A New Hybrid Imbedded Variable-Step Procedure for the Numerical Integration of the Schrödinger Equation

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Abstract—A new imbedded variable-step procedure is developed for the numerical integration of the radial Schrödinger equation. The new imbedded method is based on *P*-stable methods of exponential order eight, ten, 12, and 14. Numerical results indicate that the new procedure is more efficient than similar variable-step procedures. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords—Schrödinger equation, Second-order oscillatory initial-value problem, Phase-lag, Imbedded technique, Variable-step procedure.

1. INTRODUCTION

No other equation has been studied more profoundly in theoretical physics than the Schrödinger equation. From a computational point of view, this equation, in its radial form, has been the subject of extensive research activity. Close attention has also been paid to calculations of oscillatory systems in nuclear physics [1].

The radial Schrödinger equation can be expressed (see Section 3) as a member of the family of the initial-value problems of the form

$$y''(x) = F(x,y), \qquad y(x_0) = y_0, \qquad y'(x_0) = y'_0, \qquad (1.1)$$

involving ordinary differential equations of second order in which the derivative does not appear explicitly (see [2–13]). Equations having oscillatory solutions are of particular interest. Examples occur in celestial mechanics, in quantum mechanical scattering problems, in chemical physics and physical chemistry, and elsewhere.

The numerical solution of this equation is discussed by several authors (see [14,15]). We refer the interested reader to the works of Simos [16], Raptis and Cash [17], Raptis and Allison [18], and Ixaru and Berceanu [19], Ixaru, Rizae, and Vertse [20], Bludsky *et al.* [21], Gousheh [22] and Simos [23].

Until 1980, the most important property for the numerical solution of problem (1.1) was *the interval of periodicity and P-stability*. Brusa and Nigro [24] introduce another important property when solving problems of the form (1.1), *the phase-lag* of the method.

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Recently, several methods with minimal phase-lag have been proposed for the numerical integration of the initial-value problem (1.1) (see [25–36 and references therein]). More recently, Simos [37,2] has developed Numerov-type or hybrid explicit to implicit methods with minimal phase-lag and with good stability properties. All the methods described above are of order four and six.

The purpose of this paper is to extend the theory developed in [36] to hybrid methods. Based on this extension, we will develop two-step *predictor-corrector P-stable* methods of exponential order eight, ten, 12, and 14. Based on these methods, a new imbedded variable-step procedure is developed for the numerical integration of the one-dimensional Schrödinger equation.

Numerical results presented in Section 3 show that this new variable-step procedure is much more efficient than certain other variable-step procedures. We note here that these new methods are especially useful in cases where a large step-size is to be used.

2. DERIVATION OF THE METHODS

The derivation of the new methods is based on the theory fully described in [36].

For the numerical integration of the initial-value problem (1.1), consider the family of hybrid two-step methods

$$
\begin{aligned}
y_{n,m-j} &= y_n + h^2 \left(a_{m-j-1,0} f_{n+1} + a_{m-j-1,1} f_{n,m-j-1} + a_{m-j-1,0} f_{n-1} \right), \\
\bar{y}_{n+1/2} &= \frac{1}{2} \left(y_n + y_{n+1} \right) + h^2 \left[a f_{n,m-1} + \left(\frac{1}{8} - a \right) f_{n+1} \right], \\
\bar{y}_{n-1/2} &= \frac{1}{2} \left(y_n + y_{n-1} \right) + h^2 \left[a f_{n,m-1} + \left(\frac{1}{8} - a \right) f_{n-1} \right],
\end{aligned}
\tag{2.1}
$$

$$
b_0 y_{n+1} + b_1 y_n + b_0 y_{n-1} = -h^2 \left[a_0 f_{n+1} + a_1 f_n + a_0 f_{n-1} + a_2 \left(\bar{f}_{n+1/2} + \bar{f}_{n-1/2} \right) \right],
$$

where

$$
\begin{aligned}
&f_{n+1} = f \left(x_{n+1}, y_{n+1} \right), \qquad f_{n-1} = f \left(x_{n-1}, y_{n-1} \right), \qquad f_n = f \left(x_n, y_n \right), \\
&f_{n,i} = f \left(x_n, y_{n,i} \right), \qquad f_{n,0} = f \left(x_n, y_n \right) = f_n, \qquad \bar{f}_{n+1/2} = f \left(x_{n+1/2}, \bar{y}_{n+1/2} \right),
\end{aligned}
$$

$$
\bar{f}_{n-1/2} = f \left(x_{n-1/2}, \bar{y}_{n-1/2} \right), \qquad j = m-1, m-2, \ldots, 1.
$$

In this paper, we will investigate the cases $m = 3(1)6$. In the following, we give as an example of our new methods, the case $m = 3$. In this case, $j = 2, 1$,

$$
\begin{aligned}
y_{n,1} &= y_n + h^2 \left(a_{0,0} f_{n+1} + a_{0,1} f_{n,0} + a_{0,0} f_{n-1} \right), \\
y_{n,2} &= y_n + h^2 \left(a_{1,0} f_{n+1} + a_{1,1} f_{n,1} + a_{1,0} f_{n-1} \right),
\end{aligned}
$$

$$
\begin{aligned}
\bar{y}_{n+1/2} &= \frac{1}{2} \left(y_n + y_{n+1} \right) + h^2 \left[a f_{n,2} + \left(\frac{1}{8} - a \right) f_{n+1} \right], \\
\bar{y}_{n-1/2} &= \frac{1}{2} \left(y_n + y_{n-1} \right) + h^2 \left[a f_{n,2} + \left(\frac{1}{8} - a \right) f_{n-1} \right],
\end{aligned}
\tag{2.1a}
$$

$$
b_0 y_{n+1} + b_1 y_n + b_0 y_{n-1} = -h^2 \left[a_0 f_{n+1} + a_1 f_n + a_0 f_{n-1} + a_2 \left(\bar{f}_{n+1/2} + \bar{f}_{n-1/2} \right) \right].
$$

We note that for nonlinear problems, the above mentioned methods are implicit and a nonlinear equation must be solved at each step for the determination of y_{n+1}. It is obvious that, in our case, we do not have this problem, because the Schrödinger equation is a linear equation. We also note that the above methods are two-step methods. Assuming that y_0 is known from the boundary conditions, y_1 can be determined using high-order Runge-Kutta methods (see [3]).

Applying any symmetric two-step method to the scalar test equation

$$y'' = -w^2 y, \tag{2.2}$$

we obtain the difference equation

$$X_0(H)y_{n+1} + X_1(H)y_n + X_0(H)y_{n-1} = 0, \qquad H = wh, \tag{2.3}$$

where X_j, $j = 0, 1$, are polynomials in H, h is the integration step, and y_n is the numerical approximation to $y(x_n)$, $(n = 0, 1, \dots)$. The associated *stability polynomial* is given by

$$P(c, H) = X_0(H)c^2 + X_1(H)c + X_0(H). \tag{2.4}$$

DEFINITION 1. *(See [4].)* *A method to solve problem (1.1) is said to be P-stable if, for all $H \in (0, \infty)$, the roots of the stability polynomial (2.4) satisfy*

$$\begin{aligned} c_1 &= e^{i\vartheta(H)}, \\ c_2 &= e^{-i\vartheta(H)}, \end{aligned} \tag{2.5}$$

where $\vartheta(H)$ if the real function of $H = wh$.

DEFINITION 2. *(See [5].)* *The solution of the characteristic equation $P(c, H) = 0$ is said to be of exponential order p, if one of the roots of $P(c, H)$ (i.e., one of the roots (2.5)) satisfies*

$$e^H - c_1(H) = CH^{p+1} + O\left(H^{p+2}\right), \qquad \text{for } H \to 0, \tag{2.6}$$

where $C(\neq 0)$ is the error constant of $c_1(H)$.

Based on a proposition of Franco and Palacios [5], we have that, if we can write the *stability polynomial $P(c, r)$* as

$$P(c, r) = [T_m(ir)T_m(-ir)]\, c^2 - \left[T_m^2(ir) + T_m^2(-ir)\right] c + [T_m(ir)T_m(-ir)], \tag{2.7}$$

where $i = \sqrt{-1}$, and

$$T_m(r) = 1 + \frac{m}{2m}r + \frac{m(m-1)}{2m(2m-1)}\frac{r^2}{2!} + \cdots + \frac{m(m-1)\cdots 1}{2m(2m-1)\cdots(m+1)}\frac{r^m}{m!}, \tag{2.8}$$

the roots of (2.7) are given by

$$c_1(r) = c_2(r)^{-1} = \frac{T_m(ir)}{T_m(-ir)}, \tag{2.9}$$

i.e., we are dealing with the (m, m)-Padé approximation to $\exp(r)$. So, if we take $r = H$, those roots are going to be conjugate complex numbers and always lie on the unit circle, and they are the solution of order $2m$ of equations (2.7) (see (2.6) for $p = 2m$).

Applying (2.1) to the scalar test equation (2.2), we have the stability polynomial (2.4) with the following cases.

CASE $m = 3$.

$$\begin{aligned} X_0(H) &= b_0 - (2a_0 + a_2)\frac{H^2}{2} + a_2(1 - 8a)\frac{H^4}{8} - 2aa_{1,0}a_2 H^6 + 2aa_{0,0}a_{1,1}a_2 H^8, \\ X_1(H) &= b_1 - (a_1 + a_2)H^2 + 2aa_2 H^4 - 2aa_{1,1}a_2 H^6 + 2aa_{0,1}a_{1,1}a_2 H^8. \end{aligned} \tag{2.10}$$

CASE $m = 4$.

$$X_0(H) = b_0 - (2a_0 + a_2)\frac{H^2}{2} + a_2(1 - 8a)\frac{H^4}{8} - 2aa_{2,0}a_2H^6 + 2aa_{1,0}a_{2,1}a_2H^8$$
$$- 2aa_{0,0}a_{1,1}a_2a_{2,1}H^{10},$$

$$X_1(H) = b_1 - (a_1 + a_2)H^2 + 2aa_2H^4 - 2aa_{2,1}a_2H^6 + 2aa_{1,1}a_{2,1}a_2H^8$$
$$- 2aa_{0,1}a_{1,1}a_2a_{2,1}H^{10}.$$

(2.11)

CASE $m = 5$.

$$X_0(H) = b_0 - (2a_0 + a_2)\frac{H^2}{2} + a_2(1 - 8a)\frac{H^4}{8} - 2aa_{3,0}a_2H^6 + 2aa_{2,0}a_{3,1}a_2H^8$$
$$- 2aa_{1,0}a_{2,1}a_2a_{3,1}H^{10} + 2aa_{0,0}a_{1,1}a_2a_{2,1}a_{3,1}H^{12},$$

$$X_1(H) = b_1 - (a_1 + a_2)H^2 + 2aa_2H^4 - 2aa_{3,1}a_2H^6 + 2aa_{2,1}a_{3,1}a_2H^8$$
$$- 2aa_{1,1}a_{2,1}a_2a_{3,1}H^{10} + 2aa_{0,1}a_{1,1}a_2a_{2,1}a_{3,1}H^{12}.$$

(2.12)

CASE $m = 6$.

$$X_0(H) = b_0 - (2a_0 + a_2)\frac{H^2}{2} + a_2(1 - 8a)\frac{H^4}{8} - 2aa_{4,0}a_2H^6 + 2aa_{3,0}a_{4,1}a_2H^8$$
$$- 2aa_{2,0}a_{3,1}a_2a_{4,1}H^{10} + 2aa_{1,0}a_{2,1}a_2a_{3,1}a_{4,1}H^{12}$$
$$- 2aa_{0,0}a_{1,1}a_2a_{2,1}a_{3,1}a_{4,1}H^{14},$$

$$X_1(H) = b_1 - (a_1 + a_2)H^2 + 2aa_2H^4 - 2aa_{4,1}a_2H^6 + 2aa_{3,1}a_{4,1}a_2H^8$$
$$- 2aa_{2,1}a_{3,1}a_2a_{4,1}H^{10} + 2aa_{1,1}a_{2,1}a_2a_{3,1}a_{4,1}H^{12} - 2aa_{0,1}a_{1,1}a_2a_{2,1}a_{3,1}a_{4,1}H^{14}.$$

(2.13)

Based on the relations (2.7)–(2.9) and on the procedure described in [36], if we impose the conditions

$$X_0(H) = T_{m+1}(iH)T_{m+1}(-iH), \qquad X_1(H) = -\left[T_{m+1}^2(iH) + T_{m+1}^2(-iH)\right],$$

(2.14)

identifying terms in both of them, we obtain a system of $2(m + 2)$ equations with $2(m + 2)$ unknowns. Its solution determines the coefficients of a hybrid symmetric two-step P-stable method of order $2(m + 1)$.

CASE $m = 3$. In this case, from (2.14) with $m = 3$, we have a system of ten equations with ten unknowns, from which we find that

$$a_0 = \frac{5}{84}, \qquad a_1 = -\frac{31}{42}, \qquad a_2 = -\frac{4}{21}, \qquad b_0 = 1, \qquad b_1 = -2,$$

$$a = \frac{289}{2240}, \qquad a_{0,0} = -\frac{1}{1520}, \qquad a_{0,1} = \frac{1}{760}, \qquad a_{1,0} = \frac{1}{3468}, \qquad a_{1,1} = \frac{19}{1734}.$$

(2.15)

CASE $m = 4$. In the case of $m = 4$ and from (2.14), we have a system of 12 equations with 12 unknowns, from which we find that

$$a_0 = \frac{1}{12}, \qquad a_1 = -\frac{13}{18}, \qquad a_2 = -\frac{2}{9}, \qquad b_0 = 1,$$

$$b_1 = -2, \qquad a_{0,0} = \frac{1}{3480}, \qquad a_{0,1} = \frac{1}{1740}, \qquad a_{1,0} = -\frac{1}{13608},$$

(2.16)

$$a_{1,1} = \frac{29}{6804}, \qquad a_{2,0} = \frac{1}{10240}, \qquad a_{2,1} = \frac{81}{5120}, \qquad a = \frac{8}{63}.$$

CASE $m = 5$. From (2.14) with $m = 5$, we have a system of 14 equations with 14 unknowns, from which we find

$$a_0 = \frac{13}{1968}, \qquad a_1 = -\frac{47}{66}, \qquad a_2 = -\frac{8}{33}, \qquad b_0 = 1,$$

$$b_1 = -2, \qquad a = \frac{533}{4224}, \qquad a_{0,0} = -\frac{1}{6888}, \qquad a_{0,1} = \frac{1}{3444}, \qquad (2.17)$$

$$a_{1,0} = \frac{1}{40560}, \qquad a_{1,1} = \frac{41}{20280}, \qquad a_{2,0} = -\frac{1}{51168}, \qquad a_{2,1} = \frac{13}{1968},$$

$$a_{3,0} = \frac{1}{22386}, \qquad a_{3,1} = \frac{2}{105}.$$

CASE $m = 6$. In this case, from (2.14) with $m = 6$, we have a system of 16 equations with 16 unknowns, from which we find that

$$a_0 = \frac{17}{156}, \qquad a_1 = -\frac{55}{78}, \qquad a_2 = -\frac{10}{39}, \qquad b_0 = 1,$$

$$b_1 = -2, \qquad a = \frac{1439}{11440}, \qquad a_{0,0} = \frac{1}{12320}, \qquad a_{0,1} = \frac{1}{6160},$$

$$(2.18)$$

$$a_{1,0} = -\frac{1}{101124}, \qquad a_{1,1} = \frac{55}{50562}, \qquad a_{2,0} = \frac{3}{566840}, \qquad a_{2,1} = \frac{2809}{850260},$$

$$a_{3,0} = -\frac{25}{3398164}, \qquad a_{3,1} = \frac{14171}{1699082}, \qquad a_{4,0} = \frac{5}{207216}, \qquad a_{4,1} = \frac{11033}{518040}.$$

Based on (2.15)–(2.18), we have that the methods (2.1) with coefficients given by (2.15)–(2.18) are of exponential order eight, ten, 12, and 14.

We will prove now, that the methods produced by the family (2.1) for $m = 3(1)6$ are P-stable.

If we apply the methods produced by the family of methods (2.1) with $m = 3(1)6$ to the scalar test equation (2.2) with coefficients given by (2.15)–(2.18), we obtain the *stability polynomial* (2.4) with the following results.

CASE $m = 3$.

$$X_0(H) = 1 + \frac{H^2}{28} + \frac{3H^4}{3920} + \frac{H^6}{70560} + \frac{H^8}{2822400},$$

$$S_1(H) = \frac{X_1(H)}{-2} = 1 - \frac{13H^2}{28} + \frac{289H^4}{11760} - \frac{19H^6}{70560} + \frac{H^8}{2822400}. \qquad (2.19)$$

CASE $m = 4$.

$$X_0(H) = 1 + \frac{H^2}{36} + \frac{H^4}{2268} + \frac{H^6}{181440} + \frac{H^8}{15240960} + \frac{H^{10}}{914457600},$$

$$S_1(H) = \frac{X_1(H)}{-2} = 1 - \frac{17H^2}{36} + \frac{16H^4}{567} - \frac{H^6}{2240} + \frac{29H^8}{15240960} - \frac{H^{10}}{914457600}. \qquad (2.20)$$

CASE $m = 5$.

$$X_0(H) = 1 + \frac{H^2}{44} + \frac{5H^4}{17424} + \frac{H^6}{365904} + \frac{H^8}{43908480} + \frac{H^{10}}{5269017600} + \frac{H^{12}}{442597478400},$$

$$S_1(H) = \frac{X_1(H)}{-2} = 1 - \frac{21H^2}{44} + \frac{533H^4}{17424} - \frac{533H^6}{914760} + \frac{169H^8}{43908480} - \frac{41H^{10}}{5269017600}$$
$$+ \frac{H^{12}}{442597478400}.$$

CASE $m = 6$.

$$X_0(H) = 1 + \frac{H^2}{52} + \frac{3H^4}{14872} + \frac{5H^6}{3212352} + \frac{5H^8}{494702208} + \frac{H^{10}}{16490073600} + \frac{H^{12}}{2671391923200}$$
$$+ \frac{H^{14}}{299195895398400},$$

(2.22)

$$S_1(H) = \frac{X_1(H)}{-2} = 1 - \frac{25H^2}{52} + \frac{1439H^4}{44616} - \frac{1003H^6}{1460160} + \frac{14171H^8}{2473511040} - \frac{2809H^{10}}{148410662400}$$
$$+ \frac{H^{12}}{48570762240} - \frac{H^{14}}{299195895398400}.$$

Based on Definition 1, it can be proved (for a detailed proof, see [6]) that a symmetric two-step method is P-stable, if for all $H \in (0,\infty)$ $X_0(H) \pm S_1(H) \geq 0$. From (2.19)–(2.22), it is easy to see that the methods are P-stable.

In the following, we will prove that the family of methods (2.1) with $m = 3(1)6$ have phase-lag of order eight, ten, 12, and 14, respectively.

DEFINITION 3. *(See [31].) For any method corresponding to the stability polynomial (2.19)–(2.22), the quantity*

$$t(H) = H - \theta(H) = H - \cos^{-1}\left[\frac{S_1(H)}{X_0(H)}\right]$$

(2.23)

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

REMARK 1. (See [32].) If the phase-lag order is $q = 2r$, so that

$$t(H) = cH^{2r+1} + O\left(H^{2r+3}\right),$$

(2.24)

then

$$\cos(H) - \frac{S_1(H)}{X_0(H)} = \cos(H) - \cos(H - t) = cH^{2r+2} + O\left(H^{2r+4}\right).$$

(2.25)

Based on formula (2.25), we have the following results.

CASE $m = 3$.

$$\cos(H) - \frac{S_1(H)}{X_0(H)} = \frac{H^{10}}{25401600} + O\left(H^{12}\right).$$

(2.26)

CASE $m = 4$.

$$\cos(H) - \frac{S_1(H)}{X_0(H)} = \frac{H^{12}}{10059033600} + O\left(H^{14}\right).$$

(2.27)

CASE $m = 5$.

$$\cos(H) - \frac{S_1(H)}{X_0(H)} = \frac{H^{14}}{5753767219200} + O\left(H^{16}\right).$$

(2.28)

CASE $m = 6$.

$$\cos(H) - \frac{S_1(H)}{X_0(H)} = \frac{H^{16}}{4487938430976000} + O\left(H^{18}\right).$$

(2.29)

From the above, we see that the new methods are *P-stable and have phase-lag of order eight, ten, 12, and 14, i.e., much higher order than the known P-stable methods.*

3. NUMERICAL ILLUSTRATION

3.1. The Radial Schrödinger Equation

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

$$y''(x) = g(x)\, y(x), \qquad x \in [0, \infty), \tag{3.1}$$

where $g(x) = W(x) - E$, and $W(x) = (l(l+1))/x^2 + V(x)$ is an effective potential with $W(x) \to 0$ as $x \to \infty$, l is an integer, and E is a real number denoting energy.

The problem belongs to the boundary class of problems. The boundary conditions include $y(0) = 0$, while the second boundary condition for large values of x is determined by physical considerations.

In this paper, we will investigate the case for which $E = p^2 > 0$. In this case, in general, the potential function $V(x)$ dies away faster than the term $(l(l+1))/x^2$. Equation (3.1) then effectively reduces to

$$y''(x) + \left[E - \frac{l(l+1)}{x^2}\right] y(x) = 0,$$

for x greater than some value R, which depends upon the potential function $V(x)$. The above equation has linearly independent solutions $pxlj_l(px)$ and $pxn_l(px)$, where $j_l(px)$ and $n_l(px)$ are the spherical *Bessel and Neumann functions*, respectively. Thus, the solution of equation (3.1) has the asymptotic form

$$y(x) \underset{x \to \infty}{\cong} Apxj_l(px) - Bpxn_l(px)$$

$$\underset{x \to \infty}{\cong} C\left[\sin\left(px - \frac{l\pi}{2}\right) + \tan\delta_l \cos\left(px - \frac{l\pi}{2}\right)\right],$$

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

$$\tan\delta_l = \frac{y(x_2)G(x_l) - y(x_1)G(x_2)}{y(x_1)C(x_2) - y(x_2)C(x_1)}, \tag{3.2}$$

for x_l and x_2 distinct points on the asymptotic region with $G(x) = pxj_l(px)$ and $C(x) = pxn_l(px)$. The calculation of the phase shifts is based on the procedure fully described in [36].

We illustrate the new methods derived in Section 2 by applying them to the solution of (3.1) where $V(x)$ is the Lennard-Jones potential, which has been widely discussed in the literature. For this problem, the potential $V(x)$ is given by

$$V(x) = m\left(\frac{1}{x^{12}} - \frac{1}{x^6}\right), \qquad m = 500. \tag{3.3}$$

The problem we consider is the computation of the relevant phase shifts correct to six decimal places (analogous conclusions follow from the calculation of phase shifts correct to four and three decimal places). We will consider four separate approaches,

(i) based on the combination of the "classical" method described in [7] and the exponential fitting method described in [17],

(ii) based on the combination of the "classical" method described in [7] and the Bessel fitting method described in [17],

(iii) based on the two methods described in [36], and

(iv) based on the four methods described in Section 2.

We note that procedures (i) and (ii) consist of methods in which the coefficients must be calculated for each step-size change (procedure (i)), or during each step (procedure (ii)). Procedures (iii) and (iv) consist of methods with constant coefficients.

We will describe the numerical integration procedure and the associate local error estimation for the new procedure called an *"imbedded"* technique.

Procedures (i) and (ii) are exactly described in [17] and are used without modification. Procedure (iii) is exactly described in [36] and is used, also without modification.

Denoting the solution obtained using a lower exponential order formula as y^N and the solution obtained using a higher exponential order formula as y^H and under the assumption that h is sufficiently small, so that the local error on y_{n+1}^H can be neglected compared with that in y_{n+1}^N an estimate of the local truncation error in y_{n+1}^N is

$$\text{LTE} = \left| y_{n+1}^H - y_{n+1}^N \right|. \tag{3.4}$$

So, the step-size control procedure is the following:

(1) if LTE $\leq$ TOL, $h_{n+1} = 2h_n$,

(2) if 100TOL $>$ LTE $>$ TOL, $h_{n+1} = h_n$, and

(3) if LTE $\geq$ 100TOL, $h_{n+1} = h_n/2$.

Based on the above step-size control procedure, we will describe our new variable-step method, called an *"imbedded variable-step method"*.
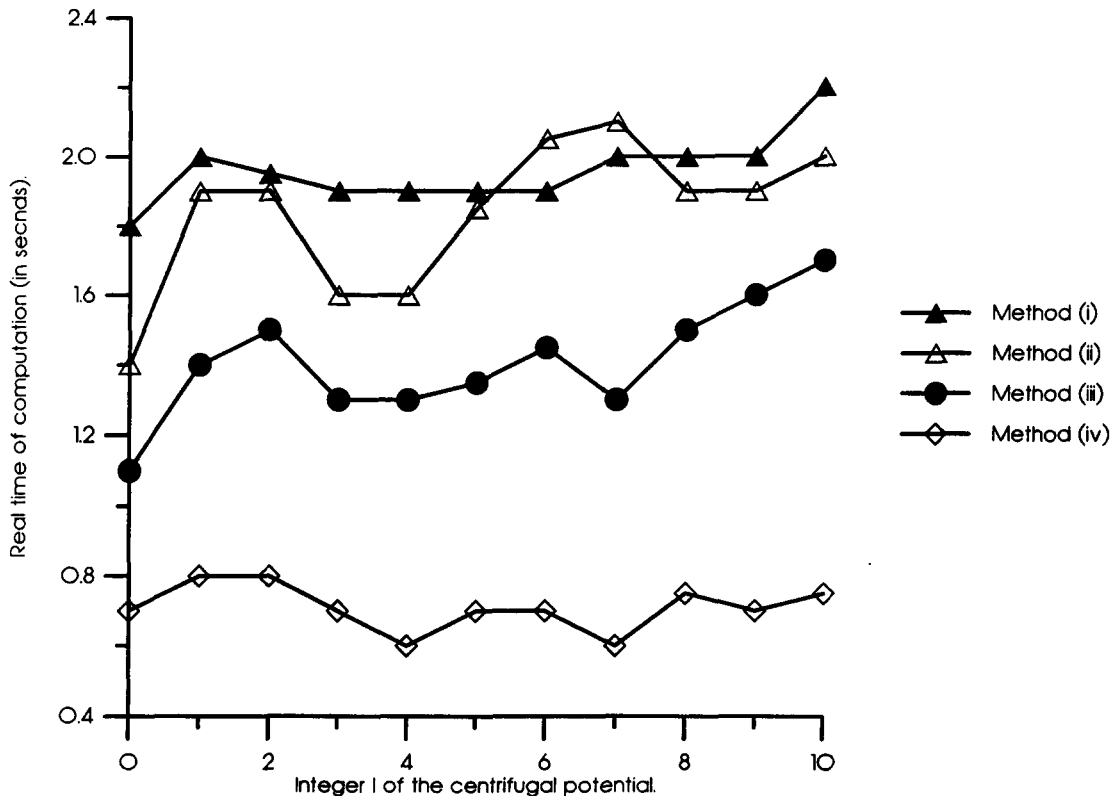

Figure 1. Real time of computation for the calculation of each of the phase shifts of the Schrödinger equation (3.1). Accuracy in phase shifts six decimal places. $h_0 = 0.04 = $ initial stepsize. $E = 1.0$.

At every step, we start to estimate (3.4) using as y^H the tenth-order method and as y^N the eighth-order method. If LTE $\leq$ TOL, then the stepsize is doubled, else we continue to estimate (3.4) using, now, as y^H the twelfth-order method and as y^N the tenth-order method. If again,
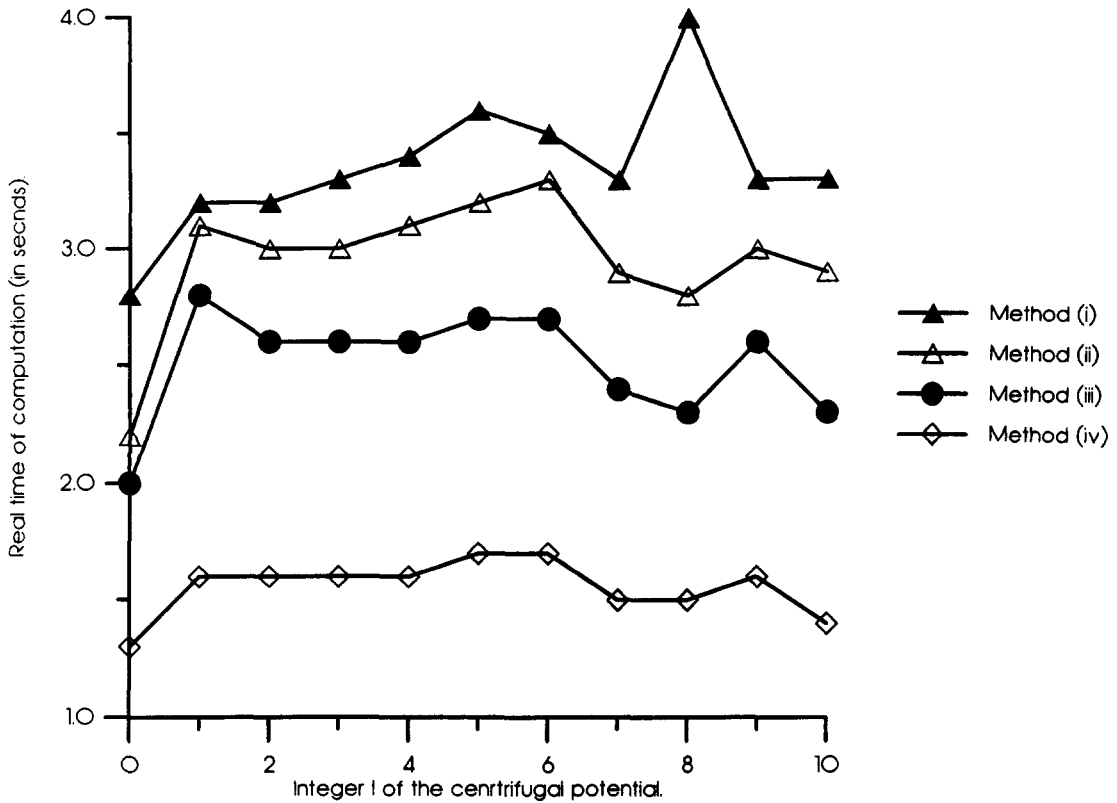
Figure 2. Real time of computation for the calculation of each of the phase shifts of the Schrödinger equation (3.1). Accuracy in phase shifts six decimal places. $h_0 = 0.01 =$ initial stepsize. $E = 25.0$.

LTE $\leq$ TOL, then the stepsize is doubled, else we continue to estimate (3.4) using now, as y^H the fourteenth-order method and as y^N the twelfth-order method. If LTE $\leq$ TOL, then the stepsize is doubled, else, we check conditions (2) and (3) of the above mentioned step-size control procedure. If the stepsize is to be doubled, then the information required to continue the calculation is computed using high-order interpolation formulae (see, for details, [3, pp. 397–400]). We call this procedure an "*imbedded technique*".

In Figures 1–3, we present the real time of computation needed for the calculation of each of the phase shifts correct to six decimal places of the Schrödinger equation (3.1) for $l = 0(1)10$ and for the potential given by (3.3).

3.2. Close-Coupling Differential Equations

There are many problems in theoretical physics, atomic physics, physical chemistry, and chemical physics which can be transformed to the solution of close coupling differential equations, which may be written in the form

$$\left[\frac{d^2}{dx^2} + k_i^2 - \frac{l(l+1)}{x^2} - V_{ii} \right] y_{ij} = \sum V_{im} y_{mj}, \tag{3.5}$$

for $1 \leq i \leq N$ and $m \neq i$ (see, for details, [8]).

We have investigated the case in which all channels are open. So, we have the following boundary boundary conditions (for details, see [8]):
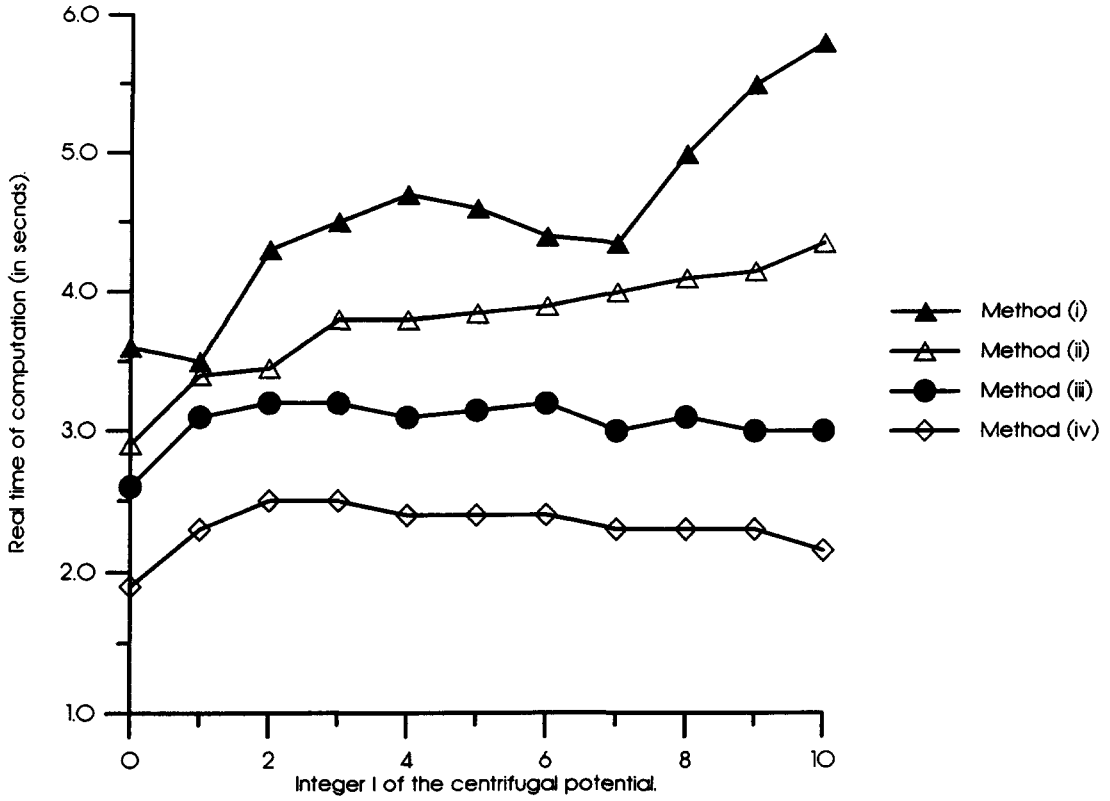
Figure 3. Real time of computation for the calculation of each of the phase shifts of the Schrödinger equation (3.1). Accuracy in phase shifts six decimal places. $h_0 = 0.01 =$ initial stepsize. $E = 100.0$.

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

$$y_{ij} \approx k_i x j_{l_i}\,(k_i x)\,\delta_{ij} + \left(\frac{k_i}{k_j}\right)^{1/2} X_{ij} k_i x n_{l_i}\,(k_i x),$$

$$(3.6)$$

where $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions, respectively.

Based on the analysis developed in [8] and defining a matrix X' and diagonal matrices M and N by

$$X'_{ij} = \left(\frac{k_i}{k_j}\right)^{1/2} X_{ij},$$

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

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

the asymptotic condition of (3.6) may be written as

$$y \approx M + N\dot{X}'.$$

The most well-known method for numerical solution of the close-coupling differential equations arising from Schrödinger equation is the Iterative Numerov method of Allison [8].

A real problem in theoretical physics, atomic physics, and molecular physics, which can be transformed to close-coupling differential equations is the rotational excitation of a diatomic molecule by neutral particle impact. Denoting, as in [8], 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

$$\left[\frac{d^2}{dx^2} + k_{j'j}^2 - \frac{l'(l'+1)}{x^2} \right] y_{j'l'}^{Jjl}(x) = \frac{2\mu}{\hbar^2} \sum_{j''} \sum_{l''} \langle j'l'; J|V|j''l''; J\rangle \, y_{j''l''}^{Jjl}(x), \qquad (3.7)$$

where

$$k_{j'j} = \frac{2\mu}{\hbar^2} \left[E + \frac{\hbar^2}{2I} \left\{ j(j+1) - j'(j'+1) \right\} \right], \qquad (3.8)$$

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 [8], the potential V may be expanded as

$$V\left(x, k_{j'j} k_{jj} \right) - V_0(x) P_0 \left(k_{j'j} k_{jj} \right) + V_2(x) P_2 \left(k_{j'j} k_{jj} \right),$$

and the coupling matrix element can then be written

$$\langle j'l'; \ |V|j''l''; J\rangle = \delta_{j'j''} \delta_{l'l''} V_0(x) + f_2 \left(j'l', j''l''; J \right) V_2(x), \qquad (3.9)$$

where the f_2 coefficients can be evaluated from formulas given by Berstein *et al.* [9]. The boundary conditions are

$$y_{j'l'}^{Jjl} = 0, \qquad \text{at } x = 0,$$

$$y_{j'l'}^{Jjl} \approx \delta_{jj'} \delta_{ll'} \exp\left[-i \left(k_{jj} x - \frac{l\pi}{2} \right) \right] + \left(\frac{k_i}{k_j} \right)^{1/2} S^J \left(jl; \ j'l' \right) \exp\left[i \left(k_{j'j} x - \frac{l'\pi}{2} \right) \right], \qquad (3.10)$$

where the scattering S matrix is related to the X matrix of (3.6) by the relation

$$S = (I + iX)(I - iX)^{-1}. \qquad (3.11)$$

To calculate the cross sections for rotational excitation of molecular hydrogen by impact of various heavy particles, a computer program has been written. In this program, the numerical method for step-by-step integration from the initial value to matching points is included. This program is based on an analogous program which has been written for the numerical applications of [8].

For numerical purposes, we choose the S matrix, which is calculated using the following parameters (see [8]):

$$\frac{2\mu}{\hbar^2} = 1000, \qquad \frac{\mu}{I} = 2.351, \qquad E = 1.1,$$

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

As is described in [8], 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 4, 9, and 16 differential equations, respectively.

Following the procedure obtained by Berstein [10] and Allison [8], the potential is considered infinite for values of x less than some x_0. The wavefunctions are then vanished in this region and effectively the first boundary condition (3.10) may be written as

$$y_{j'l'}^{Jjl} (x_0) = 0. \qquad (3.12)$$

Table 1. Real time of computation (in seconds) to calculate $|S|^2$ for the variable-step methods (1)–(3). Accuracy = TOL = 10^{-6}, h_{max} is the maximum stepsize.

Method	N	h_{max}	Real Time of Computation (in seconds)
Iterative Numerov [8]	4	0.014	3.25
	9	0.014	23.51
	16	0.014	99.15
Method of Simos [36]	4	0.112	1.43
	9	0.112	8.22
	16	0.112	40.13
Present Method	4	0.448	0.53
	9	0.448	2.31
	16	0.448	8.47

For the numerical solution of this problem, we have used

(1) the well-known Iterative Numerov method of Allison [8],

(2) the variable-step method of Simos [36], and

(3) the new imbedded 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 (given in equation (3.11)) for sets of 4, 9, and 16 close-coupling differential equations. We note here that the $|S|^2$ is very critical for the calculation of the total cross-sections for the excitation of the diatomic molecule (see [11, Chapter 6]).

From the results presented, it can be seen that the new imbedded method is much more efficient than other variable-step procedures.

All the computations were carried out in an IBM PC Pentium with double precision arithmetic in 16 digits accuracy.

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