_2 y_n + h^2[A_3(y''_{n+1} + y''_{n-1}) + A_4 y''_n] \\
& \overline{y}_{n-1/2} = B_1(y_{n+1} + y_{n-2}) + B_2(y_n + y_{n-1}) + h^2[B_3(y''_{n+1} + y''_{n-2}) + \\
& \qquad B_4(y''_n + y''_{n-1})] \qquad (25)
\end{aligned}
$$

where the coefficinets of the schems given by (**??**), (**??**), (**??**) or (**??**).

The **local truncation error** of the new method (**??**) - (**??**), with the coefficients given by (**??**), (**??**) and (**??**), is given by:

$$L.T.E. = \frac{h^8}{120960}[-v^8 y + 4v^6 y^{(ii)} - 6v^4 y^{(iv)} + 4v^2 y^{(vi)} - y^{(viii)}] \; . \qquad (26)$$

For comparison purposes in Table 1 we list the properties of the two-step exponentially fitted method introduced in this paper, together with the corresponding properties of the two-step exponentially fitted methods presented previously in the literature.

Table 1. Properties of the two-step exponentially-fitted methods.
The quantities m and p are defined by (3). A.O. is the algebraic order of the method.
$*$ = hybrid two-step method

Method	A. O.	Integrated Exponential Functions
Numerov's method	4	$1, x, x^2, x^3, x^4, x^5$
Derived by Raptis and Allison [6]	4	m=0, p=3
Derived by Ixaru and Rizea [3]	4	m=1, p=1
Derived by Raptis [7]	4	m=2, p=0
Derived by Raptis and Cash [8]*	6	m=0, p=5
Derived by Cash, Raptis and Simos [2]*	6	m=1, p=3
Present method*	6	m=3 p=0

The new method is of algebraic order six, i.e. it has the same algebraic order with the other hybrid methods listed in Table 1. However, the new method integrate exactly more functions of the form (**??**) than the previous developed hybrid exponential fitted methods. The crucial concern when solving the Schrödinger equation is that the numerical method should integrate exactly the functions (**??**) with m as large as possible, as shown by [3] and [9].

3. Comparative Error Analysis

To compare the two known sixth order exponentially fitted methods (of Raptis and Cash[8] and Cash, Raptis and Simos[2]) with the new one we make a comparative error analysis.

This is done as follows. First we consider the one-dimensional Schrödinger equation:

$$y'' = f(x)y,\ \mathrm{f}(x) = V(x) - E,\ \mathrm{x} \in [a,b],\ \mathrm{y}(a) = y_0,\ \mathrm{y}'(a) = y_0' \tag{27}$$

with a real, nonsingular potential $V(x)$. E denotes the energy.

We write $f(x)$ of eq. (**??**) in a form in which the energy dependence is conveniently separated. We thus define $g(x) = V(x) - V_c$, where V_c is the constant approximation of the potential. We also define as $f_c = V_c - E$. So, we have:

$$f(x) = g(x) + f_c \tag{28}$$

where $g(x)$ depends on the potential and its constant approximation and f_c embeds the energy dependence. We also express the derivatives $y^{(ii)}, y^{(iv)}, y^{(vi)}$ and $y^{(viii)}$ which are in the **local truncation error expression** in terms of the equation to be solved, i.e. $y'' = fy$. We take into account the fact that $g^{(n)} = V^{(n)}$ for any nth order derivative with respect to x. So for instance we have:

$$y^{(ii)} = f_c y + gy,$$
$$y^{(iv)} = f_c^2 y + 2f_c gy + [(V^{(2)} + g^2) + 2V'y']$$

etc. Finally we introduce these formulae into the **local truncation** errors terms to obtain expressions in powers of f_c. The asymptotic expansions of these expressions are:

$$\mathbf{L.T.E_{Raptis\ and\ Cash}} = -h^8/120960 f_c^3 gy$$

$$\mathbf{L.T.E_{Cash,\ Raptis\ and\ Simos}} = -h^8/120960\{f_c^2[(g^2 + 9V^{(2)})y + 2V'y']\}$$

$$\mathbf{L.T.E_{New\ method}} = -h^8/120960\{f_c[(12V^{(4)} + 16gV^{(2)} + 12V^{(2)})y + 8V^{(3)}y']\}$$

From these asymptotic expansions it is obvious that the new method is much more accurate than the others especially in cases of high energy, i.e. f_c to be a big number. Because in these cases the **local truncation error (L.T.E)** of the method of Raptis and Cash increases as the third power of f_c and the L.T.E. of the method of Cash, Raptis and Simos increases as the second power of f_c, while the L.T.E of the new method increases linearly with f_c.

We note that for the problems consider in this paper, i.e. the scattering problems of the Schrödinger equation, f_c is a big number (because we have high energies) and for the cases of the most well known potentials $V^{(4)}$ and $V^{(3)}$ are usually small.

4. Numerical Illustrations

In this section we present some numerical results to illustrate the performance of our method. We consider the numerical integration of the Schrödinger equation.

4.1. Radial Schrödinger equation

Consider the radial Schrödinger equation

$$y''(x) = (V(x) - E)y(x) \tag{29}$$

in the well-known case where the potential $V(x)$ is the Woods-Saxon potential

$$W(x) = V(x) = u_0/(1+z) - u_0 z/[a(1+z)^2] \tag{30}$$

with $z = \exp[(x - X_0)/a], u_0 = -50, a = 0.6$ and $X_0 = 7.0$. In order to solve this problem numerically we need to approximate the true (infinite) interval of integration $[0, \infty)$ by a finite interval. For the purpose of our numerical illustration we take the domain of integration as $0 \leq x \leq 15$. We consider (**??**) in a rather large domain of energies i.e. [1, 1000]. The problem we consider is the so-called *resonance problem.*

4.1.1. The Resonance Problem

In the case of positive energies $E = k^2$ the potential dies away faster than the term $l(l+1)/x^2$; equation (**??**) effectively reduces to

$$y''(x) + (k^2 - l(l+1)/x^2)y(x) = 0, \tag{31}$$

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 (**??**) has the asymptotic form (when $x \to 0$)

$$\begin{aligned} y(x) &\simeq Akxj_l(kx) - Bn_l(kx) \\ &\simeq AC[\sin(kx - \pi l/2) + \tan\delta_l \cos(kx - \pi l/2)] \ , \end{aligned} \tag{32}$$

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

$$tan\delta_l = \frac{y(x_2)S(x_1) - y(x_1)S(x_2)}{y(x_1)C(x_2) - y(x_2)C(x_1)} \tag{33}$$

for x_1 and x_2 distinct points on the asymptotic region 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, $y_0 = 0$, we show that, for values of x close to the origin, the solution behaves as $y(x) = cx^{l+1}$. With these starting values we evaluate at some point of the asymptotic region the phase shift δ_l and the normalization factor C from the above relations.

For positive energies one has the so-called resonance problem. This problem consists either of finding **the phase shift** $\delta(E)$ or finding those E, for $E \in [1, 1000]$, at which δ equals $\pi/2$. We actually solve the latter problem, known as *"the resonance problem"* when *the positive eigenenergies lie under the potential barrier.*

The boundary conditions for this problem are:

$$\begin{aligned} &y(0) = 0, \\ &y(x) = \cos(\sqrt{E}x) \text{ for large } x \end{aligned} \tag{34}$$

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

Table 2. Deviations of the computed positive eigenvalues from the exact ones in 10^{-6} units, for the methods I-V

Exact eigenenergies	h	Method I	Method II	Method III	Method IV	Method V
53.588872	1/16	228323	313	11	1	0
	1/32	14059	28	5	0	0
	1/64	870	1	0	0	0
163.215341	1/16		633	117	5	0
	1/32	476488	55	12	1	0
	1/64	29378	3	2	0	0
341.495874	1/16		1284	2542	37	0
	1/32		115	85	2	0
	1/64	435752	8	5	1	0
989.701916	1/16		2228		681	2
	1/32		304	2428	55	0
	1/64		21	115	7	0

In our numerical illustration we find the positive *eigenenergies or resonances* by the five methods:
Method I: Numerov's method
Method II: Derived by Raptis[7]
Method III: Derived by Raptis and Cash[8]
Method IV: Derived by Cash, Raptis and Simos[2]
Method V: Proposed in this paper.

The numerical results obtained for the five methods were compared to the true solution to the Woods-Saxon potential resonance problem. This true solution were obtained corrected to six decimal places using the analytic solution. Table 2 shows the absolute errors of the eigenenergies in 10^{-6} units for different choices of constant stepsize, which are shown in column 2. The empty areas indicate that the corresponding absolute errors are larger than 1.

The performance of the different methods is dependent on the choice of the fitting parameter v. For the purpose of obtaining our numerical results it is appropriate to choose v in the way suggested by Ixaru and Rizea[3]. That is, we choose:

$$v = \begin{cases} (-50+E)^{1/2} & \text{for x} \in [0, 6.5] \\ (-E)^{1/2} & \text{for x} \in (6.5, 15] \end{cases}$$

For a discussion of the reasons for choosing the values 50 and 6.5 and the extent to which the results obtained depend on these values see [3, pp.25].

4.1.2. Another potential

In Table 3 we present some results obtained with another potential in (**??**). This potential is

$$V(x) = V_{Woods-Saxon} + C/x + l(l+1)/x^2 \tag{35}$$

where $V_{Woods-Saxon}$is the Woods-Saxon potential (**??**). For the purpose of our numerical experiments we use the same parameters as in [3], i.e. $C = 20, l = 2$.

Table 3. Deviations of the computed positive eigenvalues from the exact ones in 10^{-6} units, for the methods I-V

Exact eigenenergies	h	Method I	Method II	Method III	Method IV	Method V
61.482588	1/16	253692	1265	275	11	0
	1/32	15621	108	105	5	0
	1/64	967	4	72	0	0
173.075711	1/16		5200	2925	115	3
	1/32	618815	327	300	35	0
	1/64	38361	18	48	0	0
352.682070	1/16		9171	63500	856	8
	1/32		885	2125	117	0
	1/64	573357	64	125	7	0
1002.768393	1/16		545667		80927	12
	1/32		3377	60700	813	1
	1/64		263	2875	17	0

Since $V(x)$ is singular at the origin, we use the special strategy of [3]. We start the forward integration from a point $\epsilon > 0$ and the initial values $y(\epsilon)$ and $y(\epsilon + h)$ for the integration scheme are obtained by a perturbative method[12]. As in [3] we use the value $\epsilon = 1/4$ for our numerical tests.

It is appropriate to choose v in the way suggested by Ixaru and Rizea[3]. That is we choose:

$$v = \begin{cases} [V(a_1) + V(\epsilon)]/2, & \text{for x} \in [\epsilon, a_1] \\ V(a_1)/2, & \text{for x} \in (a_1, a_2] \\ V(a_3), & \text{for x} \in (a_2, a_3] \\ V(15), & \text{for x} \in (a_3, 15] \end{cases}$$

where a_1 is taken so that $V(a_1) = V(\epsilon)/2, a_2$ is approximately the first mode of $V(x)$, and $a_3 = 6.25$ is the point where $V(x)$ is approximately half of its minimum negative value.

4.2. Error estimation-Local error

When integrating first order systems of initial value ordinary differential equations several methods have been proposed for the estimation of the local truncation error (see for example [18]).

Denoting the solution obtained using the new sixth algebraic order exponential fitted method by y_{n+1}^H and the solution obtained using the lower order (fourth algebraic order) exponential fitted method proposed by Raptis [7] by y_{n+1}^L we obtain an estimate of the local truncation error in y_{n+1}^L which is

$$LTE = \mid y_{n+1}^H - y_{n+1}^L \mid \tag{36}$$

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

Thus the step-control procedure is

$$If\ LTE < ACC/100,\ \mathrm{h}_{n+1} = 2h_n$$
$$If\ ACC > LTE > ACC/100,\ \mathrm{h}_{n+1} = h_n$$
$$If\ LTE > ACC,\ \mathrm{h}_{n+1} = h_n/2 \text{ and repeat the } step$$

where ACC is a local error requested.

It is important to note that the local error estimate always is in the **lower order solution**. Thus, although we actually controlling an estimate of the local error in the lower order solution y_n^L it is the higher order solution y_n^H which we accept at each point.

In coupled differential equations, it is obvious, that we can use the same technique, but now the local truncation error is given by

$$LTE = max_{1<i,j<N} \| y_{i,j}^H - y_{i,j}^L \| \ . \tag{37}$$

4.3. Close coupled equations

Rotational excitation of a diatomic molecule by neutral particle impact is one problem in theoretical physics that may be described in terms of coupled differential equations. Denoting 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 obtain

$$[\frac{d^2}{dR^2} + k_{j'j}^2 - \frac{l'(l'+1)}{R^2}] y_{j'l'}^{Jjl}(R) = \frac{2\mu}{\hbar^2} \sum_{j^n} \sum_{l^n} < j'l'; J \mid V \mid j''l''; J > y_{j''l''}^{Jjl}(R) \tag{38}$$

where

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

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.

The potential V may be expanded as $V(R, \hat{\mathbf{k}}_{j'j}.\hat{\mathbf{k}}_{jj}) = V_0(R)P_0(\hat{\mathbf{k}}_{j'j}.\hat{\mathbf{k}}_{jj}) + V_2(R)P_2(\hat{\mathbf{k}}_{j'j}.\hat{\mathbf{k}}_{jj})$, where $\hat{\mathbf{k}}_{j'j}$ is a unit vector parallel to the wave vector $\mathbf{k}_{jj}$.

The coupling matrix element can then be written

$$< j'l'; J \mid V \mid j''l''; J >= \delta_{j'j''}\delta_{l'l''}V_0(R) + f_2(j'l', j''l''; J)V_2(R) \tag{40}$$

where the f_2 coefficients can be evaluated from formulas given by Bernstein et al.[13]. The boundary conditions are

$$y^{Jjl}_{j'l'}(R) = 0 \text{ at } R = 0 \tag{41}$$

$$y^{Jjl}_{j'l'}(R) \sim \delta_{jj'}\delta_{ll'} \exp[-i(k_{jj}R - 1/2l\pi)] - \left(\frac{k_i}{k_j}\right)^{1/2} S^J(jl; j'l') \exp[i(k_{j'j}R - 1/2l'\pi)] \tag{42}$$

where the scattering S matrix is related to the R matrix of (**??**) by the relation

$$\mathbf{S} = (\mathbf{I} + \mathbf{iR})(\mathbf{I} - \mathbf{iR})^{-1} \ . \tag{43}$$

Table 4. Real time of computation (in seconds) to calculate $\mid S \mid^2$ for the three variable-step methods. $ACC = 10^{-6}$. hmax is the maximum stepsize

Method	N	hmax	Real time of computation (in seconds)
Iterative Numerov [16]	4	0.014	3.25
	9	0.014	23.51
	16	0.014	99.15
Raptis and Cash [8]	4	0.056	1.00
	9	0.056	5.35
	16	0.056	24.53
New method	4	0.112	0.72
	9	0.112	3.20
	16	0.112	14.35

A program has been written to solve this problem and has been used to calculate cross sections for rotational excibition of molecular hydrogen by impact of various heavy particles. This program has a subroutine that deals exclusively with the step-by-step integration from the initial value to matching points. This program is also based on an analogous program which has been written for the numerical applications of [16].

As noted by several authors (see for example [16]), a good check on the calculation is furnished by inspection of the symmetry of the calculated **R** matrix, which guarantees the unitarity of the **S** matrix. We note that this check gives no information about the

Table 5. Comparison of $|S|^2$ calculated by the three methods

		Values of j and l								
j′	l′	0 6	2 4	2 6	2 8	4 2	4 4	4 6	4 8	4 10
0	6	0.4353	0.1538	0.1244	0.2045	0.0153	0.0122	0.0128	0.0151	0.0266
0	6	0.4351	0.1544	0.1249	0.2049	0.0154	0.0122	0.0128	0.0151	0.0266
0	6	0.4350	0.1546	0.1250	0.2050	0.0155	0.0123	0.0128	0.0150	0.0267
2	4	0.1538	0.3768	0.0974	0.0301	0.2317	0.0823	0.0189	0.0071	0.0019
2	4	0.1544	0.3768	0.0970	0.0300	0.2317	0.0824	0.0187	0.0070	0.0019
2	4	0.1546	0.3769	0.0967	0.0299	0.2318	0.0824	0.0188	0.0069	0.0020
2	6	0.1244	0.0974	0.4737	0.0561	0.0156	0.0208	0.0910	0.1103	0.0107
2	6	0.1248	0.0970	0.4738	0.0560	0.0157	0.0207	0.0911	0.1104	0.0106
2	6	0.1250	0.0967	0.4738	0.0559	0.0158	0.0207	0.0911	0.1105	0.0106
2	8	0.2044	0.0300	0.0561	0.3780	0.0014	0.0012	0.0030	0.0241	0.3017
2	8	0.2049	0.0300	0.0559	0.3782	0.0014	0.0012	0.0029	0.0242	0.3012
2	8	0.2050	0.0299	0.0559	0.3782	0.0014	0.0012	0.0029	0.0244	0.3014
4	2	0.0153	0.2317	0.0156	0.0014	0.6513	0.0759	0.0080	0.0007	0.0001
4	2	0.0154	0.2316	0.0157	0.0014	0.6512	0.0758	0.0081	0.0007	0.0001
4	2	0.0155	0.2318	0.0158	0.0014	0.6512	0.0757	0.0082	0.0007	0.0001
4	4	0.0122	0.0823	0.0208	0.0012	0.0759	0.7001	0.1017	0.0058	0.0001
4	4	0.0122	0.0824	0.0207	0.0012	0.0758	0.7000	0.1016	0.0058	0.0001
4	4	0.0123	0.0824	0.0207	0.0012	0.0757	0.6999	0.1015	0.0059	0.0001
4	6	0.0128	0.0189	0.0910	0.0030	0.0080	0.1016	0.7039	0.0602	0.0006
4	6	0.0128	0.0187	0.0911	0.0029	0.0081	0.1016	0.7038	0.0603	0.0007
4	6	0.0128	0.0188	0.0911	0.0029	0.0082	0.1015	0.7038	0.0604	0.0007
4	8	0.0152	0.0071	0.1102	0.0241	0.0007	0.0058	0.0602	0.7668	0.0099
4	8	0.0151	0.0070	0.1104	0.0242	0.0007	0.0062	0.0603	0.7667	0.0100
4	8	0.0150	0.0069	0.1105	0.0244	0.0007	0.0065	0.0604	0.7666	0.0100
4	10	0.0266	0.0019	0.0107	0.3016	0.0001	0.0001	0.0006	0.0099	0.6485
4	10	0.0265	0.0019	0.0106	0.3012	0.0001	0.0001	0.0007	0.0100	0.6479
4	10	0.0266	0.0020	0.0106	0.3014	0.0001	0.0001	0.0007	0.0100	0.6475

convergence of the **R** matrix but shows only that the numerical errors are not swamping the required solutions.

For numerical purposes we choose the **S** matrix which is calculated using the following parameters

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

We take $J = 6$ and consider excitation of the rotator from $j = 0$ state to levels up to $j' = 2, 4$ and 6 giving rise to sets of **four, nine and sixteen coupled differential equations**, respectively. Following the procedure obtained by Bernstein[17] we assumed the potential infinite for values of R less than some R_0. The wavefunctions will then

Table 6. Accurate values of $|S|^2$ calculated by method proposed in [1] with stepsize equal to 0.001

Values of j and l										
j′	l′	0 6	2 4	2 6	2 8	4 2	4 4	4 6	4 8	4 10
0	6	0.4349	0.1548	0.1251	0.2051	0.0158	0.0123	0.0128	0.0150	0.0268
2	4	0.1548	0.3770	0.0968	0.0300	0.2318	0.0825	0.0188	0.0068	0.0019
2	6	0.1251	0.0968	0.4739	0.0559	0.0158	0.0207	0.0912	0.1108	0.0108
2	8	0.2051	0.0300	0.0559	0.3783	0.0014	0.0012	0.0028	0.0245	0.3015
4	2	0.0158	0.2318	0.0158	0.0014	0.6511	0.0757	0.0082	0.0007	0.0001
4	4	0.0123	0.0825	0.0207	0.0012	0.0757	0.6998	0.1016	0.0059	0.0001
4	6	0.0128	0.0188	0.0912	0.0028	0.0082	0.1016	0.7037	0.0604	0.0008
4	8	0.0150	0.0068	0.1108	0.0245	0.0007	0.0059	0.0604	0.7666	0.0101
4	10	0.0268	0.0019	0.0108	0.3015	0.0001	0.0001	0.0008	0.0101	0.6482

be zero in this region and effectively the boundary condition (**??**) may be written as

$$y_{j'l'}^{Jjl}(R_0) = 0 \ . \tag{44}$$

Using a single channel phase shift program with the same potential and parameters corresponding to the smallest wavenumber we found that succesive values of the phase shift had converged to whithin 0.0001 around $R = 6.2$. We make the assumption that, for coupled equations, the **R** matrix elements will have converged by the same radial distance, a situation that has been verified in practice (the same assumption has been made in [16]).

For the exponentially-fitted methods we choose $v_{j'j} = k_{j'j}$. So, for the coupled differential equations we shall have $w_{j'j} = v_{j'j}h$.

In Table 4 we present the real time of computation required by the Iterative Numerov method (proposed by Allison[16]), the variable-step method (proposed by Raptis and Cash[8]) and the new variable-step method (proposed in the previous section) to calculate the square of the modulus of the **S** matrix for sets of 4, 9 and 16 coupled differential equations. In Table 5 we present the matrix $|S|^2$ for $N = 9$ and for the above mentioned methods.

For comparison purposes in the Table 6 we present the accurate values of the elements of the $|S|^2$ calculate by the method proposed in [1] with stepsize 0.001.

5. Conclusions

It can be seen from the theoretical and numerical results that the new method is considerably more accurate than the other numerical methods we have considered in both cases of radial Schrödinger equation and a set of coupled differential equations of the Schrödinger type.

All computations were carried out on the VAX/VMS 6000/410 of the Agricultural University of Athens using double precision arithmetic (16 significant digits accuracy).

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