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Comparison of Numerical Solutions of the Partial-Wave Schrödinger Differential and Integral Equations

M. S. STERN

Department of Applied Mathematics and Computing Science,
University of Sheffield, Sheffield S10 2TN, England

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Various methods for computing radial wave functions and scattering phase shifts of short-range local interactions are briefly discussed and numerical results are presented for a static electron–hydrogen potential. It is found that a quadrature solution of the integral equation is highly competitive in terms of accuracy, particularly at very low energies where it has superior numerical stability over differential equation methods and is also less demanding in computer time.

1. DISCUSSION OF METHODS

Radial wave functions $u_l(r)$ and scattering phase shifts $\delta_l(k)$ of short-range local interactions $V(r)$ are most frequently determined at positive energies k^2 (in the center of mass frame) by solving numerically the partial-wave Schrödinger differential equation

$$\frac{d^2u_l}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2} - V(r)\right] u_l = 0 \tag{1}$$

under the boundary conditions

$$\begin{aligned} u_l(r) &\sim \alpha_l(k)\, r^{l+1} && \text{as} \quad r \to 0, \\ &\sim kr[j_l(kr) - \tan \delta_l(k)\, n_l(kr)] && \text{as} \quad r \to \infty, \end{aligned} \tag{2}$$

where j_l and n_l are the spherical Bessel and Neumann functions, respectively. The solution of this boundary value problem is usually computed by employing a convenient initial value method, such as the standard fourth-order Runge–Kutta process [1] or Numerov's finite difference scheme [1], which starts the integration of the differential equation from the boundary condition at $r = 0$ and progresses outward until an arbitrary large value of r is reached where the numerical solution is matched to the prescribed asymptotic behavior of the wave function.

The objective of this note is to compare the phase shifts computed via the Runge–Kutta and Numerov methods against each other and against the phase shifts obtained via alternative numerical methods which are presented below. The boundary con-

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ditions at $r = 0$ and $r = \infty$ are both applied simultaneously in these latter methods which are derived from an integral equation formulation of the problem.

Differential equation (1), together with the boundary conditions (2), can be transformed into the integral equation [2]

$$u_l(r) = krj_l(kr) + \int_0^\infty G_l(r, r')\, V(r')\, u_l(r')\, dr' \tag{3}$$

in which the Green's function takes the form

$$\begin{aligned} G_l(r, r') &= krr'j_l(kr)\, n_l(kr') \qquad \text{for} \quad r \leqslant r', \\ &= krr'j_l(kr')\, n_l(kr) \qquad \text{for} \quad r \geqslant r'. \end{aligned} \tag{4}$$

By comparing the second of the boundary conditions (2) with integral equation (3) when $r \geqslant r'$ we obtain the phase shift formula

$$\tan \delta_l(k) = -\int_0^\infty r'j_l(kr')\, V(r')\, u_l(r')\, dr'. \tag{5}$$

The infinite upper limits of the integrals in Eqs. (3) and (5) can be removed by using the substitution

$$r = x/(1 - x), \tag{6}$$

which maps the interval $0 \leqslant r \leqslant \infty$ onto the interval $0 \leqslant x \leqslant 1$, to obtain

$$u_l(r) = krj_l(kr) + \int_0^1 \frac{1}{(1 - x')^2}\, G_l(r, r')\, V(r')\, u_l(r')\, dx' \tag{7}$$

and

$$\tan \delta_l(k) = -\int_0^1 \frac{x}{(1 - x)^3}\, j_l(kr)\, V(r)\, u_l(r)\, dx \tag{8}$$

in which the local interaction $V(r)$ vanishes when x (or x') equals unity.

The standard numerical approach for solving Fredholm integral equations of the second kind is now followed: The integrals on the right-hand sides of Eqs. (7) and (8) are replaced by a quadrature formula to yield

$$u_l(r) = krj_l(kr) + \sum_m \frac{w_m}{(1 - x_m')^2}\, G_l(r, r_m')\, V(r_m')\, u_l(r_m') \tag{9}$$

and

$$\tan \delta_l(k) = -\sum_m \frac{w_m x_m}{(1 - x_m)^3}\, j_l(kr_m)\, V(r_m)\, u_l(r_m) \tag{10}$$

where the weights w_m and pivotal points x_m are determined by the chosen quadrature formula. Equation (9) is transformed into a closed system of simultaneous linear algebraic equations for the radial wave function if r is restricted to the pivotal points $r_m = x_m/(1 - x_m)$ of the numerical integration. The solution of these linear equations may then be substituted into Eq. (10) in order to compute the phase shift $\delta_l(k)$. (Equation (9) may, of course, be used as an interpolation formula to evaluate $u_l(r)$ at any nonpivotal value of r when the $u_l(r_m)$ are known.)

Some comments concerning the application of quadrature formulas are appropriate at this stage. The use of such a formula requires the integrand to be differentiable a sufficient number of times (depending on the chosen formula) at all points within the open interval of the integration (i.e., excluding the end points of the interval). This condition is necessary for the existence of a finite error term [3]. However, as $\partial G_l/\partial r'$ is discontinuous at $r' = r$ in Eq. (3), i.e., at $x' = x$ in Eq. (7), care must be exercised when setting up the quadrature approximation (9) and the resulting system of linear equations for the radial wave function.

If the composite trapezoidal rule is employed as the chosen quadrature formula in (9) and (10) then the closed system of linear equations for the wave function takes the form

$$u_l(r_t) - h \sum_{m=1}^{n-1} \frac{1}{(1 - x_m)^2} G_l(r_t, r_m) V(r_m) u_l(r_m) = kr_t j(kr_t) \tag{11}$$

where $t = 0, 1, 2, \ldots, n - 1$ and

$$h = 1/n, \qquad x_m = mh, \qquad r_m = x_m/(1 - x_m). \tag{12}$$

(In (11), use has been made of the fact that the integrand in (7) vanishes at $x' = 0$ and 1.) In view of transformation (6) it can be seen that half of the pivotal points in (11) lie in the interval $0 \leqslant r \leqslant 1$, that is, in the region where the most rapid change in the potential $V(r)$ usually occurs. The discontinuity in $\partial G_l/\partial r'$, which occurs along the principal diagonal in the system of Eqs. (11), does not pose any problems with this particular quadrature approximation because it coincides with the common end point of the subintervals $[x_{t-1}, x_t]$ and $[x_t, x_{t+1}]$ over which the basic trapezoidal rule is applied (x_t being the pivotal point on the principal diagonal).

The application of the composite trapezoidal rule to the approximate phase shift formula (10) yields

$$\tan \delta_l(k) = -h \sum_{m=1}^{n-1} \frac{x_m}{(1 - x_m)^3} j_l(kr_m) V(r_m) u_l(r_m) \tag{13}$$

where h, x_m, and r_m take the values defined in (12) (and use has been made of the fact that the integrand in (8) vanishes at $x = 0$ and 1). Half of the $(n - 1)$ terms on the right-hand side of this formula represent the region of most rapid change in $V(r)$. Furthermore, it is obvious that half of the pivotal points will always lie in the interval $0 \leqslant r \leqslant 1$ whenever the quadrature approximations (9) and (10) are represented by a closed Newton–Cotes formula (either basic or composite), the trapezoidal rule being the simplest example. The discontinuity in $\partial G_l/\partial r'$ will also always occur along the principal diagonal in the system of linear equations derived from (9).

When Eqs. (9) and (10) are represented by the composite version of Simpson's rule the closed system of linear equations for the radial wave function takes the form

$$u_l(r_t) - \frac{h}{3} \sum_{m=1}^{2n-1} \frac{c_m}{(1-x_m)^2} G_l(r_t, r_m)\, V(r_m)\, u_l(r_m) = kr_t j_l(kr_t) \tag{14}$$

where $t = 0, 1, 2, \ldots, 2n-1$ and

$$\begin{gathered} h = 1/2n, \qquad x_m = mh, \qquad r_m = x_m/(1-x_m), \\ c_1 = c_3 = \cdots = c_{2n-1} = 4, \qquad c_2 = c_4 = \cdots = c_{2n-2} = 2, \end{gathered} \tag{15}$$

whilst the approximate phase shift formula becomes

$$\tan \delta_l(k) = -\frac{h}{3} \sum_{m=1}^{2n-1} \frac{c_m x_m}{(1-x_m)^3} j_l(kr_m)\, V(r_m)\, u_l(r_m) \tag{16}$$

(remembering that the integrands in (7) and (8) vanish at each end of the interval of integration). For those equations with an *even* value of t in (14), the discontinuity in $\partial G_l/\partial r'$ does not pose any problems because it coincides with the common end point of the subintervals $[x_{t-2}, x_t]$ and $[x_t, x_{t+2}]$ over which the basic form of Simpson's rule is applied. However, in the equations with an *odd* value of t, the discontinuity in $\partial G_l/\partial r'$ occurs at the center of the subinterval $[x_{t-1}, x_{t+1}]$ and thus could possibly lead to an undefined error term in the quadrature approximation. But, as can be seen from numerical results presented below (Table VII), Eqs. (14) and (16) are stable, the rate of convergence with respect to the number of pivotal points used being only slightly slower than for Eqs. (11) and (13).

If Gauss–Legendre quadrature formulas are to be employed then it is more appropriate to use the transformation

$$r = (1+x)/(1-x), \tag{17}$$

which maps the interval $0 \leqslant r \leqslant \infty$ on to the interval $-1 \leqslant x \leqslant 1$, rather than (6) so that Eqs. (3) and (5) become, respectively,

$$u_l(r) = krj_l(kr) + \int_{-1}^{1} \frac{2}{(1-x')^2} G_l(r, r')\, V(r')\, u_l(r')\, dx' \tag{18}$$

and

$$\tan \delta_l(k) = -2 \int_{-1}^{1} \frac{(1+x)}{(1-x)^3} j_l(kr)\, V(r)\, u_l(r)\, dx. \tag{19}$$

Replacing the above integrals by an n-point Gauss–Legendre formula leads to the system of linear equations

$$u_l(r_t) - \sum_{m=1}^{n} \frac{2w_m}{(1-x_m)^2} G_l(r_t, r_m) V(r_m) u_l(r_m) = kr_t j_l(kr_t) \tag{20}$$

with $t = 1, 2, 3, \ldots, n$ and the approximate phase shift formula

$$\tan \delta_l(k) = -2 \sum_{m=1}^{n} w_m \frac{(1+x_m)}{(1-x_m)^3} j_l(kr_m) V(r_m) u_l(r_m) \tag{21}$$

where the weights w_m and pivotal points x_m are available from tables for various values of n [4]. As the use of an n-point Gauss–Legendre formula normally requires the integrand to be differentiable at least $2n$ times [3] within the open interval $(-1, 1)$, there is the possibility of an undefined error term in the system of Eqs. (20) due to the discontinuity in $\partial G_l/\partial r'$. However, as can be seen from numerical results presented below (Table VIII), Eqs. (20) and (21) yield stable results, the rate of convergence being approximately the same as that for Eqs. (14) and (16). (As the abscissas in a Gauss–Legendre quadrature formula are distributed symmetrically with respect to $x = 0$, half of the pivotal points in (20) and (21) lie in the interval $0 < r \leqslant 1$, the region of most rapid change in $V(r)$.) As a Gauss–Legendre formula is an *open* integration formula the discontinuity in $\partial G_l/\partial r'$ cannot be made to coincide with the end points of subintervals if a composite version of the two-point Gauss–Legendre formula is employed to solve either Eq. (7) or (18), in contrast to the situation experienced with the composite trapezoidal rule.

2. NUMERICAL RESULTS

Five ALGOL 60 programs have been developed to compute radial wave functions and scattering phase shifts of local interactions of the form

$$V(r) = \sum_{t=1}^{M} A_t \exp(-\mu_t r)/r + \sum_{t=1}^{N} B_t \exp(-\rho_t r) \tag{22}$$

($\mu_t > 0$, $\rho_t > 0$) for any value of the orbital angular momentum l ($= 0, 1, 2, 3, \ldots$) over any (user) specified range of positive energies k^2 via

(i) the standard fourth-order Runge–Kutta method with step length h and matching points determined from a (user) specified upper bound on the product kr;

(ii) the Numerov method with the same parameters as in (i);

(iii) Eqs. (11) and (13);

(iv) Eqs. (14) and (16);
(v) Eqs. (20) and (21).

Table I displays the approximate times taken on a CDC 7600 computer by the Runge–Kutta program to solve Eq. (1), as a function of k, the step length h, and the position of the matching points, whilst Table II contains the corresponding times for the Numerov method program. It can be seen from these tables that the Runge–Kutta and Numerov method programs take approximately 0.06 and 0.02 seconds per 100 pivotal points, respectively. Table III indicates the approximate times taken, per k value, on a CDC 7600 computer by the three quadrature method programs to set up and solve their respective equations in terms of the number of pivotal points used. The composite trapezoidal rule program requires slightly less time than the composite Simpson's rule program because of the simpler weights in the former quadrature approximation. The time taken by each of the quadrature method programs varies quadratically with respect to the number of pivotal points employed, in contrast to the linear time variation of the differential equation programs.

This note contains numerical results obtained from the five programs for the static electron–hydrogen potential

$$V(r) = -2(1 + (1/r))\exp(-2r), \tag{23}$$

the phase shifts of which have also been determined via other methods [5, 6]. S-, P-, D-, and F-wave phase shifts computed via the fourth-order Runge–Kutta method are displayed in Table IV with $h = (0.1, 0.05, 0.01)$ and matching points determined from $kr \approx 25$. It can be clearly seen that the Runge–Kutta method is unstable for $\delta_3(0.1)$ with each value of h. Further calculations performed with $kr \approx (25, 50, 100, 200)$ have shown that the method is unstable for $\delta_l(k)$ when $l \geqslant 3$ and $k < 0.5$. It has also been found that instability arises for $\delta_2(0.1)$ when $kr = 100$ and 200. It has been observed that there is little change in the values of any of the phase shifts (with the exception of the instabilities mentioned above) with $h = 0.01$ when kr is doubled from 25 to 50 and then to 100. However, the process of moving the matching points further and further from the origin leads to a loss of accuracy which grows appreciably with increasing energy when the $\delta_l(k)$ are computed with $h = 0.1$; there is also a parallel but smaller loss of accuracy when $h = 0.05$. When calculations were performed with matching points determined from $kr \approx 12.5$ the accuracy remained unchanged at low energies but it was found to deteriorate with increasing energy for all l irrespective of the value of h. Hence, the optimum rate of convergence with respect to h obtained from the Runge–Kutta program appears to occur when the matching points are determined from $kr \approx 25$.

The corresponding phase shifts computed via the Numerov method are presented in Table V. Once again instability is present for $\delta_3(0.1)$, irrespective of the value of h, and further calculations have indicated that the method is unstable for $\delta_l(k)$ when $l \geqslant 3$ and $k < 0.5$. Instability has also been found to occur for $\delta_2(0.1)$ with $h = 0.01$ when $kr = 50$ and 100. The results for $\delta_l(0.1)$ deteriorate even further when the

TABLE I

Approximate Times (in Seconds) Taken on a CDC 7600 Computer by the Fourth-Order Runge–Kutta (ALGOL 60) Program to Solve Eq. (1) with Step Length h and Matching Points Determined from the Condition $kr \approx 25$[a]

k	$h = 0.1$	$h = 0.05$	$h = 0.01$
0.1	1.48	2.93	14.49
0.5	0.32	0.61	2.92
1.0	0.18	0.32	1.49
2.0	0.10	0.18	0.76
3.0	0.08	0.13	0.52
4.0	0.07	0.10	0.40
5.0	0.06	0.09	0.32

[a] For $kr \approx 50$ and $kr \approx 100$ the above times should be multiplied approximately by two and four, respectively.

TABLE II

Approximate Times (in Seconds) Taken on a CDC 7600 Computer by the Numerov Method (ALGOL 60) Program to Solve Eq. (1) with Step Length h and Matching Points Determined from the Condition $kr \approx 25$[a]

k	$h = 0.1$	$h = 0.05$	$h = 0.01$
0.1	0.52	1.01	4.84
0.5	0.13	0.23	1.00
1.0	0.09	0.14	0.53
2.0	0.06	0.08	0.28
3.0	0.05	0.07	0.20
4.0	0.05	0.06	0.16
5.0	0.05	0.06	0.14

[a] For $kr \approx 50$ and $kr \approx 100$ the above times should be multiplied approximately by two and four, respectively.

TABLE III

Approximate Times (in Seconds) Taken on a CDC 7600 Computer by the Quadrature Method (ALGOL 60) Programs to Set Up and Solve Their Respective Equations Per k Value[a]

	Equations (11) and (13)			Equations (14) and (16)			Equations (20) and (21)		
	$n = 20$	$n = 40$	$n = 50$	$2n = 20$	$2n = 40$	$2n = 50$	$n = 20$	$n = 40$	$n = 48$
0	0.12	0.59	1.04	0.13	0.60	1.08	0.13	0.61	0.98
1	0.12	0.62	1.08	0.13	0.63	1.12	0.13	0.64	1.02
2	0.18	0.88	1.48	0.19	0.89	1.52	0.19	0.90	1.42
3	0.23	1.09	1.82	0.24	1.10	1.86	0.24	1.11	1.76

[a] n and $2n$ specify the number of pivotal points used. The dependence on l is due to the Green's function (4).

TABLE IV

S-, *P*-, *D*-, and *F*-Wave Phase Shifts (in Degrees), for the e$^-$–H Interaction (23), Computed Via the Standard Fourth-Order Runge–Kutta Method with Step Length *h* and Matching Points Determined from the Condition $kr \approx 25$

	$\delta_0(k)$			$\delta_1(k)$			$\delta_2(k)$			$\delta_3(k)$		
k	$h = 0.1$	$h = 0.05$	$h = 0.01$	$h = 0.1$	$h = 0.05$	$h = 0.01$	$h = 0.1$	$h = 0.05$	$h = 0.01$	$h = 0.1$	$h = 0.05$	$h = 0.01$
0.1	41.3825	41.3800	41.3801	0.0153546	0.0153549	0.0153548	3.789×10^{-5}	3.797×10^{-5}	3.796×10^{-5}	2.2×10^{-8}	9.2×10^{-8}	7.8×10^{-8}
0.5	59.8552	59.8545	59.8546	1.49132	1.49141	1.49141	0.079606	0.079655	0.079659	0.004606	0.004651	0.004654
1.0	51.8809	51.8824	51.8826	6.38563	6.38696	6.38698	1.01978	1.02056	1.02062	0.17815	0.17886	0.17891
1.5	44.941	44.948	44.949	10.5434	10.5498	10.5500	2.8233	2.8272	2.8275	0.8084	0.8120	0.8122
2.0	39.793	39.815	39.817	12.806	12.825	12.826	4.602	4.614	4.615	1.7386	1.7499	1.7506
2.5	35.850	35.902	35.905	13.819	13.865	13.868	5.961	5.991	5.993	2.682	2.709	2.711
3.0	32.70	32.80	32.81	14.142	14.236	14.242	6.887	6.950	6.954	3.486	3.542	3.546
3.5	30.09	30.28	30.29	14.08	14.25	14.26	7.47	7.58	7.59	4.107	4.211	4.218
4.0	27.86	28.16	28.18	13.80	14.08	14.10	7.79	7.98	8.00	4.55	4.73	4.74
4.5	25.89	26.36	26.40	13.36	13.81	13.84	7.91	8.22	8.24	4.83	5.11	5.13
5.0	24.09	24.80	24.86	12.80	13.48	13.52	7.86	8.34	8.37	4.97	5.39	5.42

TABLE V

S-, *P*-, *D*-, and *F*-Wave Phase Shifts (in Degrees), for the e^-–H Interaction (23), Computed Via Numerov's Method with Step Length *h* and Matching Points Determined from the Condition $kr \approx 25$

	$\delta_0(k)$			$\delta_1(k)$			$\delta_2(k)$			$\delta_3(k)$		
k	$h=0.1$	$h=0.05$	$h=0.01$	$h=0.1$	$h=0.05$	$h=0.01$	$h=0.1$	$h=0.05$	$h=0.01$	$h=0.1$	$h=0.05$	$h=0.01$
0.1	39.57	40.89	41.36	0.015357	0.015355	0.015357	3.80×10^{-5}	3.81×10^{-5}	3.99×10^{-5}	1.4×10^{-7}	1.7×10^{-7}	1.7×10^{-6}
0.5	59.04	59.64	59.85	1.49177	1.49146	1.49141	0.079673	0.079660	0.079659	0.0046643	0.0046544	0.0046538
1.0	51.30	51.73	51.88	6.3899	6.3873	6.3870	1.02085	1.02063	1.02062	0.17902	0.17892	0.17891
1.5	44.41	44.81	44.94	10.559	10.551	10.550	2.8287	2.8276	2.8275	0.81258	0.81228	0.81224
2.0	39.28	39.67	39.81	12.846	12.829	12.826	4.6190	4.6154	4.6151	1.7512	1.7508	1.7506
2.5	35.35	35.76	35.90	13.902	13.872	13.868	6.0031	5.9940	5.9934	2.7111	2.7113	2.7111
3.0	32.24	32.66	32.80	14.295	14.249	14.242	6.975	6.956	6.954	3.5432	3.5465	3.5461
3.5	29.71	30.13	30.28	14.34	14.27	14.26	7.633	7.594	7.591	4.2087	4.2186	4.2181
4.0	27.62	28.02	28.18	13.20	14.11	14.10	8.072	8.000	7.997	4.716	4.738	4.738
4.5	25.86	26.22	26.39	13.97	13.86	13.84	8.368	8.246	8.240	5.089	5.130	5.130
5.0	24.37	24.67	24.85	13.69	13.55	13.52	8.59	8.38	8.37	5.359	5.420	5.420

matching points are determined from $kr = 200$; the following were obtained (in degrees)

$$h = 0.1\colon\ \delta_0 = 39.57,\quad \delta_1 = 0.015358,\quad \delta_2 = 3.88 \times 10^{-5},\quad \delta_3 = 8.8 \times 10^{-7},$$

$$h = 0.05\colon\ \delta_0 = 40.89,\quad \delta_1 = 0.015358,\quad \delta_2 = 4.05 \times 10^{-5},\quad \delta_3 = 2.3 \times 10^{-6},$$

$$h = 0.01\colon\ \delta_0 = 60.79,\quad \delta_1 = -29.49,\quad \delta_2 = 60.29,\quad \delta_3 = -30.64.$$

It has been observed again that there is little change in the values of the phase shifts (with the exception of the instabilities mentioned above) with $h = 0.01$ when kr is doubled from 25 to 50 and then to 100, and it is seen that there is good agreement with the results obtained via the Runge–Kutta method with $h = 0.01$. However, it should be noted that the Runge–Kutta method yields low energy S-wave phase shifts with more significant figures than does Numerov's method. It has been found from calculations performed with $kr \approx (25, 50, 100, 200)$ that with $h = 0.1$ the value of $\delta_l(k)$, for any given k, is increased as the matching points are moved further and further from the origin, the effect becoming more noticeable as the energy rises; there is also parallel but smaller increase in the phase shift values where $h = 0.05$. However, when calculations were carried out with $kr \approx 12.5$, the results obtained were analogous to those yielded by the Runge–Kutta method with $kr \approx 12.5$, that is, the accuracy experienced little or no change at low energies but it deteriorated with increasing energy for all l irrespective of the value of h. Thus, in order to compute reliable phase shifts via Numerov's method the choice of step length and matching points should probably satisfy the inequalities $h \leqslant 0.01$ and $kr \geqslant 25$, respectively.

Tables VI–VIII contain the phase shifts of the e$^-$–H interaction (23) computed via the three quadrature methods. It can be clearly seen that each of these methods is completely stable for $\delta_2(0.1)$ and $\delta_3(0.1)$. (Further calculations have shown that the methods are also stable for all $k \geqslant 0$ when $l > 3$.) At most energies the composite trapezoidal rule provides the fastest rate of convergence with respect to the number of pivotal points employed (due to the discontinuity in $\partial G_l/\partial r'$ discussed earlier in this note) whilst the composite Simpson's rule and the Gauss–Legendre formulas exhibit approximately the same rates of convergence. The results obtained with the use of 40 to 50 pivotal points in each of the quadrature methods are in good agreement at most energies with the $h = 0.01$ differential equation results (and often with the $h = 0.05$ results as well). At medium and high energies the 20-point quadrature phase shifts are usually of higher accuracy than those computed via the Runge–Kutta or Numerov methods with $h = 0.1$.

All the numerical results presented in this section have been obtained via single precision arithmetic carried out on a CDC 7600 computer whose core store has a word length of 60 binary bits; floating point numbers are stored to an accuracy of 14 or 15 significant figures. Double precision arithmetic is not available in ALGOL 60. However, it should be noted that the computer time requirements of each of the methods examined in this section would increase considerably if calculations were performed with double precision arithmetic. (Single precision on a CDC 7600 is almost equivalent to double precision on IBM 360/370 computers.)

TABLE VI

S-, *P*-, *D*-, and *F*-Wave Phase Shifts (in Degrees) for the e$^-$–H Interaction (23)[a]

	$\delta_0(k)$			$\delta_1(k)$			$\delta_2(k)$			$\delta_3(k)$		
k	$n=20$	$n=40$	$n=50$	$n=20$	$n=40$	$n=50$	$n=20$	$n=40$	$n=50$	$n=20$	$n=40$	$n=50$
0.1	41.609	41.437	41.416	0.015372	0.015359	0.015358	3.8000×10^{-5}	3.7983×10^{-5}	3.7982×10^{-5}	1.00001×10^{-7}	1.00156×10^{-7}	1.00154×10^{-7}
0.5	59.940	59.876	59.868	1.4932	1.4919	1.4917	0.079718	0.079670	0.079666	0.00466116	0.00465403	0.00465394
1.0	51.919	51.892	51.888	6.3972	6.3896	6.3887	1.02195	1.02084	1.02076	0.178712	0.178933	0.178925
1.5	44.961	44.952	44.951	10.572	10.555	10.553	2.8303	2.8284	2.8280	0.81193	0.81241	0.81234
2.0	39.799	39.814	39.815	12.860	12.833	12.831	4.6150	4.6168	4.6162	1.7594	1.7512	1.7510
2.5	35.893	35.898	35.901	13.881	13.875	13.872	6.0194	5.9957	5.9950	2.7048	2.7122	2.7116
3.0	32.756	32.800	32.805	14.299	14.250	14.247	6.947	6.958	6.956	3.5603	3.5477	3.5469
3.5	30.253	30.276	30.280	14.263	14.270	14.269	7.635	7.596	7.594	4.2145	4.2187	4.2194
4.0	28.080	28.169	28.173	14.184	14.106	14.105	7.970	8.002	7.999	4.767	4.738	4.740
4.5	26.383	26.372	26.383	13.794	13.849	13.842	8.328	8.240	8.243	5.089	5.136	5.132
5.0	24.655	24.834	24.842	13.656	13.529	13.528	8.293	8.380	8.376	5.522	5.420	5.420

[a] *n* is the number of pivotal points used in Eqs. (11) and (13).

TABLE VII

S-, *P*-, *D*-, and *F*-Wave Phase Shifts (in Degrees) for the e^-–H Interaction (23)[a]

	$\delta_0(k)$			$\delta_1(k)$			$\delta_2(k)$			$\delta_3(k)$		
k	$2n=20$	$2n=40$	$2n=50$	$2n=20$	$2n=40$	$2n=50$	$2n=20$	$2n=40$	$2n=50$	$2n=20$	$2n=40$	$2n=50$
0.1	42.41	41.63	41.54	0.015354	0.015360	0.015358	3.79728×10^{-5}	3.79835×10^{-5}	3.79827×10^{-5}	1.0254×10^{-7}	1.0021×10^{-7}	1.0014×10^{-7}
0.5	60.27	59.96	59.92	1.4936	1.4921	1.4918	0.0790970	0.0796690	0.0796690	0.004670	0.004652	0.004654
1.0	52.16	51.95	51.92	6.400	6.391	6.389	1.02879	1.02076	1.02083	0.1757	0.1790	0.1789
1.5	45.13	45.00	44.98	10.590	10.556	10.554	2.8118	2.8288	2.8284	0.8293	0.8128	0.8122
2.0	40.05	39.87	39.85	12.862	12.833	12.832	4.644	4.620	4.617	1.718	1.749	1.751
2.5	36.10	35.94	35.93	13.846	13.884	13.876	6.032	5.991	5.994	2.754	2.716	2.713
3.0	32.84	32.86	32.84	14.443	14.244	14.246	6.848	6.965	6.959	3.587	3.545	3.547
3.5	30.62	30.32	30.32	14.17	14.28	14.27	7.776	7.589	7.595	4.078	4.222	4.218
4.0	28.40	28.24	28.20	14.07	14.10	14.11	8.03	8.02	8.00	4.84	4.73	4.75
4.5	26.39	26.41	26.43	14.01	13.88	13.84	8.12	8.22	8.25	5.27	5.16	5.12
5.0	24.77	24.93	24.87	13.83	13.50	13.53	8.23	8.42	8.37	5.44	5.39	5.43

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[a] $2n$ is the number of pivotal points used in Eqs. (14) and (16).

TABLE VIII

S-, *P*-, *D*-, and *F*-Wave Phase Shifts (in Degrees) for the e^-–H Interaction (23)[a]

	$\delta_0(k)$			$\delta_1(k)$			$\delta_2(k)$			$\delta_3(k)$		
k	$n=20$	$n=40$	$n=48$	$n=20$	$n=40$	$n=48$	$n=20$	$n=40$	$n=48$	$n=20$	$n=40$	$n=48$
0.1	42.67	41.70	41.60	0.015390	0.015364	0.015361	3.8008×10^{-5}	3.7988×10^{-5}	3.7985×10^{-5}	1.00215×10^{-7}	1.00160×10^{-7}	1.00158×10^{-7}
0.5	60.38	59.99	59.95	1.4956	1.4925	1.4922	0.079758	0.079682	0.079675	0.0046499	0.0046543	0.0046541
1.0	52.20	51.96	51.94	6.412	6.393	6.391	1.0216	1.0211	1.0210	0.17940	0.17895	0.17894
1.5	45.19	45.01	44.99	10.591	10.562	10.558	2.8380	2.8295	2.8289	0.81514	0.81255	0.81246
2.0	40.04	39.87	39.85	12.885	12.841	12.837	4.638	4.619	4.618	1.7394	1.7516	1.7514
2.5	36.03	35.95	35.94	13.956	13.884	13.879	5.988	6.000	5.998	2.7622	2.7124	2.7123
3.0	33.04	32.85	32.84	14.291	14.259	14.254	7.023	6.962	6.960	3.4877	3.5487	3.5479
3.5	30.44	30.32	30.31	14.277	14.286	14.277	7.647	7.595	7.597	4.288	4.227	4.221
4.0	28.13	28.22	28.20	14.386	14.109	14.114	7.857	8.012	8.001	4.835	4.738	4.744
4.5	26.83	26.43	26.42	13.633	13.857	13.844	8.562	8.247	8.251	4.894	5.135	5.130
5.0	24.94	24.88	24.88	13.560	13.541	13.537	6.365	8.380	8.377	5.636	5.433	5.424

[a] n is the number of pivotal points used in Eqs. (20) and (21).

3. Conclusion

The numerical results presented above show that the various methods employed to solve the partial-wave Schrödinger equation yield phase shifts of similar accuracy, provided that the step length is small enough in the Runge–Kutta and Numerov methods and that a sufficient number (40 to 50) of pivotal points are used in the quadrature methods. The most reliable of the latter methods is the composite trapezoidal rule because it should always be unaffected by the discontinuity in the first derivative of the kernel in Eq. (3). This simple quadrature method is strongly recommended for computing phase shifts at very low energies, i.e., with $k \leqslant 0.5$, particularly when $l > 1$, because of its superior stability over differential equation methods in this energy region (confirmed by further calculations) and its more economic computer time requirements. The most accurate low energy ($k \leqslant 2$) S-wave phase shifts are obtained by using either the fourth-order Runge–Kutta method or the composite trapezoidal rule, with the average time requirements (Tables I and III) over this energy region generally favouring the latter.

As expected, Numerov's method (with step length and matching points as suggested at the end of the penultimate paragraph in Section 2) requires the minimum computer time averaged over all energies above $k^2 = 0.25$ when compared with the other numerical methods for determining scattering phase shifts of short-range local interactions. However, the composite trapezoidal rule appears to yield results of greater accuracy when averaged over all energies and all orbital angular momenta than do the other methods investigated in Section 2. It is, of course, well known that the Runge–Kutta and Numerov methods may be used in a self-correcting manner whereby the step length is automatically adjusted until a result of specified accuracy is achieved, but the computer time required for such a procedure cannot be easily predicted.

The general conclusions outlined above have been confirmed by performing calculations with other central potentials of the form (22), including neutron–proton $^3S_1$ and $^1S_0$ interactions consisting of sums of two and three Yukawa potentials, respectively.

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