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On the Numerical Solution of Schroedinger's Radial Equation*

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Higher-order difference schemes are considered for the numerical solution of Schroedinger's radial equation. They are a family of difference equations which are extensions of the well-known Numerov difference equation and give highly convergent approximate solutions, the least being $O(h^6)$ compared to $O(h^4)$ in the Numerov equation. An algorithm to find eigenvalues and eigenfunctions using one-directional "shooting" is discussed. The stability and convergence of these schemes are also discussed. An example and numerical results are given, and the order of convergence which is estimated from the results is found to be close to the theoretical value.

1. INTRODUCTION

In diatomic molecules, the problem of finding the eigenvalues and eigenfunctions can be simplified by the Born–Oppenheimer approximation. With this approximation, the Schroedinger equation reduces to a radial equation which governs the vibrational and rotational states of a diatomic molecule. Such problems can be formulated as to find the couple $\{E, y(r)\}$ such that

$$y''(r) = k[V(r) - E]\, y(r), \qquad 0 \leqslant r < \infty, \tag{1}$$

where $k = 8\pi^2\mu/h^2$, subject to the "boundary" conditions

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

$$\lim_{r\to\infty} y(r) = 0. \tag{2b}$$

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A normalization condition may be added resulting simply in multiplying y by a constant.

Typically, problem (1)–(2) is a singular Sturm–Liouville system, and theoretical knowledge about the point spectrum is available (see, for example [1, pp. 107–128]). In particular, if the potential $V(r)$ vanishes as r tends to infinity, the point-spectrum is contained in the negative part of the energy axis. Closed forms or series solutions of the problem are available only in few cases of simple potentials [2, 3], and it becomes necessary, therefore, to look for approximate solutions. This is usually done as follows. The differential equation is replaced by some suitable difference equation, and condition (2b) is replaced by some *finite* end-point boundary condition such as $y(\bar{r}) = 0$, where $\bar{r}$ is a "large" positive number. For a difference scheme to be useful, it has to be *stable* and *accurate*, i.e., not sensitive to small changes due to round-off errors and provides a good approximation to the exact solution. In recent years, the trend has been towards higher-order approximation schemes, and the methods proposed in Section 2 are of the higher-order type. Related aspects of convergence and stability of these schemes are studied in Section 3. Algorithmic implementation is finally discussed in Section 4. In Section 5, we give a numerical example and results.

2. Difference Equations

The Schroedinger radial equation (1) can be put in the more general form

$$y'' = f(r, y). \tag{3}$$

If $f(r, y)$ is linear in y, then (3) reduces to (1). To derive difference equations corresponding to (3), one can either (i) proceed directly from (3) by noting that it does not contain y', or (ii) transform (3) into a system of two first-order equations to which one applies numerous existing methods. As in [4, Chap. 6], we shall take the first point of view.

Consider a uniform partition of the finite interval $(0, \bar{r})$.

$$0 = r_0 < r_1 = h < \cdots < r_k = kh < \cdots < r_N = Nh = \bar{r}.$$

We shall make use of Taylor's formula, assuming henceforth that f and $y(r)$ are sufficiently smooth. Such method has been extensively used [5, p. 620 *et seg.*].

Taylor's expansion of $y(r_{i+1})$ at $r = r_i$ gives

$$y(r_{i+1}) = y(r_i) + hy'(r_i) + (h^2/2!)\, y''(r_i) + \cdots. \tag{4}$$

Replacing h by $-h$ in (4) and adding to (4), we obtain

$$y(r_{i+1}) - 2y(r_i) + y(r_{i-1}) = (2h^2/2!)\, y''(r_i) + (2h^4/4!)\, y^{(4)}(r_i) + \cdots. \tag{5}$$

Differentiating (5) twice, we obtain

$$y''(r_{i+1}) - 2y''(r_i) + y''(r_{i-1}) = (2h^2/2!)\, y^{(4)}(r_i) + (2h^4/4!)\, y^{(6)}(r_i) + \cdots . \quad (6)$$

Elimination of $y^{(4)}(r_i)$ from (5) and (6) gives

$$y(r_{i+1}) - 2y(r_i) + y(r_{i-1}) = (h^2/12)[y''(r_{i+1}) + 10y''(r_i) + y''(r_{i-1})] - (3h^6/6!)\, y^{(6)}(r_i) + O(h^8). \quad (7)$$

Using (3) and eliminating sixth-order terms in (7), one obtains Numerov's difference scheme [6]

$$y_{i+1} - 2y_i + y_{i-1} = (h^2/12)(f_{i+1} + 10f_i + f_{i-1}), \quad (8)$$

where y_i denotes the approximation of $y(r_i)$ and f_i denotes the approximation of $f(r_i, y(r_i))$. Numerov's difference equation (8) is a fourth-order, two-step method which is generally implicit and is reducible to an explicit equation when f is linear (as in the case of the radial equation).

Higher-order schemes can be obtained by two methods: (i) by keeping the same number of steps and then using the derivatives of f (i.e., f_r, f_v, f_{rv}, etc.) if these are easily obtained, or (ii) by increasing the number of steps if one uses $f(x, y)$ only. In general, the potential $V(r)$ may be given discretely, and hence the derivatives are difficult to obtain. It is certainly more practical to extend the size of the interval and use only function values of f.

Replacing h by $2h$ in (5) and (6), we obtain

$$y(r_{i+2}) - 2y(r_i) + y(r_{i-2}) = (2(2h)^2/2!)\, y''(r_i) + (2(2h)^4/4!)\, y^{(4)}(r_i) + (2(2h)^6/6!)\, y^{(6)}(r_i) + \cdots . \quad (9)$$

$$y''(r_{i+2}) - 2y''(r_i) + y''(r_{i-2}) = (2(2h)^2/2!)\, y^{(4)}(r_i) + (2(2h)^4/4!)\, y^{(6)}(r_i) + \cdots . \quad (10)$$

Eliminating $y^{(4)}(r_i)$ from (9) and (10), and then eliminating $y^{(6)}(r_i)$ from the resulting equation and from (7), we obtain

$$y(r_{i+2}) - 2y(r_i) + y(r_{i-2}) = (h^2/15)[y''(r_{i+2}) + 16y''(r_{i+1}) + 26y''(r_i) + 16y''(r_{i-1}) + y''(r_{i-2})] + O(h^8), \quad (11)$$

and

$$y_{i+2} - 2y_i + y_{i-2} = (h^2/15)(f_{i+2} + 16f_{i+1} + 26f_i + 16f_{i-1} + f_{i-2}) + \cdots . \quad (12)$$

This is a sixth-order difference equation. By extending this derivation to $2k$ intervals, one obtains a general form for these difference schemes

$$y_{i+k} - 2y_i + y_{i-k} = h^2 \sum_{j=0}^{k} a_j (f_{i+j} + f_{i-j}). \quad (13)$$

The stability and convergence of these schemes will be discussed in the next section.

3. Stability and Convergence

From the derivation of these schemes, it can be easily shown, by using Taylor's formula, that these are *consistent* $2k$-step methods of order $2k + 2$; i.e., if $y(r)$ is a solution of (3), then

$$y(r_{i+k}) - 2y(r_i) + y(r_{i-k}) = h^2 \sum_{j=0}^{k} a_j[f(r_{i+j}, y(r_{i+j})) + f(r_{i-j}, y(r_{i-j}))] + O(h^{2k+4}). \tag{14}$$

To show that the schemes (13) are *stable*, we shall consider the stability or root condition [4, p. 300]: the modulus of any root of the polynomial which is, in our case,

$$\rho(z) = z^{2k} - 2z^k + 1,$$

may not exceed 1 and the multiplicity of the roots with moduli 1 may not exceed 2. This condition is easily verified in our case since this polynomial is equal to $(z^k - 1)^2$. Thus, every root has modulus 1 and multiplicity 2. Moreover, the difference equations (13) are optimal since the maximum order of a $2k$-step method cannot exceed $2k + 2$.

Since the schemes (13) are consistent and stable, then they are convergent. Moreover, the order of convergence is $2k + 2$, [4, pp. 314–315].

4. Practical Considerations

The implementation of difference schemes to solve two-point boundary value problems and, in particular, the Schroedinger equation is widely discussed by Fox [7, pp. 72–94]. The existing methods are either direct, using matrix methods, or indirect, using "shooting methods." It is recognized [7, pp. 58–72] that shooting methods are simpler, due to smaller storage and programming, and we have thus preferred their use. The simplest shooting method is the one-directional (outward) method. It has been recently formalized by Bhatia and Madan [8]. Due to the existence of undesired "extraneous" solutions which grow to a significant value at large r, Cooley [9] prefers to shoot from both ends of the interval $(0, \bar{r})$; the matching point is chosen inside that interval; a correction formula is used to estimate E for each trial solution.

We have, for simplicity, chosen a one-directional outward shooting method. The present method does not require any a priori knowledge about the solution at $\bar{r}$. Moreover, this method, as will be seen, has exactly the same accuracy as that of Cooley's method, if the same difference equation is used. The experimental results of the present method and the very recent theoretical considerations of Bhatia and Madan were developed independently and are essentially similar. One difference is that we have developed a bisector algorithm to pinpoint the eigenvalue quickly. Another development is how to choose a "convenient" $\bar{r}$. Our main interest is to find the eigenvalues. For this purpose, the normalizing of y is not needed. However, if one is also interested in finding the *normalized* eigenfunctions, a point r_m has to be found as will be explained.

In using (8) or (12), one faces a starting-value problem. Indeed, (8) and (12) are, respectively, two- and four-step methods. In (8), we put $y_0 = 0$ and choose y_1 arbitrarily (about 10^{-12}). As can be seen from (8), y_1 is a factor of the solution and will be adjusted later to normalize y. In (12), however, one needs y_0, y_1, y_2 and y_3 before starting the method. This problem can be solved by using (8) to find y_2 and y_3, and by decreasing the step size on $(0, 3h)$ for the sake of accuracy.

To compute E_n and the corresponding eigenfunction y_n, we start by a first estimate E_n^0 of E_n. If the solution has the correct number of zeros corresponding to E_n, then E_n^0 is acceptable. The eigensolution y_n does not tend to zero at large r. After it approaches the r axis as expected, it either (i) crosses the r axis (at y_m) and goes to infinity, or (ii) reaches a minimum distance (at r_m), turns, and goes to infinity with a sign apposite to that of the first case. The first and second cases depend on whether E_n^0 is larger or smaller than E_n. As the estimated E_n approaches the exact E_n, r_m increases. The interval $(0, y_m)$ is where y_n is "valid." This interval is used in integrating y_n^2 for normalization. The part of y_n beyond r_m may be called the "tail." The reason that the tail goes to infinity is the existence of extraneous solutions. Since y tends to zero asymptotically, the asymptotic solution is the sum of two independent solutions, e^{-sr} and e^{sr}, where s is the positive square root of $-E$. The second solution is the undesired extraneous solution and its coefficient vanishes if $E \neq E_n$. However, due to small errors in estimating E_n and in the computing scheme, this coefficient (and e^{sr}) grows as r increases.

The point $\bar{r}$ is chosen on the tail not too near r_m so that r_m would not increase beyond $\bar{r}$. The point $\bar{r}$ is not chosen too far from r_m in order that $y_n(\bar{r})$ might not have strange behavior due to accumulated error. Next, E_n^0 is increased by a small amount e_0. If $|y_n(\bar{r})|$ decreases, then e_0 is added to E_n^0 several times until $y_n(\bar{r})$ changes sign; if $|y_n(\bar{r})|$ increases, then e_0 is subtracted from E_n^0 until $y_n(\bar{r})$ changes sign at, say, E_n^1. The next choice of E is

$$E_n^2 = \tfrac{1}{2}(E_n^0 + E_n^1). \tag{15}$$

This cycle is repeated until the accuracy of the computer is overshot.

$$e_i = \tfrac{1}{2}e_{i-1}\,, \tag{16b}$$

$$E_n^{i+2} = \tfrac{1}{2}(E_n^{\,i} + E_n^{i+1}), \tag{16b}$$

where e_i is the error. About 20 such iterations are usually done (automatically as indicated above) to compute E_n to 9 or 10 significant figures.

The above method can also be applied, with equal ease, to find the eigenvalues and eigenfunctions of any parameter that may be contained in the expression of $V(r)$. In future work, this advantage may be used to deduce an analytic expression for V from the experimental eigenvalues.

5. Numerical Example

The example is the diatomic molecule H_2^+. The potential is a Morse potential [10],

$$V(r) = D[1 - \exp(-a(r - r_e))] - D,$$

where r_e is the equilibrium internuclear distance and D is the dissociation energy; $r_e = 1.9975$, $a = 0.711248$ and $D = 188.4355$ in units of 2μ a.u. The Morse potential allows an analytic solution for the eigenvalues and the eigenfunctions which can be evaluated exactly. We shall solve the radial equation numerically using (8) and (12) and compare the results with the exact analytic results and with Cooley's results [9]. Cooley used (8) and used the two-directional shooting method.

The present computations were made on an IBM 1130 computer. The eigenvalues computed by the present scheme or method using (8) are exactly the same as those computed by Cooley. The eigenvalues computed by the present method using (12) are presented in Table I where they are compared with the "exact" eigenvalues and with those computed by Cooley. The errors which are presented in Table I, and which are put in brackets, are also presented in Fig. 1 for more clarity. Clearly, the mesh $h = 1/20$ overshot machine accuracy when Eq. (12) was used.

Table II presents the values of the zeroth eigenfunction corresponding to E_0, as computed by different methods. The errors (deviations from the exact value) are used to estimate the order of convergence of the difference scheme, theoretically given as 4 in (8) and 6 in (12). For this purpose, we compute the maximum absolute deviation d_h. Assuming $d_h = ch^\alpha$, then $d_h/d_{h'} = (h/h')^\alpha$, giving

$$\alpha = \log(d_h/d_{h'})/\log(h/h'),$$

where $h = 0.1$ and $h' = h/2 = 0.05$. The last row in Table II gives the estimates of the order of convergence for each computed solution. As one observes, these practical estimates are very close to their respective theoretical values.

TABLE I

Eigenvalues Computed by Different Methods[a]

h	$0.2 = 1/5$	$0.1 = 1/10$	$0.067 = 1/15$	$0.05 = 1/20$
		E_0 (Exact) $= -178.79850$		
E_0(Sixth-order)	-178.79555 (295)	-178.79850 (0)	-178.79853 (3)	-178.79853 (3)
E_0 (Fourth-order)	-178.81052 (1202)	-178.79924 (74)	-178.79866 (16)	-178.79857 (7)
		E_1 (Exact) $= -160.28182$		
E_1 (Sixth-order)	-160.25877 (2305)	-160.28316 (134)	-160.28340 (158)	-160.28342 (160)
E_1 (Fourth-order)	-160.35850 (7668)	-160.28784 (602)	-160.28428 (246)	-160.28368 (186)
		E_2 (Exact) $= -142.77990$		
E_2 (Sixth-order)	-142.67714 (10276)	-142.77902 (88)	-142.77998 (8)	-142.78004 (14)
E_2 (Fourth-order)	-143.02059 (24069)	-142.79397 (1407)	-142.78276 (286)	-142.78090 (100)
		E_3 (Exact) $= -126.28824$		
E_3 (Sixth-order)	-125.99424 (29400)	-126.28562 (262)	-126.28821 (3)	-126.28840 (16)
E_3 (Fourth-order)	-126.83300 (54476)	-126.31918 (4094)	-126.29441 (617)	-126.29031 (207)
		E_4 (Exact) $= -110.80832$		
E_4 (Sixth-order)	-110.14662 (66170)	-110.80258 (574)	-110.80809 (23)	-110.80849 (17)
E_4 (Fourth-order)	-111.81094 (1.00272)	-110.86348 (5516)	-110.81921 (1089)	-110.81191 (359)

[a] Those computed by the method of this article using the sixth-order Eq. (12) are presented in rows indicated by "Sixth-order." Those computed by Cooley using the fourth-order Eq. (8) are indicated by "Fourth-order." Those computed from the analytic solution are indicated by "Exact". All eigenvalues are computed for different mesh sizes h. Numbers in brackets immediately under the eigenvalues are the errors of these eigenvalues (deviations from the exact value). The errors are also shown in Fig. I.

TABLE II

Values of the Zeroth Eigenfunction (corresponding to E_0) at Different Points r and for Different Mesh Sizes h[a]

r	Exact	Sixth-order HKN	Fourth-order HKN	Fourth-order Cooley
		$h = 0.1$		
1.2	0.0223746	0.0223724 (22)	0.0223865 (119)	0.0223875 (129)
1.6	0.4859927	0.4859831 (96)	0.4858638 (1289)	0.4858844 (1093)
2.0	1.3101405	1.3100755 (650)	1.3102091 (686)	1.3102630 (1225)
2.4	0.734876	0.7348251 (225)	0.7347070 (1406)	0.7347376 (1100)
2.8	0.1265004	0.1264950 (54)	0.1264854 (150)	0.1264907 (97)
3.2	0.0089541	0.0089540 (1)	0.0089547 (7)	0.0089544 (3)
		$h = 0.05$		
1.2	0.0223746	0.0223745 (1)	0.0223753 (7)	0.0223754 (8)
1.6	0.4859927	0.4859931 (4)	0.4859863 (24)	0.4859864 (23)
2.0	1.3101405	1.3101393 (12)	1.3101471 (66)	1.3101471 (66)
2.4	0.7348476	0.7348480 (4)	0.7348412 (64)	0.7348413 (63)
2.8	0.1265004	0.1265003 (1)	0.1264996 (8)	0.1264998 (6)
3.2	0.0089541	0.0089540 (1)	0.0089531 (10)	0.0089541 (0)
Order of convergence		5.8	4.4	4.2

[a] Columns headed "Exact" are computed from the analytic solution; columns headed "Sixth-order HKN" and "Fourth-order HKN" are computed by the method of this article using Eq. (12) and Eq. (8), respectively. Values computed by Cooley are in the last column. Numbers in brackets immediately under the values are the errors of these values (deviations from the exact value). The order of convergence is presented in the last row.

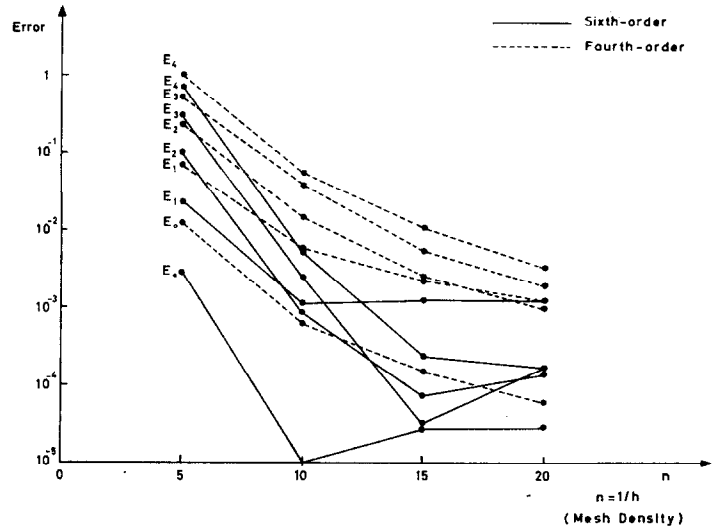

FIG. 1. The plot of the error of the eigenvalues shown in Table I vs mesh density $n = 1/h$. The vertical scale is a logarithmic scale. The errors in the $n = 1$ eigenvalues are larger than one would expect, based on the results for other eigenvalues. This is probably due to a small error in the computed "exact" value (taken from Cooley).

In the above computations, r_m ranged from about 4.0 for E_0 to about 5.0 for E_4. To find the normalization factor, a five-point Newton–Cotes formula was used to evaluate the integral, since the error in this formula is about the same order as that in (12).

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