The generalized log-derivative method for inelastic and reactive collisions[a)]

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A generalization of the log-derivative method is presented which is useful for both reactive and nonreactive scattering problems. In the coupled system of radial equations for this problem a first derivative term is included for complete generality. Thus, this method may be used when, as is often the case in reactive or curve crossing problems, the equations contain a first derivative term. When no first derivative term is present and no reactive channels are present, the method reduces to the standard log-derivative method. A reactive scattering problem is solved as an example.

INTRODUCTION

A recent study[1] has shown that for most scattering calculations a hybrid method is the most efficient. The close range part of the problem is most efficiently handled by an approximate solution approach while the long range part of the interaction is best handled by an a approximate potential approach.[2–5] The invariant imbedding technique, because of its great stability,[6–9] is the most convenient in practice. The various techniques have been discussed in detail in the literature[6] so it is unnecessary to expand on them here. The VIVAS program[7,10] is a hybrid program of this sort, which uses the log-derivative method[8] for the close in part of the potential and variant of the R-matrix method[7] for the long range part. This program is ideally suited for inelastic scattering problems for which the radial Schrödinger equation contains no first derivative term.

Reactive scattering problems may be treated by the R-matrix method or its variant used in VIVAS. The R-matrix method is efficient because it allows a large step size in regions in which the interaction potential is slowly varying. In the close in and nonclassical region, a method such as the log-derivative is preferable. This type of approach always requires a small step size but the computational effort per step is less than that required in the R-matrix method. Thus there is a need to generalize the log-derivative method to reactive scattering. Often reactive problems are formulated in such a way that a first derivative term appears in the radial equations. This first derivative term shows up in the adiabatic formulation of inelastic scattering and curve crossing problems also.

In the present paper we present a generalization of the log-derivative method which will handle any reactive or inelastic scattering problem. For problems in which no first derivative term appears and only inelastic channels are considered our algorithm reduces to the standard log-derivative method.

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We begin by reviewing the existing propagators of solutions to the general coupled radial equations for a scattering problem, and we introduce a new propagator L, which serves as the basic quantity in the derivation. Enough details are given in the derivation so that it is obvious how one may modify the method for special purposes. No derivation was given in the original publication of the log-derivative method,[8,11] and as a result such simple procedures as changing step size during a calculation are obscure.

I. PROPAGATORS FOR THE SOLUTION OF THE SCHRÖDINGER EQUATION

The most general form taken by the equations for reactive or inelastic scattering is

$$\left[\frac{d^2}{dr^2}+A(r)\frac{d}{dr}+B(r)\right]\psi(r)=0\,, \tag{1}$$

where we have included the energy and potential matrix together in the matrix $B(r)$. The problem is usually formulated such that the matrix $A(r)$ is zero. Such a formulation of course simplifies the problem, but it is not always a convenient thing to do. In the adiabatic representation of these problems this first derivative term arises naturally. Since the method discussed here handles such a term conveniently we carry it in this derivation, though, as we shall show, the technique simplifies somewhat when the A matrix is zero. A solution to Eq. (1) is a vector function and the complete set of solution vectors is the solution matrix $\psi(r)$. In general the matrices A, B, and ψ are infinite, but in practice we truncate the basis set at some convenient number N and henceforth we will assume that they are $N\times N$ matrices.

We will call a propagator in an interval $[r', r'']$ a $(2N\times 2N)$ block matrix which connects values of any solution of Eq. (1), ψ and its derivative ψ' at the endpoints r' and r''. The standard propagator, well known from the theory of differential equations, is the Cauchy matrix [12]

$$\Omega=\begin{pmatrix}\Omega_1\Omega_2\\ \Omega_3\Omega_4\end{pmatrix}$$

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for which the defining relation takes the form

$$\begin{pmatrix}\psi(r'')\\ \psi'(r'')\end{pmatrix}=\begin{pmatrix}\Omega_1(r'',r') & \Omega_2(r'',r')\\ \Omega_3(r'',r') & \Omega_4(r'',r')\end{pmatrix}\begin{pmatrix}\psi(r')\\ \psi'(r')\end{pmatrix}, \quad (2)$$

the existence of which is guaranteed in all intervals $[r', r'']$ where the matrices $A(r)$ and $B(r)$ are continuous functions of r. The basic properties of Ω are

$$\Omega(x'',x')=\Omega(x'',y)\Omega(y,x') \quad \text{for } y\in[x',x''], \quad (3)$$

$$\Omega(x',x')=1. \quad (4)$$

The determination of the fundamental solutions forming the matrix $\Omega(x'',x')$ requires solving of an appropriate number of initial value problems for the system of equations [Eq. (1)] in the interval $[x',x'']$. There are a number of other types of propagators but they all are intimately involved with boundary value problems rather than initial value problems for the system [Eq. (1)]. They are called invariant imbedding type propagators. The invariant imbedding process consists of solving a series of simple problems imbedded in the space of the complete problem. The inherent stability of these techniques derives from the fact that the bounded scattering amplitude of intermediate problems rather than the wave function for the entire system is propagated through the space. The quantities used in the original formulation of the invariant imbedding technique[13]—the "reflection" and "transmission" matrices $Y^{\pm}$ and $Z^{\pm}$ form the propagator

$$\begin{pmatrix}Y^{+} & Z^{-}\\ Z^{+} & Y^{-}\end{pmatrix}$$

satisfying the following relation for any solution ψ:

$$\begin{pmatrix}\psi'(x')\\ \psi(x'')\end{pmatrix}=\begin{pmatrix}Y^{+}(x',x'') & Z^{-}(x',x'')\\ Z^{+}(x',x'') & Y^{-}(x',x'')\end{pmatrix}\begin{pmatrix}\psi(x')\\ \psi'(x'')\end{pmatrix}. \quad (5)$$

Another type of invariant imbedding propagator is the matrix $\mathfrak{R}$ introduced by Zvijac, Light *et al.*[3-5] in their widely used method for solving coupled equations for scattering. The matrix

$$\mathfrak{R}=\begin{pmatrix}\mathfrak{R}_1\mathfrak{R}_2\\ \mathfrak{R}_3\mathfrak{R}_4\end{pmatrix}$$

fulfills its propagation role through the relation

$$\begin{pmatrix}\psi(r')\\ \psi(x'')\end{pmatrix}=\begin{pmatrix}\mathfrak{R}_1(x',x'') & \mathfrak{R}_2(x',x'')\\ \mathfrak{R}_3(x',x'') & \mathfrak{R}_4(x',x'')\end{pmatrix}\begin{pmatrix}\psi'(x')\\ \psi'(x'')\end{pmatrix}. \quad (6)$$

For the purpose of the present paper, we define here still another propagator—a matrix

$$L=\begin{pmatrix}L^{(1)}L^{(2)}\\ L^{(3)}L^{(4)}\end{pmatrix}$$

by rewriting the above relation in the form

$$\begin{pmatrix}\psi'(x')\\ \psi'(x'')\end{pmatrix}=\begin{pmatrix}L^{(1)}(x',x'') & L^{(2)}(x',x'')\\ L^{(3)}(x',x'') & L^{(4)}(x',x'')\end{pmatrix}\begin{pmatrix}\psi(x')\\ \psi(x'')\end{pmatrix}. \quad (7)$$

The specific form of the boundary value problems to which any of the above listed invariant imbedding type propagators is related can be easily established on the basis of the defining relations [Eqs. (5)–(7)].

In particular, the relation [Eq. (7)] suggests as a way for the evaluation of the matrix $L(x',x'')$, solving of the following boundary value problems for the matrices $\psi^{+}(x)$ and $\psi^{-}(x)$:

$$\left[\frac{d^2}{dx^2}+A(x)\frac{d}{dx}+B(x)\right]\psi^{\pm}(x)=0, \quad (8a)$$

$$\psi^{\pm}(x')=\begin{cases}1\\ 0\end{cases} \quad \psi^{\pm}(x'')=\begin{cases}0\\ 1\end{cases}. \quad (8b)$$

The derivatives of these matrices at the endpoints of the interval $[x',x'']$ can be identified as

$$\psi^{\pm\prime}(x')=\begin{cases}L^{(1)}(x',x'')\\ L^{(2)}(x',x'')\end{cases}, \quad \psi^{\pm\prime}(x'')=\begin{cases}L^{(3)}(x',x'')\\ L^{(4)}(x',x'')\end{cases}. \quad (9)$$

As a direct consequence of the fact that solutions of particular boundary value problems do not always exist, all invariant imbedding type propagators fail to exist for some intervals $[x',x'']$. This is the well-known problem of singularities in the invariant imbedding approach.[14-16] Fortunately, this problem can be easily overcome, at least in scattering calculations.

Obviously, each of the above mentioned propagators is related to all others. Consequently, the basic properties of the standard propagator Ω [Eqs. (3) and (4)] can be expressed in terms of the properties of any other propagator. In that way we can get the well-known recurrence relations for the matrices $Y^{\pm}$ and $Z^{\pm}$ (listed, e.g., in Ref. 17) as well as the $\mathfrak{R}$-matrix propagation relations derived originally by Zvijac and Light.[3] The relevant relations for the matrix L will be given below. To begin with we specify the connection of the matrix L with the standard propagator Ω:

$$L(x',x'')=\hat{L}[\Omega(x'',x')]. \quad (10)$$

This is done by defining the operation $\hat{L}$ as the following rearrangement of a $2N\times 2N$ block matrix

$$C=\begin{pmatrix}C_1 & C_2\\ C_3 & C_4\end{pmatrix}:$$

$$\hat{L}[C]=\begin{pmatrix}-C_2^{-1}C_1 & C_2^{-1}\\ -C_4C_2^{-1}C_1+C_3 & C_4C_2^{-1}\end{pmatrix}. \quad (11)$$

From this definition it follows that:

$$\hat{L}\hat{L}=\hat{1}. \quad (12)$$

Thus, acting $\hat{L}$ on both sides of Eq. (3) we get the formula

$$L(x',x'')=\hat{L}\{\hat{L}[L(y,x'')]\cdot\hat{L}[L(x',y)]\}, \quad (13)$$

which after performing the necessary matrix operations, leads to the following recurrence relations for the blocks $L^{(i)}(x',x'')$, $i=1, 2, 3, 4$:

$$L^{(1)}(x',x'')=L^{(1)}(x',y)-L^{(2)}(x',y)1(x',y,x'')L^{(3)}(x',y), \quad (14a)$$

$$L^{(2)}(x',x'')=L^{(2)}(x',y)1(x',y,x'')L^{(2)}(y,x''), \quad (14b)$$

$$L^{(3)}(x',x'') = -L^{(3)}(y,x'')1(x',y,x'')L^{(3)}(x',y)\,, \tag{14c}$$

$$L^{(4)}(x',x'') = L^{(4)}(y,x'') + L^{(3)}(y,x'')1(x',y,x'')L^{(2)}(y,x'')\,, \tag{14d}$$

where

$$1(x',y,x'') = [L^{(4)}(x',y) - L^{(1)}(y,x'')]^{-1}\,. \tag{15}$$

In addition, from Eqs. (4), (10), and (11) we obtain

$$L(x',x') = \begin{pmatrix} -1 & 1 \\ -1 & 1 \end{pmatrix} c\,, \tag{16}$$

where c is a constant: $c \to \infty$.

The L matrix can be simply related to the other invariant imbedding formulations. For example, the relation to the $\mathcal{R}$ matrices is given by

$$L(x',x'') = [\mathcal{R}(x',x'')]^{-1} \tag{17}$$

and further

$$\mathcal{R}(x',x'') = \hat{L}(\tilde{\Omega}(x'',x'))\,, \tag{18}$$

where

$$\tilde{\Omega} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \Omega \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\,. \tag{19}$$

In consequence of Eq. (18), the recurrence relations for the matrix L must have the same structure as the appropriate relations for the matrix $\mathcal{R}$. Indeed,

$$\mathcal{R}(x',x'') = \hat{L}[\tilde{\Omega}(x'',x')] = \hat{L}[\tilde{\Omega}(x'',y)\tilde{\Omega}(y,x')] = \hat{L}\{\hat{L}[\mathcal{R}(y,x'')]\cdot\hat{L}[\mathcal{R}(x',y)]\}\,. \tag{20}$$

The existence of a connection between the matrices L, $Y^{\pm}$, and $Z^{\pm}$ enables us to apply the same procedure as described in Ref. 18 to convert the recurrence relations [Eqs. (14a)–(14d)] to the following differential form in the limit of $(x''-y)\to 0$:

$$\frac{d}{dy}L^{(1)}(x',y) = -L^{(2)}(x',y)A_2(y)L^{(3)}(x',y)\,, \tag{21a}$$

$$\frac{d}{dy}L^{(2)}(x',y) = -L^{(2)}(x',y)[A_1(y) + A_2(y)L^{(4)}(x',y)]\,, \tag{21b}$$

$$\frac{d}{dy}L^{(3)}(x',y) = [A_4(y) - L^{(4)}(x',y)A_2(y)]L^{(3)}(x',y)\,, \tag{21c}$$

$$\frac{d}{dy}L^{(4)}(x',y) = A_3(y) + A_4(y)L^{(4)}(x',y) - L^{(4)}(x',y)A_1(y) - L^{(4)}(x',y)A_2(y)L^{(4)}(x',y)\,. \tag{21d}$$

The A_i, $i=1, 2, 3, 4$, denote blocks of the coupling matrix in the system of first order differential equations equivalent to the system Eq. (1), i.e.,

$$\begin{pmatrix} A_1 & A_2 \\ A_3 & A_4 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -B & -A \end{pmatrix}\,. \tag{22}$$

In conclusion of this section we should point out that the new propagator L is an extension of the log-derivative matrix L_D, which is defined by the relation

$$\bar{\psi}'(x) = L_D\bar{\psi}(x)\,,$$

where $\bar{\psi}(x)$ is a solution of Eq. (1) satisfying the initial condition: $\bar{\psi}(x') = 0$. Indeed, if one substitutes $\bar{\psi}$ into Eq. (7) one can see that $L_D = L^{(4)}$. For inelastic scattering $L^{(4)}$ alone is sufficient. Thus, we may propagate $L^{(4)}$ using only Eq. (14d) and the present method becomes the generalization of the log-derivative method for equations containing a first derivative.

II. AN ALGORITHM FOR THE MATRIX L

In an attempt to construct an algorithm for the matrix $L(x',x'')$ we will follow the same idea that was followed many times in cases of other algorithms, i.e., we will apply the appropriate recurrence relations to approximate propagators for subsequent small sectors of the interval $[x',x'']$. The crucial point in the realization of this idea, influencing the final shape and properties of the entire algorithm, is, of course, the evaluation of the sector propagators. From the two approaches to this task mentioned in the Introduction, we decided to apply here the approximate solution approach. We start by choosing a discretization procedure to the boundary value problems for the sector L matrices.

As a preparatory step to a description of our choice we convert the Eq. (8) to the integral equation form using the Green's function technique. Thus, treating the second derivative term as the homogeneous part of the Eq. (8a) and denoting by $\varphi^{+}(x)$ and $\varphi^{-}(x)$ the diagonal matrices defined by

$$\frac{d^2}{dx^2}\varphi^{\pm}(x) = 0\,, \tag{23a}$$

$$\varphi^{\pm}(x') = \begin{cases} 1 \\ 0 \end{cases}\,, \qquad \varphi^{\pm}(x'') = \begin{cases} 0 \\ 1 \end{cases}\,, \tag{23b}$$

we get

$$\psi^{\pm}(x) = \varphi^{\pm}(x) - \int_{x'}^{x''} W^{-1}\varphi^{-}(x_<)\varphi^{+}(x_>) \times [B(y)\psi^{\pm}(y) + A(y)\psi^{\pm\prime}(y)]\,dy\,, \tag{24a}$$

$$\psi^{\pm\prime}(x) = \varphi^{\pm\prime}(x) - \int_{x'}^{x''} W^{-1}\frac{d}{dx}[\varphi^{-}(x_<)\varphi^{+}(x_>)] \times [B(y)\psi^{\pm}(y) + A(y)\psi^{\pm\prime}(y)]\,dy\,, \tag{24b}$$

where

$$W = \varphi^{-}\varphi^{+\prime} - \varphi^{-\prime}\varphi^{+}\,, \tag{25}$$

and $x_<$ is the lesser of x and y, with a similar definition for $x_>$. In Eq. (25) we have made use of the fact that φ^{+} and φ^{-} are diagonal. As a $2N$ by N order matrix equation,

$$\Psi^{\pm}(x) = \Phi^{\pm}(x) - \int_{x'}^{x''} G(x,y)P(y)\Psi^{\pm}(y)\,dy\,. \tag{26}$$

Above we use the abbreviated notation

$$\Psi^{\gamma} = \begin{pmatrix} \psi^{\gamma} \\ \psi^{\gamma\prime} \end{pmatrix}\,, \quad \Phi^{\gamma} = \begin{pmatrix} \varphi^{\gamma} \\ \varphi^{\gamma\prime} \end{pmatrix} \qquad \text{for } \gamma = +, -\,,$$

$$P = (B, A)\,,$$

$$G(x,y) = \begin{cases} W^{-1}\Phi^{+}(x)\varphi^{-}(y) & \text{for } y < x\,, \\ W^{-1}\Phi^{-}(x)\varphi^{+}(y) & \text{for } y > x\,, \end{cases} \tag{27}$$

After dividing the interval $[x', x'']$ into sectors $[x_l, x_{l+2}]$ of length $2h$, i.e.; $x_{l+2}-x_l=2h$ for $l=0, 2, 4, \ldots, 2M-2$ and $x_0=x', x''=x_{2M}$; we may analogously formulate the problems related to the sector propagators $L(x_l, x_{l+2})$:

$$\Psi^{\pm}_{l,l+2}(x)=\Phi^{\pm}_{l,l+2}(x)-\int_{x_l}^{x_{l+2}} G_{l,l+2}(x,y)P(y)\Psi^{\pm}_{l,l+2}(y)\,dy\ . \tag{28}$$

The subscripts in the Green's function $G_{l,l+2}(x,y)$ indicate that it is formed from the solutions $\varphi^{\pm}_{l,l+2}(x)$ of the Eqs. (23a)–(23b) in the interval $[x_l, x_{l+2}]$. Now, rewriting the integrals from the above equations in the abbreviated form

$$\int_{x_l}^{x_{l+2}} K(x,y)\,dy\ ,$$

we evaluate them approximately at

$$x=x_l\ ,\quad x_{l+1}, x_{l+2}, (x_{l+1}=x_{l+2}-h=x_l+h)$$

by means of the formula[19]

$$\int_{x_l}^{x_{l+2}} K(x_l,y)\,dy \sim \frac{h}{3}\left[K(x_l,x_l)+4K(x_l,x_{l+1})+K(x_l,x_{l+2})\right] + C(x_{l+1})\delta_{l,l+1}\ , \tag{29}$$

which differs from the standard Simpson rule by the additional term C,

$$C(x_{l+1})=\frac{h^2}{6}\left[\lim_{(y-x_{l+1})\to 0^+}\frac{d}{dy}K(x_{l+1},y) - \lim_{(y-x_{l+1})\to 0^-}\frac{d}{dy}K(x_{l+1},y)\right]\ ; \tag{30}$$

necessary in the case of an integrand having a discontinuous first derivative. This term must be included if one wishes to preserve the accuracy of the Simpson formula. After inserting the explicit form of $K(x_{l+1},y)$ into Eq. (30) and performing some elementary operations we obtain the expressions

$$C(x_{l+1})=\frac{h^2}{6}\begin{pmatrix} P(x_{l+1})\Psi^{\pm}_{l,l+2}(x_{l+1}) \\ -\frac{d}{dy}\left[P(y)\Psi^{\pm}_{l,l+2}(y)\right]\big|_{y=x_{l+1}}\end{pmatrix}, \tag{31}$$

or

$$C(x_{l+1})=\alpha\tilde{Q}(x_{l+1})\Psi^{\pm}_{l,l+2}(x_{l+1})\ , \tag{32}$$

where

$$\alpha=\frac{h^2}{6}\ , \tag{33}$$

$$\tilde{Q}=\begin{pmatrix} B & A \\ -B'+AB & -B-A'+A^2\end{pmatrix}\ . \tag{34}$$

Equation (32) is derived with the help of Eq. (8a). Thus, in consequence of the above discretization procedure we arrive at the algebraic equations for the matrices

$\Psi^{\pm}_{l,l+2}(x_l)$ at $x_l=x_l,\ x_{l+1},\ x_{l+2}$,

$$\Psi^{\pm}_{l,l+2}(x_l)=\Phi^{\pm}_{l,l+2}(x_l) - \sum_{k=l}^{l+2}\omega_k G_{l,l+2}(x_l,x_k)P(x_k)\Psi^{\pm}_{l,l+2}(x_k) - \delta_{l,l+1}\alpha\tilde{Q}(x_{l+1})\Psi^{\pm}_{l,l+2}(x_{l+1})\ , \tag{35}$$

where

$$\omega_l=\omega_{l+2}=\frac{h}{3}\ ,\quad \omega_{l+1}=\frac{4}{3}h\ , \tag{36}$$

or

$$F^{\pm}_{l,l+2}(x_l)=\Phi^{\pm}_{l,l+2}(x_l) - \sum_{k=l}^{l+2}\omega_k G_{l,l+2}(x_l,x_k)P(x_k)Q(x_k)F^{\pm}_{l,l+2}(x_k) \tag{37}$$

for matrices $F^{\pm}_{l,l+2}(x_l)$ defined as

$$F^{\pm}_{l,l+2}(x_l)=[Q(x_l)]^{-1}\Psi^{\pm}_{l,l+2}(x_l)\ , \tag{38}$$

where

$$Q(x_l)=[1+\delta_{l,l+1}\alpha\tilde{Q}(x_l)]^{-1}\ . \tag{39}$$

The approximate sector L matrices that we are seeking will be hereafter denoted by

$$L_{l,l+2}=\begin{pmatrix} L^{(1)}_{l,l+2} & L^{(2)}_{l,l+2} \\ L^{(3)}_{l,l+2} & L^{(4)}_{l,l+2}\end{pmatrix}\ . \tag{40}$$

Of course, they are related also to the matrices $F^{\pm}_{l,l+2}$ introduced above by

$$F^{+}_{l,l+2}(x_l)=\begin{pmatrix} 1 \\ L^{(1)}_{l,l+2}\end{pmatrix}\ , \tag{41a}$$

$$F^{-}_{l,l+2}(x_l)=\begin{pmatrix} 0 \\ L^{(2)}_{l,l+2}\end{pmatrix}, \tag{41b}$$

$$F^{+}_{l,l+2}(x_{l+2})=\begin{pmatrix} 0 \\ L^{(3)}_{l,l+2}\end{pmatrix}\ , \tag{41c}$$

$$F^{-}_{l,l+2}(x_{l+2})=\begin{pmatrix} 1 \\ L^{(4)}_{l,l+2}\end{pmatrix}\ . \tag{41d}$$

The determination of the $L_{l,l+2}$ matrices, being now a matter of solving Eq. (37), is much simplified by inserting the Green's function $G_{l,l+2}(x_l,x_k)$ constructed according to Eq. (27) with $\varphi^{\pm}_{l,l+2}$ having the form

$$\varphi^{+}_{l,l+2}(x)=\frac{x-x_{l+2}}{x_l-x_{l+2}}1\ ,\quad \varphi^{-}_{l,l+2}(x)=\frac{x-x_l}{x_{l+2}-x_l}1\ . \tag{42}$$

As a result of solving Eq. (37) we get the following formulas for the matrices $L^{(i)}_{l,l+2}$; $i=1, 2, 3, 4$:

$$hL^{(1)}_{l,l+2}=(1-s_l)^{-1}\left[-1+\tfrac{1}{2}(1-hS_{l+1})^{-1}(1-s_{l+1})+hS_l\right]\ , \tag{43a}$$

$$hL^{(2)}_{l,l+2}=\tfrac{1}{2}(1-s_l)^{-1}(1-hS_{l+1})^{-1}(1+s_{l+1})\ , \tag{43b}$$

$$hL^{(3)}_{l,l+2}=-\tfrac{1}{2}(1+s_{l+2})^{-1}(1-hS_{l+1})^{-1}(1-s_{l+1})\ , \tag{43c}$$

$$hL^{(4)}_{l,l+2}=(1+s_{l+2})^{-1}\left[1-\tfrac{1}{2}(1-hS_{l+1})^{-1}(1+s_{l+1})-hS_{l+2}\right]\ , \tag{43d}$$

where

$$(S_k, s_k)=\bar{\omega}_k P(x_k)Q(x_k) \quad \text{for } k=l,\ l+1,\ l+2\ ,$$

$$\bar{\omega}_k=\frac{h}{3}(1+\delta_{k,l+1})\ .$$

Equations (43a)–(43d) give us the means of computing the L matrix over a small region. The algorithm

$$L_{0,l+2}=\hat{L}\{\hat{L}[L_{l,l+2}]\cdot\hat{L}[L_{0,l}]\}\ , \tag{44}$$

with the initial condition

$$L_{0,0}=\begin{pmatrix}-1 & 1\\ -1 & 1\end{pmatrix} c \quad \text{for } c\gg 1 \tag{45}$$

gives us a method of solving the general scattering problem, or, in general, the boundary value problem associated with Eq. (1). As it stands this is an extremely complex and cumbersome algorithm. A much more efficient algorithm can be obtained by carrying the derivation a step further.

To accomplish this we first show that the formulas given by Eq. (43) can be obtained by the transformation

$$L_{l,l+2}=\hat{L}\{\hat{L}[\tilde{L}_{l+1,l+2}]\cdot\hat{L}[\tilde{L}_{l,l+1}]\}\,. \tag{46}$$

The matrices $\tilde{L}_{r,r+1}$ for $r=l,\ l+1$ are defined analogously to the matrices $L_{l,l+2}$, Eq. (41), but in terms of the solutions $F^{\pm}_{r,r+1}$ of the following algebraic equations:

$$F^{\pm}_{r,r+1}(x_i)=\Phi^{\pm}_{r,r+1}(x_1) - \sum_{k=r}^{r+1}\tilde{\omega}_k G_{r,r+1}(x_i,x_k)P(x_k)Q(x_k)F^{\pm}_{r,r+1}(x_k) \tag{47}$$

for $i=r, r+1$ and $r=l, l+1$.

The $\Phi^{\pm}_{r,r+1}$ and $G_{r,r+1}$ matrices are constructed from the solutions of Eq. (23) in the interval $[x_r, x_{r+1}]$, i.e., from the matrices

$$\varphi^{+}_{r,r+1}(x)=-\frac{x-x_{r+1}}{h}\,1\,, \tag{48a}$$

$$\varphi^{-}_{r,r+1}(x)=\frac{x-x_r}{h}\,1\,. \tag{48b}$$

It should be pointed out that the matrices $\tilde{L}_{r,r+1}$ for $r=l,\ l+1$ cannot be considered as the approximate L propagators in the corresponding halfsectors. This is because of the fact that the matrices $Q(x_k)$ present in Eqs. (46) contain contributions from both halves of the sectors. The straightforward way of verifying the relation [Eq. (46)] is to insert into it the following formulas for the matrices $\tilde{L}_{r,r+1}$, $r=l,\ l+1$, obtained by solving Eq. (47):

$$\tilde{L}^{(1)}_{r,r+1}=-\tilde{L}^{(2)}_{r,r+1}(1-hS_r)\,, \tag{49a}$$

$$\tilde{L}^{(2)}_{r,r+1}=\frac{1}{h}(1-s_r)^{-1}\,, \tag{49b}$$

$$\tilde{L}^{(3)}_{r,r+1}=-\frac{1}{h}(1+s_{r+1})^{-1}\,, \tag{49c}$$

$$\tilde{L}^{(4)}_{r,r+1}=-\tilde{L}^{(3)}_{r,r+1}(1-hS_{r+1})\,, \tag{49d}$$

where

$$\tilde{L}=\begin{pmatrix}\tilde{L}^{(1)} & \tilde{L}^{(2)}\\ \tilde{L}^{(3)} & \tilde{L}^{(4)}\end{pmatrix}\,. \tag{50}$$

Now we can replace one operation [Eq. (44)] with the following two operations:

$$\tilde{L}_{0,l+1}=\hat{L}[\hat{L}(\tilde{L}_{l,l+1})\cdot\hat{L}(L_{0,l})]\,, \tag{51a}$$

$$L_{0,l+2}=\hat{L}[\hat{L}(\tilde{L}_{l+1,l+2})\cdot\hat{L}(\tilde{L}_{0,l+1})]\,. \tag{51b}$$

The first of them defines the matrix $\tilde{L}$ for any odd numbered halfsector; the second operation can be checked by inserting Eq. (46) and Eq. (12) into the right-hand side of Eq. (44):

$$\hat{L}[\hat{L}(\tilde{L}_{l+1,l+2})\cdot\hat{L}(\tilde{L}_{l,l+1})\cdot\hat{L}(L_{0,l})] = \hat{L}\{\hat{L}(\tilde{L}_{l+1,l+2})\hat{L}\hat{L}[\hat{L}(\tilde{L}_{l,l+1})\hat{L}(L_{0,l})]\}\,. \tag{52}$$

In this way we have also shown that the global matrix L (for any number of sectors) can be built by an accumulation of the appropriate matrices for subsequent half-sectors. This completes the description of the basic ideas involved in the derivation of our algorithm.

To specify the final form of this algorithm, we introduce working quantities matrices $\mathfrak{L}^{(i)}_k$ $i=1,\ 2,\ 3,\ 4$, related to the matrices $L^{(i)}_{0,k}$ for $k=0, 2, \ldots, 2M$ through the formulas

$$\mathfrak{L}^{(1)}_k=L^{(1)}_{0,k}\,, \tag{53a}$$

$$\mathfrak{L}^{(2)}_k=hL^{(2)}_{0,k}\,, \tag{53b}$$

$$\mathfrak{L}^{(3)}_k=(1+s_k)L^{(3)}_{0,k}\,, \tag{53c}$$

$$\mathfrak{L}^{(4)}_k=[h(1-s_k)L^{(4)}_{0,k}+1-hS_k]^{-1}\,, \tag{53d}$$

and through the analogous formulas to the matrices $\tilde{L}^{(i)}_{0,k}$ for $k=1,\ 3,\ 5,\ \ldots,\ 2\tilde{M}-1$. The final shape of our algorithm is

$$\mathfrak{L}^{(1)}_1=-\mathfrak{L}^{(2)}_1\left(\frac{1}{h}-\frac{h}{3}B_0\right), \tag{54a}$$

$$\mathfrak{L}^{(2)}_1=\left(1-\frac{h}{3}A_0\right)^{-1}, \tag{54b}$$

$$\mathfrak{L}^{(3)}_1=-\frac{1}{h}\,, \tag{54c}$$

$$\mathfrak{L}^{(4)}_1=0\,, \tag{54d}$$

and

$$\mathfrak{L}^{(3)}_k=(Y_{k-1}-\mathfrak{L}^{(4)}_{k-2})^{-1}\mathfrak{L}^{(3)}_{k-1}\,, \tag{54e}$$

$$\mathfrak{L}^{(1)}_k=\mathfrak{L}^{(1)}_{k-1}-\mathfrak{L}^{(2)}_{k-1}\mathfrak{L}^{(3)}_k\,, \tag{54f}$$

$$\mathfrak{L}^{(2)}_k=\mathfrak{L}^{(2)}_{k-1}\mathfrak{L}^{(4)}_{k-1} \quad \text{for } k=2,3,\ldots,2\tilde{M}\,, \tag{54g}$$

and

$$\mathfrak{L}^{(4)}_k=(Y_k-\mathfrak{L}^{(4)}_{k-1})^{-1}(Z_k-1) \quad \text{for } k=1,2,\ldots,2\tilde{M}-1\,, \tag{54h}$$

where

$$Z_k=2(1-s_k)^{-1}\,, \tag{55}$$

$$Y_k=Z_k(1-hS_k)\,, \tag{56}$$

$$(S_k, s_k)=\tilde{\omega}_k(B_k, A_k) \times\begin{pmatrix}1+\alpha_k B_k & \alpha_k A_k\\ -\alpha_k(B'_k-A_kB_k) & 1-\alpha_k(B_k-A_k^2+A'_k)\end{pmatrix}^{-1}, \tag{57}$$

$$B_k=B(r_k)\,,\quad A_k=A(r_k), \tag{58}$$

$$\tilde{\omega}_k=\begin{cases}\frac{h}{3}\\ \frac{2h}{3}\end{cases}, \quad \alpha_k=\begin{cases}0 & \text{for } k=0,2,\ldots,2\tilde{M}\,,\\ \frac{h^2}{6} & \text{for } k=1,3,\ldots,2\tilde{M}-1\,.\end{cases} \tag{59}$$

Finally,

$$L^{(1)}_{0,M}=\mathfrak{L}^{(1)}_M\,, \tag{60a}$$

$$L^{(2)}_{0,M}=\frac{1}{h}\mathfrak{L}^{(2)}_M\,, \tag{60b}$$

$$L^{(3)}_{0,M}=\left(1+\frac{h}{3}A_M\right)^{-1}\mathfrak{L}^{(3)}_M\,, \tag{60c}$$

$$L_{0,M}^{(4)}=\frac{1}{h}\left(1+\frac{h}{3}A_M\right)^{-1}\left[1-\frac{h^2}{3}B_M-\mathcal{L}_{M-1}^{(4)}\right], \tag{60d}$$

where $M=2\tilde{M}$.

The starting expressions for the matrices $\mathcal{L}^{(i)}$, i.e., Eqs. (54a)–(54d), result directly from Eq. (45) in the case of $\mathcal{L}_0^{(4)}$, and from the relation

$$\tilde{L}_{0,1}=\hat{L}[\hat{L}(\tilde{L}_{0,1})\hat{L}(L_{0,0})] \tag{61}$$

in the cases of the matrices $\mathcal{L}_1^{(i)}$ for $i=1$, 2, 3. Whereas setting the initial values for $\mathcal{L}^{(2)}$ and $\mathcal{L}^{(3)}$ matrices at the point x_1 is only a matter of convenience, the addition in Eq. (61) must be definitely performed analytically for the matrix $\mathcal{L}_1^{(1)}$. This is because of the structure of the relation Eq. (14a) which for large values of $L(x', y)$, i.e., for $L(x', y)=L_{0,0}$, would lead to a loss of accuracy in numerical calculations. In the back transformation to the matrices $L^{(i)}$, i.e., in Eqs. (60), performed at the end of the calculations, when $k=2\tilde{M}$, use is made of the fact that for even values of k we have

$$S_k=\frac{h}{3}B_k, \quad s_k=\frac{h}{3}A_k. \tag{62}$$

Equation (60d) includes additionally the operation Eq. (54h) for $k=2\tilde{M}$.

The algorithm we have presented here will solve the general boundary value problem which is the solution to Eq. (1). In particular, it solves the reactive scattering problem when the radial equation contains first derivative terms. If one is interested only in the inelastic scattering problem the algorithm is much simpler. In that case, only $L_{0,M}^{(4)}$ is of interest. One starts with Eq. (54d) and iterates using Eq. (54b) until $k=2\tilde{M}-1$ and finishes with Eq. (60d). The other $\mathcal{L}_k^{(i)}$ for $i\neq 4$ are not needed.

In scattering calculations, usually one uses a radial equation with no first derivative and the B matrix is symmetric. In this special case

$$A(x)=0 \text{ and } B^T(x)=B(x), \tag{63}$$

the algorithm simplifies greatly. The exact and approximate propagators, $L(x_0, x_k)$ and $L_{0,k'}$, respectively, reveal the following symmetry properties:

$$[L^{(i)}]^T=L^{(i)} \quad \text{for } i=1,4 \tag{64}$$

and

$$[L^{(3)}]^T=-L^{(2)}. \tag{65}$$

Moreover, we have

$$s_k=0, \quad S_k=\bar{\omega}_k B_k(1+\alpha_k B_k)^{-1}. \tag{66}$$

Thus, defining the quantities r_k, t_k, and z_k as

$$r_k=\mathcal{L}_k^{(1)}, \tag{67}$$

$$t_k=\mathcal{L}_k^{(3)}=-\frac{1}{h}[\mathcal{L}_k^{(2)}]^T, \tag{68}$$

$$z_k=[\mathcal{L}_k^{(4)}]^{-1}, \tag{69}$$

we get from Eqs. (54) and (60),

$$z_0^{-1}=0, \tag{70a}$$

$$t_1=-\frac{1}{h}, \tag{70b}$$

$$r_1=-\frac{1}{h}+\frac{h}{3}B_0, \tag{70c}$$

and

$$z_k=2-2hS_k-z_{k-1}^{-1} \quad \text{for } k=1,2,\ldots,M-1, \tag{71a}$$

$$t_k=z_{k-1}^{-1}t_{k-1}, \tag{71b}$$

$$r_k=r_{k-1}+ht_{k-1}^T t_k \quad \text{for } k=2,3,\ldots,M. \tag{71c}$$

Finally,

$$L_{0,M}^{(1)}=r_M, \tag{72a}$$

$$L_{0,M}^{(2)}=-t_M^T, \tag{72b}$$

$$L_{0,M}^{(3)}=t_M, \tag{72c}$$

$$L_{0,M}^{(4)}=\frac{1}{h}\left(1-\frac{h^2}{3}B_M-z_{M-1}^{-1}\right). \tag{72d}$$

The part containing the Eqs. (70a), (71a), and (72d) is recognized as the log-derivative algorithm of Johnson.[8] The basic formulas of this algorithm are known rather in the form[11]

$$z_k=-6+\left[0.125+\frac{h^2}{48}B_k\right]^{-1}-z_{k-1}^{-1} \quad \text{for } k=1,3,5,\ldots,M-1, \tag{73}$$

$$z_k=2-\frac{2h^2}{3}B_k-z_{k-1}^{-1} \quad \text{for } k=2,4,6,\ldots,M-2. \tag{74}$$

The above is easy to obtain after substitution of Eqs. (66) and (59) into Eq. (71a). The z_k and that in Ref. 11 are the z_k of Ref. 8 plus 1.

III. NUMERICAL TEST AND CONCLUDING REMARKS

In order to test the derived algorithm we applied it to solving the problem considered by Wu *et al.*[20] in their studies of chemical reactions. This is the boundary value problem

$$\left[\frac{d^2}{dx^2}+A(x)\frac{d}{dx}+B(x)\right]\psi(x)=0, \tag{75a}$$

$$\psi(x) \underset{x\to-\infty}{\sim} \exp(ik^R x)+\exp(-ik^R x)R, \tag{75b}$$

$$\psi(x) \underset{x\to\infty}{\sim} \exp(ik^P x)T, \tag{75c}$$

describing collinear $A+BC\rightarrow AB+C$ reaction in the close coupling approximation (formulated in an adiabatic representation of wave function):

$$\lim_{x\to\pm\infty} A(x)=0,$$

$$\lim_{x\to-\infty} B(x)=k^R, \quad \lim_{x\to+\infty} B(x)=k^P,$$

k^R and k^P are constant diagonal matrices. The formulas for the evaluation of the $A(x)$ and $B(x)$ matrices at any x and other details concerning the derivation of the above problem from the quantum mechanical principles are given in Refs. 20 and 21. We have repeated a part of the calculations presented in Sec. 4 of Ref. 20, devoted to the role of so-called nonadiabatic static coupling in creating resonances in chemical reactions. The solutions of the problem Eqs. (75) were sought in the

TABLE I. Probability matrices P^R and P^T for collinear reaction on potential surface V of Ref. 20.

	E[a]	N[b]	P^R		P^T[c]		Σ_0/Σ_2[d]	t[e]
(A)[f]	39	3	0.4311(−1)		0.8719		0.999 990	6
					0.8500(−1)			
		4	0.4308(−1)		0.8708		0.999 986	11
					0.8610(−1)			
		5	0.4308(−1)		0.8707		0.999 986	18
					0.8624(−1)			
	44	5	0.2450(−2)	0.3854(−2)	0.7951	0.2010	0.999 972	18
			0.3845(−2)	0.3612(−1)	0.1986	0.7590	0.999 969	
		6	0.2455(−2)	0.3863(−2)	0.7952	0.2010	0.999 972	28
			0.3854(−2)	0.3635(−1)	0.1985	0.7588	0.999 971	
(B)[g]	39	3	0.4312(−1)		0.8718		0.999 963	13
					0.8501(−1)			
		4	0.4309(−1)		0.8708		0.999 963	24
					0.8610(−1)			
		5	0.4309(−1)		0.8706		0.999 963	40
					0.8624(−1)			
	44	5	0.2456(−2)	0.3857(−2)	0.7950	0.2010	0.999 926	40
			0.3856(−2)	0.3616(−1)	0.1986	0.7589	0.999 975	
		6	0.2461(−2)	0.3866(−2)	0.7951	0.2009	0.999 926	62
			0.3866(−2)	0.3639(−1)	0.1985	0.7588	0.999 975	

[a] E-total energy (in kcal/mol).
[b] N-number of vibrational states included. Only states with the same parity are coupled in this problem.
[c] Elements of P^R and P^T matrices are: $\begin{pmatrix} 0,0 & 0,2 \\ 2,0 & 2,2 \end{pmatrix}$.
[d] $\Sigma_I = \sum_n (P^R_{n,I} + P^T_{n,I})$.
[e] t-execution time (in s) on VAX....
[f] Results by method of this paper.
[g] Results by method of Ref. 21.

form of matrices P^T and P^R,

$$P^T_{m,n} = \frac{k^P_m}{k^R_n} |T_{m,n}|^2 , \quad P^R_{m,n} = \frac{k^R_m}{k^R_n} |R_{m,n}|^2 .$$

These matrices give probabilities of all possible vibrational transitions in the reactive system with and without simultaneous change of the chemical structure of the diatomic molecule, respectively. Our procedure of evaluation of these probabilities consisted of finding the propagator $L(x_{-\infty}, x_{+\infty})$ for the system [Eq. (75a)]. The matrices R and T were then obtained by means of the transformation resulting from insertion of the matrices $\psi(x_{-\infty})$, $\psi(x_{+\infty})$ and their derivatives into Eq. (7). With this procedure we have reconstructed the overall energy dependence of the $P^T_{m,n}$ probabilities plotted in Fig. 7(a) of Ref. 20.

For a more detailed testing of our method, we performed also calculations by the method described in Ref. 21. In this method, the probabilities were extracted from the standard propagator, determined with the aid of the Runge–Kutta algorithm. A sample of the results obtained by both methods is given in Table I. The agreement between the corresponding probabilities from parts (A) and (B) of this table confirms the correctness of our algorithm for the matrix L. The values of sums of probabilities Σ_I calculated for each case indicate that the conservation of the probability flux is not automatically guaranteed by either method. Therefore, these sums may serve to some extent as measures of the accuracy of the numerical integration.

Though both methods are of the fourth order, the step-size requirements in solving a given problem may be quite different. This is because of the fact that, in contrast to the Runge–Kutta, any invariant imbedding type of propagator is determined not by solving the system of linear differential equations but by solving a related but structurally different system of equations. The algorithm for the matrix L can be, in fact, considered as an algorithm for an integration of the differential equations [Eqs. (21)].

In the cases reported in Table I, the same accuracy, of the results obtained by both methods was reached at the expense of using three times smaller step size in the Runge–Kutta method (B). Thus, the method (A) turned out to be more efficient in these cases. But, as the last column of the table shows, this superiority is not so large that it can always be expected. One must take into account, however, that in these test cases there was little need for exploiting the major advantage of our method: its complete numerical stability.

A more exhaustive estimation of the method developed for the matrix L requires, of course, further investigations. The essential question arises as to whether these investigations should be undertaken at the present stage of this method. Obviously, the answer depends on the properties of the problems to be solved. As was already stated, the method is formulated for systems of linear differential equations of general form—no symmetry restrictions on coupling matrices

are imposed. Such general equations occurred in some early papers on the quantum mechanical description of chemical reactions.[22] In recent years, however, factorization[23] of the wave function allows the same problems to be formulated in a much more symmetrical form. The general algorithm we have described does not require such symmetrization. It is possible that our algorithm could be simplified for matrices which have symmetry properties. In the special case described at the end of the preceding section, the use of the symmetry of the B matrix along with the absence of the first derivative term lead to great simplification. This gave a direct extension of the log-derivative method. This algorithm is, in our opinion, ideally suited for collinear reactive scattering problems formulated in the quasi-adiabatic representation. It would also be useful, at least for providing more flexibility in handling these problems, to have a simple method for solving the appropriate equations in the adiabatic representation. These are, of course, equations with first derivative coupling. The coupling matrix, however, is skew-symmetric and this fact should be somehow exploited in deriving a simpler version of our general algorithm. Investigations in this direction will be undertaken in the near future.

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