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Note

The Multichannel Log-Derivative Method for Scattering Calculations*

A new method for solving multichannel scattering problems is presented. The key to the method is an efficient algorithm for numerically solving the matrix Ricatti equation for the logarithmic derivative of the wave function. This method has several advantages: it is simple to program, no special difficulties are encountered with closed channels, it is self-starting, the step size can be easily changed, no difficulties arise from starting the solution well inside the classically forbidden region, and it is somewhat more efficient of computer time than the matrix Numerov method [1] for computing an S-matrix.

The matrix Schroedinger equation can be written in the form

$$[d^2/dx^2 + \mathscr{V}(x)]\,\psi(x) = \mathbf{0}, \tag{1}$$

where

$$\mathscr{V}(x) = (2\mu/\hbar^2)[E\mathbf{I} - \mathbf{V}(x) - \mathscr{E}]. \tag{2}$$

E is the total energy, μ is the reduced mass, $\mathbf{V}(x)$ is the symmetric potential matrix that includes the centrifugal potential which approaches zero as x approaches infinity, and $\mathscr{E}$ is a diagonal matrix whose elements are the threshold energies of the various channels. Channels with thresholds greater than E are said to be closed; otherwise they are open. The wave function $\psi(x)$ is a square matrix, each column being a linearly independent solution of the problem.

The log-derivative matrix is defined to be

$$\mathbf{y}(x) = \psi'(x)\,\psi^{-1}(x), \tag{3}$$

where the prime means differentiation with respect to x. Differentiating Eq. (3) and using Eq. (1) to eliminate the second derivative term, we obtain the matrix Ricatti equation

$$\mathbf{y}'(x) + \mathscr{V}(x) + \mathbf{y}^2(x) = \mathbf{0}, \tag{4}$$

which is well known [2, 3], at least in its single channel version. Methods of

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solution for the single channel case based on continued fractions [4, 5] and quasi-linearization [6] have been published.

The usual boundary condition at the origin for a scattering problem is, $\psi(0) = \mathbf{0}$, $\psi'(0)$ is arbitrary as long as it leads to linearly independent solutions. A convenient choice is $\psi'(0) = \mathbf{I}$ ($\mathbf{I}$ is the unit matrix). This means (see Eq. (3)) that $\mathbf{y}(0)$ is a diagonal matrix with infinite diagonal elements. Since $\mathbf{y}(x)$ is initially diagonal and since $\mathscr{V}(x)$ is symmetric, Eq. (4) requires $\mathbf{y}(x)$ to be a symmetrix matrix.

Equation (4) cannot be integrated by the usual numerical techniques for solving differential equations because $\mathbf{y}(x)$ diverges for certain values of x and it is impossible to integrate across these points.

The nature of this problem is illustrated by the solution to a simple one channel problem in which $\mathscr{V}$ is a constant

$$y(x) = \mathscr{V}^{1/2} \operatorname{ctn}[\mathscr{V}^{1/2} x]. \tag{5}$$

Although our algorithm for numerically integrating Eq. (4) is quite simple, its derivation by invariant imbedding techniques is too lengthy to be presented here.[1]

The algorithm is as follows:

$$\mathbf{y}_n = (\mathbf{I} + h\mathbf{y}_{n-1})^{-1}\, \mathbf{y}_{n-1} - (h/3)\, w_n \mathbf{u}_n\,, \tag{6}$$

where h is the spacing between integration points and

$$\mathbf{u}_n = \begin{cases} \mathscr{V}(x_n) & n = 0, 2, 4, \ldots, N, \\ [\mathbf{I} + (h^2/6)\, \mathscr{V}(x_n)]^{-1}\, \mathscr{V}(x_n) & n = 1, 3, 5, \ldots, N-1. \end{cases} \tag{7}$$

The weights, w_n, are the same as in the Simpson integration rule, i.e.,

$$w_n = \begin{cases} 1 & n = 0, N, \\ 4 & n = 1, 3, 5, \ldots, N-1, \\ 2 & n = 2, 4, 6, \ldots, N-2. \end{cases} \tag{8}$$

Just as in a Simpson integration the total number of integration points must be odd. The truncation error varies as the fourth power of h,

$$\mathbf{y}(x_N) = \mathbf{y}_N + \mathbf{C}h^4 + \mathbf{O}(h^6), \tag{9}$$

where $\mathbf{C}$ is some unknown constant matrix, $\mathbf{O}(h^6)$ is a matrix of order h^6, $\mathbf{y}(x_N)$ is the exact value, and $\mathbf{y}_N$ is the approximate value computed by our method. Equation (9) can be used to derive a Richardson extrapolation formula [7].

[1] The derivation will appear in a future article which will deal in greater detail with log-derivative techniques and applications to bound state and scattering problems.

It should be noted that only at the final integration point $n = N$ is the numerical value of $\mathbf{y}_n$ a good approximation to the value of $\mathbf{y}(x_n)$. This, however, is no problem, since in scattering calculations we are only interested in the value of $\mathbf{y}(x)$ at the final integration point.

In practice we can save one multiplication per step by solving for the quantity $\mathbf{z}_n = h\mathbf{y}_n$. Multiplying Eq. (6) across by h gives

$$\mathbf{z}_n = (\mathbf{I} + \mathbf{z}_{n-1})^{-1}\,\mathbf{z}_{n-1} - (h^2/3)\,w_n\mathbf{u}_n\,. \tag{10}$$

The matrix $\mathbf{y}_N$ is then recovered in a final calculation

$$\mathbf{y}_N = h^{-1}\mathbf{z}_N\,. \tag{11}$$

In making a numerical calculation, the infinite diagonal elements of $\mathbf{y}(0)$ can be replaced by finite but very large numbers, such as 10^{20}; thus, initially we could take

$$\mathbf{y}_0 = 10^{20}\mathbf{I}, \qquad \text{or} \quad \mathbf{z}_0 = 10^{20}\,\mathbf{I}. \tag{12}$$

The reaction matrix $\mathbf{K}$ is defined by the asymptotic behavior of the wave function. In the region $x \geqslant x_N$, in which all but the centrifugal part of the potential has become negligible, the wave function is

$$\Psi(x) \underset{x\geqslant x_N}{=} \mathbf{J}(x) + \mathbf{N}(x)\,\mathbf{K}. \tag{13}$$

The matrices $\mathbf{J}(x)$ and $\mathbf{N}(x)$ are diagonal. The matrix elements of the open channels are made up of Riccati–Bessel functions [8, 9]

$$[\mathbf{J}(x)]_{ij} = \delta_{ij}k_j^{-1/2}\hat{\jmath}_{l_j}(k_jx), \tag{14}$$

$$[\mathbf{N}(x)]_{ij} = \delta_{ij}k_j^{-1/2}\hat{n}_{l_j}(k_jx), \tag{15}$$

and the matrix elements for the closed channels are made up of modified spherical Bessel functions of the first and third kinds [8]

$$[\mathbf{J}(x)]_{ij} = \delta_{ij}(k_jx)^{1/2}\,I_{l_j+1/2}(k_jx), \tag{16}$$

$$[\mathbf{N}(x)]_{ij} = \delta_{ij}(k_jx)^{1/2}\,K_{l_j+1/2}(k_jx), \tag{17}$$

where k_j is the channel wave number. Differentiate Eq. (13) with respect to x, then multiply from the right by the inverse of this equation, set $x = x_N$, and solve the resulting equation for $\mathbf{K}$ in terms of $\mathbf{y}(x_N)$.

$$\mathbf{K} = -[\mathbf{y}(x_N)\,\mathbf{N}(x_N) - \mathbf{N}'(x_N)]^{-1} \times [\mathbf{y}(x_N)\,\mathbf{J}(x_N) - \mathbf{J}'(x_N)]. \tag{18}$$

The matrix **K** is an augmented reaction matrix containing elements connecting closed as well as open channels, i.e., **K** can be written in the form

$$\mathbf{K} = \begin{pmatrix} \mathbf{K}_{oo} & \mathbf{K}_{oc} \\ \mathbf{K}_{co} & \mathbf{K}_{cc} \end{pmatrix} \tag{19}$$

where $\mathbf{K}_{oo}$, $\mathbf{K}_{oc}$, $\mathbf{K}_{co}$, and $\mathbf{K}_{cc}$ are open–open, open–closed, closed–open, and closed–closed submatrices of **K**. The S-matrix is given in terms of the open–open submatrix, $\mathbf{K}_{oo}$, by the familiar formula

$$\mathbf{S} = (\mathbf{I} + i\mathbf{K}_{oo})^{-1}(\mathbf{I} - i\mathbf{K}_{oo}). \tag{20}$$

The closed channel functions defined by Eq. (16) increase exponentially and those defined by Eq. (17) decrease exponentially with increasing x. This is a possible source of numerical difficulties in evaluating Eq. (18). The problem is easily eliminated by the following simple replacement of the closed channel matrix elements of the matrices $\mathbf{J}(x_N)$, $\mathbf{N}(x_N)$, $\mathbf{J}'(x_N)$, and $\mathbf{N}'(x_N)$:

$$[\mathbf{J}(x_N)]_{ii} \to 1, \tag{21}$$

$$[\mathbf{J}'(x_N)]_{ii} \to [\mathbf{J}'(x_N)]_{ii} \times [\mathbf{J}(x_N)]_{ii}^{-1} \tag{22}$$

along with the expressions obtained from (21) and (22) by replacing the symbol **J** by the symbol **N**. It is easily verified that this transformation will leave the open–open submatrix $\mathbf{K}_{oo}$ unchanged.

As one example of the use of this method we have repeated the calculations of Olson and Smith [10] on the He^+–Ne collision at an energy of 70.9 eV (2.60566 a.u.). The potential used is given by Eq. (45) with the parameters of Table I in Ref. [10]. This is a two channel curve crossing problem, both channels being open. The reduced mass used was 6089 a.u. It was found that $|S_{12}^{(l)}|^2$ could be computed to three-figure accuracy by integrating out to a radius of 6 a.u. with a spacing between integration points of 0.001 a.u. The angular momentum quantum number l was varied from $l = 0$ to $l = 350$. The initial point of the integration was always taken at the origin, although computer time could have been reduced somewhat by moving the initial point to the right as the classical turning points moved to the right with increasing values of l. This was done for two reasons: first, for simplicity of programming, and second, to demonstrate that this method does not suffer from any of the usual problems encountered by starting far inside the classically forbidden region. The calculation was done on an IBM model 370-165 computer using Fortran IV programming language and double precision floating point variables. The total time required to compute the S-matrices for the 351 l values was about 60 sec. A few selected values of $|S_{12}^{(l)}|^2$ for l values in low, mid, and high ranges are presented in Table I.

TABLE I

$|S_{12}|^2$ for Selected Values of l

l	$\|S_{12}^{(l)}\|^2$
0	0.279(−3)[a]
10	0.164(−2)
20	0.110(−1)
200	0.215(−1)
202	0.552(−1)
205	0.900(−1)
209	0.553(−1)
214	0.487(−3)
290	0.167(−4)
300	0.146
310	0.202
320	0.941(−1)
330	0.226(−1)
350	0.329(−3)

[a] The number in parentheses is the power of ten involved.

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