A new explicit Bessel and Neumann fitted eighth algebraic order method for the numerical solution of the Schrödinger equation

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An explicit eighth algebraic order Bessel and Neumann fitted method is developed in this paper for the numerical solution of the Schrödinger equation. The new method has free parameters which are defined in order the method is fitted to spherical Bessel and Neumann functions. A variable-step procedure is obtained based on the newly developed method and the method of Simos [17]. Numerical illustrations based on the numerical solution of the radial Schrödinger equation and of coupled differential equations arising from the Schrödinger equation indicate that this new approach is more efficient than other well known methods.

KEY WORDS: Schrödinger equation, coupled differential equations, Bessel and Neumann fitting, finite difference, multistep methods, scattering problems

1.   Introduction

Last years a significant activity has been developed on the construction of numerical methods for solving the Schrödinger equation. The result of this activity is a large number of methods (see [1–21]).

The radial Schrödinger equation is a boundary value problem which can be written in the form

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

with one boundary condition given by

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

and the other boundary condition, for large values of r, determined by physical considerations. Equations of this type occur very frequently in quantum physics, in nuclear physics, in theoretical physics and chemistry, in quantum chemistry and elsewhere (see [12,22]) and there is a real need to be able to solve them both efficiently and reliably by

343

numerical methods. In (1) the function $W(r) = l(l+1)/r^2 + V(r)$ denotes *the effective potential*, which satisfies $W(r) \to 0$ as $r \to \infty$, k is a constant which may be complex but in this paper we will work exclusively with the case where k is a real number, l is a given integer and V is a given function which denotes the potential.

It is known that the form of the second boundary condition depends crucially on the sign of energy E. In this paper we will investigate the case $E = k^2 > 0$. In this case, in general, the potential function $V(r)$ dies away faster than the term of centrifugal potential $l(l+1)/r^2$. Equation (1) then effectively reduces to

$$y''(r) + \left(E - \frac{l(l+1)}{r^2} \right) y(r) = 0 \tag{3}$$

for large r. The above equation has linearly independent solutions $kr j_l(kr)$ and $kr n_l(kr)$, where $j_l(kr)$ and $n_l(kr)$ are the spherical Bessel and Neumann functions, respectively. Thus, the solution of equation (1) has the asymptotic form:

$$y(r) \underset{r \to \infty}{\cong} A kr j_l(kr) - B kr n_l(kr)$$

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

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

$$\tan \delta_l = \frac{y(r_2) S(r_1) - y(r_1) S(r_2)}{y(r_1) C(r_2) - y(r_2) C(r_1)} \tag{4}$$

for r_1 and r_2 distinct points on the asymptotic region with $S(r) = kr j_l(kr)$ and $C(r) = -kr n_l(kr)$.

One of the most well-known methods for solving the scattering problem of the Schrödinger equation (see [12]) is the iterative Numerov's method of Allison [1].

An alternative approach in production of efficient methods is introduced by Raptis and Cash [8]. In [8] they have constructed a second algebraic order Bessel and Neumann fitted methods which are more efficient than the Numerov method or the iterative Numerov method of Allison [1]. More recently Simos and Raptis [16] have obtained a fourth algebraic order Bessel and Neumann fitted methods. Simos and Williams [13] have constructed a fourth and a fifth algebraic order Bessel and Neumann fitted methods. Finally, Simos [17] has developed an explicit sixth algebraic order Bessel and Neumann fitted method.

The purpose of the present paper is the construction of an explicit eighth algebraic order Bessel and Neumann fitted method. In section 2 the construction of the new explicit eighth algebraic order Bessel and Neumann fitted method is presented. Based on the new method and on the explicit sixth algebraic order Bessel and Neumann fitted method developed by Simos [17] a variable-step method is introduced in section 3. An application of the variable-step method to the radial Schrödinger equation and to the coupled differential equations arising from the Schrödinger equation is presented in section 4. Conclusions are presented in section 5.

2. A new explicit eighth algebraic order Bessel and Neumann fitted method

Consider, now, the two parameter family of two-step eighth order methods $M_8(w_i, \ i = 0, 1)$

$$\overline{y}_{n+1} = 2y_n - y_{n-1} + h^2 y_n'',$$

$$\overline{\overline{y}}_{n+1} = 2y_n - y_{n-1} + \frac{h^2}{12}\left(\overline{y}_{n+1}'' + 10y_{n+1}'' + y_{n-1}''\right),$$

$$\overline{y}_{n+1/2} = \frac{1}{64}\left(19\overline{\overline{y}}_{n+1} + 58y_n - 13y_{n-1}\right)$$
$$+ \frac{h^2}{768}\left(-25\overline{y}_{n+1}'' + 62y_n'' + 23y_{n-1}''\right),$$

$$\overline{y}_{n-1/2} = \frac{1}{64}\left(-13\overline{\overline{y}}_{n+1} + 58y_n + 19y_{n-1}\right)$$
$$+ \frac{h^2}{768}\left(23\overline{y}_{n+1}'' + 62y_n'' - 25y_{n-1}''\right),$$

$$\overline{y}_n = y_n - w_0 h^2\left[\overline{y}_{n+1}'' - 2y_n'' + y_{n-1}'' - 4\left(\overline{y}_{n+1/2}'' - 2y_n'' + \overline{y}_{n-1/2}''\right)\right],$$

$$\tilde{y}_{n+1} = 2y_n - y_{n-1} + \frac{h^2}{60}\left[\overline{y}_{n+1}'' + 26y_n'' + y_{n-1}'' + 16\left(\overline{y}_{n+1/2}'' + \overline{y}_{n-1/2}''\right)\right],$$

$$\overline{\overline{y}}_{n+1/2} = \frac{1}{64}\left(19\tilde{y}_{n+1} + 58y_n - 13y_{n-1}\right)$$
$$+ \frac{h^2}{768}\left(-25\overline{\overline{y}}_{n+1}'' + 62y_n'' + 23y_{n-1}''\right),$$

$$\overline{\overline{y}}_{n-1/2} = \frac{1}{64}\left(-13\tilde{y}_{n+1} + 58y_n + 19y_{n-1}\right)$$
$$+ \frac{h^2}{768}\left(23\overline{\overline{y}}_{n+1}'' + 62y_n'' - 25y_{n-1}''\right),$$

$$\overline{y}_{n+1/4} = \frac{1}{2048}\left(535\tilde{y}_{n+1} + 1490y_n + 23y_{n-1}\right)$$
$$+ \frac{h^2}{24576}\left(-101\overline{\overline{y}}_{n+1}'' - 722y_n'' - 13y_{n-1}'' - 1744\overline{\overline{y}}_{n+1/2}''\right),$$

$$\overline{y}_{n-1/4} = \frac{1}{2048}\left(23\tilde{y}_{n+1} + 1490y_n + 535y_{n-1}\right)$$
$$+ \frac{h^2}{24576}\left(-13\overline{\overline{y}}_{n+1}'' - 722y_n'' - 101y_{n-1}'' - 1744\overline{\overline{y}}_{n-1/2}''\right),$$

$$\overline{\overline{y}}_n = y_n - w_1 h^2\left[\tilde{y}_{n+1}'' - 90\overline{y}_n'' + y_{n-1}''\right.$$
$$\left. - 20\left(\overline{\overline{y}}_{n+1/2}'' + \overline{\overline{y}}_{n-1/2}''\right) + 64\left(\overline{y}_{n+1/4}'' + \overline{y}_{n-1/4}''\right)\right],$$

$$y_{n+1} - 2y_n + y_{n-1} = \frac{h^2}{3780}\left[47\left(\tilde{y}_{n+1}'' + y_{n-1}''\right) + 3078\overline{\overline{y}}_n''\right.$$
$$\left. + 1328\left(\overline{y}_{n+1/2}'' + \overline{y}_{n-1/2}''\right) - 1024\left(\overline{y}_{n+1/4}'' + \overline{y}_{n-1/4}''\right)\right],$$

$$(5)$$

where $y_p'' = f(r_p, y_p)$, $p = n-1(1)n+1$, $\overline{y}_{n+1} = f(r_{n+1}, \overline{y}_{n+1})$, $\overline{\overline{y}}_{n+1} = f(r_{n+1}, \overline{\overline{y}}_{n+1})$, $\tilde{y}_{n+1} = f(r_{n+1}, \tilde{y}_{n+1})$, $\overline{y}_q'' = f(r_q, \overline{y}_q)$, $q = n$, $\overline{\overline{y}}_q'' = f(r_q, \overline{\overline{y}}_q)$, $q = n$, $\overline{y}_{n\pm1/2}'' = f(r_{n\pm1/2}, \overline{y}_{n\pm1/2})$, $\overline{\overline{y}}_{n\pm1/2}'' = f(r_{n\pm1/2}, \overline{\overline{y}}_{n\pm1/2})$, $\overline{y}_{n\pm1/4}'' = f(r_{n\pm1/4}, \overline{y}_{n\pm1/4})$.

The corresponding local truncation error is given by

$$LTE(h) = h^{10}\left(-\frac{57}{35840}w_1 y_n^{(8)} + \frac{513}{112}w_1 w_0 y_n^{(6)} + \frac{31}{8164800}y_n^{(4)}\right.$$

$$\left. + \frac{31}{72576000}y_n^{(6)} + \frac{629}{4877107200}y_n^{(8)} - \frac{31}{232243200}y_n^{(10)}\right). \qquad (6)$$

Demanding now that the family of methods $M_8(w_i,\ i = 0, 1)$ integrate exactly the functions $kr j_l(kr)$ and $kr n_l(kr)$, where $j_l(kr)$ and $n_l(kr)$ are the spherical Bessel and Neumann functions respectively, we have the equations

$$\overline{J}_{n+1} = 2J_n - J_{n-1} + h^2 F_n J_n,$$

$$\overline{\overline{J}}_{n+1} = 2J_n - J_{n-1} + \frac{h^2}{12}\left(F_{n+1}\overline{J}_{n+1} + 10F_{n+1}J_{n+1} + F_{n-1}J_{n-1}\right),$$

$$\overline{J}_{n+1/2} = \frac{1}{64}\left(19\overline{\overline{J}}_{n+1} + 58J_n - 13J_{n-1}\right)$$

$$+ \frac{h^2}{768}\left(-25F_{n+1}\overline{J}_{n+1} + 62F_n J_n + 23F_{n-1}J_{n-1}\right),$$

$$\overline{J}_{n-1/2} = \frac{1}{64}\left(-13\overline{\overline{J}}_{n+1} + 58J_n + 19J_{n-1}\right)$$

$$+ \frac{h^2}{768}\left(23F_{n+1}\overline{J}_{n+1} + 62F_n J_n - 25F_{n-1}J_{n-1}\right),$$

$$\overline{J}_n = J_n - w_0 h^2\left[F_{n+1}\overline{\overline{J}}_{n+1} - 2F_n J_n + F_{n-1}J_{n-1}\right.$$

$$\left. - 4\left(F_{n+1/2}\overline{J}_{n+1/2} - 2F_n J_n + F_{n-1/2}\overline{J}_{n-1/2}\right)\right], \qquad (7a)$$

$$\tilde{J}_{n+1} = 2J_n - J_{n-1} + \frac{h^2}{60}\left[F_{n+1}\overline{\overline{J}}_{n+1} + 26F_n J_n + F_{n-1}J_{n-1}\right.$$

$$\left. + 16\left(F_{n+1/2}\overline{J}_{n+1/2} + F_{n-1/2}\overline{J}_{n-1/2}\right)\right],$$

$$\overline{\overline{J}}_{n+1/2} = \frac{1}{64}\left(19\tilde{J}_{n+1} + 58J_n - 13J_{n-1}\right)$$

$$+ \frac{h^2}{768}\left(-25F_{n+1}\overline{\overline{J}}_{n+1} + 62F_n J_n + 23F_{n-1}J_{n-1}\right),$$

$$\overline{\overline{J}}_{n-1/2} = \frac{1}{64}\left(-13\tilde{J}_{n+1} + 58J_n + 19J_{n-1}\right)$$

$$+ \frac{h^2}{768}\left(23F_{n+1}\overline{\overline{J}}_{n+1} + 62F_n J_n - 25F_{n-1}J_{n-1}\right),$$

$$\overline{J}_{n+1/4} = \frac{1}{2048}\big(535\tilde{J}_{n+1} + 1490J_n + 23J_{n-1}\big)$$
$$+ \frac{h^2}{24576}\big(-101F_{n+1}\overline{\overline{J}}_{n+1} - 722F_nJ_n - 13F_{n-1}J_{n-1}$$
$$- 1744F_{n+1/2}\overline{\overline{J}}_{n+1/2}\big),$$

$$\overline{J}_{n-1/4} = \frac{1}{2048}\big(23\tilde{J}_{n+1} + 1490J_n + 535J_{n-1}\big)$$
$$+ \frac{h^2}{24576}\big(-13F_{n+1}\overline{\overline{J}}_{n+1} - 722F_nJ_n - 101F_{n-1}J_{n-1}$$
$$- 1744F_{n-1/2}\overline{\overline{J}}_{n-1/2}\big),$$

$$\overline{\overline{J}}_n = J_n - w_1h^2\big[F_{n+1}\tilde{J}_{n+1} - 90F_n\overline{J}_n + F_{n-1}J_{n-1}$$
$$- 20\big(F_{n+1/2}\overline{\overline{J}}_{n+1/2} + F_{n-1/2}\overline{\overline{J}}_{n-1/2}\big)$$
$$+ 64\big(F_{n+1/4}\overline{J}_{n+1/4} + F_{n-1/4}\overline{J}_{n-1/4}\big)\big], \tag{7b}$$

$$J_{n+1} - 2J_n + J_{n-1} = \frac{h^2}{3780}\big[47\big(F_{n+1}\tilde{J}_{n+1} + F_{n-1}J_{n-1}\big) + 3078F_n\overline{\overline{J}}_n$$
$$+ 1328\big(F_{n+1/2}\overline{\overline{J}}_{n+1/2} + F_{n-1/2}\overline{\overline{J}}_{n-1/2}\big)$$
$$- 1024\big(F_{n+1/4}\overline{J}_{n+1/4} + F_{n-1/4}\overline{J}_{n-1/4}\big)\big],$$

and

$$\overline{Y}_{n+1} = 2Y_n - Y_{n-1} + h^2F_nY_n,$$
$$\overline{\overline{Y}}_{n+1} = 2Y_n - Y_{n-1} + \frac{h^2}{12}\big(F_{n+1}\overline{Y}_{n+1} + 10F_{n+1}Y_{n+1} + F_{n-1}Y_{n-1}\big),$$
$$\overline{Y}_{n+1/2} = \frac{1}{64}\big(19\overline{\overline{Y}}_{n+1} + 58Y_n - 13Y_{n-1}\big)$$
$$+ \frac{h^2}{768}\big(-25F_{n+1}\overline{Y}_{n+1} + 62F_nY_n + 23F_{n-1}Y_{n-1}\big),$$
$$\overline{Y}_{n-1/2} = \frac{1}{64}\big(-13\overline{\overline{Y}}_{n+1} + 58Y_n + 19Y_{n-1}\big)$$
$$+ \frac{h^2}{768}\big(23F_{n+1}\overline{Y}_{n+1} + 62F_nY_n - 25F_{n-1}Y_{n-1}\big), \tag{8a}$$
$$\overline{Y}_n = Y_n - w_0h^2\big[F_{n+1}\overline{\overline{Y}}_{n+1} - 2F_nY_n + F_{n-1}Y_{n-1}$$
$$- 4\big(F_{n+1/2}\overline{Y}_{n+1/2} - 2F_nY_n + F_{n-1/2}\overline{Y}_{n-1/2}\big)\big],$$
$$\tilde{Y}_{n+1} = 2Y_n - Y_{n-1} + \frac{h^2}{60}\big[F_{n+1}\overline{\overline{Y}}_{n+1} + 26F_nY_n + F_{n-1}Y_{n-1}$$
$$+ 16\big(F_{n+1/2}\overline{Y}_{n+1/2} + F_{n-1/2}\overline{Y}_{n-1/2}\big)\big],$$

$$\overline{\overline{Y}}_{n+1/2} = \frac{1}{64}\left(19\tilde{Y}_{n+1} + 58Y_n - 13Y_{n-1}\right)$$

$$+ \frac{h^2}{768}\left(-25F_{n+1}\overline{\overline{Y}}_{n+1} + 62F_nY_n + 23F_{n-1}Y_{n-1}\right),$$

$$\overline{\overline{Y}}_{n-1/2} = \frac{1}{64}\left(-13\tilde{Y}_{n+1} + 58Y_n + 19Y_{n-1}\right)$$

$$+ \frac{h^2}{768}\left(23F_{n+1}\overline{\overline{Y}}_{n+1} + 62F_nY_n - 25F_{n-1}Y_{n-1}\right),$$

$$\overline{Y}_{n+1/4} = \frac{1}{2048}\left(535\tilde{Y}_{n+1} + 1490Y_n + 23Y_{n-1}\right)$$

$$+ \frac{h^2}{24576}\left(-101F_{n+1}\overline{\overline{Y}}_{n+1} - 722F_nY_n - 13F_{n-1}Y_{n-1}\right.$$

$$\left. - 1744F_{n+1/2}\overline{\overline{Y}}_{n+1/2}\right),$$

$$\overline{Y}_{n-1/4} = \frac{1}{2048}\left(23\tilde{Y}_{n+1} + 1490Y_n + 535Y_{n-1}\right)$$

$$\text{(8b)}$$

$$+ \frac{h^2}{24576}\left(-13F_{n+1}\overline{\overline{Y}}_{n+1} - 722F_nY_n - 101F_{n-1}Y_{n-1}\right.$$

$$\left. - 1744F_{n-1/2}\overline{\overline{Y}}_{n-1/2}\right),$$

$$\overline{\overline{Y}}_n = Y_n - w_1h^2\big[F_{n+1}\tilde{Y}_{n+1} - 90F_n\overline{Y}_n + F_{n-1}Y_{n-1}$$

$$- 20\big(F_{n+1/2}\overline{\overline{Y}}_{n+1/2} + F_{n-1/2}\overline{\overline{Y}}_{n-1/2}\big)$$

$$+ 64\big(F_{n+1/4}\overline{Y}_{n+1/4} + F_{n-1/4}\overline{Y}_{n-1/4}\big)\big],$$

$$Y_{n+1} - 2Y_n + Y_{n-1} = \frac{h^2}{3780}\big[47\big(F_{n+1}\tilde{Y}_{n+1} + F_{n-1}Y_{n-1}\big) + 3078F_n\overline{\overline{Y}}_n$$

$$+ 1328\big(F_{n+1/2}\overline{\overline{Y}}_{n+1/2} + F_{n-1/2}\overline{\overline{Y}}_{n-1/2}\big)$$

$$- 1024\big(F_{n+1/4}\overline{Y}_{n+1/4} + F_{n-1/4}\overline{Y}_{n-1/4}\big)\big],$$

where

$$F_q = \left[\frac{l(l+1)}{r_q} - k^2\right]h^2, \qquad J_q = kr_q\,j_l(kr_q), \qquad Y_q = kr_q\,y_l(kr_q),$$

$$q = n - 1,\ n - \tfrac{1}{2}\left(\tfrac{1}{4}\right)n + \tfrac{1}{2},\ n + 1.$$

We note that in figure 1 we present a Maple program in order one to construct the above system of equations.

Solving the above system of equations we obtain the values of the parameters w_i, $i = 0, 1$.

```
> jpnp1:=2*J[n]-J[n-1]+F[n]*J[n];
> jppnp1:=2*J[n]-J[n-1]+1/12*(F[n+1]*jpnp1+10*F[n]*J[n]+F[n-1]*J[n-1]);
> jpnp12:=1/64*(19*jppnp1+58*J[n]-13*J[n-1])+1/768*(-25*F[n+1]*jpnp1
+58*F[n]*J[n]+19*F[n-1]*J[n-1]);
> jpnm12:=1/64*(-13*jppnp1+58*J[n]+19*J[n-1]) +1/768*(23*F[n+1]*jpnp1
+62*F[n]*J[n]-25*F[n-1]*J[n-1]);
> jpn:=J[n]-w[0]*(F[n+1]*jppnp1-2*F[n]*J[n]+F[n-1]*J[n-1]-4*(F[n+1/2]*jpnp12-
2*F[n]*J[n]+F[n-1/2]*jpnm12));
> jpppnp1:=2*J[n]-J[n-1]+1/60*(F[n+1]*jppnp1+26*F[n]*J[n]+F[n-1]*J[n-1] +16*
(F[n+1/2]*jpnp12+F[n-1/2]*jpnm12));
> jppnp12:=1/64*(19*jpppnp1+58*J[n]-13*J[n-1])+1/768*(-25*F[n+1]*jppnp1
+58*F[n]*J[n]+19*F[n-1]*J[n-1]);
> jppnm12:=1/64*(-13*jpppnp1+58*J[n]+19*J[n-1])+1/768*(23*F[n+1]*jppnp1
+62*F[n]*J[n]-25*F[n-1]*J[n-1]);
> jpnp14:=1/2048*(535*jpppnp1+1490*J[n]+23*J[n-1])+1/24576*(-101*F[n+1]
*jppnp1-722*F[n]*J[n]-13*F[n-1]*J[n-1]-1744*F[n+1/2]*jpnp12);
> jpnm14:=1/2048*(23*jpppnp1+1490*J[n]+535*J[n-1])+1/24576*(-13
*F[n+1]*jppnp1-722*F[n]*J[n]-101*F[n-1]*J[n-1]-1744*F[n-1/2]*jpnm12);
> jppn:=J[n]-w[1]*(F[n+1]*jpppnp1-90*F[n]*jpn+F[n-1]*J[n-1]-20*(F[n+1/2]
*jppnp12+F[n-1/2]*jppnm12)+64*(F[n+1/4]*jpnp14+F[n-1/4]*jpnm14));
eq1:=simplify(J[n+1]-2*J[n]+J[n-1]-1/3780*(47*(F[n+1]*jpppnp1+F[n-1]
*J[n-1])+1328*(F[n+1/2]*jppnp12+F[n-1/2]*jppnm12)-1024*(F[n+1/4]*jpnp14+F[n-
1/4]*jpnm14)+3078*F[n]*jppn))=0;
>
> ypnp1:=2*Y[n]-Y[n-1]+F[n]*Y[n];
> yppnp1:=2*Y[n]-Y[n-1]+1/12*(F[n+1]*ypnp1+10*F[n]*Y[n]+F[n-1]*Y[n-1]);
> ypnp12:=1/64*(19*yppnp1+58*Y[n]-13*Y[n-1])+1/768*(-25*F[n+1]*ypnp1
+58*F[n]*Y[n]+19*F[n-1]*Y[n-1]);
> ypnm12:=1/64*(-13*yppnp1+58*Y[n]+19*Y[n-1])+1/768*(23*F[n+1]*ypnp1
+62*F[n]*Y[n]-25*F[n-1]*Y[n-1]);
> ypn:=Y[n]-w[0]*(F[n+1]*yppnp1-2*F[n]*Y[n]+F[n-1]*Y[n-1]-4*(F[n+1/2]
*ypnp12-2*F[n]*Y[n]+F[n-1/2]*ypnm12));
> ypppnp1:=2*Y[n]-Y[n-1]+1/60*(F[n+1]*yppnp1+26*F[n]*Y[n]+F[n-1]*Y[n-1]
+16*(F[n+1/2]*ypnp12+F[n-1/2]*ypnm12));
> yppnp12:=1/64*(19*ypppnp1+58*Y[n]-13*Y[n-1])+1/768*(-25*F[n+1]*yppnp1
+58*F[n]*Y[n]+19*F[n-1]*Y[n-1]);
> yppnm12:=1/64*(-13*ypppnp1+58*Y[n]+19*Y[n-1])+1/768*(23*F[n+1]*yppnp1
+62*F[n]*Y[n]-25*F[n-1]*Y[n-1]),
> ypnp14:=1/2048*(535*ypppnp1+1490*Y[n]+23*Y[n-1])+1/24576*(-101*F[n+1]
*yppnp1-722*F[n]*Y[n]-13*F[n-1]*Y[n-1]-1744*F[n+1/2]*ypnp12);
> ypnm14:=1/2048*(23*ypppnp1+1490*Y[n]+535*Y[n-1])+1/24576*(-
13*F[n+1]*yppnp1-722*F[n]*Y[n]-101*F[n-1]*Y[n-1]-1744*F[n-1/2]*ypnm12);
> yppn:=Y[n]-w[1]*(F[n+1]*ypppnp1-90*F[n]*ypn+F[n-1]*Y[n-1]-
20*(F[n+1/2]*yppnp12+F[n-1/2]*yppnm12)+64*(F[n+1/4]*ypnp14+F[n-
1/4]*ypnm14));
> eq2:=simplify(Y[n+1]-2*Y[n]+Y[n-1]-1/3780*(47*(F[n+1]*ypppnp1+F[n-1]*Y[n-
1])+1328*(F[n+1/2]*yppnp12+F[n-1/2]*yppnm12)-1024*(F[n+1/4]*ypnp14+F[n-
1/4]*ypnm14)+3078*F[n]*yppn))=0;
> solut:=solve({eq1,eq2},{w[0],w[1]});
>
```

Figure 1. Maple program for the construction of explicit eighth algebraic order Bessel and Neumann fitted method.

3.   Error estimation

In the literature there are many methods for the estimation of the local truncation error (*LTE*) in the numerical solution of systems of differential equations (see, for example, [7,8,23]).

In this work we base our local error estimation technique on an embedded pair of integration methods and on the fact that when the order is maximal then the approximation of the solution for the problems with oscillatory or periodical solution is better.

The new variable-step procedure consists of the following parts:

(1) We divide the integration range into two distinct parts.

(2) The first part of the integration runs from $r = 0$ to r_c, where r_c is a point such that $|V(r)|$ is small. In practice we consider that $V(r)$ is small when $|V(r)| < 1/8$. In the range $0 \leqslant r \leqslant r_c$ the variable-step method is exactly described in [18].

(3) For $r \geqslant r_c$ we use the following variable-step procedure.

We use as lower order solution y_{n+1}^{L}, for the purpose of local error estimation, the explicit sixth order Bessel and Neumann fitted method developed in [17]. As higher order solution y_{n+1}^{H} we use the explicit eighth order Bessel and Neumann fitted method obtained above. Now, the local truncation error in y_{n+1}^{L} is estimated by

$$LTE = \left| y_{n+1}^{H} - y_{n+1}^{L} \right|. \tag{9}$$

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

$$h_{n+1} = h_n \left(\frac{acc}{LTE} \right)^{1/q}, \tag{10}$$

where q is the algebraic order of the method.

However, for ease of programming, we have reduced all step changes to halving and doubling. Thus, based on the procedure developed in [18] the step control procedure which we have used is:

$$
\begin{aligned}
&\text{If } LTE < acc, & &h_{n+1} = 2h_n. \\
&\text{If } 100acc > LTE \geqslant acc, & &h_{n+1} = h_n. \\
&\text{If } LTE \geqslant 100acc, & &h_{n+1} = \frac{h_n}{2} \text{ and repeat the step.}
\end{aligned}
\tag{11}
$$

We note that the local truncation 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.

4. Numerical illustrations

4.1. Radial Schrödinger equation

We apply the new variable-step procedure developed above to the solution of (1), where $V(r)$ is the *Lennard-Jones potential* which has been widely discussed in the literature. For this problem the potential $V(r)$ is given by

$$V(r) = m\left(\frac{1}{r^{12}} - \frac{1}{r^6}\right), \quad \text{where } m = 500. \tag{12}$$

We solve this problem as an initial value one and, in order to be able to use a two-step method, we need an extra initial condition to be specified, e.g., $y_1 (= y(h))$. It is well known that, for values of x close to the origin, the solution of (1) behaves like

$$y(r) \simeq Cr^{l+1} \quad \text{as } r \to 0. \tag{13}$$

In view of this we use $y_1 = h^{l+1}$ as our extra initial condition.

The problem we consider is the computation of the relevant phase shifts correct to 4 decimal places for energies $k = 1$, $k = 5$ and $k = 10$ and for $l = 0(1)10$. We will consider ten approaches:

Method MI: the iterative Numerov's method developed by Allison [1],

Method MII: based on the well-known variable step method of Raptis and Cash [7],

Method MIII: based on the well-known variable step method of Raptis and Cash [8],

Method MIV: based on the variable step procedure developed by Simos [10],

Method MV: based on the variable step procedure developed by Simos and Mousadis [11],

Method MVI: based on the variable step procedure developed by Avdelas and Simos [3],

Method MVII: based on the method developed by Simos [17],

Method MVIII: The Runge–Kutta–Nyström method developed by Dormand and Prince (see [24, table 13.4]),

Method MIX: the Runge–Kutta–Nyström method developed by Dormand et al. (see [25]),

Method MX: based on the variable-step method developed above.

In table 1 we present the average time of computation of the eleven phase shifts (for $l = 0(1)10$) correct to four decimal places for energies $k = 1$, $k = 5$ and $k = 10$.

4.2. Coupled differential equations

There are many problems in quantum chemistry, theoretical physics, atomic physics, physical chemistry and chemical physics which can be transformed to the solution of coupled differential equations of the Schrödinger type.

Table 1
Phase shift problem. Average time of computation for the calculation of the eleven phase shifts (for $l = 0(1)10$) correct to 4 decimal places for energies $k = 1$, $k = 5$ and $k = 10$ using the ten methods mentioned in the text.

Method	Average time of computation (in seconds)
MI	2.750
MII	2.144
MIII	1.716
MIV	1.623
MV	1.543
MVI	1.204
MVII	0.734
MVIII	1.446
MIX	1.056
MX	0.588

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

$$\left[\frac{d^2}{dx^2} + k_i^2 - \frac{l_i(l_i + 1)}{x^2} - V_{ii} \right] y_{ij} = \sum_{m=1}^{N} V_{im} y_{mj} \tag{14}$$

for $1 \leqslant i \leqslant N$ 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 [1]):

$$y_{ij} = 0 \quad \text{at } x = 0, \tag{15}$$

$$y_{ij} \sim k_i x j_{l_i}(k_i x)\delta_{ij} + \left(\frac{k_i}{k_j} \right)^{1/2} K_{ij} k_i x n_{li}(k_i x), \tag{16}$$

where $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions, respectively. We can also use the present method for problems involving closed channels.

Based on the detailed analysis developed in [1] and defining a matrix $\mathbf{K}'$ and diagonal matrices $\mathbf{M}, \mathbf{N}$ 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 (16) may be written as

$$\mathbf{y} \sim \mathbf{M} + \mathbf{N}\mathbf{K}'. \tag{17}$$

One of the most well-known methods for the numerical solution of the coupled differential equations arising from the Schrödinger equation is the iterative Numerov method of Allison [1].

A real problem in quantum chemistry, theoretical physics, atomic physics 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 [1], 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

$$\left[\frac{d^2}{dx^2} + k_{j'j}^2 - \frac{l'(l'+1)}{x^2}\right] y_{j'l'}^{Jjl}(x) = \frac{2\mu}{\hbar^2} \sum_{j''} \sum_{l''} \langle j'l'; J|V|j''l''; J\rangle y_{j''l''}^{Jjl}(x), \quad (18)$$

where

$$k_{j'j} = \frac{2\mu}{\hbar^2}\left[E + \frac{\hbar^2}{2I}\{j(j+1) - j'(j'+1)\}\right], \quad (19)$$

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 [1], the potential V can be expanded as

$$V\left(x, \hat{\mathbf{k}}_{j'j}\hat{\mathbf{k}}_{jj}\right) = V_0(x)P_0\left(\hat{\mathbf{k}}_{j'j}\hat{\mathbf{k}}_{jj}\right) + V_2(x)P_2\left(\hat{\mathbf{k}}_{j'j}\hat{\mathbf{k}}_{jj}\right), \quad (20)$$

and the coupling matrix element may then be written as

$$\langle j'l'; J|V|j''l''; J\rangle = \delta_{j'j''}\delta_{l'l''}V_0(x) + f_2\left(j'l', j''l''; J\right)V_2(x), \quad (21)$$

where the f_2 coefficients can be obtained from formulas given by Bernstein et al. [14], $\hat{\mathbf{k}}_{j'j}$ is a unit vector parallel to the wave vector $\mathbf{k}_{j'j}$ and P_i, $i = 0, 2$, are Legendre polynomials (see [15] for details). The boundary conditions are

$$y_{j'l'}^{Jjl}(x) = 0 \quad \text{at } x = 0, \quad (22)$$

$$y_{j'l'}^{Jjl}(x) \sim \delta_{jj'}\delta_{ll'} \exp\left[-i\left(k_{jj}x - \frac{1}{2}l\pi\right)\right]$$
$$- \left(\frac{k_i}{k_j}\right)^{1/2} S^J\left(jl; j'l'\right) \exp\left[i\left(k_{j'j}x - \frac{1}{2}l'\pi\right)\right], \quad (23)$$

where the scattering **S** matrix is related to the **K** matrix of (16) by the relation

$$\mathbf{S} = (\mathbf{I} + i\mathbf{K})(\mathbf{I} - i\mathbf{K})^{-1}. \quad (24)$$

To calculate the cross sections for rotational excitation of molecular hydrogen by impact of various heavy particles an algorithm in which the numerical method for step-by-step integration from the initial value to matching points is included. This algorithm is based on an analogous algorithm which has been developed for the numerical applications of [1].

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

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

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

As described in [1], we take $J = 6$ and consider excitation of the rotator from the $j = 0$ state to levels up to $j' = 2$, 4 and 6 giving sets of *four, nine and sixteen coupled differential equations*, respectively. Following the procedure obtained by Bernstein [15] and Allison [1] the potential is considered infinite for values of x less than some x_0. The wave functions then zero in this region and effectively the boundary condition (22) may be written as

$$y_{j'l'}^{Jjl}(x_0) = 0. \tag{25}$$

For the numerical solution of this problem we have used the most well-known methods for the above problem:

  (i) the Iterative Numerov method of Allison [1],

 (ii) the variable-step method of Raptis and Cash [7],

(iii) the variable step method of Raptis and Cash [8],

(iv) the variable-step method developed by Simos [17],

 (v) the Runge–Kutta–Nyström method developed by Dormand and Prince (RKN1) (see [24, table 13.4]),

(vi) the Runge–Kutta–Nyström method developed by Dormand et al. (RKN2) (see [25]), and

(vii) the new variable-step method.

In table 2 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 2 N indicates the number of equations of the set of coupled differential equations.

In all cases the embedded variable step method developed in this paper is more efficient than other well-known finite difference ones for a given value of $h_{\max}$ so that the new variable-step method can use a larger value of $h_{\max}$ and still gets converged results.

5.   Conclusions

In the present paper an explicit eighth algebraic order Bessel and Neumann fitted method for the numerical solution of the phase shift problem of the radial Schrödinger

Table 2
Coupled differential equations. RTC is real time of computation (in s) to calculate $|\mathbf{S}|^2$ for the variable-step methods (i)–(vii). $acc = 10^{-6}$. $h_{\max}$ is the maximum stepsize.

Method	N	$h_{\max}$	RTC
Iterative Numerov [1]	4	0.014	3.25
	9	0.014	23.51
	16	0.014	99.15
Variable-step method of Raptis and Cash [7]	4	0.056	1.65
	9	0.056	8.68
	16	0.056	45.21
Variable-step method of Raptis and Cash [8]	4	0.056	1.55
	9	0.056	8.43
	16	0.056	43.32
Variable-step method of Simos [17]	4	0.448	0.14
	9	0.448	0.85
	16	0.224	4.90
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
The new variable-step method	4	0.896	0.07
	9	0.448	0.54
	16	0.448	2.05

equation and of the coupled differential equations arising from the Schrödinger equation is constructed. We also give the Maple program in order one can develop the new approach. Based on this new method we introduce a new variable step method for the solution of the Schrödinger equation (radial and coupled differential equations). The obtained numerical results show that the new method is better than those of the most well known variable-step methods of Raptis and Cash [7,8], the iterative Numerov method of Allison [1], the Runge–Kutta–Nyström method developed by Dormand and Prince (see [24, table 13.4]) and the Runge–Kutta–Nyström method developed by Dormand et al. (see [25]).

All computations were carried out on a PC i586 using double precision arithmetic (16 significant digits accuracy).

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