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Eighth-Order Methods for Elastic Scattering Phase Shifts

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Two new hybrid eighth-algebraic-order two-step methods with phase lag of order 12 and 14 are developed for computing elastic scattering phase shifts of the one-dimensional Schrödinger equation. Based on these new methods we obtain a new variable-step procedure for the numerical integration of the Schrödinger equation. Numerical results obtained for the integration of the phase shift problem for the well-known case of the Lennard-Jones potential show that these new methods are better than other finite-difference methods.

1. INTRODUCTION

The one-dimensional Schrödinger equation has the form

$$y''(r) + f(r)y(r) = 0 \tag{1}$$

where $0 \leq r < \infty$ and $f(r) = E - l(l + 1)/r^2 - V(r)$. We call the term $l(l + 1)/r^2$ *the centrifugal potential* and the function $V(r)$ *the potential*, where $V(r) \to 0$ as $r \to \infty$. According to the sign of the energy E there are two main categories of problems for (1) [for details see Simos and Tougelidis (1996)].

The numerical solution of the Schrödinger equation is needed in many areas of nuclear physics, physical chemistry, theoretical physics, and chemistry (Cooley, 1961; Blatt, 1967; Herzberg, 1950).

There has been much activity in the area of the solution of the one-dimensional Schrödinger equation (1). The result of this activity has been the development of a great number of methods. The most important characteristics of an efficient method for the solution of problem (1) are accuracy

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and computational efficiency. The development of methods with the above-mentioned characteristics is an open problem.

One of the most important properties for the numerical solution of the general second-order differential equations with periodic solution is the algebraic order of the method. Another important new insight is the *phase lag*, first introduced by Bruca and Nigro (1980). The most widely used technique for the numerical integration of (1) is *Numerov's method*, with interval of periodicity (0, 6) and phase lag of order four. Many authors (Chawla and Rao, 1984, 1986, 1987; Simos, 1992a,b; Coleman, 1989; van der Houwen and Sommeijer, 1987; Thomas, 1984; Simos and Tougelidis, 1996) have developed methods with minimal phase lag for the solution of general second-order differential equations with periodic solutions. All these methods have algebraic orders of four and six.

The purpose of this paper is to introduce two explicit eighth-algebraic-order methods with phase lag of order 12 and 14 for the numerical solution of the phase-shift problem of the one-dimensional Schrödinger equation. The new methods are very simple because they are explicit. The phase shifts calculated by these methods are more accurate than those given by Riehl *et al.* (1974) and Hepburn and Le Roy (1978). We introduce a new error control procedure, which is based on the property of the phase lag. Based on these new methods, we introduce a new variable-step method for the solution of (1). The numerical results given by this new variable-step method are better than those of the best-known variable-step method of Raptis and Cash (1985).

2. PHASE-LAG ANALYSIS

We investigate the numerical integration of the problem

$$y'' = f(r, y), \qquad y(r_0) = y_0, \qquad y'(r_0) = y'_0 \tag{2}$$

To examine the stability properties of the methods for solving the initial-value problem (2), Lambert and Watson (1976) introduced the scalar test equation

$$y'' = -w^2 y \tag{3}$$

and the *interval of periodicity*. When we apply a symmetric two-step method to the scalar test equation (3) we obtain a difference equation of the form

$$y_{n+1} - 2Q(s)y_n + y_{n-1} = 0 \tag{4}$$

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

The characteristic equation associated with (4) is

$$z^2 - 2Q(s)z + 1 = 0 \tag{5}$$

We have the following definitions.

Definition 1 (Thomas, 1984). The method (4) with the characteristic equation (5) is unconditionally stable if $|z_1| \leq 1$ and $|z_2| \leq 1$ for all values of wh.

Definition 2. Following Lambert and Watson (1976), we say that the numerical method (4) has an interval of periodicity $(0, H_0^2)$ if for all $s^2 \in (0, H_0^2)$, z_1 and z_2 satisfy

$$z_1 = e^{i\theta(s)} \quad \text{and} \quad z_2 = e^{-i\theta(s)} \tag{6}$$

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

Definition 3 (Lambert and Watson, 1976). The method (4) is *P-stable* if its *interval of periodicity* is $(0, \infty)$.

Based on the above we have the following theorems [for the proofs see Simos and Tougelidis (1996)].

Theorem 1. A method which has the characteristic equation (5) has an interval of periodicity $(0, H_0^2)$ if for all $s^2 \in (0, H_0^2)$, $|Q(s)| < 1$.

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

$$\cos[\theta(s)] = Q(s), \quad \text{where} \quad s^2 \in (0, H_0^2) \tag{7}$$

Definition 4 (van der Houwen and Sommeijer, 1987). For any method corresponding to the characteristic equation (5) the quantity

$$t = s - \cos^{-1}[B(s)/A(s)] \tag{8}$$

is called the dispersion or the phase error or the phase lag of the method. If $t = O(s^{q+1})$ as $s \to 0$, the order of the phase lag is q.

Based on the above definition, Coleman (1989) arrived at the following remark. If the order of dispersion is $2r$, then we have

$$\begin{aligned} t &= cs^{2r+1} + O(s^{2r+3}) \Rightarrow \cos(s) - Q(s) = \cos(s) - \cos(s - t) \\ &= cs^{2r+2} + O(s^{2r+4}) \end{aligned} \tag{9}$$

where t is the *phase lag of the method.*

3. THE NEW EXPLICIT EIGHTH-ORDER METHODS

Consider the family of two-step formulas $M_8(a_i,\ i = 1(1)3)$ given by

$$\bar{y}_{n+1} = 2y_n - y_{n-1} + h^2 f_n$$

$$\bar{f}_{n+1} = f(r_{n+1}, \bar{y}_{n+1}) \tag{10}$$

$$\bar{\bar{y}}_{n+1} = 2y_n - y_{n-1} + \frac{h^2}{12}(\bar{f}_{n+1} + 10f_n + f_{n-1})$$

$$\bar{\bar{f}}_{n+1} = f(r_{n+1}, \bar{\bar{y}}_{n+1}) \tag{11}$$

$$\bar{y}_{n+1/2} = \frac{1}{104}(5\bar{\bar{y}}_{n+1} + 146y_n - 47y_{n-1}) + \frac{h^2}{4992}(-59\bar{\bar{f}}_{n+1} + 1438f_n + 253f_{n-1})$$

$$\bar{f}_{n+1/2} = f(r_{n+1/2}, \bar{y}_{n+1/2}) \tag{12}$$

$$\bar{y}_{n-1/2} = \frac{1}{52}(3\bar{\bar{y}}_{n+1} + 20y_n + 29y_{n-1}) + \frac{h^2}{4992}(41\bar{\bar{f}}_{n+1} - 682f_n - 271f_{n-1})$$

$$\bar{f}_{n-1/2} = f(r_{n-1/2}, \bar{y}_{n-1/2}) \tag{13}$$

$$\tilde{y}_{n+1} = 2y_n - y_{n-1} + \frac{h^2}{60}[\bar{\bar{f}}_{n+1} + 26f_n + f_{n-1} + 16(\bar{f}_{n+1/2} + \bar{f}_{n-1/2})]$$

$$\tilde{f}_{n+1} = f(r_{n+1}, \tilde{y}_{n+1}) \tag{14}$$

$$\bar{\bar{y}}_{n+1/2} = \frac{1}{128}(-25\tilde{y}_{n+1} + 205y_n - 15y_{n-1} - 37y_{n-2}) + \frac{h^2}{1536}(23\tilde{f}_{n+1} + 761f_n + 509f_{n-1} + 27f_{n-2}) \tag{15}$$

$$\bar{\bar{f}}_{n+1/2} = f(r_{n+1/2}, \bar{\bar{y}}_{n+1/2})$$

$$\bar{\bar{y}}_{n-1/2} = \frac{1}{128}[37(\tilde{y}_{n+1} + y_{n-2}) + 27(y_n + y_{n-1})] + \frac{h^2}{512}[-9(\tilde{f}_{n+1} + f_{n-2}) - 171(f_n + f_{n-1})] \tag{16}$$

$$\bar{\bar{f}}_{n-1/2} = f(r_{n+1/2}, \bar{\bar{y}}_{n-1/2})$$

$$\bar{y}_{n+1/4} = \frac{1}{4096}[605\tilde{y}_{n+1} + 4070y_n - 579y_{n-1} - 160(y_{n+1/2} - y_{n-1/2})] - \frac{h^2}{49152}[113\tilde{f}_{n+1} - 1390f_n - 103f_{n-1} + 1944(f_{n+1/2} - f_{n-1/2})] \tag{17}$$

$$\bar{f}_{n+1/4} = f(r_{n+1/4}, \bar{y}_{n+1/4})$$

$$\bar{y}_{n-1/4} = -\frac{1}{4096}[579\tilde{y}_{n+1} - 4070y_n - 605y_{n-1} - 160(y_{n+1/2} - y_{n-1/2})] + \frac{h^2}{49152}[103\tilde{f}_{n+1} + 1390f_n - 113f_{n-1} + 1944(f_{n+1/2} - f_{n-1/2})] \quad (18)$$

$$\bar{f}_{n-1/4} = f(r_{n-1/4}, \bar{y}_{n-1/4})$$

$$\bar{y}_n^{(i)} = y_n - a_i h^2[\tilde{y}_{n+1} - 90f_n + y_{n-1} - 20(\bar{\bar{y}}_{n+1/2} + \bar{\bar{y}}_{n-1/2}) + 64(\bar{\bar{y}}_{n+1/4} + \bar{\bar{y}}_{n-1/4})]$$

$$\bar{f}_n^{(i)} = f(r_n, \bar{y}_n^{(i)}), \qquad i = 1(1)3 \quad (19)$$

Then for $n \geq 1$ we derive the following two-parameter family $M_8(a_i, i = 1(1)3)$ of explicit methods of order eight:

$$y_{n+1} - 2y_n + y_{n-1} = \frac{h^2}{3780}[47(\tilde{f}_{n+1} + f_{n-1}) + 1328(\bar{\bar{f}}_{n+1/2} + \bar{\bar{f}}_{n-1/2}) - 1024(\bar{f}_{n+1/4} + \bar{f}_{n-1/4}) + 3078\bar{f}_n^{(3)}] \quad (20)$$

The local truncation error (LTE) of the method is given by

$$\text{LTE} = \frac{h^{10}}{951035904000}[126945y_n^{(10)} + (1512529200a_3 + 1010945)y_n^{(8)}F_n - 1001952y_n^{(6)}F_nF'_n - 636160y_n^{(4)}F'_nF_n^2] + O(h^{12}) \quad (21)$$

where $F_n = (\partial f/\partial y)_n$, $F'_n = (dF/dr)_n$, $y_n^{(2)} = (d^2y/dr^2)_n$, $y_n^{(4)} = (d^4y/dr^4)_n$, $y_n^{(6)} = (d^6y/dr^6)_n$, $y_n^{(8)} = (d^8y/dr^8)_n$, and $y_n^{(10)} = (d^{10}y/dr^{10})_n$.

We apply this method to the scalar test equation (3). Setting $s = wh$, we obtain the *difference equation* (4) and the corresponding characteristic equation (5) with $A(s) = 1$ and

$$B(s) = 1 - \frac{1}{2}s^2 + \frac{1}{24}s^4 - \frac{1}{720}s^6 + \frac{1}{40320}s^8 + \frac{900315a_3 + 3332}{1132185600}s^{10} + \frac{52 - 89775a_3 - 108037800a_2a_3}{1509580800}s^{12} + \frac{19a_3(5054400a_1a_2 + 4200a_2 - 1)}{14909440}s^{14} + \frac{171a_2a_3(1 - 4200a_1)}{1490944}s^{16} - \frac{7695a_1a_2a_3}{745472}s^{18}$$

For the proof of the following theorem see Simos and Tougelidis (1996).

Theorem 3. The phase lag of a symmetric two-step method with characteristic equation (5) is the leading term in the expansion of

$$[\cos(s) - Q(s)]/s^2, \qquad Q(s) = B(s)/A(s) \tag{22}$$

Theorem 4. The family of methods $M_8(a_1, a_2, a_3)$ produces methods with phase lag of order 12 and 14 for the values of a_1, a_2, and a_3 given in Table I. The intervals of periodicity of these methods are given in Table I.

Proof. Considering (22), we have that

$$\begin{aligned}
&[\cos(s) - Q(s)]/s^2 \\
&= s^8 \frac{900315a_3 + 3644}{1132185600} \\
&+ s^{10} \frac{1612 - 2962575a_3 - 3565247400a_2a_3}{49816166400} \\
&+ s^{12} \frac{16 - 1777545a_3 + 7465689000a_2a_3 + 8984423448000a_1a_2a_3}{1394852659200} \\
&- s^{14} \frac{1 - 2399685750a_2a_3 + 10078680150000a_1a_2a_3}{20922789888000} \\
&+ s^{16} \frac{1 - 660873455555000a_1a_2a_3}{6402373705728000}
\end{aligned} \tag{23}$$

To have maximal phase-lag order it follows from (23) that we must have the following system of equations:

$$\begin{aligned}
900315a_3 + 3644 \\
1612 - 2962575a_3 - 3565247400a_2a_3 \\
16 - 1777545a_3 + 7465689000a_2a_3 + 8984423448000a_1a_2a_3
\end{aligned} \tag{24}$$

Based on this system and on (23) we have Table I.

Table I. Characteristics of the New Methods

	Method 1	Method 2
a_1	0	−122158423/117312708240
a_2	−3644/900315	−198943/211042260
a_3	−198943/211042260	−3644/900315
Phase lag	$2.6 \times 10^{-8}\ s^{14}$	$2.4 \times 10^{-9}\ s^{16}$
Interval of periodicity	(0, 12.9394)	(0, 12.6756)

To prove the property of nonempty interval of periodicity, we note first that considering (5), it is clear that the roots $z_{1,2}$ will be distinct, complex conjugate, and each of modulus one for $s^2 \in (0, H_0)$ provided $|Q(s)| < 1$ for all $s^2 \in (0, H_0)$. Considering (5) and Theorem 1 and for a_i, $i = 1(1)3$, given in Table I, we have the intervals of periodicity mentioned in the same table. ■

4. NUMERICAL ILLUSTRATION

The methods developed in Section 3 can be applied in both the open-channel problem and the bound-state problem. We investigate the open-channel problem, i.e., the case $E = k^2 > 0$.

In this case, in general, the potential function $V(r)$ dies away much faster than $l(l + 1)/r^2$, so the latter is the predominant term. Then equation (1) effectively reduces to $y''(r) + (k^2 - l(l + 1)/r^2)y(r) = 0$ for large r. It is well known that equation (1) has two linearly independent solutions $krj_l(kr)$ and $krn_l(kr)$, where $j_l(kr)$ and $n_l(kr)$ are the spherical Bessel and Neumann functions, respectively. Thus the asymptotic solution of (1) (i.e., for $r \to \infty$) has the form

$$\begin{aligned} y(r) &\cong Akrj_l(kr) - Bkrn_l(kr) \\ &\cong AD[\sin(kr - l\pi/2) + \tan \delta_l \cos(kr - l\pi/2)] \end{aligned} \tag{25}$$

where δ_l is the real scattering phase shift of the lth partial wave induced by the potential $V(r)$. The value of δ_l can be computed using the formula

$$\tan \delta_l = \frac{y(r_b)S(r_a) - y(r_a)S(r_b)}{y(r_a)C(r_b) - y(r_b)C(r_a)} \tag{26}$$

where r_a and r_b are two distinct points in the asymptotic region, $S(r) = krj_l(kr)$ and $C(r) = -krn_l(kr)$.

The term $l\pi/2$ in (25) is conventional. The reason for inserting it is that, with this definition, all phase shifts vanish when the potential function vanishes itself.

Based on (25) and (26), we have that the normalization factor D is given by [for details see Simos (1990)]

$$D \approx \frac{y(r_a)}{kr_a[\cos(\delta_l)\, S(r_a) + (-1)^l \sin(\delta_l)\, C(r_a)]} \tag{27}$$

In this section we present some numerical results to illustrate the performance of our methods on a problem of practical interest. We consider the

Table II. Phase Shifts Computed for $k = 10$ and $l = 0(10)50$ Using the Methods of (a) Riehl *et al.* (1974) and (b) Hepburn and Le Roy (1978) and the Present Method with Phase Lag of Order (c) 12 and (d) 14

l	Method a	Method b	Method c	Method d
0	−0.4311	−0.4310043	−0.431004370	−0.43100438189
10	0.3778	0.3779001	0.37789991	0.3779001041
20	0.4659	0.4659448	0.46594470	0.4659446969
30	0.0566	0.0566391	0.05663870	0.0566390356
40	0.0135	0.0135798	0.01357903	0.0135796944
50	0.0045	0.0044945	0.00449447	0.0044944736

numerical integration of the Schrödinger equation (1) in the well-known case where the potential $V(r)$ is the Lennard-Jones potential:

$$V(r) = 500(1/r^{12} - 1/r^{6}) \tag{28}$$

In Table II we present the calculated phase shifts of the Schrödinger equation (1) for $k = 10$ and for $l = 0(10)50$ using the present methods, the method of Riehl *et al.* (1974), and the method of Hepburn and Le Roy (1978). From the results presented it is obvious that our new methods are much more accurate than the other methods.

4.1. Error Estimation

For the integration of systems of initial-value problems, several methods have been proposed for the estimation of the local truncation error (LTE) [see, for example, Shampine *et al.* (1976) and references therein]. Here we will introduce a new error control procedure.

In this paper we base our local error estimation technique on an embedded pair of integration methods and on the fact that when the local phase-lag error is of higher order, then the approximation of the solution for the problems with a periodic solution is better.

We denote the solution obtained with higher order phase lag as y_{n+1}^{H} and the solution obtained with lower order phase lag as y_{n+1}^{L}; we have the following definition.

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

$$\text{LPLE} = |y_{n+1}^{H} - y_{n+1}^{L}| \tag{29}$$

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

We assume that the solution y_{n+1}^{H} is obtained using the family of methods with phase lag of order 14 described above and the solution y_{n+1}^{L} is obtained using the family of methods with phase lag of order 12 described above.

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

$$h_{n+1} = h_n\left(\frac{acc}{\mathrm{LPLE}}\right)^{1/q} \tag{30}$$

where q is the order of the local phase-lag error.

However, for ease of programming we have restricted all step changes to halving and doubling. Thus, based on the procedure developed in Raptis and Cash (1985) for the local phase-lag error, the step control procedure which we actually used is

$$\text{If} \quad \mathrm{LPLE} < acc, \qquad h_{n+1} = 2h_n$$

$$\text{If} \quad 100acc > \mathrm{LPLE} \geq acc, \qquad h_{n+1} = h_n \tag{31}$$

$$\text{If} \quad \mathrm{LPLE} \geq 100acc, \qquad h_{n+1} = \frac{h_n}{2} \quad \text{and repeat the step} \tag{32}$$

We note that the local phase-lag 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.

We investigate now the computational cost of the application of the new embedded method. The new embedded method is a variable-step method. So, for comparison purposes we could apply only variable-step methods, such as those developed by the Raptis and Cash (1985).

In Table III we present the phase shifts for $k = 10$ and for $acc = 10^{-6}$ using the variable-step algorithm described above and the variable-step method presented in Raptis and Cash (1985). In all cases the embedded variable-step method developed in this paper is more accurate and requires less computation time.

All computations were carried out on a PC-AT 80486 using double-precision arithmetic of 16-digit accuracy.

5. CONCLUSION

It is obvious that the new method and the new variable-step procedure are more efficient than other well-known methods in the literature.

Table III. Computed Phase Shifts and Real Time of Computation for Variable-Step Method of Raptis and Cash (1985) and for Our New Embedded Variable-Step Method

	Method of Reptis and Cash (1995)		New embedded variable-step method	
l	Phase shift	Real time of computation	Phase shift	Real time of computation
0	−0.4311	0.330	−0.43100438189	0.045
1	1.0449	0.330	1.04500892188	0.045
2	0.7158	0.330	−0.71580734152	0.045
3	0.5687	0.340	0.56880699288	0.045
4	−1.3858	0.340	−1.38576629936	0.045
5	−0.2984	0.340	−0.29834219581	0.045
6	0.6867	0.340	0.68682979399	0.045
7	1.5662	0.340	1.56630306556	0.045
8	−0.8060	0.330	−0.80593975405	0.040
9	−0.1525	0.330	−0.15240773446	0.040
10	−0.3778	0.335	0.3779001041	0.040

REFERENCES

Blatt, J. M. (1967). *Journal of Computational Physics,* **1**, 382.

Brusa, L., and Nigro, L. (1980). *International Journal for Numerical Methods in Engineering,* **15**, 685.

Chawla, M. M., and Rao, P. S. (1984). *Journal of Computational and Applied Mathematics,* **11**, 277.

Chawla, M. M., and Rao, P. S. (1986). *Journal of Computational and Applied Mathematics,* **15**, 329.

Chawla, M. M., and Rao, P. S. (1987). *Journal of Computational and Applied Mathematics,* **17**, 365.

Coleman, J. P. (1989). *IMA Journal of Numerical Analysis,* **9**, 145.

Cooley, J. W. (1961). *Mathematics of Computation,* **15**, 363.

Hepburn, J. W., and Le Roy, R. J. (1978). *Chemical Physics Letters,* **57**, 304.

Herzberg, G. (1950). *Spectra of Diatomic Molecules,* Van Nostrand, New York.

Lambert, J. D., and Watson, I. A. (1976). *Journal of the Institute of Mathematics and Its Applications,* **18**, 189.

Raptis, A. D., and Cash, J. R. (1985). *Computer Physics Communications,* **36**, 113.

Riehl, J. P., Diestler, D. J., and Wagner, A. F. (1974). *Journal of Computational Physics,* **15**, 212.

Shampine, L. F., Watts, H. A., and Davenport, S. M. (1976). *SIAM Review,* **18**, 376.

Simos, T. E. (1900). Numerical solution of ordinary differential equations with periodical solution, Doctoral dissertation, National Technical University of Athens.

Simos, T. E. (1992a). *Applied Mathematics and Computation,* **49**, 261.

Simos, T. E. (1992b). *Journal of Computational and Applied Mathematics,* **39**, 89.

Simos, T. E., and Tougelidis, G. (n.d.). *Computers and Chemistry,* **20**, 397.

Thomas, R. M. (1984). *BIT,* **24**, 225.

Van der Houwen, P. J., and Sommeijer, B. P. (1987). *SIAM Journal on Numerical Analysis,* **24**, 595.