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NOTE

On an Eighth Order Formula for Solving a Schrödinger Equation

The study of finite difference multi-step schemes for constructing the solutions of second order linear ordinary differential equations, needed for example in investigations of atomic and molecular structure and scattering, has long been established. Popular amongst the available choices are Numerov's method because of its small leading error and symmetry and de Vogelaere's method because of the ease of applying it to sets of coupled differential equations [1] and also various invariant embedding schemes such as Johnson's log-derivative method [2]. The leading global truncation errors in all these are proportional to the fourth power of the step length, h. Attempts to derive integration schemes with errors of higher order in h are comparatively few because of the success of the cited methods. One such higher order method is the eighth order formula of Allison *et al.* [3] with global error $\mathcal{O}(h^8)$. These authors demonstrated that this method works well for a number of examples but their illustration of calculating phase shifts induced by a 6–12 Lennard–Jones potential requires further study because of the strong repulsion at the origin; the variation of the error with step length must be studied carefully when finite difference methods are applied in the presence of such strong singularities [4]. The 6–12 form is a potential with a well at medium range, a long range van der Waals attraction, and a very repulsive core at short range. The core can complicate the error analysis.

The equation solved by Allison *et al*. is, for zero angular momentum,

$$d^2y(r)/dr^2 + \left(c_6 r^{-6} - c_{12} r^{-12} + k^2\right) y(r) = 0 \tag{1}$$

with boundary conditions

$$y(0) = 0 \qquad y(r) \to A(\sin kr + \tan\delta \cos kr) \text{ as } r \to \infty, \tag{2}$$

where r is the independent variable, c_6 and c_{12} are coefficients each equal to 500 in appropriate units, k is the wave number, A is a constant, and δ is the phase shift. Near the origin the equation is dominated by the r^{-12} term and its solutions contain modified Bessel functions as factors [5] which are asymptotically like $r^{11/2}\exp[\pm\sqrt{(c_{12})}/5r^5]$ for small r. Finite difference formulae, including the eighth order one, cannot follow these functions adequately. It has been shown that when Hartree's method is used to solve this equation a starting error occurs which vanishes when $\exp[-\sqrt{(c_{12})}/5h^5]$ is small (as it is for small h)

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TABLE I
Rotationless Phase Shifts

k	h	Exact[a]	Numerov[a]	Eighth Order[b]
1	0.04	0.15442	0.15491	
1	0.08	0.15442	0.16270	0.154
5	0.03	−0.48303	−0.48302	
5	0.06	−0.48303	−0.47438	−0.484
10	0.025	−0.43100	−0.42593	
10	0.05	−0.43100	−0.34910	−0.431[c]

[a] This calculation.
[b] Ref. [3].
[c] Incorrect sign displayed in Ref. [3].

leaving the expected $\mathcal{O}(h^2)$ error [6]. Similar error behaviour is expected for any finite difference method applied to Eq. (1) but accurate values of the phase shifts can be produced if sufficiently small step lengths are used; the results shown as "exact" in Table I were obtained with small step lengths. In the examples studied below, the angular momentum is chosen as zero because otherwise the centrifugal barrier tends to keep the colliding particles out of the core region, as is reflected in the results of Allison *et al*.

Table I shows that the eighth order formula is much more accurate than Numerov's method. The term $\exp[-\sqrt{(c_{12})}/5h^5]$ is very small for all the step lengths quoted in Table I, and the inability of Numerov's method to follow the Bessel functions near the origin can be discounted in these calculations; surprisingly, this problem matters most when the coefficient of the r^{-12} term is very small [6]. However, as we show, the r^{-12} term is still responsible for the marked superiority of the eighth order formula but to some extent this is an artefact of the problem under consideration. The differential equation may be written

$$d^2y(r)/dr^2 - K^2(r)y(r) = 0, \tag{3}$$

where $K(r)$ is a local quantity analogous to a wave number. The leading term of the local relative truncation error of Numerov's method has magnitude of $(hK)^6/240$ approximately and the ratio of the next term to it is about $(hK)^2/23$. The leading term of the local relative truncation error of the eighth order method has magnitude approximately $(hK)^{10}/10^6$. (A factor f was omitted from the first term of Eq. 2.1 of Ref. [3]). The wave function is extremely small near the origin because of the strong repulsion and remains very small until $r \approx 0.8$; numerical experiments show that when the integration is started between the origin and $r = 0.8$ the calculated phase shift is correct to five significant figures but not otherwise. This means that, for five figure accuracy, the local errors become significant in both the Numerov and eighth order calculations only when $r \geq 0.8$.

Table II shows the truncation errors for $k = 1$ (they are not much different for $k = 5$ and $k = 10$). It can be seen that for step length 0.08 the Numerov errors are substantial and, from the last column, that for $r < 0.83$ the h^8 Numerov term is larger than the h^6 term and cannot be ignored. The large errors arise from the r^{-12} term in the potential which causes $K(r)$ to be large, as can be seen in the second column. For $h = 0.04$ the Numerov errors are much smaller; values in the last column would be divided by four. The errors for the eighth order method are much smaller than the Numerov values for $h = 0.08$; while they start large they

TABLE II

Local Truncation Errors with $k = 1$

r	$K(r)$[a]	$(hK)^6/240$[b] ($h = 0.04$)	$(hK)^6/240$[b] ($h = 0.08$)	$(hK)^{10}/10^6$[c] ($h = 0.08$)	$(hK)^2/23$[d] ($h = 0.08$)
0.80	73.3	2.6	170.	50.	1.5
0.81	67.1	1.6	99.	21.	1.3
0.82	61.4	0.9	58.	8.5	1.1
0.83	56.1	0.5	34.	3.5	0.9
0.84	51.3	0.3	20.	1.4	0.7
0.85	46.8	0.2	11.	0.6	0.6
0.86	42.7	0.1	6.6	0.2	0.5
0.87	38.8	0.1	3.7	0.1	0.4

[a] Local wave number.
[b] Numerov.
[c] Eighth order, Ref. [3].
[d] Ratio of Numerov h^8 term to h^6 term.

fall very rapidly. It is by chance that they fall so quickly just in the region where the wave function starts to grow, thus flattering the eighth order method.

The fourth differences of phase shifts induced by a nonsingular potential and calculated by Numerov's method, with its global $\mathcal{O}(h^4)$ error, should be almost constant. In Table III, showing differences of phase shifts calculated for the 6–12 potential at wave number $k = 1$, they start to be constant for step lengths around 0.04; they are constant for smaller step lengths but not for step lengths near 0.08, where the higher power terms in the error expansion can be important. The constant fourth differences allow very accurate phase shifts to be found

TABLE III

Differences and Extrapolation for Numerov's Method with $k = 1$

h	Phase shift	2nd	4th	Extrapolated
0.005	0.15442116	0.00000590	0.00000293	0.15442110
0.010	0.15442293	0.00001302	0.00000302	
0.015	0.15443059	0.00002308		
0.020	0.15445128	0.00003616		
0.025	0.15449505			
0.030	0.15457498			
0.01	0.15442293	0.00009535	0.00005269	0.15442519
0.02	0.15445128	0.00021277	0.00005851	
0.03	0.15457498	0.00038288		
0.04	0.15491144	0.00061150		
0.05	0.15563079			
0.06	0.15696164			
0.02	0.15445128	0.00159003	−0.00073171	Invalid
0.04	0.15491144	0.00369093	0.02088290	
0.06	0.15696164	0.00506013		
0.08	0.16270277	0.02731222		
0.10	0.17350403			
0.12	0.21161752			

by extrapolation. When the step length is increased, the exponential behaviour referred to earlier must eventually be considered. Table III shows the Numerov calculations with a step length of 0.04 to be almost acceptable although less accurate than eighth order calculations; the higher order (in h) errors become less important around the point where the wave function starts to grow.

It is concluded that caution is needed when applying any finite difference method to solve a differential equation with singularities. In particular, the results obtained when testing a new method, such as the eighth order formula, on such an equation must be examined carefully. The eighth order formula is more accurate than Numerov's method (as might be expected) for evaluating scattering by a Lennard–Jones 6–12 potential but it is flattered by this example because the wave function grows significantly just when the local truncation error decreases acceptably.

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