A Dissipative Exponentially-Fitted Method for the Numerical Solution of the Schrödinger Equation

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A dissipative exponentially fitted method is constructed in this paper for the numerical integration of the Schrödinger equation. We note that the present method is a nonsymmetric multistep method (dissipative method) An application to the bound-states problem and the resonance problem of the radial Schrödinger equation indicates that the new method is more efficient (i.e. more accurate and more rapid) than the classical dissipative method and other well-known methods. Based on the new method and the method of Raptis and Allison[19] a new variable-step method is obtained. The application of the new variable-step method to the coupled differential equations arising from the Schrödinger equation indicates the efficiency of the new approach.

1. INTRODUCTION

The one-dimensional or radial Schrödinger equation can be written as

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

Equations of this type occur very frequently in theoretical physics and chemistry, quantum physics and chemistry, and physical chemistry (see for example, refs 6, 7, 14, 27), and it is needed to be able to solve them both efficiently and reliably by numerical methods. In (1) the function $W(r) = l(l+1)/r^2 + V(r)$ denotes *the effective potential*, which satisfies $W(r) \rightarrow 0$ as $r \rightarrow \infty$, 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

$$y(0) = 0 \quad (2)$$

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

There is a great activity for the numerical solution of the Schrödinger equation (see refs 1−3, 5−12, 15−26, 28, 31). The aim of this activity is the construction of a fast and reliable method that generates a numerical solution.

A fruitful way for developing efficient methods for the solution of (1) is to use exponential fitting. Until today the exponential fitting was applied to **symmetric multistep methods**. Raptis and Allison[19] have derived a Numerov type exponentially fitted method. The computational results obtained in ref 19 indicate that these fitted methods are much more efficient than Numerov's method for the solution of (1). Since then, exponential fitting has been the subject of great activity for the construction of symmetric exponentially fitted multistep methods. An interesting paper in this general area is that of Ixaru and Rizea.[7] They showed that for the resonance problem defined by (1) it is generally more efficient to derive methods which exactly integrate functions of the form

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

where υ is the frequency of the problem, than to use classical exponential fitting methods. The reason for this is explained in ref 25. We note here that the resonance problem is a stiff oscillatory problem. For the method obtained by Ixaru and Rizea[7] we have $m = 1$ and $p = 1$. Another low order method of this type (with $m = 2$ and $p = 0$) was developed by Raptis.[16] Simos[22] has derived a four-step method of this type which integrates more exponential functions and gives much more accurate results than the four-step methods of Raptis.[15,17] For this method we have $m = 3$ and $p = 0$. Simos[23] has derived a family of four-step methods which give more efficient results than other four-step methods. In particular, he has derived methods with $m = 0$ and $p = 5$, $m = 1$ and $p = 3$, $m = 2$ and $p = 1$, and finally $m = 3$ and $p = 0$. Also Raptis and Cash[20] have derived a two-step method fitted to (3) with $m = 0$ and $p = 5$ based on the well-known Runge−Kutta-type sixth order formula of Cash and Raptis.[2] The method of Cash, Raptis, and Simos[3] is also based on the formula proposed in ref 2 and is fitted to (3) with $m = 1$ and $p = 3$. Recently Simos and Williams[34] have developed Numerov-type exponentially fitted methods with $m = 0$ and $p = 9$, $m = 1$ and $p = 7$, $m = 2$ and $p = 5$, $m = 3$ and $p = 3$, $m = 4$ and $p = 1$, and $m = 5$ and $p = 0$. Recently Thomas, Simos, and Mitsou[33] have developed Numerov-type exponentially fitted methods with $m = 0$ and $p = 7$, $m = 1$ and $p = 5$, $m = 2$ and $p = 3$, and $m = 3$ and $p = 1$. More recently Thomas and Simos[35] have developed hybrid expo-

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nentially fitted methods with $m = 0$ and $p = 9$, $m = 1$ and $p = 7$, $m = 2$ and $p = 5$, $m = 3$ and $p = 3$, and $m = 4$ and $p = 1$.

In this paper we introduce a nonsymmetric (dissipative) two-step exponentially fitted method. This method is more efficient (i.e. more accurate and more rapid) than the exponentially fitted method of Raptis and Allison (which is an exponentially fitted method of the same kind) and the classical dissipative two-step method. We have applied the new methods to *the resonance problem* (which arises from the one-dimensional Schrödinger equation) with two different types of potential. We have also applied the new methods to *the bound-states problem*. Based on the new method and the method of Raptis and Allison[19] a new variable-step method is obtained. The application of the new variable-step method to the coupled differential equations arising from the Schrödinger equation indicates the efficiency of the new approach. We note here that the exponentially fitted form of the new method can be used in any eigenvalue or bound states problem of the Schrödinger type, while the trigino-metrically fitted form of the new method can be used in any scattering problem arising from the Schrödinger equation.

2. EXPONENTIAL MULTISTEP METHODS

For the numerical solution of the rth order initial value problem

$$y^{(r)} = f(x, y), y^{(j)}(A) = 0, j = 0, 1, \ldots, r-1 \quad (4)$$

the multistep methods of the form

$$\sum_{i=0}^{k} a_i y_{n+i} = h^r \sum_{i=0}^{k} b_i f(x_{n+i}, y_{n+i}) \quad (5)$$

over the equally spaced intervals $\{x_i\}_{i=0}^{k}$ in $[A, B]$ can be used, where A and B are the bounds of the interval of integration and are real numbers.

The method (5) is associated with the operator

$$L(x) = \sum_{i=0}^{k} [a_i z(x + ih) - h^r b_i z^{(r)}(x + ih)] \quad (6)$$

where z is a continuously differentiable function.

Definition 1. The multistep method (5) called algebraic (or exponential) of order p if the associated linear operator L vanishes for any linear combination of the linearly independent functions

$$\{1, x, x^2, \ldots, x^{p+r-1}\} \quad (7)$$

(or

$$\{exp(v_0 x), exp(v_1 x), \ldots, exp(v_{p+r-1} x)\} \quad (8)$$

where v_i, $i = 0, 1, \ldots, p + r - 1$ are real or complex numbers).

Remark 1. (See refs 30 and 21.) If $v_i = v$ for $i = 0, 1, \ldots, n$, $n \leq p + r - 1$, then the operator L vanishes for any linear combination of

$$\{exp(vx), xexp(vx), x^2 exp(vx), \ldots, x^n exp(vx), exp(v_{n+1}x), \ldots, exp(v_{p+r-1}x)\} \quad (9)$$

Remark 2. (See refs 30 and 21.) Every exponential multistep method corresponds in a unique way, to an algebraic multistep method (by setting $v_i = 0$ for all i).

Lemma 1. (For proof see refs 29 and 30.) Consider an operator L of the form (6). With $v \in C$, $h \in R$, $n \geq r$ if $v = 0$, and $n \geq 1$ otherwise, then we have

$$L[x^m exp(vx)] = 0, m = 0, 1, \ldots, n-1, \quad L[x^n exp(vx)] \neq 0 \quad (10)$$

if and only if the function φ has a zero of exact multiplicity s at $exp(vh)$, where $s = n$ if $v \neq 0$, and $s = n - r$ if $v = 0$, $\varphi(w) = \rho(w)/log^r w - \sigma(w)$, $\rho(w) = \sum_{i=0}^{k} a_i w^i$, and $\sigma(w) = \sum_{i=0}^{k} b_i w^i$.

In the present paper we investigate the case $r = 2$.

3. THE NEW FAMILY OF EXPONENTIALLY-FITTED METHODS

Consider the following family of methods

$$\bar{y}_a = \frac{1}{2}(-y_{n-1} + 3y_n) + \frac{h^2}{16}(f_{n-1} + 5f_n)$$

$$\bar{y}_b = \frac{1}{2}(y_{n-1} + y_n) + \frac{h^2}{144}(-7f_{n-1} - 15f_n + 4\bar{f}_a)$$

$$\bar{y}_c = -y_{n-1} + 2y_n + \frac{h^2}{9}(9zf_{n-1} + 9qf_n + 2\bar{f}_a + 6\bar{f}_b)$$

$$y_{n+1} - 2y_n + y_{n-1} = h^2[c_0 f_{n-1} + c_1 f_n + c_2 \bar{f}_a + c_2 \bar{f}_b + c_0 \bar{f}_c] \quad (11)$$

where $\bar{f}_a = f(x_{n+1/2})$, $\bar{f}_b = f(x_{n-1/2})$ and $\bar{f}_c = f(x_{n+1})$.

This method for appropriate values of z, qc_i, $i = 0(1)2$ is of algebraic order six.

For the present case we choose $q = 1/3$. We require that the methods (11) should integrate exactly any linear combination of the functions

$$\{1, x, x^2, x^3, x^4, x^5, \exp(\pm vx)\} \quad (12)$$

To construct a method of the form (11) which integrates exactly the functions (12), we follow the procedure described below:

The method (11) integrates exactly the functions 1, x. Demanding that (11) integrates exactly x^2, x^3, x^4, x^5 the following system of equations is obtained

$$2c_0 + c_1 + 2c_2 = 1 \quad (13)$$

$$\frac{44}{9}c_0 + c_2 + 4zc_0 = \frac{1}{3} \quad (14)$$

$$c_0(9z + 2) = 0 \quad (15)$$

Demanding, now, that the method (11) integrates exactly $\exp(\pm\upsilon x)$ we obtain the following system of equations

$$e^{(w)} - 2 + \frac{1}{e^{(w)}} - c_1 w^2 - 2c_2 w^2 - \frac{1}{4}c_2 w^4 - \frac{1}{576}\frac{c_2 w^6}{e^{(w)}} - \frac{5}{576}c_2 w^6 - 2c_0 w^2 - \frac{c_0 b_5 w^4}{e^{(w)}} - c_0 w^4 - \frac{2c_0 w^4}{9\,e^{(w)}} + \frac{1}{36}\frac{c_0 w^6}{e^{(w)}} - \frac{1}{36}c_0 w^6 - \frac{1}{864}\frac{c_0 w^8}{e^{(w)}} - \frac{5}{864}c_0 w^8 = 0 \quad (16)$$

where $w = \upsilon h$.

Solving the above system of eqs 13−16 we obtain the following values of parameters c_i, $i = 0(1)2$, and z

$$c_0 = -\frac{\frac{1}{2}-1728(e^w)^2 + 3456e^w - 1728 + 1728w^2e^w + 144w^4e^w + w^6 = 5w^6e^w}{w^6(-30 - 6e^w + w^2 + 5w^2e^w)}$$

$$c_1 = \frac{1}{3}(-39w^6 - 51w^6e^w + w^8 + 5w^8e^w + 15552(e^w)^2 - 31104e^w + 15552 - 15552w^2e^w - 1296w^4e^w)/(w^6(-30 - 6e^w + w^2 + 5w^2e^w))$$

$$c_2 = \frac{1}{3}(-24w^6 + 24w^6e^w + w^8 + 5w^8e^w - 10368(e^w)^2 + 20736e^w - 10368 + 10368w^2e^w + 864w^4e^w)/(w^6(-30 - 6e^w + w^2 + 5w^2e^w))$$

$$z = \frac{-2}{9} \quad (17)$$

For small values of υ the above formulas are subject to heavy cancelations. In this case the following Taylor series expansions must be used.

$$c_0 = \frac{1}{60} + \frac{1}{630}w^2 + \frac{13}{15120}w^3 + \frac{61}{113400}w^4 + \frac{181}{544320}w^5 + \frac{20143}{89812800}w^6 + \frac{39187}{269438400}w^7 + \frac{2501021}{26747884800}w^8 + \frac{213962299}{3530720793600}w^9 + \frac{4169557177}{105921623808000}w^{10} + \frac{1473599509}{57775431168000}w^{11} + \frac{535489581001}{32412016885248000}w^{12} + \frac{4165137497293}{388944202622976000}w^{13} + \dots$$

$$c_1 = \frac{13}{30} + \frac{1}{105}w^2 + \frac{13}{2520}w^3 + \frac{61}{18900}w^4 + \frac{181}{90720}w^5 + \frac{20143}{14968800}w^6 + \frac{39187}{44906400}w^7 + \frac{2501021}{4457980800}w^8 + \frac{213962299}{588453465600}w^9 + \frac{4169557177}{17653603968000}w^{10} + \frac{1473599509}{9629238528000}w^{11} + \frac{535489581001}{5402002814208000}w^{12} + \frac{4165137497293}{64824033770496000}w^{13} + \dots$$

$$c_2 = \frac{4}{15} - \frac{2}{315}w^2 - \frac{13}{3780}w^3 - \frac{61}{28350}w^4 - \frac{181}{136080}w^5 - \frac{20143}{22453200}w^6 - \frac{39187}{67359600}w^7 - \frac{2501021}{6686971200}w^8 - \frac{213962299}{882680198400}w^9 - \frac{4169557177}{2648040595000}w^{10} - \frac{1473599509}{14443857792000}w^{11} - \frac{535489581001}{8103004221312000}w^{12} - \frac{4165137497293}{97236050655744000}w^{13} + \dots \quad (18)$$

The local trunction error is given by

$$L.T.E.(h) = \frac{h^8}{120960}(-8y_n^{(8)} - 7y_n^{(4)} + 14y_n^{(6)} + 8\upsilon^2 y_n^{(6)} - 20\upsilon^2 y_n^{(4)}) \quad (19)$$

4. THE NEW FAMILY OF TRIGONOMETRICALLY-FITTED METHODS

Consider the above family of methods (11). We require that the methods (11) should integrate exactly any linear combination of the functions

$$\{1, x, x^2, x^3, x^4, x^5, \cos(\pm wx), \sin(\pm wx)\} \quad (20)$$

The above is equivalent with the requirement that the methods (11) should integrate exactly any linear combination of the functions

$$\{1, x, x^2, x^3, x^4, x,^5 \exp(\pm Iwx)\} \quad (21)$$

where $I = \sqrt{-1}$.

To construct a method of the form (11) which integrates exactly the functions (21), we follow the procedure described below:

The method (11) integrates exactly the functions 1, x. Demanding that (11) integrates exactly x^2, x^3, x^4, x^5 the following system of equations is obtained

$$2c_0 + c_1 + 2c_2 = 1 \quad (22)$$

$$4c_0 + c_2 + 4zc_0 = \frac{1}{3} \quad (23)$$

$$c_0(9z + 2) = 0 \quad (24)$$

Demanding, now, that the method (11) integrates exactly $\exp(\pm Iwx)$ we obtain the following system of equations

$$\cos(\upsilon x + \upsilon h) - 2\cos(\upsilon x) + \cos(\upsilon x - \upsilon h) + h^2 c_1 \upsilon^2 \cos(\upsilon x) + 2h^2 c_2 \upsilon^2 \cos(\upsilon x) - \frac{1}{4}h^4 c_2 \upsilon^4 \cos(\upsilon x) + \frac{1}{576}h^6 c_2 \upsilon^6 \cos(\upsilon x - \upsilon h) + \frac{5}{576}h^6 c_2 \upsilon^6 \cos(\upsilon x) + 2h^2 c_0 \upsilon^2 \cos(\upsilon x) - h^4 c_0 z \upsilon^4 \cos(\upsilon x - \upsilon h) - h^4 c_0 q \upsilon^4 \cos(\upsilon x) - \frac{2}{9}h^4 c_0 \upsilon^4 \cos(\upsilon x - \upsilon h) - \frac{2}{3}h^4 c_0 \upsilon^4 \cos(\upsilon x) - \frac{1}{36}h^6 c_0 \upsilon^6 \cos(\upsilon x - \upsilon h) + \frac{1}{36}h^6 c_0 \upsilon^6 \cos(\upsilon x) - \frac{1}{864}h^8 c_0 \upsilon^8 \cos(\upsilon x - \upsilon h) - \frac{5}{864}h^8 c_0 \upsilon^8 \cos(\upsilon x) = 0$$

$$\sin(vx+vh)-2\sin(vx)+\sin(vx-vh)+h^2c_1v^2\sin(vx)+2h^2c_2v^2\sin(vx)-\frac{1}{4}h^4c_2v^4\sin(vx)+\frac{1}{576}h^6c_2v^6\sin(vx-vh)+\frac{5}{576}h^6c_2v^6\sin(vx)+2h^2c_0v^2\sin(vx)-h^4c_0zv^4\sin(vx-vh)-h^4c_0qv^4\sin(vx)-\frac{2}{9}h^4c_0v^4\sin(vx-vh)-\frac{2}{3}h^4c_0v^4\sin(vx)-\frac{1}{36}h^6c_0v^6\sin(vx-vh)+\frac{1}{36}h^6c_0v^6\sin(vx)-\frac{1}{864}h^8c_0v^8\sin(vx-vh)-\frac{5}{864}h^8c_0v^8\sin(vx)=0 \quad (25)$$

Solving the above system of eqs 22−25 we obtain the following values of parameters c_i, $i = 0(1)2$, and z

$$c_0=\frac{1}{2}\frac{1}{30+w^2}$$

$$c_1=\frac{1}{3}\frac{39+w^2}{30+w^2}$$

$$c_2=\frac{1}{3}\frac{24+w^2}{30+w^2},\ z=\frac{-2}{9}$$

$$q=-\frac{4}{3}\frac{-90\cos(w)-3w^2\cos(w)+90-42w^2+2w^4}{w^4} \quad (26)$$

where $w = vh$. For small values of v the above formulas are subject to heavy cancelations. In this case the following Taylor series expansions must be used.

$$c_0=\frac{1}{60}-\frac{1}{1800}w^2+\frac{1}{54000}w^4-\frac{1}{1620000}w^6+\frac{1}{48600000}w^8-\frac{1}{1458000000}w^{10}+\frac{1}{43740000000}w^{12}-\frac{1}{1312200000000}w^{14}+\ldots$$

$$c_1=\frac{13}{30}-\frac{1}{300}w^2+\frac{1}{9000}w^4-\frac{1}{270000}w^6+\frac{1}{8100000}w^8-\frac{1}{243000000}w^{10}+\frac{1}{7290000000}w^{12}-\frac{1}{218700000000}w^{14}+\ldots$$

$$c_2=\frac{4}{15}+\frac{1}{450}w^2-\frac{1}{13500}w^4+\frac{1}{405000}w^6-\frac{1}{12150000}w^8+\frac{1}{364500000}w^{10}-\frac{1}{10935000000}w^{12}+\frac{1}{328050000000}w^{14}+\ldots$$

$$q=\frac{1}{3}-\frac{13}{5040}w^4+\frac{1}{15120}w^6-\frac{17}{19958400}w^8+\frac{19}{2724321600}w^{10}-\frac{1}{24908083200}w^{12}+\frac{23}{133382785536000}w^{14}+\ldots \quad (27)$$

The local trunction error is given by

$$L.T.E.(h)=\frac{h^8}{604800}(-40y_n^{(8)}-35y_n^{(4)}+70y_n^{(6)}-14v^2y_n^{(6)}+35v^2y_n^{(4)}+26v^4y_n^{(4)}-26v^4y_n^{(2)}) \quad (28)$$

5. NUMERICAL ILLUSTRATIONS

In this section we present some numerical results to illustrate the performance of our new methods. Consider the numerical integration of the Schrödinger eq 1.

All computations were carried out on a IBM PC-AT compatible 80486 using double precision arithmetic with 16 significant digits accuracy (IEEE standard).

5.1. Resonance Problem. In the asymptotic region the eq 1 effectively reduces to

$$y''(x)+\left(k^2-\frac{l(l+1)}{x^2}\right)y(x)=0 \quad (29)$$

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 eq 1 has the asymptotic form (when $x \rightarrow \infty$)

$$y(x)\simeq Akxj_l(kx)-Bn_l(kx)\simeq D[\sin(kx-\pi l/2)+\tan\delta_l\cos(kx-\pi l/2)] \quad (30)$$

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

$$\tan\delta_l=\frac{y(x_2)S(x_1)-y(x_1)S(x_2)}{y(x_1)C(x_2)-y(x_2)C(x_1)} \quad (31)$$

for x_1 and x_2 distinct points on the asymptotic region (for which we have that x_1 is the right-hand end point of the interval of integration and $x_2 = x_1 - h$, h is the stepsize) with $S(x) = kxj_l(kx)$ and $C(x) = kxn_l(kx)$.

Since the problem is treated as an initial-value problem, one needs y_0 and y_1 before starting a two-step method. From the initial condition, $y_0 = 0$. The value y_1 is computed using the Runge−Kutta-Nyström 12 (10) method of Dormand et al.[36−38] With these starting values we evaluate at x_1 of the asymptotic region the phase shift δ_l from the above relation.

5.1.1. The Woods-Saxon Potential. As a test for the accuracy of our methods we consider the numerical integration of the Schrödinger eq 1 with $l = 0$ in the well-known case where the potential $V(r)$ is the Woods-Saxon one

$$V(r)=V_w(r)=\frac{u_0}{(1+z)}-\frac{u_0z}{[a(1+z)^2]} \quad (32)$$

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

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

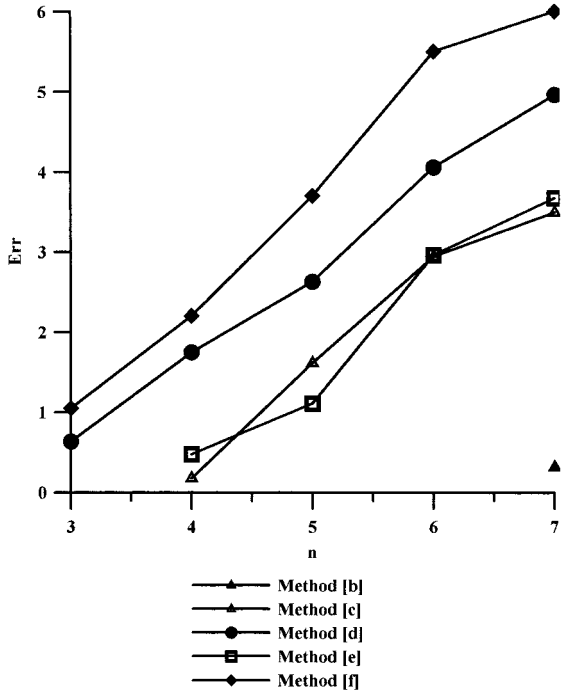

Figure 1. Values of Err for several values of n for the resonance E = 989.7019159. The nonexistence of a value for a method indicates that Err is negative.

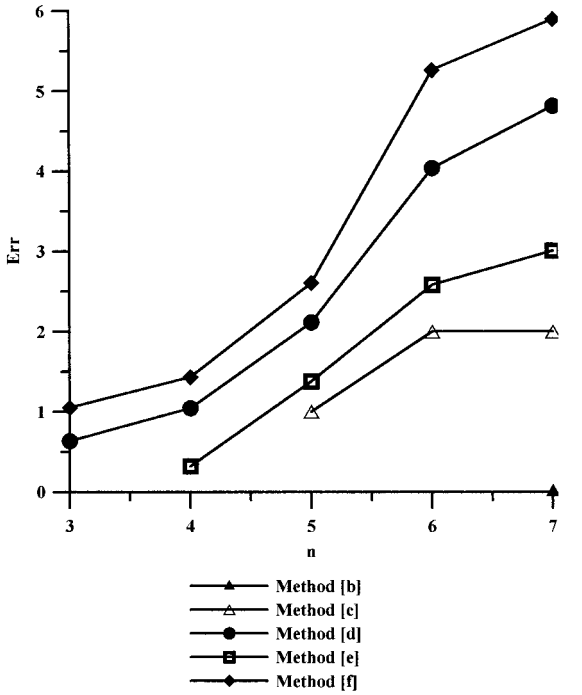

Figure 2. Values of Err for several values of n for the resonance E = 1002.768393. The nonexistence of a value for a method indicates that Err is negative.

The boundary conditions for this problem are

$$y(0) = 0$$

$$y(x) \sim \cos[\sqrt{E}x] \text{ for large } x.$$

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

For comparison purposes in our numerical illustration we use the well-known Numerov's method (which is indicated as method [a]), the exponentially fitted method of Raptis and Allison[19] (which is indicated as method [b]), the exponentially fitted method of Raptis and Cash (which is indicated as method [c]), the exponentially fitted method (Case I) of Thomas, Simos, and Mitsou (which is indicated as method [d]), the classical dissipative two-step method (which is indicated as method [e]), and the exponentially fitted dissipative two-step method developed in this paper (which is indicated as method [f]). We note that the method of Raptis and Allison[19] has been proved that it is much more efficient than the well-known Numerov's method (see for details refs 19, 21, 24, 25, and 33−35).

The numerical results obtained for the four methods, with stepsizes equal to $h = 1/2^n$, were compared with the analytic solution of the Woods-Saxon potential resonance problem, rounded to six decimal places. Figure 1 show the errors $Err = -log_{10}|E_{\text{calculated}} - E_{\text{analytical}}|$ of the highest eigenenergy $E_3 = 989.701916$ for several values of n.

The performance of the present method 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.[7] That is, we choose

$$v = \begin{cases} (-50 - E)^{1/2} & \text{for } x \in [0, 6.5] \\ (-E)^{1/2} & \text{for } x \in (6.5, 15] \end{cases} \tag{33}$$

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 ref 7, p 25.

5.1.2. Modified Woods-Saxon Potential. In Figure 2 some results for $Err = -log_{10}|E_{\text{calculated}} - E_{\text{analytical}}|$ of the highest eigenenergy $E_3 = 1002.768393$, for several values of n, obtained with another potential in (1) using the methods mentioned above are shown. This potential is

$$V(x) = V_W(x) + \frac{D}{x} \tag{34}$$

where V_W is the Woods-Saxon potential (32). For the purpose of our numerical experiments we use the same parameters as in ref 7, i.e., $D = 20$, $l = 2$.

Since $V(x)$ is singular at the origin, we use the special strategy of 7. We start the integration from a point $\epsilon > 0$ and the initial values $y(\epsilon)$ and $y(\epsilon + h)$ for the integration scheme are obtained using a perturbative method (see ref 6). As in ref 7 we use the value $\epsilon = 1/4$ for our numerical experiments.

For the purpose of obtaining our numerical results it is appropriate to choose v in the way suggested by Ixaru and Rizea.[7] That is, we choose

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

where a_i, $i = 1(1)3$ are fully defined in ref 7.

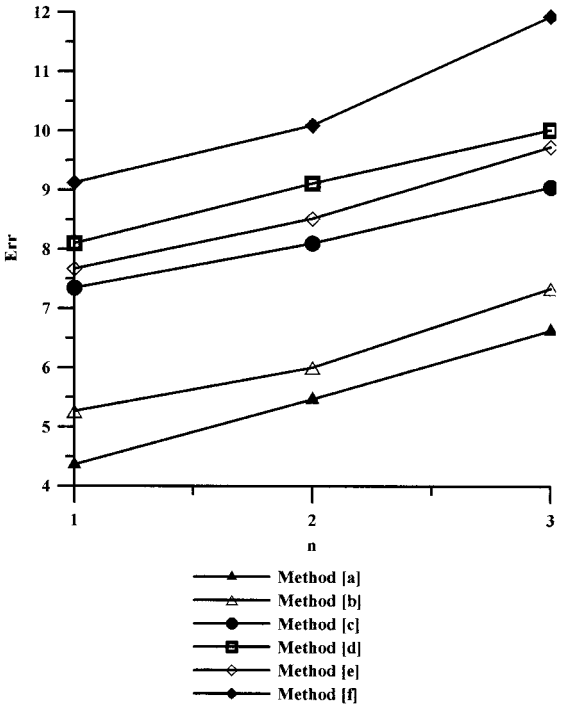

Figure 3. Values of Err for several values of n for the eigenvalue E = 49.457788728.

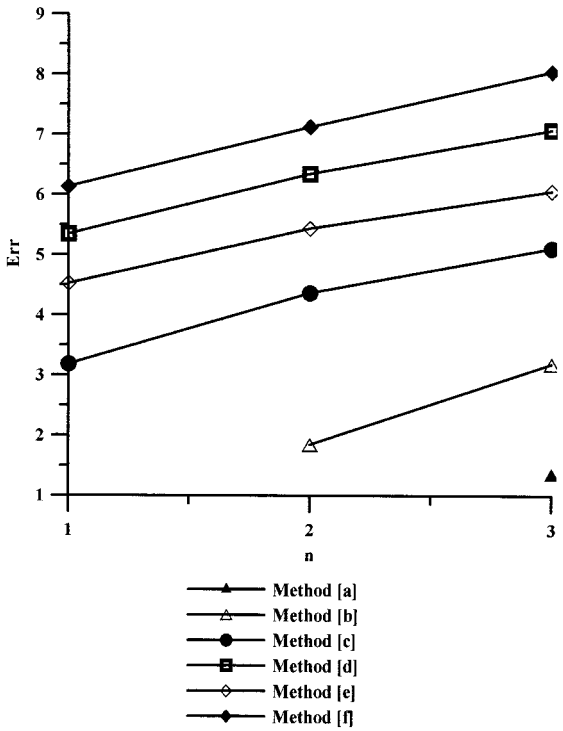

Figure 4. Values of Err for several values of n for the eigenvalue E = 8.676081670. The nonexistence of a value for a method indicates that Err is negative.

5.2. The Bound-States Problem. For negative energies we solve the so-called bound-states problem, i.e., the eq 1 with $l = 0$ and boundary conditions given by

$$y(0) = 0$$

$$y(x) \sim exp(-\sqrt{-E}x) \text{ for large } x.$$

To solve this problem numerically we use a strategy which has been proposed by Cooley[5] and has been improved by Blatt.[1] This strategy involves integrating forward from the point $x = 0$, backward from the point $x_b = 15$, and matching up the solution at some internal point in the range of integration. As initial conditions for the backward integration we take (see ref 3)

$$y(x_b) = exp(-\sqrt{E}x_b) \text{ and } y(x_b - h) = exp[-\sqrt{E}(x_b - h)] \quad (35)$$

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

The true solutions to the Woods-Saxon bound-states problem were obtained correct to nine decimal places using the analytic solution, and the numerical results obtained for the six methods mentioned above were compared to this true solution. In Figure 3 some results for $Err = -log_{10}|E_{calculated} - E_{analytical}|$ of the eigenenergy $E_0 = -49.457788728$ using stepsizes equal to $h = 1/2^n$ for several values of n are shown. In Figure 4 some results for $Err = -log_{10}|E_{calculated} - E_{analytical}|$ of the eigenenergy $E_{12} = -8.676081670$ using stepsizes equal to $h = 1/2^n$ for several values of n are also shown.

5.3. Local Error Estimation. In the literature there are many methods for the estimation of the local truncation error (LTE) for the integration of systems of initial-value problems (see for example refs 36−39 and references therein).

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

We have the following definition.

Definition 2. We define the **local truncation error** estimate in the lower order solution y^L_{n+1} by the quantity

$$L.T.E = |y^H_{n+1} - y^L_{n+1}| \quad (36)$$

where y^H_{n+1} is the solution obtained with higher order method and y^L_{n+1} is the solution obtained with lower order method. In the present case y^H_{n+1} is the solution obtained using the exponentially fitted method presented in this paper, while y^L_{n+1} is the solution obtained using the method of Raptis and Allison.[19] Under the assumption that h is sufficiently small, the **local error** in y^H_{n+1} can be neglected compared with that in y^L_{n+1}.

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

$$h_{n+1} = h_n\left(\frac{acc}{L.T.E}\right)^{1/q} \quad (37)$$

where q is the algebraic order of the method.

However, for ease of programming we have restricted all step changes to halving and doubling. Thus, based on the procedure developed in ref 39, the step control procedure which we have actually used is

$$If\ L.T.E < acc,\ h_{n+1} = 2h_n$$

$$If\ 100\ acc > L.T.E \geq acc,\ h_{n+1} = h_n \qquad (38)$$

$$If\ L.T.E \geq 100\ acc,\ h_{n+1} = \frac{h_n}{2}\ and\ repeat\ the\ step$$

We note, here, that the local truncation error estimate is in the lower order solution y^L_{n+1}. 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 algebraic order solution y^L_{n+1}, it is the higher algebraic order solution y^H_{n+1} which we actually accept at each point. We note here that other methods of selection of stepsizes can be used.

5.4. Coupled Differential Equations of the Schrödinger Type. There are many problems in theoretical physics and chemistry, molecular physics, physical chemistry, quantum chemistry, atomic physics, chemical physics, electronics, and molecular biology which can be transformed to the solution of coupled differential equations of the Schrödinger type.

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

$$\left[\frac{d^2}{dx^2} + k_i^2 - \frac{l_i(l_i+1)}{x^2} - V_{ii}\right] y_{ij} = \sum_{m=1}^{N} V_{im} y_{mj} \qquad (39)$$

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

We have investigated the case in which all channels are open. So we have the following boundary conditions (see for details ref 40):

$$y_{ij} = 0\ at\ x = 0 \qquad (40)$$

$$y_{ij} \sim k_i x j_{l_i}(k_i x)\delta_{ij} + \left(\frac{k_i}{k_j}\right)^{1/2} K_{ij} k_i x n_{li}(k_i x) \qquad (41)$$

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

Based on the detailed analysis developed in ref 40 and defining a matrix K' and diagonal matrices M, N by

$$K'_{ij} = \left(\frac{k_i}{k_j}\right)^{1/2} K_{ij}$$

$$M_{ij} = k_i x j_{l_i}(k_i x)\delta_{ij}$$

$$N_{ij} = k_i x n_{l_i}(k_i x)\delta_{ij}$$

we find that the asymptotic condition (41) may be written as

$$\boldsymbol{y} \sim \boldsymbol{M} + \boldsymbol{N}\boldsymbol{K}' \qquad (42)$$

One of the most popular methods for the approximate solution of the coupled differential equations arising from the Schrödinger equation is the Iterative Numerov method of Allison.[40]

A real problem in theoretical physics and chemistry, atomic physics, quantum chemistry and molecular physics, which can be transformed to close-coupling differential equations of the Schrödinger type is the rotational excitation of a diatomic molecule by neutral particle impact. Denoting, as in ref 40, the entrance channel by the quantum numbers (j,l), the exit channels by (j', l'), and the total angular momentum by $J = j + l = j' + l'$, we find that

$$\left[\frac{d^2}{dx^2} + k_{j'j}^2 - \frac{l'(l'+1)}{x^2}\right] y^{Jjl}_{j'l'}(x) = \frac{2\mu}{\hbar^2} \sum_{j''} \sum_{l''} < j'l'; J|V|j''l''; J > y^{Jjl}_{j''l''}(x) \qquad (43)$$

where

$$k_{j'j} = \frac{2\mu}{\hbar^2}\left[E + \frac{\hbar^2}{2I}\{j(j+1) - j'(j'+1)\}\right] \qquad (44)$$

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 ref 40 the potential V may be written as

$$V(x, \hat{\mathbf{k}}_{j'j}\hat{\mathbf{k}}_{jj}) = V_0(x)P_0(\hat{\mathbf{k}}_{j'j}\hat{\mathbf{k}}_{jj}) + V_2(x)P_2(\hat{\mathbf{k}}_{j'j}\hat{\mathbf{k}}_{jj}) \qquad (45)$$

and the coupling matrix element is given by

$$\langle j'l'; J|V|j''l''; J\rangle = \delta_{j'j''}\delta_{l'l''}V_0(x) + f_2(j'l', j''l''; J)V_2(x) \qquad (46)$$

where the f_2 coefficients can be obtained from formulas given by Berstein et al.[41] and $\hat{\mathbf{k}}_{j'j}$ is a unit vector parallel to the wave vector $\mathbf{k}_{j'j}$ and P_i, $i = 0, 2$ are Legendre polynomials (see for details ref 41). The boundary conditions may then be written as (see ref 40)

$$y^{Jjl}_{j'l'}(x) = 0 \text{ at } x = 0 \qquad (47)$$

$$y^{Jjl}_{j'l'}(x) \sim \delta_{jj'}\delta_{ll'}\exp[-i(k_{jj}x - 1/2l\pi)] - \left(\frac{k_i}{k_j}\right)^{1/2} \times S^J(jl; j'l')\exp[i(k_{j'j}x - 1/2l'\pi)] \qquad (48)$$

where the scattering $\boldsymbol{S}$ matrix is related to the $\mathbf{K}$ matrix of (41) by the relation

$$\boldsymbol{S} = (\mathbf{I} + \mathbf{iK})(\mathbf{I} - \mathbf{iK})^{-1} \qquad (49)$$

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

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

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

As is described in ref 40, 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 **4, 9, and 16 coupled differential equations**, respectively. Following Berstein[42] and Allison[40] the reduction of the interval $[0, \infty)$ to $[0, x_0]$ is obtained. The wave functions are then vanished in this region

Table 1. RTC (Real Time of Computation (in s)) and MErr (Maximum Absolute Error) in the Calculation of $|S|^2$ for the Variable-Step Methods (i)−(v)

method	*N*	hmax	RTC
Iterative Numerov[40]	4	0.014	3.25
	9	0.014	23.51
	16	0.014	99.15
variable-step method of Raptis and Cash[39]	4	0.056	1.65
	9	0.056	8.68
	16	0.056	45.21
RKN1	4	0.224	1.02
	9	0.224	6.33
	16	0.112	22.14
RKN2	4	0.224	0.82
	9	0.224	5.01
	16	0.224	13.43
new variable-step method			
	4	0.224	0.39
	9	0.224	4.18
	16	0.224	11.35

[a] $acc = 10^{-6}$; hmax is the maximum stepsize.

and consequently the boundary condition (47) may be written as

$$y^{Jjl}_{j'l'}(x_0) = 0 \tag{50}$$

For the numerical solution of this problem we have used (i) the well-known Iterative Numerov method of Allison,[40] (ii) the variable-step method of Raptis and Cash,[39] (iii) the Runge−Kutta-Nyström method developed by Dormand and Prince (RKN1) (see Table 13.4 of[38]), (iv) the Runge−Kutta-Nyström method developed by Dormand, El-Mikkawy and Prince (RKN2) (see ref 37), and (v) the new variable-step method. In Table 1 we present the real time of computation required by the methods mentioned above to calculate the square of the modulus of the **S** matrix for sets of 4, 9, and 16 coupled differential equations. In Table 1 *N* indicates the number of equations of the set of coupled differential equations.

6. CONCLUSIONS

In this paper a new approach for constructing exponentially fitted methods is introduced. Using this new approach we can construct nonsymmetric methods which exactly integrate functions of the form

$$\{1, x, x^2, x^3, x^4, x^5, \exp(\pm \upsilon x)\} \tag{51}$$

or

$$\{1, x, x^2, x^3, x^4, x^5, \cos(\pm wx), \sin(\pm wx)\} \tag{52}$$

Numerical and theoretical results show that these methods are much more accurate than than other well-known methods. Using the method of Raptis and Allison a variable-step method is also constructed. The application of the new variable-step method to the coupled differential equations arising from the Schrödinger equation indicates the efficiency of the new approach.

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