JOURNAL OF COMPUTATIONAL PHYSICS 105, 169–172 (1993)

NOTE

Johnson's Log Derivative Algorithm Rederived

1. INTRODUCTION

A variety of scattering and bound state problems in chemistry and physics can, to a good approximation, be reduced to the solution of a radial matrix Schrödinger equation with the general form

$$\Psi''(r) = W(r)\,\Psi(r), \tag{1}$$

where $W(r)$ and $\Psi(r)$ are N by N matrices and the primes denote differentiation with respect to r. Johnson's log derivative algorithm is a stable and efficient numerical method for integrating these "close coupled" equations [1]. Since it was first introduced in 1973 it has found wide application in the chemical physics literature, two recent examples being provided by the hyperspherical coordinate $F+H_2$ reactive scattering calculations of Bačić *et al.* [2], and the related hyperspherical coordinate H_3^+ bound state calculations of Hutson and Jain [3].

Despite this continuing popularity, no really transparent derivation of the log derivative algorithm has yet appeared. Johnson's own derivation [4], which was based on the amplitude density method [5], has never been published in full. The only derivation which *has* appeared in the open literature is that of Mrugała and Secrest [6]. This derivation has already proved useful as a basis for several improvements [7, 8] and extensions [9, 10] to the original algorithm. However, since it relies on a highly sophisticated form of invariant embedding [6, 11], it is inevitably quite complicated to describe. This short note contains a simpler derivation based solely on finite difference approximations to $\Psi(r)$.

2. JOHNSON'S ALGORITHM

Johnson's algorithm focusses on the log derivative matrix $Y(r)$, which is defined in terms of the regular solution matrix $\Psi(r)$ of Eq. (1) by the matrix Riccati transformation

$$\Psi'(r) = Y(r)\,\Psi(r). \tag{2}$$

Differentiating this defining relation throughout with respect to r, and using Eq. (1) to remove the second derivative term $\Psi''(r)$, we obtain the matrix Riccati equation [1]

$$Y'(r) = W(r) - Y(r)^2. \tag{3}$$

This first-order differential equation can be solved to give $Y(r)$ at all r once some appropriate initial value has been found [8], and the asymptotic ($r \to \infty$) form of $Y(r)$ then contains essentially *all* of the physically relevant information that can be extrated from Eq. (1). This follows, both for scattering [1] and for bound state [12] problems, because any irrelevant constant post-multiplicative matrix factor in $\Psi(r)$, which cancels from both sides of Eq. (1), also cancels from both sides of Eq. (2).

It should be clear from Eq. (2) that the definition of $Y(r)$ breaks down whenever $|\Psi(r)| = 0$. These singularities prohibit the naive numerical integration of Eq. (3) by adaptive quadrature methods [13], because it is not clear how these methods would propagate the solution across a pole. The difficulty can be avoided for single channel problems by switching between the Riccati equations satisfied by the log derivative $Y(r)$ and its inverse $R(r) = Y(r)^{-1}$ [14]. This procedure cannot reliably be extended to multichannel problems, however, because different eigenvalues of the $Y(r)$ and $R(r)$ matrices can simultaneously become undefined.

The singularities implied by Eq. (2) *are* effectively avoided in Johnson's algorithm [1], which does not approximate $Y(r)$ continuously at all r. Instead, the solution $\Psi(r)$ of Eq. (1), which remains well defined and continuous for all r, is approximated using the finite difference formulae

$$\Psi_{n+1} - h\Psi'_{n+1} + \frac{h^2}{3}\Psi''_{n+1} = \Psi_n - \frac{h^2}{6}\Psi''_n + \frac{h^4}{24}\Psi^{\mathrm{iv}}_n + O(h^5), \tag{4}$$

$$\Psi_{n-1} + h\Psi'_{n-1} + \frac{h^2}{3}\Psi''_{n-1} = \Psi_n - \frac{h^2}{6}\Psi''_n + \frac{h^4}{24}\Psi^{\mathrm{iv}}_n + O(h^5), \tag{5}$$

0021-9991/93 $5.00

and

$$\Psi_{n+1}+\Psi_{n-1}=2\left(\Psi_n+\frac{h^2}{2}\Psi_n''+\frac{h^4}{24}\Psi_n^{\mathrm{iv}}\right)+O(h^6), \quad (6)$$

where $f_n \equiv f(r_n)$ and $h=r_{n+1}-r_n=r_n-r_{n-1}$. (Equation (6) is the well-known central difference approximation for a second derivative, and Eqs. (4) and (5) are related by symmetry in $\pm h$.)

The derivation of the algorithm from these formulae is straightforward. First, we use Eqs. (1) and (2) to rearrange Eqs. (4) to (6):

$$\Psi_{n+1}=\left(I-hY_{n+1}+\frac{h^2}{3}W_{n+1}\right)^{-1}\left(I-\frac{h^2}{6}W_n\right)\times\left(\Psi_n+\frac{h^4}{24}\Psi_n^{\mathrm{iv}}\right)+O(h^5), \quad (7)$$

$$\Psi_{n-1}=\left(I+hY_{n-1}+\frac{h^2}{3}W_{n-1}\right)^{-1}\left(I-\frac{h^2}{6}W_n\right)\times\left(\Psi_n+\frac{h^4}{24}\Psi_n^{\mathrm{iv}}\right)+O(h^5), \quad (8)$$

and

$$\Psi_{n+1}+\Psi_{n-1}=2\left(I+\frac{h^2}{2}W_n\right)\left(\Psi_n+\frac{h^4}{24}\Psi_n^{\mathrm{iv}}\right)+O(h^6). \quad (9)$$

Next, we note that the error terms involving even powers of h in Eqs. (7) and (8) have the same sign, whereas those involving odd powers of h have opposite signs. (For example, the leading $O(h^5)$ error term in Eq. (7) is $+(h^5/45)\,\Psi_n^{\mathrm{v}}$, whereas that in Eq. (8) is $-(h^5/45)\,\Psi_n^{\mathrm{v}}$.) The odd error terms therefore cancel when we add Eqs. (7) and (8), subtract Eq. (9), post-multiply by

$$\left(\Psi_n+\frac{h^4}{24}\Psi_n^{\mathrm{iv}}\right)^{-1}\left(I-\frac{h^2}{6}W_n\right)^{-1}$$

and use the identity

$$2\left(I+\frac{h^2}{2}W_n\right)\left(I-\frac{h^2}{6}W_n\right)^{-1}=8\left(I-\frac{h^2}{6}W_n\right)^{-1}-6I, \quad (10)$$

to give

$$\left(I-hY_{n+1}+\frac{h^2}{3}W_{n+1}\right)^{-1}+\left(I+hY_{n-1}+\frac{h^2}{3}W_{n-1}\right)^{-1}=8\left(I-\frac{h^2}{6}W_n\right)^{-1}-6I+O(h^6), \quad (11)$$

in which only the even error terms remain.

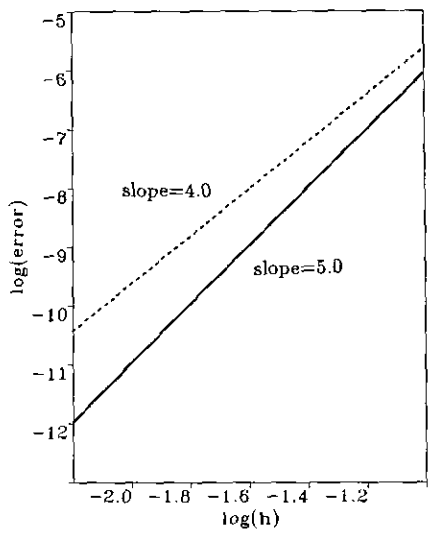

FIG. 1. Numerical test of the log derivative algorithm for a single channel problem with $W(r)=1$ and $Y(r)=1$. The differential equation $Y'(r)=W(r)-Y(r)^2$ is integrated numerically from $r=0$ to $r=1$ in a total of $m=1/(2h)$ steps using Eq. (11). The two curves show the log of the error in the calculated $Y(r)$ at $r=2h$ (solid line) and at $r=1$ (dashed line) as a function of $\log(h)$. Clearly, the local error in $Y(r)$ after one step is $O(h^5)$, whereas the global error after integrating across a fixed interval is $O(h^4)$.

This final propagation relation forms the basis of the algorithm [1]. It is easily rearranged to give Y_{n+1} in terms of Y_{n-1} and the intermediate coefficient matrices W_{n-1}, W_n, and W_{n+1}. Equation (11) gives the local error in hY_{n+1} as $O(h^6)$, so that the local error in Y_{n+1} is $O(h^5)$. Repeated application of the equation gives a global error of $O(h^4)$, because the number of steps required to cross a given interval scales as $O(h^{-1})$ (Fig. 1). These errors have the same orders as those in the renormalised Numerov method [15], which can be derived in an analogous way (i.e., starting from a finite difference approximation to $\psi(r)$ with a local error of $O(h^6)$).

Johnson has described how both scattering [1] and bound state [12] boundary conditions can be applied in the solution of Eq. (1). Several other implementational details of the algorithm are also well explained in his papers [1, 12], so they need not be repeated here.

3. MRUGAŁA'S EXTENSION

Mrugała [9] has derived an extension of Johnson's algorithm for inhomogeneous close coupled equations of the form

$$\psi''(r)=W(r)\,\psi(r)+w(r), \quad (12)$$

in which the matrices $\psi(r)$ and $w(r)$ are in general N by M. Equations of this form arise naturally via perturbation

theory approximations to problems involving both strong and weak coupling, such as the driven equation approach to molecular photodissociation described by Band *et al.* [16]. Mrugała's extension for solving Eq. (12) has recently been used, for example, in a study of quantum flux redistribution during the photodissociation of CH_3I [17]. We now quickly rederive this extension in a way which highlights the connection with Section 2.

The starting point for solving Eq. (12) by the log derivative method is the inhomogeneous matrix Riccati transformation [14]

$$\psi'(r) = Y(r)\,\psi(r) + y(r), \tag{13}$$

in which the matrix $y(r)$ is again obviously N by M. The first-order differential equation satisfied by $y(r)$ can be found by differentiating Eq. (13) throughout with respect to r, using Eq. (12) to remove the second derivative term $\psi''(r)$, and noting that $Y(r)$ satisfies Eq. (3):

$$y'(r) = w(r) - Y(r)\,y(r). \tag{14}$$

The quickest way to proceed from here is to note that Eqs. (3) and (14) can be combined in the single equation

$$\mathbf{Y}'(r) = \mathbf{W}(r) - \mathbf{Y}(r)^2, \tag{15}$$

where $\mathbf{W}(r)$ and $\mathbf{Y}(r)$ are the $N+M$ by $N+M$ matrices

$$\mathbf{W}(r) = \begin{bmatrix} W(r) & w(r) \\ 0 & 0 \end{bmatrix} \tag{16}$$

and

$$\mathbf{Y}(r) = \begin{bmatrix} Y(r) & y(r) \\ 0 & 0 \end{bmatrix}. \tag{17}$$

Since Eq. (15) has the same form as Eq. (3), it can be integrated using the same methods. The appropriate extension of Johnson's algorithm for solving Eq. (12) is therefore given immediately by Eq. (11) as

$$\left(\mathbf{I} - h\mathbf{Y}_{n+1} + \frac{h^2}{3}\mathbf{W}_{n+1}\right)^{-1} + \left(\mathbf{I} + h\mathbf{Y}_{n-1} + \frac{h^2}{3}\mathbf{W}_{n-1}\right)^{-1} = 8\left(\mathbf{I} - \frac{h^2}{6}\mathbf{W}_n\right)^{-1} - 6\mathbf{I}. \tag{18}$$

As it stands, this algorithm is not particularly efficient, because it does not exploit the special form of the matrices $\mathbf{W}(r)$ and $\mathbf{Y}(r)$. However, any matrix $\mathbf{M}$ with the partitioned form

$$\mathbf{M} = \begin{bmatrix} M & m \\ 0 & I \end{bmatrix}, \tag{19}$$

can be inverted to give

$$\mathbf{M}^{-1} = \begin{bmatrix} M^{-1} & -M^{-1}m \\ 0 & I \end{bmatrix}, \tag{20}$$

so that the inversions in Eq. (18) can be streamlined. (This is especially true when, as is usually the case, the matrices $W(r)$ and $Y(r)$ are real symmetric [18].) We have checked in detail that the resulting streamlined algorithm is equivalent to the algorithm described by Mrugała [9]. Moreover, in the present form, it is easy to see how this algorithm can be programmed with only a slight modification of a standard inelastic scattering code.

The application of outgoing wave photodissociation boundary conditions in the solution of Eq. (12) has been described in some detail by Mrugała [9]. The only thing worth adding here is that, since it does not involve any new numerical approximations, the error analysis given in Section 2 for Johnson's algorithm applies equivalently to Mrugała's extension. Equation (15) also suggests how other log derivative algorithms [7, 8] might be adapted to solve Eq. (12).

4. SUMMARY

According to Secrest, in his early review of numerical methods for solving Eq. (1), Johnson's algorithm can be classified as an approximate solution method of the invariant embedding type [19]. It is an approximate solution method, rather than an approximate potential method, because the solution $\Psi(r)$ is fit to a low-order polynomial rather than the coefficient matrix $W(r)$. It is an invariant embedding method because the propagated quantity is the log derivative matrix $Y(r)$ rather than the solution matrix $\Psi(r)$.

In general, approximate solution methods are expected to be more efficient than approximate potential methods when the solution is more slowly varying than the potential; this is typically the case for low-energy scatering and bound-state calculations. Thus Johnson's algorithm is a stable and efficient method for solving Eq. (1) in regions where the solution $\Psi(r)$ is slowly varying. In practice, for higher energy scattering problems, it is recommended to combine the algorithm with an approximate potential algorithm at long range (large r), where the potential is varying more slowly than the wavefunction [20].

The present derivation of Johnson's algorithm makes its approximate solution nature abundantly clear—via Eqs. (4) to (6)—and shows that even though it is an invariant embedding method it can be derived without recourse to specialised invariant embedding techniques [6, 11]. The present error analysis also reveals that the global error in the propagated log derivative matrix only contains even powers of h behond h^4.

ACKNOWLEDGMENT

A.D.P. is supported by the National Science Foundation through its funding of the Institute for Theoretical Atomic and Molecular Physics.

REFERENCES

1. B. R. Johnson, *J. Comput. Phys.* **13**, 445 (1973).
2. Z. Bačić, J. D. Kress, G. A. Parker, and R. T. Pack, *J. Chem. Phys.* **92**, 2344 (1990).
3. J. M. Hutson and S. Jain, *J. Chem. Phys.* **91**, 4197 (1989).
4. B. R. Johnson, private communication, 1986.
5. B. R. Johnson and D. Secrest, *J. Math. Phys.* **7**, 2187 (1966).
6. F. Mrugała and D. Secrest, *J. Chem. Phys.* **78**, 5954 (1983).
7. D. E. Manolopoulos, *J. Chem. Phys.* **85**, 6425 (1986).
8. D. E. Manolopoulos, Ph.D. thesis, Cambridge University, 1988 (unpublished).
9. F. Mrugała, *J. Comput. Phys.* **58**, 113 (1985).
10. M. H. Alexander, G. Parlant, and T. Hemmer, *J. Chem. Phys.* **91**, 2388 (1989).
11. J. V. Lill, T. G. Schmalz, and J. C. Light, *J. Chem. Phys.* **78**, 4456 (1983).
12. B. R. Johnson, *J. Chem. Phys.* **67**, 4086 (1977).
13. J. D. Lambert, *Computational Methods for Ordinary Differential Equations* (Wiley, New York, 1986).
14. M. R. Scott, *Invariant Imbedding and its Applications to Ordinary Differential Equations* (Addison–Wesley, Reading, MA, 1973).
15. B. R. Johnson, *J. Chem. Phys.* **69**, 4678 (1978).
16. Y. B. Band, K. F. Freed, and D. J. Kouri, *J. Chem. Phys.* **74**, 4380 (1981).
17. D. E. Manolopoulos and M. H. Alexander, *J. Chem. Phys.* **97**, 2527 (1992).
18. J. J. Dongarra, C. B. Moler, J. R. Bunch, and G. W. Steward, *Linpack User's Guide* (SIAM, Philadelphia, 1979), Chap. 5.
19. D. Secrest, in *Atom–Molecule Collision Theory: A Guide for the Experimentalist*, edited by R. B. Bernstein (Plenum, New York, 1979).
20. L. D. Thomas, M. H. Alexander, R. B. Walker, B. R. Johnson, W. A. Lester, J. C. Light, K. D. McLenithan, G. A. Parker, M. J. Redmond, T. G. Schmalz, and D. Secrest, *J. Comput. Phys.* **41**, 407 (1981).

Received October 30, 1990; accepted June 17, 1992

DAVID E. MANOLOPOULOS

Department of Chemistry
University of Nottingham, Nottingham, England

MICHAEL J. JAMIESON

Department of Computing Science
University of Glasgow, Glasgow, Scotland

ATUL D. PRADHAN

Harvard-Smithsonian Center for Astrophysics
60 Garden Street, Cambridge, Massachusetts