JOURNAL OF COMPUTATIONAL PHYSICS 11, 458–462 (1973)

Letter to the Editor

Comparison of the Finite Difference Boundary Value Method and the Cooley–Cashion–Zare Method for Solving One-Dimensional Eigenvalue Equations

Truhlar [1] has recently described a finite difference boundary value method (FDBV method) for determining eigenvalues and eigenfunctions of the one-dimensional Schrodinger equation. In this note it is shown that his implementation of this method is inferior in several important respects to the method introduced by Cooley [2] and developed by Cashion [3] and Zare [4] (CCZ method), and since then widely used [5–7]. Both methods are considered and compared.

It is required to obtain solutions of the radial Schrodinger equation

$$[(d^2/dR^2) - U(R)]\,\phi_n(R) = \lambda_n \phi_n(R), \tag{1}$$

satisfying

$$\phi_n(0) = 0 \qquad \text{and} \qquad \phi_n(R) \xrightarrow[R\to\infty]{} 0, \tag{2}$$

where $U(R) = (2\mu/\hbar^2)\,V(R) + l(l+1)/R^2$, $\lambda_n = -(2\mu/\hbar^2)\,E_n$ and the parameters have their usual significance. Trivial modifications to the boundary conditions (2) are required if a real one-dimensional problem is considered, and they do not affect the following discussion. The boundary conditions (2) are approximated by $\phi_n(R_s) = \phi_n(R_r) = 0$, where the precise values chosen for R_s and R_r depend on the potential $U(R)$ and λ_n. More efficient procedures for satisfying the right-hand boundary condition will be mentioned below.

Both methods use a finite difference approximation to the differential operator to convert the problem to that of determining the eigenvalues of a band matrix of high order. Significant differences exist both in the choice of finite difference approximation and in the method of solving for the eigenvalues.

Consider a grid of N mesh points, $R_i = R_s + ih$, $1 \leqslant i \leqslant N$, where $h = (R_r - R_s)/(N+1)$. The use of varying step sizes [8] makes no significant difference to the comparison between the two methods. In the FDBV method a three point central difference formula [9] is used for the differential operator. Then Eq. (1) is approximated, with a truncation error of order h^4, by the matrix equation

$$(\mathbf{A} - \lambda \mathbf{I})\,X = 0, \tag{3}$$

where **A** is a symmetric, tridiagonal matrix with elements $A_{i,i} = -(2/h^2 + U_i)$, $A_{i,i\pm1} = 1/h^2$, $U_i = U(R_i)$, $(X)_i = \phi_n(R_i)$ and the suffix has been dropped on the eigenvalue and eigenvector. Alternatively, the CCZ method uses the Numerov formula [9]. This yields, with a truncation error of order h^6,

$$(\mathbf{A}' - \lambda\mathbf{B})\, X = 0, \tag{4}$$

where $\mathbf{A}'$ and **B** are tridiagonal matrices with elements $A'_{i,i} = -(2/h^2 + 5U_i/6)$, $A'_{i,i\pm1} = 1/h^2 - (1/12)\, U_{i\pm1}$, $B_{i,i} = 5/6$, $B_{i,i\pm1} = 1/12$. Typically the matrices may be of order up to 1000.

The FDBV method apparently uses the Sturm sequence technique [10] to determine the eigenvalues of **A**. (In [1] the Givens-Householder method is quoted. Both the Givens method and the Householder method are used to transform real symmetric matrices to tridiagonal form [11]. Since **A** is already tridiagonal this transformation is not required. However the method used in the program in [10] to find the eigenvalues of a symmetric tridiagonal matrix is the Sturm sequence technique). This technique involves bisection of an interval known to contain the required root, so, if eigenvalues are required to an accuracy of 10^{-6} of their separation, then roughly 20 iterations will be necessary. The advantages of this technique are that it is very stable and that a specified eigenvalue can be calculated without finding all the eigenvalues of the matrix [11]. This property is almost essential when perhaps less than 50 of the eigenvalues are of interest. The Sturm sequence technique does not yield the corresponding eigenvector, which is usually obtained by inverse iteration [11].

The technique used by the CCZ method to solve Eq. (4) employs Newton's method to determine the zeroes of a function closely related to the characteristic polynomial. Since the vibrational energy levels of diatomic molecules are well separated the characteristic polynomial has single roots, so quadratic convergence is obtained. The technique may also be considered as an inverse iteration to find the eigenvalue of Eq. (4) which is closest to a trial eigenvalue λ^*, followed by a correction to λ^* [11]. An approximate eigenvector X_1 is generated by solving $X_1 = (\mathbf{A}' - \lambda^*\mathbf{B})^{-1} X_0$, where X_0 can be almost arbitrary [11]. An improved eigenvalue is obtained from

$$\begin{aligned}\lambda &\approx \lambda^* + [X_1^T(\mathbf{A}' - \lambda^*\mathbf{B})\, X_1]/(X_1^T X_1) \\ &= \lambda^* + X_1^T X_0/(X_1^T X_1).\end{aligned} \tag{5}$$

The trial eigenvector X_0 has all elements except the r-th equal to zero, so finding X_1 is similar to evaluating a three term recurrence relation. The application of this technique to Eq. (3) has been discussed in detail by Osborne [12] and Sykes [13]. For this case it is equivalent to obtaining an improved eigenvalue using the Rayleigh quotient of the approximate eigenvector X_1.

However no matrix theory has been obtained for the full Numerov approximation, Eq. (4). Since $\mathbf{A}'$ in Eq. (4) is unsymmetric a direct application of the Rayleigh quotient [12] to improve the eigenvalue would require the eigenvector of both Eq. (4) and its transpose. A symmetric form of Eq. (4) can be obtained by introducing $Y = \mathbf{D}X$, where $D_{ij} = \delta_{i,j}[1 - (h^2/12)(U_i + \lambda)]$. Then Y satisfies

$$(\mathbf{A}'' - \lambda\mathbf{B})\ Y = 0 \tag{6}$$

where $A''_{i,i\pm1} = (1/h^2) - U_i/12$, $A''_{i,i} = -((2/h^2) + 5U_i/6)$. While the Rayleigh quotient method could be used, with $\mathbf{D}X_1$, to improve λ^*, this would yield

$$\lambda = \lambda^* + (X_1{}^T\mathbf{D}\mathbf{D}X_0)/(X_1{}^T\mathbf{D}\mathbf{B}\mathbf{D}X_0), \tag{7}$$

which is slightly different from Eq. (5). The CCZ method writes Eq. (4) as

$$[\mathbf{A} + \lambda\mathbf{D}^{-1} + (\mathbf{D}^{-1} - \mathbf{I})\ \mathbf{U}]\ Y = 0, \tag{8}$$

$$\text{where } U_{ij} = \delta_{i,j}U_i\,.$$

Since Eq. (8) is nonlinear in λ, no simple direct connection with matrix methods seems possible. However, because of the closeness of Eqs. (5) and (7) it seems reasonable to assume that the convergence properties of the two methods for improving the eigenvalue will be similar. Equation (5) should then converge on the desired eigenvalue, if λ^* lies in the interval bounded by the pair of adjacent roots of D_{r-1}, the $(r-1)$-th principal minor of the determinant of $(\mathbf{A}'' - \lambda\mathbf{B})$ [12].

With the use of a trial eigenvalue λ^* it is possible to employ a WKB type solution to approximate the boundary condition for large R. The calculation required to improve a trial eigenvalue is comparable with that for a single bisection in the Sturm sequence technique. Blatt [14] has discussed how the number of changes of sign in X_1 can be used to check that convergence to the desired eigenvalue is occurring, thus almost eliminating this disadvantage of iterative methods. Counting the number of sign changes, which is related to the Sturm sequence property, was used by Harrison and Bernstein [15] for finding eigenvalues and eigenvectors. It should be noted that Le Roy and Bernstein [5] switched to the CCZ method partly because of its superior convergence. The general eigenvalue problem of the form of Eq. (6) has been discussed by Peters and Wilkinson [16]. They recommend the use of the Sturm sequence to isolate an eigenvalue, followed by interpolation in the characteristic polynomial to improve it. They mention the use of inverse iteration and the Rayleigh quotient but say that it is not easy to ensure convergence to specific vectors. For the vibrational eigenvalue problem this does not seem to be a serious difficulty.

Generally spectroscopic information allows quite good initial estimates to be employed, so that four or five iterations are normally sufficient to obtain an eigenvalue with a precision limited only by the machine wordlength. Cooley [2, Table 1] gives examples of the convergence for the pathological case of the trial eigenvalue lying about midway between λ_0 and λ_1. There when λ^* was slightly closer to λ_0, convergence to λ_0 occurred in nine iterations, while with λ^* slightly closer to λ_1 convergence to λ_1 occurred in six iterations, in both cases with an accuracy of about one part in 10^7.

Hence, it may be seen that this technique shares with the Sturm sequence technique the ability to obtain a particular eigenvalue, and, while it does not have the same stability in general, it has second order rather than first order convergence properties for vibrational eigenvalues.

Truhlar [1] discusses in detail the extrapolation of the calculated eigenvalues of (3) to zero step size. With the central difference formula used in [1] the cumulative error is of order h^2 and is an even function of h [1]. Because of the h^2 error a fairly large correction, 0.4% of the eigenvalue separation, was necessary even with $N = 1000$ for the $v = 9$ level. For the Numerov method the cumulative error behaves as h^4 [17] and it has seldom been considered worthwhile running several grids and extrapolating to zero step size, although the success of this procedure in [1] suggests that some savings might be obtained. It is interesting that a simple extrapolation to zero step size, as a function of h^4, applied to the two smallest step sizes in Table 2 of [2] improves the agreement with the exact results by between a factor of 2 for $v = 0$ and a factor of 17 for $v = 4$. (There is a misprint in this table for the exact value of E_1. It should read -160.28332.)

A direct comparison between the FDBV and CCZ 150 point integrations for the $v = 0$ and $v = 2$ levels shows that in both cases the ratio of the error in the eigenvalue to the eigenvalue separation is about 100 times smaller in the CCZ method than in the FDBV method.

Hence, as well as determining the eigenvalues more efficiently the CCZ method finds the eigenvalues resulting from a superior finite difference approximation to the differential Eq. (1).

The success of the inverse iteration technique for determining the eigenvalues of the finite difference matrix suggests that this technique should also be useful for eigenvalue methods employing expansion in a basis set (see refs. in [1, 18–20]), since the eigenvalue distribution will be very similar. A related quadratically convergent method has been employed [18] and a Rayleigh quotient method has also been used successfully [21]. The quadratically convergent techniques should make expansion-in-a-basis-set methods very competitive with finite difference methods [20], since they should be able to use much smaller matrices in many cases.

ACKNOWLEDGMENTS

I wish to thank Mr. D. Banks and Mr. J. McB. Wilson for their comments on this manuscript and Dr. S. Bell for a useful discussion.

RECEIVED: October 4, 1972

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Printed in Belgium