

# A symmetrized generalized log-derivative method for inelastic and reactive scattering<sup>a)</sup>

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A new invariant imbedding approximate solution algorithm related to the log-derivative method is derived. The method makes use of the symmetry of the scattering equations and is particularly well suited to problems with a first derivative term. Comparisons of efficiency are made in the use of this method on both a reactive scattering problem and a nondiabatic inelastic scattering problem.

## I. INTRODUCTION

It appears that for scattering calculations hybrid methods have distinct advantages in efficiency.<sup>1</sup> In the asymptotic regions of the collision the approximate potential approaches are most efficient while in the strongly interacting regions approximate solution approaches appear to be more efficient. The present paper is part of a continuing effort to extend the hybrid method to reactive scattering problems. We concentrate on the development of the approximate solution approach for the close in region. The equations describing the reactive scattering processes in the close-coupling approximation are, of course, ordinary second order differential equations but the boundary conditions are usually more general than in the case of inelastic processes. Moreover, first derivative terms are more likely to occur. The need to limit the number of coupled equations for a numerical treatment has given rise to the practice of using curvilinear coordinates to describe the reactive system. For the same reason, basis sets which are more flexible than the diabatic ones must be employed to represent the total wave function along the reaction coordinate. The curvature of the reaction coordinate was eventually eliminated<sup>2</sup> as the source of the first derivative coupling in the system of equations, but the possibility of including terms related to the reaction coordinate dependence of the basis functions still seems to be desirable for better handling of the transition state regions of the potential surfaces. These are also the regions where the approximate solution approach should be more advantageous than the approximate potential approach. Unfortunately, no efficient and stable approximate solution-type procedure capable of solving the coupled equations for reactive collisions has been proposed so far. Thus, the task of primary importance for our investigations is to develop such a procedure.

Proceeding in this direction, we started in a previous paper<sup>3</sup> the project of extending the range of applicability of the log-derivative algorithm<sup>4</sup> well known for its usefulness in inelastic scattering calculations. In connection with this project we have introduced a new invariant

imbedding-type propagator for systems of linear second order differential equations—the matrix  $L$ —one block of which coincides with the log-derivative matrix. The original algorithm of Johnson<sup>4</sup> has been supplied with the operations necessary for finding the entire  $L$ -propagator for the coupled equations in the diabatic representation.<sup>3</sup>

The straightforward generalization of this method for the equations with first derivative coupling has been also carried out.<sup>3</sup> However, the algorithm, though competitive with others in some circumstances, seems to be too complicated for problems possessing symmetry properties, as is the case for coupled equations formulated in the nondiabatic representation.

The goal of the present paper is to derive an algorithm which is more efficient in dealing with these equations. We achieve this goal by rederiving the previous generalized version of the log-derivative method and by inserting into it the relations for the propagator  $L$  appropriate for the nondiabatic representations.

These relations are derived in Sec. II. The details of the new generalization of the log-derivative method are described in Sec. III and the resulting algorithm is given at the end of it. The last section contains a comparison of this algorithm with two other  $L$ -propagator based algorithms.

## II. THE PROPAGATOR $L$ FOR THE COUPLED EQUATIONS OF SCATTERING

The time independent Schrödinger equation for a scattering problem is usually treated in the form of a coupled system of radial equations obtained by expanding the wave function in some complete set of basis functions for the internal coordinates. The basis set may be chosen to depend parametrically on the radial coordinate  $x$ . Thus we may write

$$\Psi(x, y) = \sum_i \eta_i(y; x) \psi_i(x), \quad (1)$$

or in matrix notation,

$$\Psi(x, y) = \eta^T(y; x) \psi(x). \quad (2)$$

Here  $x$  is the separation parameter or radial coordinate and  $y$  is all of the internal coordinates of both colliding systems and the angular coordinates of the separation

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vector. We are treating  $\eta$  and  $\psi$  as column vectors with elements  $\eta_i$  and  $\psi_i$ , respectively. The complete basis set satisfies the orthonormality relation

$$\langle \eta(y; x) \eta^T(y; x) \rangle = 1, \quad (3)$$

where 1 is the unit matrix. The brackets denote integration over all internal coordinates  $y$  and Eq. (3) holds for every value of  $x$ . For simplicity, we will restrict our discussion here to real basis sets, though no difficulty is encountered in working with complex basis functions.

The Schrödinger equation (expressed in reduced units),

$$(E - H) \Psi = \left( \frac{d^2}{dx^2} + E - H' \right) \Psi = 0, \quad (4)$$

can be replaced by the coupled system of ordinary differential equations,

$$(K + V) \psi = 0 \quad (5)$$

with  $K$  and  $V$  standing for the matrix representations of the  $d^2/dx^2$  and  $E - H'$  operators, respectively, i. e.,

$$K = \left\langle \eta \frac{d^2}{dx^2} \eta^T \right\rangle = 1 \frac{d^2}{dx^2} + 2 \langle \eta \dot{\eta}^T \rangle \frac{d}{dx} + \langle \eta \ddot{\eta}^T \rangle, \quad (6)$$

$$V = \langle \eta (E - H') \eta^T \rangle \quad (7)$$

(dot denotes a derivative with respect to  $x$ ). If the basis  $\eta$  is complete the operator  $K$  can be converted to the form

$$K = \left( 1 \frac{d}{dx} + \frac{1}{2} A \right)^2 \quad (8)$$

with

$$A = 2 \langle \eta \dot{\eta}^T \rangle. \quad (9)$$

Equation (5) becomes equivalent to the equation

$$D[\psi] = 0, \quad (10)$$

for the differential operator  $D$ ,

$$D = \frac{d^2}{dx^2} + A(x) \frac{d}{dx} + B(x), \quad (11)$$

where

$$B(x) = V(x) + \frac{1}{2} \dot{A}(x) + \frac{1}{4} A^2(x). \quad (12)$$

Here we have made use of the fact that  $A$  is skew symmetric, which follows from Eq. (3), giving

$$A^T = -A \quad (13)$$

and

$$A^2 = -A^T A = -4 \langle \dot{\eta} \dot{\eta}^T \rangle. \quad (14)$$

The  $V$  matrix is symmetric.

In general neither the matrix  $K$  nor the matrix  $V$  is diagonal. The exceptions are: the adiabatic case leading to the diagonal matrix  $V$  and the diabatic cases where the operator  $K$  is represented by the matrix  $1(d^2/dx^2)$ .

A change from the basis set  $\eta(y; x)$  to the diabatic one can be performed by means of any transformation diagonalizing the matrix  $K$ , given by Eq. (8). It is easy to see following Baer, *et al.*<sup>5</sup> that such a transforma-

tion should satisfy the differential equation

$$\left( 1 \frac{d}{dx} + \frac{1}{2} A \right) \mathcal{T}(x; \bar{x}) = 0 \quad (15)$$

and the condition

$$\mathcal{T}(\bar{x}; \bar{x}) = 1 \quad (16)$$

at an arbitrarily chosen point  $\bar{x}$ .

Using Eq. (13) we can show that the transformations  $\mathcal{T}$  are orthogonal,

$$\mathcal{T}^T(x; \bar{x}) = \mathcal{T}^{-1}(x; \bar{x}). \quad (17)$$

In addition, they satisfy the following relations

$$\mathcal{T}(x; \bar{x}) = \mathcal{T}(x; \bar{x}_1) \mathcal{T}(\bar{x}_1; \bar{x}), \quad (18)$$

$$\mathcal{T}^{-1}(x; \bar{x}) = \mathcal{T}(\bar{x}; x). \quad (19)$$

The transformation of the basis set

$$\eta_{\bar{x}}(y) = \mathcal{T}^T(x; \bar{x}) \eta(y; x) \quad (20)$$

changes the expansion coefficients

$$\psi_{\bar{x}}(x) = \mathcal{T}^T(x; \bar{x}) \psi(x) \quad (21)$$

and implies also a transformation of the operator  $D$ ,

$$D_{\bar{x}} = \mathcal{T}^T(x; \bar{x}) D [\mathcal{T}(x; \bar{x})]. \quad (22)$$

The coupled equations now take the form<sup>5</sup>

$$D_{\bar{x}}[\psi_{\bar{x}}] = 0 \quad (23)$$

with

$$D_{\bar{x}} = 1 \frac{d^2}{dx^2} + B_{\bar{x}}(x), \quad (24)$$

where

$$B_{\bar{x}}(x) = \mathcal{T}^T(x; \bar{x}) V(x) \mathcal{T}(x; \bar{x}). \quad (25)$$

Using Eq. (18) it is easy to show that Eqs. (20)–(22) may be written,

$$\eta_{\bar{x}}(y) = \mathcal{T}^T(\bar{x}_1; \bar{x}) \eta_{\bar{x}_1}(y), \quad (26)$$

$$\psi_{\bar{x}}(x) = \mathcal{T}^T(\bar{x}_1; \bar{x}) \psi_{\bar{x}_1}(x), \quad (27)$$

$$D_{\bar{x}} = \mathcal{T}^T(\bar{x}_1; \bar{x}) D_{\bar{x}_1} \mathcal{T}(\bar{x}_1; \bar{x}). \quad (28)$$

Now they express the connection between two diabatic basis sets and between the corresponding diabatic representations of the wave function and the  $E - H$  operator, respectively.

The basic symmetry properties of the  $D$  and  $D_{\bar{x}}$  operators are:

(i)  $\bar{D} = D^T$ , where  $\bar{D}$  denotes the adjoint operator which acting on a vector  $\phi^T$  gives

$$\bar{D}[\phi^T] = \frac{d^2}{dx^2} \phi^T - \frac{d}{dx} (\phi^T A) + \phi^T B \quad (29)$$

and  $D^T$  is the transposed operator defined by the relation

$$D^T[\phi^T] = (D[\phi])^T. \quad (30)$$

(ii)

$$D_{\bar{x}} = D_{\bar{x}}^T, \quad (31)$$

where,

$$\bar{D}_{\bar{x}} = \bar{D}[\mathcal{T}^T(x; \bar{x})] \mathcal{T}(x; \bar{x}) . \tag{32}$$

Thus, taking into account the following relation<sup>6</sup> satisfied by any vectors  $\psi$  and  $\phi$ ;

$$\psi^T D[\phi] - \bar{D}[\psi^T] \phi = \frac{d}{dx} W[\psi, \phi] , \tag{33}$$

where

$$W[\psi, \phi] = \psi^T \dot{\phi} - \dot{\psi}^T \phi + \psi^T A \phi ; \tag{34}$$

and its equivalent form for the operator  $D_{\bar{x}}$ ;

$$\psi_{\bar{x}}^T D_{\bar{x}}[\phi_{\bar{x}}] - \bar{D}_{\bar{x}}[\psi_{\bar{x}}^T] \phi_{\bar{x}} = \frac{d}{dx} w[\psi_{\bar{x}}, \phi_{\bar{x}}] , \tag{35}$$

where

$$w[\psi_{\bar{x}}, \phi_{\bar{x}}] = W[\mathcal{T}(x; \bar{x}) \psi_{\bar{x}}, \mathcal{T}(x; \bar{x}) \phi_{\bar{x}}] = \psi_{\bar{x}}^T \dot{\phi}_{\bar{x}} - \dot{\psi}_{\bar{x}}^T \phi_{\bar{x}} ; \tag{36}$$

we can state that

$$\frac{d}{dx} W[\psi, \phi] = 0 \tag{37}$$

and

$$\frac{d}{dx} w[\psi_{\bar{x}}, \phi_{\bar{x}}] = 0 \tag{38}$$

if  $\psi$  and  $\phi$  are solutions to Eq. (10) or, equivalently, if  $\psi_{\bar{x}}$  and  $\phi_{\bar{x}}$  are solutions to Eq. (23).

The information collected above will be exploited now in the discussion of the properties of the propagator  $L$  for the coupled equations of scattering. The propagator

$$L(x', x'') = \begin{pmatrix} L^{(1)}(x', x'') & L^{(2)}(x', x'') \\ L^{(3)}(x', x'') & L^{(4)}(x', x'') \end{pmatrix} \tag{39}$$

for Eq. (10) is defined in Ref. 3 in the form

$$\begin{pmatrix} \psi'(x') \\ \psi'(x'') \end{pmatrix} = \begin{pmatrix} L^{(1)}(x', x'') & L^{(2)}(x', x'') \\ L^{(3)}(x', x'') & L^{(4)}(x', x'') \end{pmatrix} \begin{pmatrix} \psi(x') \\ \psi(x'') \end{pmatrix} . \tag{40}$$

We may write  $L(x', x'')$  in terms of the solution to the two point boundary problems,

$$D[\psi^+(x)] = 0 , \tag{41}$$

$$\psi^+(x') = \begin{Bmatrix} 1 \\ 0 \end{Bmatrix} \text{ and } \psi^+(x'') = \begin{Bmatrix} 0 \\ 1 \end{Bmatrix} \tag{42}$$

to obtain

$$L(x', x'') = \begin{pmatrix} \dot{\psi}^+(x') & \dot{\psi}^-(x') \\ \dot{\psi}^+(x'') & \dot{\psi}^-(x'') \end{pmatrix} . \tag{43}$$

The analogously defined  $L$  propagator for Eq. (23) in the diabatic representation will be denoted by

$$L_{\bar{x}}(x', x'') = \begin{pmatrix} L_{\bar{x}}^{(1)} & L_{\bar{x}}^{(2)} \\ L_{\bar{x}}^{(3)} & L_{\bar{x}}^{(4)} \end{pmatrix} \tag{44}$$

and the solutions of the corresponding boundary value problems by  $\psi_{\bar{x}}^{\pm}(x)$ . Notice

$$\psi_{\bar{x}}^{\pm} = (\psi^{\pm})_{\bar{x}} \tag{45}$$

where according to Eq. (21)

$$(\psi^{\pm})_{\bar{x}} = \mathcal{T}^T(x, \bar{x}) \psi^{\pm} , \tag{46}$$

while  $\psi_{\bar{x}}^{\pm}$  satisfies the boundary conditions

$$\psi_{\bar{x}}^{\pm}(x') = \begin{Bmatrix} 1 \\ 0 \end{Bmatrix} \text{ and } \psi_{\bar{x}}^{\pm}(x'') = \begin{Bmatrix} 0 \\ 1 \end{Bmatrix} . \tag{47}$$

Applying Eq. (37) to the solutions  $\psi^{\pm}(x)$  we get the relations

$$W[\psi^-, \psi^-] = 0 , \quad W[\psi^+, \psi^+] = 0 , \tag{48}$$

$$W[\psi^-, \psi^+] = C , \tag{49}$$

where  $C$  is a constant matrix.

From these relations the following symmetry properties of the propagator  $L(x', x'')$  can be deduced:

$$L^{(1)}(x', x'') = [L^{(1)}(x', x'')]^T - A(x') , \tag{50}$$

$$L^{(4)}(x', x'') = [L^{(4)}(x', x'')]^T - A(x'') , \tag{51}$$

$$L^{(2)}(x', x'') = -[L^{(3)}(x', x'')]^T . \tag{52}$$

Analogously, Eq. (38), when applied to the solutions  $\psi_{\bar{x}}^{\pm}$ , yields

$$L_{\bar{x}}^{(i)}(x', x'') = [L_{\bar{x}}^{(i)}(x', x'')]^T , \text{ for } i = 1, 4 , \tag{53}$$

$$L_{\bar{x}}^{(2)}(x', x'') = -[L_{\bar{x}}^{(3)}(x', x'')]^T . \tag{54}$$

Specifying the connections between the  $\psi^{\pm}(x)$  and  $\psi_{\bar{x}}^{\pm}(x)$  matrices, resulting from the form of the boundary conditions (42) and (47), and from Eq. (21);

$$\psi^+(x) = \mathcal{T}(x; \bar{x}) \psi_{\bar{x}}^+(x) \mathcal{T}^T(x', \bar{x}) , \tag{55}$$

$$\psi^-(x) = \mathcal{T}(x; \bar{x}) \psi_{\bar{x}}^-(x) \mathcal{T}^T(x'', \bar{x}) , \tag{56}$$

we can easily establish the relation showing the effect of the transformation Eq. (20) between the nondiabatic and diabatic basis sets on the  $L$  propagators for the corresponding coupled equations. This relation is

$$L(x', x'') = \begin{pmatrix} -\frac{1}{2} A(x') & 0 \\ 0 & -\frac{1}{2} A(x'') \end{pmatrix} + \begin{pmatrix} \mathcal{T}(x'; \bar{x}) & 0 \\ 0 & \mathcal{T}(x''; \bar{x}) \end{pmatrix} L_{\bar{x}}(x', x'') \begin{pmatrix} \mathcal{T}^T(x'; \bar{x}) & 0 \\ 0 & \mathcal{T}^T(x''; \bar{x}) \end{pmatrix} . \tag{57}$$

The transformation between two diabatic representations for the  $L$  propagators take a form similar to that of Eqs. (26)–(28),

$$L_{\bar{x}}^{(i)} = \mathcal{T}(\bar{x}; \bar{z}) L_{\bar{x}}^{(i)} \mathcal{T}^T(\bar{x}; \bar{z}) , \text{ for } i = 1-4 . \tag{58}$$

It is valid, of course, for any values of  $\bar{x}$  and  $\bar{z}$ .

Making use of this fact we can rewrite Eq. (57) for the blocks  $L^{(i)}$   $i = 1, 4$  in the form

$$L^{(1)}(x', x'') = -\frac{1}{2} A(x') + L_x^{(1)}(x', x'') , \tag{59a}$$

$$L^{(4)}(x', x'') = -\frac{1}{2} A(x'') + L_x^{(4)}(x', x'') . \tag{59b}$$

Moreover, setting  $\bar{x} = x''$  we can simplify this relation also for the two remaining blocks of  $L$  and we get,

$$L^{(2)}(x', x'') = \mathcal{T}(x', x'') L_x^{(2)}(x', x'') , \tag{59c}$$

$$L^{(3)}(x', x'') = L_x^{(3)}(x', x'') \mathcal{T}^T(x', x'') . \tag{59d}$$

The final question is how the basis set transformations affect the recurrence property of the  $L$ -propagators for the corresponding coupled equations. This property is expressed by the following relation<sup>3</sup>:

$$\begin{pmatrix} L^{(1)}(x', x'') & L^{(2)}(x', x'') \\ L^{(3)}(x', x'') & L^{(4)}(x', x'') \end{pmatrix} = \begin{pmatrix} L^{(1)}(x', z) & 0 \\ 0 & L^{(4)}(z, x'') \end{pmatrix} + \begin{pmatrix} L^{(2)}(x', z) & 0 \\ 0 & L^{(3)}(z, x'') \end{pmatrix} 1(x', z, x'') \begin{pmatrix} L^{(3)}(x', z) & 0 \\ 0 & L^{(2)}(z, x'') \end{pmatrix} , \tag{60}$$

where  $1(x', z, x'')$  is the  $2 \times 2$  block matrix of the form

$$1(x', z, x'') = \begin{pmatrix} -1 & 1 \\ -1 & 1 \end{pmatrix} [L^{(4)}(x', z) - L^{(1)}(z, x'')]^{-1} \tag{61}$$

and  $z \in [x', x'']$ .

As can be easily proven this relation is invariant with respect to the transformation Eq. (57), as well as to the transformation Eq. (58), provided that they are performed on the  $L$  propagators for all intervals involved. This is, of course, to be expected since the recurrence relations are known to be valid for any system of linear differential equations and in fact they can be derived<sup>3</sup> without making use of any particular properties of the coupling matrices.

The structure of the above relation should, however, change slightly after applying the transformation (59). This is caused by the fact that the  $L$  propagators for different intervals are expressed now in different basis sets and therefore they are connected by different equations. The resulting relation is

$$\begin{pmatrix} L_x^{(1)}(x', x'') & L^{(2)}(x', x'') \\ L^{(3)}(x', x'') & L_x^{(4)}(x', x'') \end{pmatrix} = \begin{pmatrix} L_x^{(1)}(x', z) & 0 \\ 0 & L_x^{(4)}(z, x'') \end{pmatrix} + \begin{pmatrix} L^{(2)}(x', z) & 0 \\ 0 & L_x^{(3)}(z, x'') \mathcal{T}^T(z, x'') \end{pmatrix} 1(x', z, x'') \begin{pmatrix} L^{(3)}(x', z) & 0 \\ 0 & \mathcal{T}(z, x'') L_x^{(2)}(z, x'') \end{pmatrix} , \tag{62}$$

where

$$1(x', z, x'') = \begin{pmatrix} -1 & 1 \\ -1 & 1 \end{pmatrix} [L_x^{(4)}(x', z) - L_x^{(1)}(z, x'')]^{-1} , \tag{63}$$

Eqs. (61) and (63) are identical. This relation gives us the propagator  $L$  in a form which mixes the nondiabatic representation for the off-diagonal blocks with two different diabatic representations for the diagonal blocks. These diabatic representations coincide with the nondiabatic representation of  $L$  [see Eqs. (59a) and (59b)] for the intervals at the boundaries at which the coupling matrix  $A$  vanishes, i. e., where the nondiabatic equations really become diabatic ones. To maintain this convenient form of the propagator  $L$  after enlarging the interval  $[x', z]$  to the interval  $[x', x'']$  requires a proper choice of the diabatic representation of the  $L$  propagator in the interval  $[z, x'']$ . This choice depends on the location of the point  $x''$ . The matrices  $\mathcal{T}$  occurring in the above relation account for the changes of the diabatic representation from interval to interval.

### III. AN ALGORITHM FOR SOLVING THE COUPLED EQUATIONS IN THE NONDIABATIC REPRESENTATION

As was mentioned in the Introduction we are interested here in deriving a new version of the log-derivative

method which will be more efficient than the previous generalization of this method<sup>3</sup> in solving the coupled equations in the nondiabatic representation. There are two steps in using an invariant imbedding method for solving a system of differential equations:

- (i) Propagating the solution from sector to sector to accumulate the propagator  $L$  for the entire integration range  $[x', x'']$ ; and (ii) the numerical computation of the propagator for each small sector into which the range of integration was divided.

We compute the sector propagators of step ii by the Simpson's rule modified for integrands with discontinuous first derivatives<sup>7</sup> just as we did in our previous paper.<sup>3</sup> In the present paper we concentrate on testing the possible ways of realizing step i.

The direct way is to use the relations, Eq. (60) for the sector  $L$  propagators obtained from the discretized nondiabatic equations, as we considered previously.<sup>3</sup>

The second possibility is to use the relations Eq. (60) for the accumulation of the propagators  $L_{\bar{x}}$  (with fixed value of  $\bar{x}$  throughout the integration range) for small sectors of  $[x', x'']$ . These propagators are determined by applying step ii to the appropriate diabatic equations.

This is exactly the procedure used in the original version of the log-derivative method and its supplement mentioned in the Introduction. In the usual implementation  $\bar{x}$  is chosen in the asymptotic region where the basis set is independent of the choice of  $\bar{x}$ . If  $\bar{x}$  is chosen in the interaction region, one must perform the transformation at the end of the calculation using  $\mathcal{T}(x; \bar{x})$  obtained by solving Eqs. (15) and (16), in the interval  $[x', x'']$ .

The idea of treating the nondiabatic coupled equations via the related diabatic equations is not new. It can be exploited in many different combinations of algorithms for solving the diabatic equations and algorithms for finding the transformation matrix  $\mathcal{T}$ . The combination involving the original log-derivative algorithm is mentioned here with the purpose of testing it against the proposed new generalization of this algorithm for the nondiabatic equations.

The essentially new element in the present generalization of the log-derivative method is the use of Eq. (62) to assemble the propagators  $L_{x_{l+2}}(x_l, x_{l+2})$  for sectors  $[x_l, x_{l+2}]$  covering the interval of interest  $[x', x'']$ , i. e.,  $x_0 = x'$ ,  $x_M = x''$ , and  $x_{l+2} = x_l + 2h$  for  $l = 0, 2, 4, \dots, M - 2$ . The approximate formulas for these propagators neces-

sary for a construction of an algorithm are obtained by applying step ii to the Eq. (23) for the matrices  $\psi_{\bar{x}}^{\pm}$  with  $\bar{x} = x_{l+2}$  satisfying the conditions Eq. (47) at the boundaries of the interval  $[x_l, x_{l+2}]$ . Adapting the results of the previous paper<sup>3</sup> [i. e., Eqs. (43a)–(43d) of Ref. 3] we can write the recursion formulas as

$$hL_{x_{l+2}}(x_l, x_{l+2}) = \begin{pmatrix} -(1 - hS_l) & 0 \\ 0 & 1 - hS_{l+2} \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 1 & 1 \\ -1 & -1 \end{pmatrix} (1 - hS_{l+1})^{-1}, \quad (64)$$

where

$$S_k = \frac{h}{3} B_{x_{l+2}}(x_k), \quad \text{for } k = l, l + 2, \quad (65)$$

$$S_{l+1} = \frac{2h}{3} B_{x_{l+2}}(x_{l+1}) \left[ 1 + \frac{h^2}{6} B_{x_{l+2}}(x_{l+1}) \right]^{-1}, \quad (66)$$

$$x_{l+1} = x_{l+2} - h = x_l + h. \quad (67)$$

For computational purposes we transform these expressions to a simpler form

$$6hL_{x_{l+2}}(x_l, x_{l+2}) = \begin{pmatrix} -7 + 2h^2 B_{x_{l+2}}(x_l) & -1 \\ 1 & 7 - 2h^2 V(x_{l+2}) \end{pmatrix} + \begin{pmatrix} 1 & 1 \\ -1 & -1 \end{pmatrix} \left[ \frac{1}{4} - \frac{h^2}{8} B_{x_{l+2}}(x_{l+1}) \right]^{-1} \quad (68)$$

and we introduce new matrices

$$\mathcal{L}_{l,p} = \begin{pmatrix} \mathcal{L}_{l,p}^{(1)} & \mathcal{L}_{l,p}^{(2)} \\ \mathcal{L}_{l,p}^{(3)} & \mathcal{L}_{l,p}^{(4)} \end{pmatrix}, \quad \text{for } l = 0, 2, 4, \dots$$

$p = l + 2k$  with  $k = 1, 2, 3, \dots$ , defining them by the relation

$$\mathcal{L}_{l,p} = \begin{pmatrix} 0 & 0 \\ 0 & 7 - 2h^2 V(x_p) \end{pmatrix} + 6h \begin{pmatrix} L_{x_l}^{(1)}(x_l, x_p) & L^{(2)}(x_l, x_p) \\ L^{(3)}(x_l, x_p) & L_{x_p}^{(4)}(x_l, x_p) \end{pmatrix}. \quad (69)$$

In the case  $p = l + 2$  we get the expressions:

$$\mathcal{L}_{l,l+2}^{(1)} = -7 + 2h^2 V(x_l) + \mathcal{T}(x_l; x_{l+2}) S_{l,l+2} \mathcal{T}^T(x_l; x_{l+2}), \quad (70a)$$

$$\mathcal{L}_{l,l+2}^{(2)} = [(-1 + S_{l,l+2}) \mathcal{T}^T(x_l; x_{l+2})]^T, \quad (70b)$$

$$\mathcal{L}_{l,l+2}^{(3)} = -[\mathcal{L}_{l,l+2}^{(2)}]^T, \quad (70c)$$

$$\mathcal{L}_{l,l+2}^{(4)} = 14 - 4h^2 V(x_{l+2}) - S_{l,l+2}, \quad (70d)$$

where

$$S_{l,l+2} = \left[ \frac{1}{4} - \frac{h^2}{8} B_{x_{l+2}}(x_{l+1}) \right]^{-1}. \quad (70e)$$

In the derivation of these expressions use was made of the properties of  $\mathcal{T}$ , Eqs. (17)–(19) and (59), the definition of  $B_{x_{l+2}}$  [Eq. (25)] and of Eq. (52).

On the basis of the Eq. (62) we establish the following formula to assemble the matrices  $\mathcal{L}_{l,l+2}$  for  $l = 0, 2, 4, \dots, M - 2$ :

$$\begin{pmatrix} \mathcal{L}_{0,l+2}^{(1)} & \mathcal{L}_{0,l+2}^{(2)} \\ -[\mathcal{L}_{0,l+2}^{(2)}]^T & \mathcal{L}_{0,l+2}^{(4)} \end{pmatrix} = \begin{pmatrix} \mathcal{L}_{0,l}^{(1)} & 0 \\ 0 & \mathcal{L}_{l,l+2}^{(4)} \end{pmatrix} + \begin{pmatrix} \mathcal{L}_{0,l}^{(2)} & 0 \\ 0 & -[\mathcal{L}_{l,l+2}^{(2)}]^T \end{pmatrix} Y_{0,l+2} \begin{pmatrix} -[\mathcal{L}_{0,l}^{(2)}]^T & 0 \\ 0 & \mathcal{L}_{l,l+2}^{(2)} \end{pmatrix}, \quad (71)$$

where

$$Y_{0,i+2} = \begin{pmatrix} 1 & 1 \\ -1 & -1 \end{pmatrix} [\mathcal{L}_{0,i}^{(4)} - \mathcal{T}(x_i; x_{i+2}) s_{i,i+2} \mathcal{T}^T(x_i; x_{i+2})]^{-1}.$$

The resulting matrix  $\mathcal{L}_{0,M}$  gives us, through the Eqs. (69) and (59), the propagator  $L(x', x'')$  for the nondiabatic coupled equations [Eq. (10)].

For completion of the computational scheme we still need a procedure for finding the matrices  $\mathcal{T}(x; x_{i+2})$  at  $x = x_{i+1}$  and  $x = x_i$ . To this end, we rewrite Eqs. (15) and (16) with  $\bar{x} = x_{i+2}$  in the integral equation form

$$\mathcal{T}(x; x_{i+2}) = 1 + \frac{1}{2} \int_x^{x_{i+2}} A(x') \mathcal{T}(x'; x_{i+2}) dx' . \quad (72)$$

Discretizing it in the interval  $[x_{i+2} - 2H, x_{i+2}]$  with the aid of the Simpson formula

$$\begin{aligned} \mathcal{T}(x_{i+2} - 2H; x_{i+2}) \\ = 1 + \frac{1}{2} \sum_{k=0}^2 \omega_k(H) A(x_{i+2} - kH) \mathcal{T}(x_{i+2} - kH; x_{i+2}) \end{aligned} \quad (73)$$

with

$$\omega_0(H) = \omega_2(H) = \frac{H}{3}, \quad \omega_1(H) = \frac{4}{3}H,$$

we obtain the algebraic equation for the matrices  $\mathcal{T}(x_{i+1}; x_{i+2})$  and  $\mathcal{T}(x_i; x_{i+2})$  by setting  $H = (h/2)$  and  $H = h$ , respectively. Inserting the unit matrix for  $\mathcal{T}(x_{i+2}; x_{i+2})$  and the approximate expression [resulting from application of the trapezoidal formula to Eq. (72)] for the matrix  $\mathcal{T}(x_{i+(3/2)}; x_{i+2})$ ,  $x_{i+(3/2)} = x_{i+2} - \frac{1}{2}h$ ,

$$\mathcal{T}(x_{i+(3/2)}; x_{i+2}) = \left[ 1 - \frac{h}{8} A(x_{i+(3/2)}) \right]^{-1} \left[ 1 + \frac{h}{8} A(x_{i+2}) \right], \quad (74a)$$

we can derive from these equations the following formulas:

$$\begin{aligned} \mathcal{T}(x_{i+1}; x_{i+2}) &= \left[ \frac{3}{8} - \frac{h}{32} A(x_{i+1}) \right]^{-1} \\ &\times \left[ -\frac{5}{8} - \frac{3}{32} h A(x_{i+2}) + \mathcal{T}(x_{i+(3/2)}; x_{i+2}) \right], \end{aligned} \quad (74b)$$

$$\begin{aligned} \mathcal{T}(x_i; x_{i+2}) &= \left[ 1 - \frac{h}{6} A(x_i) \right]^{-1} \\ &\times \left[ 1 + \frac{h}{6} A(x_{i+2}) + \frac{2h}{3} A(x_{i+1}) \mathcal{T}(x_{i+1}; x_{i+2}) \right]. \end{aligned} \quad (74c)$$

Finally, putting together all operations described above, we form the following algorithm for solving the nondiabatic coupled equations in terms of the propagator  $L(x'; x'')$ :

- (1) Divide the interval  $[x', x'']$  into  $M/2$  sectors of length  $2h$ ; (2) calculate the matrices  $\mathcal{L}_{0,i}^{(l)}$  for  $i = 1, 2, 4$  for  $l = 2, 4, 6, \dots, M - 2$ —calculating at each of them: The matrices from the formulas

$$\mathcal{T}(x; x_{i+2}) \text{ at } x = x_i, x_{i+1} \quad (74)$$

$$V(x) \text{ at } x = x_{i+1}, x_{i+2} \quad (25)$$

$$B_{x_{i+2}}(x_{i+1}) \quad (70)$$

$$s_{i,i+2}, \mathcal{L}_{i,i+2}^{(i)}, \quad i = 2, 4 \quad (70)$$

and determining the matrices  $\mathcal{L}_{0,i+2}^{(i)}$  for  $i = 1, 2, 4$  from the recurrence relation (71); and (4) find the matrices  $L_{x_0}^{(1)}(x_0, x_M)$ ,  $L^{(2)}(x_0, x_M)$ , and  $L_{x_M}^{(4)}(x_0, x_M)$  from Eq. (69) for  $l = 0$  and  $p = M$ , and the matrices  $L^{(1)}(x_0, x_M)$ ,  $L^{(4)}(x_0, x_M)$ , and  $L^{(3)}(x_0, x_M)$  from Eqs. (59a)–(59d) and (52).

#### IV. NUMERICAL TESTS

Our numerical tests were designed to answer, at least in part, the following questions concerning the new algorithm for solving the coupled equations in the nondiabatic representation:

- (1) How much has our use of the symmetries of the problem in the present approach improved the effectiveness of the algorithm over that described in our previous<sup>3</sup> generalization of the log-derivative algorithm?; and
- (2) What practical advantages does the present approach offer as compared with the standard way of handling the first derivative coupling in the nondiabatic equations?

In calculations related to the first question we solved one of the model problems constructed by Wu, Johnson, and Levine<sup>8,9</sup> for the investigations of chemical reactions. Though the overall formulation of the reactive scattering problem by these authors did not have the usual symmetry properties of the nondiabatic coupled equations, the particular problem which we have chosen from their papers, i. e., the collinear model on potential surface  $V$  discussed in their<sup>8</sup> Sec. IV, did. Thus, this was a suitable problem for testing our first generalized version of the log-derivative method against the standard method used by Wu and Levine,<sup>9</sup> which was done in Ref. 3, as well as for comparing it with the new version proposed here.

The results of this comparison are reported in Table I. We have reported solutions to the same problem by our previous generalization of the log-derivative method<sup>3</sup> denoted by (A) in Table I and the present generalization denoted by (B). Computation time are given and the problem is solved for various sized basis sets. From these results we can discern the following points:

- (i) The new symmetric approach is on average a factor of 1.6 faster than the approach which does not take advantage of symmetry. This factor indicates roughly the reduction of the number of operations required per sector by the present approach.
- (ii) By the present approach, the sum of the probabilities are equal to one and microscopic reversibility holds exactly, even when not enough basis functions are carried to converge the results.
- (iii) The (A) and (B) approaches do not at all agree for small basis sets. Equation (10) was derived from Eq. (5) assuming a complete basis set expansion. Both Eqs. (5) and (10) are exact equations for the scattering calculation. When they are approximated by truncating the basis set, however, they represent different approximations. Thus with a small basis set we would not expect the two solutions to agree. As the size of the basis set is increased the two approximations should converge to the same result.

TABLE I. Results of testing the previous (A) and the present (B) generalized versions of the log-derivative method on the  $A+BC \rightarrow AB+C$  collinear reaction model of Wu *et al.* (Ref. 8) at energy  $E = 44$  kcal/mol.<sup>a</sup>  $N$ —basis set size<sup>b</sup>;  $P^R$ ,  $P^T$ —matrices of reflection and transmission probabilities<sup>c</sup>;  $\Sigma_I$ —sum of probabilities from the initial state  $I$ ,  $\Sigma_I = \sum_n (P_{n,I}^R + P_{n,I}^T)$ ;  $t$ —execution time (in s) on VAX 11/780.

(A)						
$N$		$P^R$		$P^T$	$\Sigma_I$	$t$
2	0.1769(-2)	0.6701(-2)	0.7869	0.2093	0.999995	3
	0.6701(-2)	0.3000(-1)	0.2046	0.7540	1.00000	
3	0.2358(-2)	0.3317(-2)	0.7939	0.2029	0.999983	6
	0.3310(-2)	0.2591(-1)	0.2005	0.7679	1.000001	
4	0.2421(-2)	0.3827(-2)	0.7946	0.2016	0.999974	11
	0.3819(-2)	0.3486(-1)	0.1991	0.7597	0.999993	
5	0.2450(-2)	0.3854(-2)	0.7951	0.2010	0.999972	18
	0.3845(-2)	0.3612(-1)	0.1986	0.7590	0.999969	
6	0.2455(-2)	0.3863(-2)	0.7952	0.2010	0.999972	28
	0.3854(-2)	0.3635(-1)	0.1985	0.7588	0.999971	
(B)						
2	0.1784(-2)	0.2495(-2)	0.7974	0.1995	1.00000	2
	0.2495(-2)	0.6434(-2)	0.1984	0.7915	1.00000	
3	0.2843(-2)	0.3543(-2)	0.8036	0.1917	1.00000	4
	0.3543(-2)	0.4944(-1)	0.1900	0.7553	1.00000	
4	0.2442(-2)	0.3942(-2)	0.7947	0.2014	1.00000	7
	0.3942(-2)	0.3691(-1)	0.1989	0.7578	1.00000	
5	0.2461(-2)	0.3854(-2)	0.7952	0.2009	1.00000	11
	0.3854(-2)	0.3638(-1)	0.1984	0.7589	1.00000	
6	0.2457(-2)	0.3864(-2)	0.7952	0.2010	1.00000	17
	0.3864(-2)	0.3641(-1)	0.1985	0.7588	1.00000	

<sup>a</sup>In all cases the integration range was  $(-4.2, 4.2)$  a.u. and the number of sectors  $M = 200$ .

<sup>b</sup>In the asymptotic regions of the reaction coordinate the basis functions describe even vibrational states of the molecules.

<sup>c</sup>Elements of these matrices are listed as:  $\begin{pmatrix} 0,0 & 0,2 \\ 2,0 & 2,2 \end{pmatrix}$ .

Whereas the difference between both methods stated in the last point is only a manifestation of the lack of convergence of the results with respect to the size of the basis set employed, the remaining points testify convincingly to the superiority of the new method in application to the nondiabatic coupled equations.

Proceeding to the second question of our computational investigations we have changed the test problem to the collinear model of inelastic atom-diatom collision of Secret and Johnson.<sup>7</sup> This choice was motivated by our wish to get at the same time some complementary information to the work by M. Baer *et al.*<sup>5</sup> recommending the adiabatic approach for studying vibrational excitation problems. Several arguments have been found<sup>5</sup> in favor of this approach. The most important of them seems to be the high rate of convergence of the calculated transition probabilities with respect to the basis set size. It was shown in the collinear model that this rate for the adiabatic basis can be considerably higher than for the asymptotic basis traditionally employed in that kind of problem. This gave the authors a good reason for expressing the opinion that the adiabatic approach, despite some complications with the first deriva-

tive coupling, should lead to computational procedures much more efficient in solving at least some problems. The procedure used by them for solving the adiabatic coupled equations was just the standard one in the sense that it required only one transformation to the appropriate diabatic representation for the entire problem. In support of the above opinion the authors pointed out the possibility of using repeatedly the same transformation to change the representation of the coupled equations for problems differing only in values of total energy. We decided to follow this suggestion with the intent to learn how profitable it can be in combination with the standard (in the above sense) procedures as well as with our new algorithm for the nondiabatic coupled equations.

Thus, solving the collinear collision model in the adiabatic representation,<sup>6</sup> we tried our algorithm:

(a) in its version from the preceding section but with additional operations for storing all calculated matrices  $\mathcal{T}$ ,  $B$ , and  $V(x_l)$  for  $l = 0, 2, 4, \dots, M$ , (b) in the abbreviated version using the previously stored information, and the corresponding two versions of the standard-type procedure. This procedure was similar to that of Ref.

TABLE II. Some transition probabilities  $P_{i-j}$  for the collinear model of He + H<sub>2</sub> collision obtained in the adiabatic (upper value) and the asymptotic approaches with different basis set sizes  $N$ . Total energy is  $E = 6\hbar\omega$ .

$P_{i-j}$	0-1	0-2	0-3	1-2	1-3	2-3	2-4	3-4
$N$								
7	0.4874 0.4887	0.1593 0.1568	0.1240(-1) 0.1195(-1)	0.3852 0.3861	0.9274(-1) 0.8848(-1)	0.3202 0.3152	0.1887(-1) 0.1690(-1)	0.1329 0.1253
8	0.4874 0.4875	0.1593 0.1590	0.1240(-1) 0.1235(-1)	0.3852 0.3853	0.9274(-1) 0.9226(-1)	0.3202 0.3197	0.1887(-1) 0.1869(-1)	0.1329 0.1324
9	0.4874	0.1593	0.1240(-1)	0.3853	0.9270(-1)	0.3202	0.1886(-1)	0.1329

5 in the part concerning the determination of the transformation matrix,<sup>11</sup> but for the diabatic equations solver the log-derivative method of Johnson<sup>4</sup> was used. In version (a) of this procedure all matrices  $\mathcal{T}(x_i; \bar{x})$  with  $\bar{x} = x_M$  and  $V(x_i)$  needed for finding the matrix  $B_{\bar{x}}(x_i)$  at  $l = 0, 1, 2, \dots, M$  were calculated, and the matrices  $B_{\bar{x}}$  were stored for version (b) where no use was made of any subroutines related to the determination of the coupling matrix for the diabatic equations.

We have repeated all calculations of Baer *et al.*<sup>5</sup> for the He + H<sub>2</sub> system, including those based on the asymptotic approach, where we also used the log-derivative algorithm. In Table II we list only those transition probabilities not given in Ref. 5.

Our primary concern here is with the efficiency of our new algorithm as compared to the more standard approach of Baer *et al.*<sup>5</sup> In Fig. 1 we plot time against basis set size. The dashed lines are for the method of Baer *et al.* and the solid lines represent the present algorithm. The curves marked A are calculations for a first energy for which all of the transformations must be computed. The curves marked B are for a second energy for which the transformations had been saved from a previous calculation. The dotted line gives the times for the standard diabatic approach as a function of basis size. From this figure we can make several interesting observations:

- (i) The new algorithm is much more efficient than the standard procedure when full versions are used and all operations needed for solving a given problem are performed.
- (ii) The improvement achieved by reusing some of the information from the previous runs, instead of calculating it every time, is much greater however, in the case of standard procedure.<sup>5</sup>
- (iii) The abbreviated version (b) of the standard procedure—the most efficient of the algorithms tested for solving the coupled equations in the adiabatic approach—appears to be approximately as fast as the log-derivative algorithm when applied to a basis set two larger.

As a comment on the points (i) and (ii), we summarize again the similarities and the differences in the construction of the algorithms.

In the derivation of both algorithms, the boundary value problems related to the sector  $L$  propagators for the

original nondiabatic coupled equations were transformed to the appropriate problems for the diabatic equations. These problems were next converted to the integral equations form and discretized by the Simpson quadrature formula in order to obtain approximate expressions for the sector propagators. The subsequent accumulation of these propagators is the essence of both algorithms. The difference in their form arises from the different choices of the diabatic representation, by which the original nondiabatic representation is replaced. In the standard algorithm we are dealing with only one diabatic representation which is defined at once for all sectors. The accumulation of the sector propagators is performed entirely in this representation; no intermediate result must be transformed to the original representation. Therefore this part of the standard algorithm is very efficient and structurally independent of the part concerning the determination of the transfor-

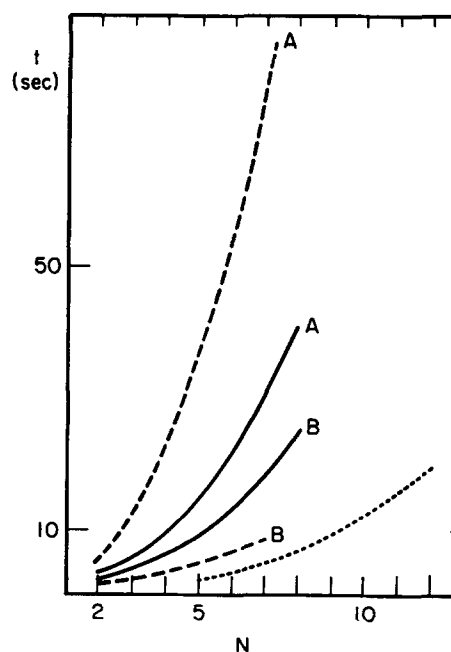


FIG. 1. Execution time  $t$  vs basis set size  $N$  for the algorithm tested on the collinear model of He + H<sub>2</sub> collision. The solid lines correspond to the new algorithm of this paper, the broken lines—to the standard procedure described in the text. A and B denote the full and the abbreviated versions of these algorithms. The dotted line corresponds to the original log-derivative algorithm used in the asymptotic approach.



mation matrix. In the present algorithm different diabatic representation are chosen for different sectors. This fact complicates to some degree, the process of the accumulation of the sector propagators.<sup>12</sup> The determination of the transformation matrices independently for each sector, however, turns out to be much less time consuming than the determination of one matrix for the entire interval in the standard algorithm. Thus, at the expense of some complications of one part, i.e., the part which remains in the abbreviated version (b), we gain quite a large improvement in the full version of the present algorithm.

Point (iii) seems to confirm to some degree the expectations of the authors of Ref. 5 concerning the computational advantages of the adiabatic approach. Due to the improvement achieved in the abbreviated version of the standard procedure the adiabatic approach becomes competitive to the asymptotic approach. In the model tested the basis size requirements of the asymptotic approach usually exceeded the requirements of the adiabatic approach by more than two functions (see Baer *et al.*<sup>5</sup> for the detailed comparison). So, the adiabatic approach was more efficient in computing the convergent results, but no cases was its superiority as large as one order of magnitude in the execution time.

As was already mentioned, the abbreviated versions of the algorithms for solving the nondiabatic coupled equations are applicable to serial calculations performed for one collisional system at many total energies. It is not surprising that the abbreviated version of the generalized log-derivative method does not compete with the abbreviated version of the standard method. Clearly, one would use a method which handles a first derivative term only for a case in which a first derivative term is necessary. Thus one should use the full approach, including the first derivative term, only when the first derivative term is intrinsically present, as in a reactive scattering problem or a curve crossing problem. The present approach might be useful also in solving the equations of the Perturbed Rotational State approximation<sup>12</sup> in the fully quantum mechanical form.<sup>14</sup>

In conclusion, we would like to say that both algorithms

tested here, i.e., the new generalization of the log-derivative method for the nondiabatic equations and the version for the diabatic equations in the standard arrangement for treating the first derivative coupling, reveal properties which encourage continuing investigation on applications of these algorithms. As invariant imbedding approximate solution algorithms, they are expected to be very useful in the reactive scattering calculations, where few procedures of this type have been tried so far.

Work on including these algorithms into Walker's RXN1D program<sup>10</sup> for solving collinear atom-diatom reactive problems is in progress.

<sup>1</sup>L. D. Thomas, M. H. Alexander, B. R. Johnson, W. A. Lester, Jr., J. C. Light, K. D. McLenithan, G. A. Parker, M. J. Redmon, T. G. Schmalz, D. Secrest, and R. B. Walker, *J. Comput. Phys.* **41**, 407 (1981).

<sup>2</sup>J. C. Light and R. B. Walker, *J. Chem. Phys.* **63**, 1598 (1976).

<sup>3</sup>F. Mrugała and D. Secrest, *J. Chem. Phys.* **78**, 5954 (1983).  
Errata: In this paper Eq. (54d) should read  $\mathcal{L}_0^{(4)} = 0$ .

<sup>4</sup>B. R. Johnson, *J. Comput. Phys.* **13**, 445 (1973).

<sup>5</sup>M. Baer, G. Drolshagen, and J. P. Toennies, *J. Chem. Phys.* **73**, 1690 (1980).

<sup>6</sup>E. L. Ince, *Ordinary Differential Equations* (Dover, New York).

<sup>7</sup>D. Secrest and B. R. Johnson, *J. Chem. Phys.* **45**, 4556 (1966).

<sup>8</sup>S.-F. Wu, B. R. Johnson, and R. D. Levine, *Mol. Phys.* **25**, 839 (1973).

<sup>9</sup>S.-F. Wu and R. D. Levine, *Mol. Phys.* **22**, 881 (1971).

<sup>10</sup>R. B. Walker, 1978, Quantum Chemistry Program Exchange, Program No. 352.

<sup>11</sup>The necessary matrix diagonalizations were performed using the HQR2 EISPACK routine.

<sup>12</sup>It should be noted that in a reactive collision, as opposed to the present inelastic collision, it is necessary to make sector transformations more often and either the present method or the more general approach of Ref. 3 are the only approximate solution approaches available.

<sup>13</sup>K. Takayanagi, *J. Phys. Soc. Jpn.* **45**, 976 (1978).

<sup>14</sup>K. Sakimoto, Institute of Space and Aeronautical Science Research Note 125, University of Tokyo (1980).