The Schwinger and Newton variational principles for the log-derivative matrix[a]

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We present the Schwinger and Newton variational principles for the log-derivative matrix. These methods have one significant advantage over their K, or T matrix analogs: the Green's functions that satisfy the log-derivative boundary conditions can be made independent of the scattering energy, which means that *all matrix elements between basis functions become energy independent, and hence need be evaluated only once*. The convergence characteristics of these functionals are compared with those of the K matrix Schwinger and Newton functionals, for potential scattering problems. The amplitude density version of the Newton variational principle is then generalized to the multichannel case, and used to compute transition probabilities for a popular inelastic scattering problem at several energies. These results are compared to those obtained from the application of a discrete representation of the Kohn variational principle for the log-derivative matrix to the same problem.

I. INTRODUCTION

In recent years, variational methods have proved to be extremely powerful in the exact quantum mechanical descriptions of collision events between atoms and diatomic molecules. Three of the most commonly used variational methods are due to Kohn (the Kohn variational principle, or the KVP),[1,2] Schwinger (the SVP),[2,3] and Newton (the NVP).[4] Miller and co-workers recently used the S matrix version of the KVP,[5] to compute the S matrix elements for the $H + H_2$,[5(b),5(c)] and $F + H_2$[6] reactions, and more recently, to compute the integral cross sections for the $H + H_2$ reaction at several energies.[7] The Schwinger method for the K matrix has been used to study collinear atom–diatom reactions,[8] and both the SVP and the NVP have been used in the study of inelastic and reactive collisions in three dimensions.[9] Recently, the amplitude density Newton method[9] for the K matrix was also used in a calculation of state-to-state cross sections for the $H + H_2$ reaction at one energy.[10]

Converged transition probabilities have also been computed for the $H + H_2$, $D + H_2$, $O + H_2$, and $H + HBr$ reactions using a method of moments[11] derived[9(b)] by inserting a resolution of the identity in the matrix elements of the NVP.

A variational method for the logarithmic derivative of the wavefunction was first presented by Kohn in 1948.[1] This stationary functional was recently applied by Manolopoulos and Wyatt to the 3D $H + H_2$ reactive scattering problem.[12] That work demonstrated that the log-derivative Kohn method becomes particularly simple and elegant, if the following boundary conditions were imposed on the scattering wave function $\Psi(R)$: $\Psi(0) = 0$, and $\Psi(a) = 1$, where a is some "sufficiently large" value of the radial coordinate R at which the log-derivative $Y(a)$ is evaluated. Once the log-derivative matrix $Y(a)$ is known, other quantities of interest, such as the K, S, or the T matrices can be computed from it in a straightforward manner.

This paper presents the Schwinger[2,3] and the Newton[4] variational functionals for the log-derivative matrix, using the same asymptotic boundary conditions as those of Ref. 12. To the best of our knowledge, these functionals have not been derived and tested previously. For simplicity, we derive the stationary expressions using potential scattering as an example. The convergence characteristics of these functionals are then tested using three one-dimensional potentials and three L^2 basis sets. We compare the convergence of the log-derivative methods to the results of the more familiar K matrix versions of the SVP and the NVP. Generalization to multichannel (including reactive) scattering is straightforward, and is illustrated by using the amplitude density version of the Newton variational principle in the Secrest–Johnson $He + H_2$ inelastic scattering problem.[13] We acknowledge the recent work of Manolopoulos and Wyatt[12] as the inspiration for the present attempt.

Variational methods reduce a scattering problem to a set of linear algebraic equations, which may be written in matrix form as $\mathbf{AC} = \mathbf{B}$. The solution to the problem is then arrived at by obtaining the unknown quantities $\mathbf{C}$ by solving the system of equations or by inverting $\mathbf{A}$, so that $\mathbf{C} = \mathbf{A}^{-1}\mathbf{B}$. The effort involved in implementing a variational method can therefore be divided into two parts: in the first, one must evaluate the matrix elements that constitute the matrices $\mathbf{A}$ and $\mathbf{B}$; in the second, the unknown quantities $\mathbf{C}$ are obtained by one of the two ways mentioned above.

It seems to us that at least two considerations become important in choosing one variational method over another, to tackle a given problem. The first is the computational effort (time) involved in evaluating the matrix elements of $\mathbf{A}$ and $\mathbf{B}$. In this regard, the Kohn methods[5–7,12] have a definite advantage. The Kohn functional is remarkably simple, and a large number of the matrix elements turn out to be energy independent[5(c),12,14] and need not be reevaluated each time the scattering energy is changed. On the other hand, the Schwinger and Newton functionals for the K matrix contain Green's functions which enforce the asymptotic, energy-dependent, boundary conditions. This makes all matrix elements in these functionals energy dependent, and so the Green's functions and their matrix elements must be reeval-

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uated each time the energy is changed. Since in general, scattering calculations need to be conducted at more than one energy, this proves to be a serious handicap for these methods. The second consideration is the minimum size of the matrices **A** and **B** for which an acceptable level of accuracy can be achieved by the method. The computational effort for the latter part of the variational problem, i.e., finding the unknowns **C**, formally scales as the third power of the order of matrix **A**. Although this step turns out to be highly vectorizable and is, therefore, rapidly executed in modern supercomputers, it is clear that for large enough problems, this step will dominate the calculation. For the large number of workers who do not have ready access to a CRAY-2 with its enormous high speed memory, the amount of memory required to store and manipulate **A** and **B** also becomes an important issue. For multichannel scattering problems, the order of **A** is determined by the quantity mN, where m is the number of channels and N, the number of basis functions used per channel. Thus, for multichannel problems, even a modest reduction in N results in a large reduction in the order of **A**. In this regard, the Schwinger and Newton methods seem to have a definite advantage. It is now well established that these methods achieve acceptable levels of accuracy with fewer basis functions than the Kohn method, for a variety of potentials.[15,16] With the inclusion of suitable distortion potentials, the SVP and the NVP have been shown to converge with extremely small values of N, for reactive scattering problems.[9,10] Therefore, even though the evaluation of individual matrix elements is a more time consuming step in the SVP and the NVP, the number of matrix elements that have to be evaluated can be small.

The present approach is the result of an attempt to combine, to the extent possible, the best features of the Kohn method and those of the Schwinger and Newton methods. This means that the matrix elements of **A** and **B** be made as independent of the scattering energy as possible, while retaining the more rapidly convergent properties of the integral equation methods. Below, we show that the Schwinger and Newton variational principles for the log-derivative matrix meet these goals. The present formulation is shown to have significant computational advantages over the SVP and the NVP for the K matrix.

The remainder of this paper is organized as follows: in Sec. II, we derive the stationary expressions for the log-derivative matrix $Y(a)$. In the process, we discuss the boundary conditions chosen and present Green's functions that satisfy these boundary conditions. The ensuing discussion shows that the log-derivative Schwinger and Newton methods promise great savings in computational effort, compared to the K matrix versions of the methods. In Sec. III we test the variational functionals using potential scattering from one-dimensional potentials. The results are compared with those of the Schwinger and Newton methods that compute the K matrix directly. In Sec. IV, we extend the amplitude density Newton method to the multichannel case, and use the method to compute transition probabilities for the Secrest–Johnson He + H_2 problem at several energies. In this section, we also apply the log-derivative Kohn method of Manolopoulos and Wyatt[12] to the same problem, and compare the results from the two methods. Finally in Sec. V we summarize the important aspects that have emerged from our studies and discuss a modification that promises to make the present method even more efficient in terms of computational effort.

II. THE LOG-DERIVATIVE SVP AND NVP

A. The variational functionals

Limiting our discussion to the case of potential scattering, we write

$$\mathscr{L}(R) = T(R) + V(R) - E, \tag{1}$$

where $T(R)$ and $V(R)$ are the kinetic and potential energy terms, respectively, of the Hamiltonian, R is the distance between the colliding particles, and E is the scattering energy. For later use, we also note that $\mathscr{L}(R)$ can be partitioned rather arbitrarily into two pieces,

$$\mathscr{L}(R) = H_0(R) + W(R), \tag{2}$$

where we demand that $H_0(R)$ contain the kinetic energy operator.

The exact scattering wave function $\Psi(R)$ satisfies $\mathscr{L}(R)\Psi(R) = 0$. We require the wave function $\Psi(R)$ to satisfy the following boundary conditions: $\Psi(0) = 0$, and $\Psi(a) = 1$, where a is chosen to be some large value of R, so that for $R > a$, $\Psi(R)$ can be satisfactorily represented as a superposition of plane waves. The first of these conditions is physically motivated, while the second is motivated by the great simplification that results in the log-derivative formulation: if $\Psi(a) = 1$, then $Y(a) = \Psi'(a)\Psi(a)^{-1} = \Psi'(a)$, where the prime indicates differentiation with respect to R. We refer to these boundary conditions as the (0,1) boundary conditions. It is then straightforward, using standard Green's function arguments,[17] to rewrite this two-point boundary value problem for $\Psi(R)$ as an integral equation in the interval $(0,a)$,

$$\Psi(R) = \phi_r(R) + \int_0^a dR'\, G^0(R,R')W(R')\Psi(R'), \tag{3}$$

where, $\phi_r(R)$ is the regular solution to the reference problem $H_0(R)\phi(R) = 0$, subject to the boundary conditions $\phi_r(0) = 0$, $\phi_r(a) = 1$ [$\phi_i(R)$ being the corresponding irregular solution, subject to the boundary conditions $\phi_i(0) \neq 0$, $\phi_i(a) = 0$], and

$$H_0(R)G^0(R,R') = -\delta(R-R'), \tag{4}$$

where we have adopted units in which $\hbar^2/2\mu = 1$. It is well known[17] that

$$G^0(R,R') = \phi_r(R_<)\Omega^{-1}\phi_i(R_>),$$

where $(R_<, R_>)$ are the lesser and greater, respectively, of (R,R'), and the constant Ω is the Wronskian given by

$$\Omega = \phi_r(R)\phi_i'(R) - \phi_i(R)\phi_r'(R).$$

The expression for the log-derivative $Y(a)$ can now be found by simply differentiating both sides of Eq. (3), and evaluating the resulting function at $R = a$. This leads to the result[18]

$$Y(a) = Y_0(a) + \int_0^a dR'\,\phi_r(R')W(R')\Psi(R'), \qquad (5)$$

where $Y_0(a) = \phi_r'(a)$, and we have used the fact that $\Omega^{-1}\phi_i'(a) = 1$.[18] Stationary expressions for the integral on the right-hand side of Eq. (5) can now be obtained in the manner suggested by the derivations of the Schwinger and the Newton K or T matrix functionals,[15] by the application of Eq. (3). We thus get the Schwinger and the Newton functionals for the log-derivative matrix elements:

$$\begin{aligned} Y(a) = Y_0(a) + [&2\langle\phi_r|W|\Psi\rangle \\ &- \langle\Psi|W - WG^0W|\Psi\rangle] \end{aligned} \qquad (6)$$

for the SVP and

$$\begin{aligned} Y(a) = Y_0(a) + [&Y_1^B + 2\langle\phi_r|WG^0W|\Psi\rangle \\ &- \langle\Psi|W(G^0 - G^0WG^0)W|\Psi\rangle] \end{aligned} \qquad (7)$$

for the NVP, where $Y_1^B = \langle\phi_r|W|\phi_r\rangle$, the first term in the Born expansion of Eq. (3). Here we introduce the notation NVP-Ψ to refer to the functional in Eq. (7), since the wave function $\Psi(R)$ is to be expanded in a set of basis functions. The Newton functional may also be written in terms of the amplitude density $F(R) = W(R)\Psi(R)$–denoted as NVP-F–as follows:

$$\begin{aligned} Y(a) = Y_0(a) + [&Y_1^B + 2<\phi_r|WG^0|F\rangle \\ &- \langle F|G^0 - G^0WG^0|F\rangle]. \end{aligned} \qquad (8)$$

Once the log-derivative is obtained at $R = a$, the K, T, or S matrix elements are evaluated in a straightforward manner. To get the K matrix elements, we write

$$\begin{aligned} Y(a) &= \Psi'(a)\Psi(a)^{-1} \\ &= k\,[\cos(ka) - K\sin(ka)]\,[\sin(ka) \\ &\quad + K\cos(ka)]^{-1} \end{aligned} \qquad (9)$$

from which K is easily obtained. It is important to realize that the quantities $Y(a)$ and K in Eq. (9) are matrices, and hence, in the case of multichannel scattering, the whole Y matrix is required before K can be computed.

B. The Green's functions

In integral equation methods for the K matrix, the Green's function is determined by the requirement that the asymptotic wavefunction be of the form

$$\lim_{R\to\infty} \Psi(R) \approx \sin(kR) + K\cos(kR).$$

The result of this requirement, as mentioned in Sec. I, is that the Green's function for these methods explicitly depends on the scattering energy, through k. Similar restrictions are present in methods for T and S matrix elements. In the case of the log-derivative formulation, however, the asymptotic boundary condition is the simple requirement that $\Psi(a) = 1$. This gives us much more freedom in the choice of the reference problem. We illustrate this below, by presenting Green's functions for a class of reference problems that have analytic solutions.

Let us consider reference problems that can be expressed as

$$\left(\frac{d^2}{dR^2} + \kappa^2\right)G^0(R,R') = \delta(R - R'). \qquad (10)$$

Then, $W(R) = V(R) - \lambda$, where $\lambda = (k^2 - \kappa^2)$, and $k^2 = E$, because of our particular choice of units. The quantity κ^2 can be viewed as a reference energy, so that Green's functions that satisfy Eq. (10) can be called "reference energy Green's functions." Subject to the boundary conditions $\phi_r(0) = 0$, $\phi_r(a) = 1$, and $\phi_i(0) = 1$, $\phi_i(a) = 0$, we get case (1) $\kappa^2 > 0$,

$$\begin{aligned} &G^0(R,R') \\ &= -\{\sin(\kappa R_<)\sin[\kappa(a - R_>)]\}[\kappa\sin(\kappa a)]^{-1}, \end{aligned} \qquad (11)$$

case (2) $\kappa^2 < 0$,

$$\begin{aligned} &G^0(R,R') \\ &= -\{\sinh(\kappa R_<)\sinh[\kappa(a - R_>)]\}[\kappa\sinh(\kappa a)]^{-1}, \end{aligned} \qquad (12)$$

and case (3) $\kappa^2 = 0$,

$$G^0(R,R') = (-1/a)R_<(a - R_>). \qquad (13)$$

It is easy to see that while any one of the Green's functions (11)–(13) are acceptable for use in the SVP functional of Eq. (6) and the NVP functionals of Eq. (7) or (8), they do not depend on the scattering energy k^2. We discuss the advantages offered by this below.

Let us now examine the behavior of $\Psi(R)$ in (3), at $R = 0$ and $R = a$. Inserting the Green's function $G^0(R,R')$ into Eq. (3), we get

$$\begin{aligned} \Psi(R) &= \phi_r(R) \\ &\quad - \phi_i(R)\left[\int_0^R dR'\,\phi_r(R')W(R')\Psi(R')\right]\Omega^{-1} \\ &\quad - \phi_r(R)\left[\int_R^a dR'\,\phi_i(R')W(R')\Psi(R')\right]\Omega^{-1}. \end{aligned}$$

The expression above reveals two aspects that deserve comment. First of all, it satisfies, as it should, the (0,1) boundary conditions – at $R = 0$, the first integral vanishes and $\phi_r(0) = 0$, and at $R = a$, the second integral vanishes, $\phi_i(a) = 0$, and $\phi_r(a) = 1$, Secondly, the expression above implies that since the Green's function enforces the (0,1) boundary conditions, the basis sets used to expand the wavefunction $\Psi(R)$ within the integrals, need not, in principle, satisfy *either* boundary condition. We illustrate this in Sec. III.

C. The half-integrated Green's functions

The difficult part of computations using integral equation methods for scattering calculations is evaluating the matrix elements of operators containing the Green's function. These matrix elements can be evaluated faster and with higher accuracy of we first evaluate the half-integrated Green's function,[9(b),15] defined as

$$g_n(R) = \int_0^a dR'\,G^0(R,R')W(R')u_n(R') \qquad (14)$$

when the wave function is expanded in terms of basis functions $\{u_n\}$, and

$$G_n(R) = \int_0^a dR'\, G^0(R,R')u_n(R') \qquad (15)$$

when the amplitude density is expanded. Then, for example, matrix elements of the type $\langle u_m|WG^0W|u_n\rangle$, which result from a basis set expansion of $\Psi(R)$ in Eq. (6), are computed as $\langle u_m|W|g_n\rangle$, and matrix elements of the type $\langle u_m|G^0WG^0|u_n\rangle$ in Eq. (8), as $\langle G_m|W|G_n\rangle$.

A closer examination of the integrals above reveals the important advantage of the log-derivative approach. As shown above, the quantity $W(R)$ is explicitly written as $V(R) - \lambda$, where λ is a constant whose value depends only on the scattering energy and the value chosen for κ in the Green's function. Using this relation in Eq. (14), we get

$$g_n(R) = \int_0^a dR'\, G^0(R,R')V(R')u_n(R') - \lambda \int_0^a dR'\, G^0(R,R')u_n(R'),$$

which we write as

$$g_n(R) = g_n^V(R) - \lambda G_n(R).$$

With this result, the system of linear algebraic equations for the expansion coefficients $\{c_n\}$ in the Schwinger method can be written as

$$\sum_{n=1}^{N} \{\langle u_m|V|u_n\rangle - \lambda\langle u_m|u_n\rangle - \langle u_m|V|g_n^V\rangle - \lambda^2\langle u_m|G_n\rangle + \lambda[\langle g_m^V|u_n\rangle + \langle u_m|g_n^V\rangle]\}c_n = \langle u_m|V|\phi_r\rangle - \lambda\langle u_m|\phi_r\rangle, \quad m = 1,...,N.$$

Recall now that the Green's function $G^0(R,R')$ used in the log-derivative formulations are independent of the scattering energy. It is then immediately obvious that the half-integrated Green's functions and *all the integrals above are also energy independent.* Similar expressions consisting only of energy independent integrals can also be written for the NVP-Ψ functional of Eq. (7), and the NVP-F functional of Eq. (8). The latter yields a particularly simple set of equations for the expansion coefficients:

$$\sum_{n=1}^{N} \{\langle u_m|G_n\rangle - \langle G_m|V|G_n\rangle + \lambda\langle G_m|G_n\rangle\}c_n = \langle G_m|V|\phi_r\rangle - \lambda\langle G_m|\phi_r\rangle, \quad m = 1,...,N. \qquad (16)$$

The full significance of this becomes apparent only when one considers the effort involved in computing the K, or T matrix directly using the Schwinger or Newton methods. As we pointed out earlier, the asymptotic boundary conditions in these methods make the Green's function explicitly *energy dependent.* This means that the Green's function must be defined at each energy. If the reference problem for $G^0(R,R')$ does not have an analytic solution, then it has to be reevaluated numerically. Moreover, the half-integrated Green's functions and their matrix elements must also be found each time the scattering energy is changed. For reactive scattering problems, this step also involves the evaluation of the exchange integrals.[19] It is thus clear that these methods require considerable amounts of computation to be repeated at each energy. If the Green's function is energy independent, then these steps have to be performed only once, for a given basis size. This helps to reduce the "setup" time in the log-derivative Schwinger and Newton methods dramatically. Section V further substantiates these arguments.

III. POTENTIAL SCATTERING

In this section, we present the results of the calculations conducted in order to test the convergence characteristics of the two variational functionals presented above. We compute the log-derivative $Y(a)$ for the following three one-dimensional potentials:

Potential A: $10[1 - e^{-(3/2)(R-2)}]^2 - 10$,
Potential B: $-10e^{-R}$,
Potential C: $10e^{-R}$,

using three types of L^2 basis functions to expand the wave function in the case of the SVP, and the wave function and the amplitude density in the case of the NVP. The L^2 basis sets are

Basis 1: $u_n(R) = \sin\left(\frac{n\pi}{a}R\right) \quad n = 1,...,N.$

Basis 2: $u_n(R) = \exp[-\alpha(R - R_n)^2]$,

$$R_n = \frac{na}{N+1}, \quad \alpha = \left(\frac{0.60a}{N+1}\right)^2;$$

Basis 3: $u_n(R) = \prod_{\substack{m=0 \\ n\neq m}}^{N} \frac{(R - R_m)}{(R_n - R_m)}, \quad n = 1,...,N.$

Basis 1 and 2 are, respectively, the 1D box eigenfunctions and the very popular distributed Gaussian basis.[20] We noted in Sec. II B, that since the Green's function enforces the (0,1) boundary conditions, the basis functions for the log-derivative Schwinger and Newton methods can be chosen without regard to these boundary conditions. We have included the distributed Gaussian basis in our calculations to illustrate this aspect. It is easily verified that the Gaussians used here have significant amplitudes at both limits of the interval $(0,a)$. Basis 3 consists of the Lobatto shape functions,[12] which are Lagrange interpolation polynomials defined over a set of nodes $\{R_m\}$ chosen to be the abscissae of the N-point Lobatto quadrature rule.[12,21]

Table I presents the absolute values of the fractional error $|\epsilon|$ in the K matrix elements as the number of basis functions is increased, for the three potentials when basis 1 is employed. The scattering energy $E = 4.0$. The Green's function of Eq. (11) is used in these calculations with $\kappa^2 = 4.0$, so that close analogy with the SVP and the NVP for the K matrix is achieved. For comparison, we also present the results of the Schwinger and the Newton variational methods that compute K directly. The notation is as follows: $|\epsilon|_f^m$, where the subscript indicates the variational principle and, where necessary (as in the case of the NVP), the quantity expanded in the L^2 basis—e.g., NVP-Ψ indicates that the wave function $\Psi(R)$ was expanded in terms of the basis, and used in Eq. (7)—and the superscript indicates the quantity computed directly, i.e., Y or K, using the functional.

TABLE I. Fractional errors in K matrix elements using basis 1. The Green's function of Eq. (11) is used with $\kappa^2 = 4.0$.

N	$\lvert\epsilon\rvert^{Y}_{\mathrm{SVP}}$	$\lvert\epsilon\rvert^{K}_{\mathrm{SVP}}$	$\lvert\epsilon\rvert^{Y}_{\mathrm{NVP}\text{-}F}$	$\lvert\epsilon\rvert^{K}_{\mathrm{NVP}\text{-}F}$	$\lvert\epsilon\rvert^{Y}_{\mathrm{NVP}\text{-}\Psi}$	$\lvert\epsilon\rvert^{K}_{\mathrm{NVP}\text{-}\Psi}$
Potential A						
20	0.0370	0.0370	0.0734	0.0734	0.0024	0.0024
21	0.0134	0.0134	0.0715	0.0714	0.0015	0.0015
22	0.0044	0.0044	0.0557	0.0556	0.0015	0.0015
23	0.0001	0.0001	0.0332	0.0331	0.0012	0.0012
24	0.0056	0.0056	0.0152	0.0151	0.0008	0.0008
25	0.0074	0.0074	0.0056	0.0056	0.0004	0.0004
Potential B						
15	0.0017	0.0017	0.0266	0.0265	0.0001	0.0001
16	0.0009	0.0009	0.0156	0.0156	a	a
17	0.0005	0.0005	0.0094	0.0094	a	a
18	0.0003	0.0003	0.0058	0.0058	a	a
19	0.0002	0.0002	0.0037	0.0037	a	a
20	0.0001	0.0001	0.0024	0.0024	a	a
Potential C						
5	0.8368	0.8368	4.7912	1.0507	0.1014	0.0360
6	0.0915	0.0915	0.1346	0.1693	0.0012	0.0024
7	0.0015	0.0015	0.0019	0.0021	a	a
8	0.0007	0.0007	0.0002	0.0002	a	a
9	0.0003	0.0003	0.0002	0.0002	a	a
10	0.0003	0.0003	0.0002	0.0002	a	a

[a] Error is less than 5.0×10^{-5}.

It is obvious from Table I that a particular log-derivative method and the corresponding K matrix method converge at the same rate. This indicates that one does not have to pay any price for using the log-derivative Schwinger and Newton methods as opposed to their K matrix analogs. Since, as discussed above and illustrated below, these methods are able to use energy independent Green's functions with all the accompanying computational advantages, using the log-derivative methods does indeed seem to be a step in the right direction. It is also seen from Table I that the NVP converges faster if the wave function, rather than the amplitude density is expanded in the L^2 basis. A tentative explanation for this behavior is given in Ref. 15(a).

A comparison of the results obtained by using basis 2 in the same set of calculations are presented in Table II. Recall that this basis does not satisfy the (0,1) boundary conditions. The results in Table II indicate that using a basis that does not satisfy the (0,1) boundary conditions does not, in itself, cause the log-derivative and K matrix methods to converge at different rates. From a comparison of Table II to Table I, one would conclude that the convergence is slower if basis 2 rather than basis 1 is used. It is well-known, however, that careful choice of the positions and widths of the Gaussians significantly alter their convergence characteristics. The present calculations are intended for illustrative purposes only, and we have made no attempts to fine-tune basis 2 for these problems.

We now come to an illustration of the most interesting and potentially the most useful feature of the log-derivative Schwinger and Newton methods, viz., the use of the reference energy Green's function to compute $Y(a)$ at many different energies. Table III presents the results of using the Green's function of Eq. (11) in the amplitude density Newton functional of Eqs. (8) and (16), where the amplitude density is expanded in basis 3. The results are presented for eight energies. We set $\kappa^2 = 4.0$, so that at $E = 4.0$, the results listed in Table III provide a fair comparison of the convergence characteristics of this basis against those of basis 1 and 2 in Tables I and II.

The results of Table III indicate that the reference energy Green's function used in the log-derivative NVP-F is capable of achieving rapid convergence of K matrix elements over a wide energy range. We also note that the convergence is fastest when the scattering energy k^2 is close to the value of κ^2, and slower when k^2 is much lower or much higher than this value. This behavior is not surprising, because at values of κ^2 that are different from the scattering energy, the distortion due to $W(R)$ becomes more significant, and the basis functions have to work harder in order to build the wave function in the internal region.

In principle, we should be able to converge the results at any energy using a given value of κ. However, practical considerations dictate that the value of κ be chosen with a view to the range of energies at which the scattering is to be studied. It is clear that the range of energies over which fast convergence can be achieved with a given value of κ will ultimately determine the usefulness of these methods over those that compute the K matrix element directly. It is gratifying therefore, that the results of Table III indicate that this range can be quite large. We shall see in the following section, that this is true even for a multichannel scattering problem.

TABLE II. Fractional errors in K matrix elements using basis 2. The Green's function of Eq. (11) is used with $\kappa^2 = 4.0$.

N	$\lvert\epsilon\rvert^{Y}_{\rm SVP}$	$\lvert\epsilon\rvert^{K}_{\rm SVP}$	$\lvert\epsilon\rvert^{Y}_{\text{NVP-}F}$	$\lvert\epsilon\rvert^{K}_{\text{NVP-}F}$	$\lvert\epsilon\rvert^{Y}_{\text{NVP-}\Psi}$	$\lvert\epsilon\rvert^{K}_{\text{NVP-}\Psi}$
Potential A						
20	0.1686	0.1686	0.1681	0.1681	0.0311	0.0310
21	0.0741	0.0741	0.1543	0.1543	0.0123	0.0123
22	0.0290	0.0290	0.1106	0.1106	0.0051	0.0051
23	0.0093	0.0093	0.0610	0.0610	0.0047	0.0047
24	0.0003	0.0003	0.0254	0.0254	0.0052	0.0052
25	0.0081	0.0081	0.0084	0.0084	0.0045	0.0045
Potential B						
15	0.1974	0.1974	0.0172	0.0172	0.0098	0.0098
16	0.1530	0.1530	0.0148	0.0148	0.0072	0.0072
17	0.1204	0.1204	0.0125	0.0125	0.0055	0.0055
18	0.0970	0.0970	0.0104	0.0104	0.0042	0.0042
19	0.0792	0.0792	0.0085	0.0085	0.0032	0.0032
20	0.0657	0.0657	0.0069	0.0069	0.0025	0.0025
Potential C						
5	1.9563	1.9563	1.2414	2.3709	0.0010	0.0018
6	0.1320	0.1320	0.8100	1.1773	0.0168	0.0211
7	0.0616	0.0616	0.2046	0.2140	0.0016	0.0020
8	0.0076	0.0076	0.0636	0.0656	0.0008	0.0012
9	0.0011	0.0011	0.0195	0.0199	a	a
10	0.0003	0.0003	0.0069	0.0070	a	a

[a] Error is less than 5.0×10^{-5}.

We do not present the results of calculations analogous to those of Table III, for the SVP and the NVP-Ψ functionals, since no new information is conveyed. The NVP-Ψ results, as one might anticipate from Tables I and II, converge faster than the NVP-F results in Table III.

We also do not present the results for the Green's function of Eq. (13). The use of this Green's function results in extremely slow convergence, which is perhaps to be expected from the extremely simple form of the Green's function, and the fact that it corresponds to zero energy. The Green's function of Eq. (12) is used in the following section.

IV. MULTICHANNEL SCATTERING

Extending the methods developed in the earlier sections to the case of multichannel scattering is straightforward. We illustrate this below, using the inelastic scattering problem of Secrest and Johnson,[13] as an example.

The problem is stated as

$$\frac{-1}{2\mu}\frac{\partial^2\Psi}{\partial R^2} - \frac{1}{2}\frac{\partial^2\Psi}{\partial r^2} + \frac{1}{2}r^2\Psi + V(R,r)\Psi = \frac{1}{2}E\Psi, \tag{17}$$

where

$$V(R,r) = V_0 \exp[-\alpha(R-r)].$$

We choose the reference problem solved for the Green's function to be

$$\left(\frac{-1}{2\mu}\frac{\partial^2}{\partial R^2} - \frac{1}{2}\frac{\partial^2}{\partial r^2} + \frac{1}{2}r^2 - \frac{1}{2}\kappa^2\right)G^0(R,R',r,r') = -\delta(R-R')\delta(r-r') \tag{18}$$

which is solved to give

$$G^0(R,R',r,r') = \sum_n G^{(n)}(R,R')\varphi_n(r)\varphi_n(r'),$$

where the φ_n are the orthonormal energy eigenfunctions of the harmonic oscillator problem corresponding to the energy eigenvalues $\epsilon_n = (n + 1/2)$; $n = 0,1,2,\ldots,$ and $G^{(n)}(R,R')$ for the channels open and closed with respect to κ^2 are

$$G^{(n)}(R,R') = \begin{cases} -\sin(\kappa_n R_<)\sin[\kappa_n(a-R_>)][\kappa_n \sin(\kappa_n a)]^{-1}; & \kappa_n^2 > 0, \\ -\sinh(\kappa_n R_<)\sinh[\kappa_n(a-R_>)][\kappa_n \sinh(\kappa_n a)]^{-1}; & \kappa_n^2 < 0, \end{cases} \tag{19}$$

where $\kappa_n^2 = \mu(\kappa^2 - 2n - 1)$, and $R = a$ is the boundary at which the log-derivative matrix is evaluated.

We focus attention on the projected amplitude densities $F_{nm}(R)$ (where n denotes the channel of interest and m is the initial channel), which are defined as

$$F_{nm}(R) = \int_{-\infty}^{\infty} dr\, \varphi_n(r)\, W(r,R)\Psi_m(r,R).$$

TABLE III. The quantities $|\epsilon|^{Y}_{\text{NVP-}F}$ at eight energies, using basis 3. The Green's function of Eq. (11) is used, with $\kappa^2 = 4.0$.

Energy	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
N								
Potential A								
20	0.0975	0.1811	0.0663	0.1327	0.2680	0.1335	0.1884	0.7676
21	0.0587	0.0997	0.0383	0.0720	0.1385	0.0644	0.0851	0.2772
22	0.0577	0.0993	0.0383	0.0720	0.1377	0.0636	0.0824	0.2584
23	0.0335	0.0592	0.0247	0.0481	0.0951	0.0459	0.0596	0.1815
24	0.0127	0.0218	0.0097	0.0187	0.0374	0.0178	0.0243	0.0736
25	0.0090	0.0140	0.0059	0.0111	0.0211	0.0098	0.0122	0.0334
26	0.0086	0.0134	0.0058	0.0109	0.0210	0.0098	0.0122	0.0334
27	0.0043	0.0074	0.0033	0.0064	0.0126	0.0059	0.0079	0.0230
28	0.0016	0.0025	0.0011	0.0022	0.0044	0.0022	0.0028	0.0077
29	0.0011	0.0017	0.0007	0.0014	0.0026	0.0012	0.0015	0.0043
30	0.0010	0.0016	0.0007	0.0013	0.0025	0.0012	0.0015	0.0043
Potential B								
10	0.0216	0.0056	0.0114	0.0133	0.0647	6.8677	1.1104	0.9798
11	0.0166	0.0055	0.0034	0.0091	0.0045	0.0760	1.4957	0.9713
12	0.0116	0.0014	0.0015	0.0024	0.0045	0.0457	0.8894	0.7988
13	0.0033	0.0013	0.0002	0.0003	0.0014	0.0076	0.1577	0.7849
14	0.0031	0.0005	0.0001	a	0.0003	0.0021	0.0410	0.1401
15	0.0017	0.0004	a	a	0.0002	0.0009	0.0070	0.0301
16	0.0013	0.0003	a	a	0.0001	0.0009	0.0026	0.0301
17	0.0009	0.0002	a	a	0.0001	0.0004	0.0002	0.0286
18	0.0007	0.0002	a	a	a	0.0003	0.0001	0.0078
19	0.0005	0.0001	a	a	a	0.0002	0.0001	0.0057
20	0.0004	0.0001	a	a	a	0.0002	a	0.0050
Potential C								
5	0.2976	8.5961	0.7497	1.0882	1.1478	1.1217	0.5464	1.1464
6	0.2532	0.9249	0.4040	1.0969	1.1487	1.5272	0.3995	1.2771
7	0.2308	0.0608	0.3972	0.1016	0.5605	1.5126	8.8815	0.1072
8	0.0719	0.0606	0.0105	0.0058	0.3599	0.6741	1.2904	0.0102
9	0.0303	0.0068	0.0100	0.0043	0.1227	0.6209	0.7289	1.0486
10	0.0178	0.0018	0.0012	0.0013	0.0385	0.1932	0.7073	0.9080
11	0.0105	0.0016	0.0002	0.0001	0.0163	0.1182	0.2285	0.6917
12	0.0065	0.0010	0.0002	a	0.0015	0.0225	0.2245	0.3484
13	0.0042	0.0006	0.0001	a	0.0003	0.0069	0.0149	0.2677
14	0.0028	0.0004	a	a	0.0001	0.0006	0.0141	0.0378
15	0.0020	0.0003	a	a	a	0.0001	0.0015	0.0180

[a] Error is less than 5.0×10^{-5}.

Expanding the $F_{nm}(R)$ in terms of an L^2 basis set $\{u_I(R)\}$, and substituting into the multichannel version of the NVP-*F* functional of Eq. (8), we get the matrix equation

$$\mathbf{Y}(a) = \mathbf{Y}_0(a) + \mathbf{Y}_1^B + \mathbf{B}^T\mathbf{C} + \mathbf{C}^T\mathbf{B} - \mathbf{C}^T\mathbf{A}\mathbf{C}, \qquad (20)$$

where the superscript T denotes the matrix transpose, and

$$(\mathbf{Y}_0)_{n,m} = [\partial(\phi_r)_n/\partial R\,]_{R=a}\delta_{nm},$$

$$(\mathbf{Y}_1^B)_{n,m} = \int_0^a dR \int_{-\infty}^{\infty} dr[\phi_r(r,R)]_n W(r,R)[\phi_r(r,R)]_m,$$

$$[\phi_r(r,R)]_n = \varphi_n(r)\sigma_n(R),$$

where

$$\sigma_n(R) = \sin(\kappa_n R)[\sin(\kappa_n a)]^{-1} \quad \text{(open channel)}$$

$$= \sinh(\kappa_n R)[\sinh(\kappa_n a)]^{-1} \quad \text{(closed channel)}.$$

Also, using lower case subscripts (n,m) to label the channels and upper case subscripts (I,J) to label the L^2 translational basis functions, we get

$$\mathbf{A}_{nI,mJ} = \{\langle u_I|G^{(n)}|u_J\rangle\delta_{nm} - \langle u_I|G^{(n)}W_{nm}G^{(m)}|u_J\rangle\}.$$

and

$$\mathbf{B}_{nI,m} = \langle u_I|G^{(n)}W_{nm}|\sigma_m\rangle,$$

where

$$W_{nm}(R) = \int_{-\infty}^{\infty} dr\,\varphi_n(r)W(r,R)\varphi_m(r)\,.$$

Extremizing the functional (20) with respect to the expansion coefficients **C**, we get a system of linear equations $\mathbf{AC} = \mathbf{B}$, to be solved for the elements of the matrix **C**. Now, recognizing that for our particular choice of the reference problem, $W(r,R)$ can be expressed in terms of $V(r,R) - \lambda$, where λ is a constant that depends only on the scattering energy E and the constant κ (see below), we get

$$\mathbf{A}_{nI,mJ} = \{\langle u_I|G^{(n)}|u_J\rangle\delta_{nm} - \langle u_I|G^{(n)}V_{nm}G^{(m)}|u_J\rangle\}$$
$$+\lambda\,\langle u_I|G^{(n)}G^{(m)}|u_J\rangle\delta_{nm},$$

and

$$\mathbf{B}_{nI,m} = \langle u_I | G^{(n)} V_{nm} | \sigma_m \rangle - \lambda \langle u_I | G^{(n)} | \sigma_m \rangle \delta_{nm},$$

where

$$V_{nm}(R) = \int_{-\infty}^{\infty} dr\, \varphi_n(r) V(r,R) \varphi_m(r),$$

and

$$\lambda = (k_n^2 - \kappa_n^2) = \mu[(E - 2n - 1) - (\kappa^2 - 2n - 1)]$$
$$= \mu(E - \kappa^2).$$

It is interesting that λ turns out to be channel independent, due to mutual cancellation of the channel-dependent internal energy ϵ_n. As in the case of potential scattering, all the matrix elements are independent of the scattering energy, and hence, need be evaluated only once.

To test the NVP-F method for the log-derivative matrix, we choose $\mu = 2/3$, and $\alpha = 0.30$. This choice of paramters, in the reduced units of Secrest and Johnson,[13] correspond to the collision of a He atom with an H_2 molecule. It was pointed out in the previous section that the usefulness of the present method would be determined by the range of scattering energies E for which the transition probabilities converge reasonably quickly (as the basis size is increased), for a given value of κ^2. To estimate this range, we set $\kappa^2 = 6.0$, $a = 40.0$, and compute the log-derivative matrix $\mathbf{Y}(a)$ at seven energies $E = 5.2$, 5.5, 5.8. 6.0, 6.2, 6.5, and 6.9, in the units of the Hamiltonian of Eq. (18). Over this range, 3 vibrational channels, corresponding to $n = 0$, 1, and 2, are open. The channel threshold for the $n = 3$ channel is at the energy $E = (2n + 1) = 7.0$. The log-derivative matrix $\mathbf{Y}$ is used to compute the $\mathbf{S}$ matrix at each energy, following the procedure of Johnson.[22] The results are presented as absolute values of fractional errors in the transition probabilities $P_{nm} = |S_{nm}|^2$. The converged transition probabilities at the energies listed above are given in Table IV.

TABLE IV. Converged transition probabilities for the Secrest–Johnson problem, of Eq. (17). The parameters are, $\mu = 2/3$, $\alpha = 0.30$, $V_0 = 12.0$ and $a = 40.0$. The numbers in parentheses indicate powers of 10.

Energy	P_{01}	P_{02}	P_{12}
4.9	4.578 356(− 3)		
5.2	7.671 344(− 3)	9.570 319(− 9)	4.970 370(− 6)
5.5	1.194 234(− 2)	2.404 123(− 7)	7.968 952(− 5)
5.8	1.755 365(− 2)	1.794 321(− 6)	4.040 532(− 4)
6.0[a]	2.211 020(− 2)	5.052 240(− 6)	9.003 375(− 4)
6.2	2.735 080(− 2)	1.208 199(− 5)	1.734 594(− 3)
6.5	3.656 356(− 2)	3.620 227(− 5)	3.864 658(− 3)
6.9	5.145 192(− 2)	1.190 143(− 4)	8.934 345(− 3)

$E = 7.2$

P_{01}	P_{02}	P_{03}
6.460 132(− 2)	2.511 798(− 4)	2.028 280(− 10)
P_{12}	P_{13}	P_{23}
1.486 627(− 2)	2.839 850(− 8)	7.495 054(− 6)

[a] The results listed are slightly different from those of Refs. 11 and 15. The results listed in Ref. 15 are $P_{01} = 2.210\,93(-2)$, $P_{02} = 5.039\,48(-6)$, and $P_{12} = 8.980\,32(-4)$. We can reproduce these numbers exactly if $a = 100.0$.

We use the basis 1 of Sec. III—the 1D box energy eigenfunctions—to expand the amplitude density. The matrix elements are evaluated as follows: the quantities $V_{nm}(R)$ are evaluated analytically, using the relationship derived by Sharp and Rapp.[23] The integrals over the coordinate R are carried out using a 200 point Gauss–Legendre quadrature rule. The half-integrated Green's functions were evaluated at each Gauss–Legendre point by integrating over R' using a high order Newton–Cotes rule with a stepsize of 0.02 in the intervals $(0,R)$ and (R,a). At the energies of interest, three channels are open. We have used a total of five channels in our calculations. Including more channels has no effect on the converged transition probabilities.

The results are presented in Table V, as fractional errors in the transition probabilities. For comparison, we also present the fractional errors computed from the log-derivative Kohn method of Manolopoulos and Wyatt.[12] Our implementation of this method parallels that of Ref. 12 in every way, and hence we refer the reader to that work for further details of this method. We also note that a recent paper by Peet and Miller[24] describes the application of a discrete representation of the S matrix Kohn method to the same inelastic problem studied here. However, their choice for the parameters μ and α differ slightly from ours.

Many items in Table V deserve comment. First of all, we note that the log-derivative NVP-F converges the transition probabilities to within 1% (0.01 fractional error) of the exact value with only 30–35 L^2 basis functions per channel, *at all energies* investigated. This shows that the log-derivative NVP-F is capable of achieving rapid convergence over an energy range large enough to make the method practically useful. Compared to the convergence rates exhibited by the NVP, the log-derivative KVP requires significantly more basis functions to achieve similar accuracies, especially as the energy increases. This is not surprising, since earlier comparisons of the KVP with the SVP and the NVP have shown[15,16] that the latter methods are capable of faster convergence.

Another item of interest in Table V is that at scattering energies that are very different from the value of κ^2, the NVP-F achieves a certain accuracy very quickly, but is somewhat slow to converge further. Examples of this behavior are the probabilities P_{02} and P_{12} at $E = 5.2$, 5.5, and 6.9. The KVP on the other hand, does require more basis functions than the NVP at these energies to reach 1% accuracy. However, as the number of basis functions is increased, the KVP continues to converge rapidly, eventually achieving higher accuracy than the NVP, for the same number of basis functions. This contrast in behavior between the two methods is a reflection of the fact that the matrix elements of the log-derivative NVP functional in Eq. (20) are not truly energy independent in the same sense as those of the Kohn method. We observed and discussed in Sec III, a similar behavior in the case of the potential scattering results presented in Table III. As mentioned there, the reference energy Green's functions are most efficient when the scattering energy E is in the vicinity of the reference energy κ^2, and when E shifts further and further away from this value, the functional progressively loses its ability to achieve high accuracy rapidly.

TABLE V. Fractional errors in transition probabilities for the Secrest–Johnson problem, of Eq. (17), as functions of the number of L^2 basis functions. The parameters used are identical to those in Table IV. For the NVP, $\kappa^2 = 6.0$.

	P_{01}		P_{02}		P_{12}	
N	NVP-F	KVP	NVP-F	KVP	NVP-F	KVP
$E = 5.2$						
25	0.0221	0.9996	0.1018	0.9997	0.0002	0.6254
30	0.0036	0.9933	0.0141	0.9921	0.0098	0.0061
35	0.0024	1.0593	0.0106	1.0604	0.0079	0.0041
40	0.0015	0.0052	0.0075	0.0052	0.0059	a
45	0.0010	a	0.0054	a	0.0043	a
			$E = 5.5$			
25	0.0190	0.9999	0.0061	0.9999	0.0177	0.8876
30	0.0014	0.9971	0.0055	0.9970	0.0072	0.0152
35	0.0001	0.8199	0.0037	0.8198	0.0039	0.0048
40	a	0.0192	0.0024	0.0192	0.0024	0.0001
45	a	a	0.0016	a	0.0016	a
			$E = 5.8$			
25	0.0026	1.0	0.0035	1.0	0.0002	0.8453
30	0.0007	0.9964	0.0004	0.9970	0.0002	0.1745
35	0.0002	0.8543	0.0001	0.8543	0.0001	0.0084
40	0.0001	0.0077	a	0.0078	a	a
45	0.0001	a	a	a	a	a
			$E = 6.0$			
25	0.0089	1.0	0.0089	1.0	a	0.9894
30	a	0.7615	a	0.5364	a	0.8180
35	a	10.1205	a	10.0951	a	0.1174
40	a	0.1613	a	0.1613	a	0.0018
45	a	0.0005	a	0.0005	a	a
			$E = 6.2$			
25	0.0094	1.0	0.0094	1.0	0.0006	0.9967
30	0.0010	0.9960	0.0012	0.9914	0.0001	0.3156
35	0.0004	0.9428	0.0005	0.9430	a	0.0071
40	0.0002	0.0861	0.0003	0.0861	a	0.0015
45	0.0001	0.0002	0.0002	0.0002	a	a
			$E = 6.5$			
25	0.0563	1.0	0.0610	0.9973	0.0003	0.9982
30	0.0010	0.9999	0.0002	1.0	0.0012	0.9180
35	0.0005	0.9921	0.0001	0.9918	0.0009	0.0684
40	0.0003	0.6626	0.0002	0.6626	0.0006	0.0135
45	0.0001	0.0055	0.0002	0.0055	a	0.0001
			$E = 6.9$			
25	0.4255	1.0	0.4116	0.9858	0.0353	0.9949
30	0.0047	1.0	0.0074	0.9892	0.0116	1.7268
35	0.0008	0.9964	0.0057	0.9972	0.0061	0.2218
40	0.0002	0.8235	0.0038	0.8283	0.0037	0.0232
45	a	0.0312	0.0026	0.0312	0.0025	0.0008

[a] Error is less than 5.0×10^{-5}.

The important point however, is that in spite of this, the NVP is able to achieve accuracies better than 1% very rapidly over a significant range of scattering energies, for a given Green's function reference energy. Within the energy range $5.8 \leqslant E \leqslant 6.5$, the NVP results do converge (to within 5.0×10^{-5}) faster than those from the KVP.

There is, however, another important question that we have to address: how does the method behave when the energy range of interest includes channel thresholds? In the case of a three-dimensional collision problem, many channels open up as the energy is increased. This would lead to the situation where the present method would attempt to treat a closed channel with an open channel Green's function (if $E < \kappa^2$), and an open channel with a closed channel Green's function (if $E > \kappa^2$). To test whether the method can achieve satisfactory convergence under these circumstances, we present two more calculations: with κ^2 fixed at 6.0, we compute the Y matrix at $E = 4.9$ where only two channels are open, using a total of five channels, and also at $E = 7.2$ where four channels are open, using a total of seven channels. In the former case, the closed channel corresponding to $n = 2$ is represented by the open channel $G^{(n)}(R,R')$ in Eq. (19), and in the latter case, the open channel $n = 3$ is represented by the $G^{(n)}$ that corresponds to a closed channel. The results are presented in Table VI, along with the KVP results at the same energies. These results indicate that the present method does achieve rapid convergence to within 1% of the exact results even when the energy range of interest includes channel thresholds.

Once again we notice in Table VI, that the NVP results achieve a certain level of convergence rapidly—generally faster than the KVP (P_{23} at $E = 7.2$ being the sole exception)—but is slow to converge further. However, from a practical point of view, accuracies greater than 1% are rarely necessary. Therefore, we believe that these results show that the log-derivative NVP-F is a viable method for scattering calculations, having significant advantages over the version of NVP-F that computes the K or T matrix directly.

V. DISCUSSION

In this paper, we have presented the Schwinger and Newton variational functionals for the log-derivative matrix **Y**. Our discussion of the boundary conditions satisfied by the Green' functions used in the present methods led to the observation that the Green's functions need not explicitly depend on the scattering energy. This is in sharp contrast to the Green's functions used in the K (or T) matrix versions of the methods. We showed that this "energy independence" of the Green's functions lead to one great advantage: the matrix elements required to set up the linear system of equations **AC** = **B** need be evaluated only once for a given basis size.

We tested the convergence characteristics of these functionals using three one-dimensional potential scattering problems to compute $Y(a)$, where a is a sufficiently large value of the translational coordinate R, that for $R > a$, the scattering wave function has essentially reached its asymptotic form. We then used the value of Y and the well-known asymptotic form of $\Psi(R)$, to compute the K matrix elements. Comparing the results of these calculations to those from the Schwinger and Newton methods that compute the K matrix directly, we established that the two classes of methods converge at similar rates. We illustrated the advantages of the "energy independence" of the Green's function by computing the K matrix elements for potential scattering

TABLE VI. Fractional errors in transition probabilities for the Secrest–Johnson problem, of Eq. (17), at energies involving channel thresholds. The parameters used are the same as those in Table IV. For the NVP, $\kappa^2 = 6.0$.

	$E = 4.9$ P_{01}	
N	NVP-F	KVP
25	0.2090	0.9680
30	0.0357	0.8764
35	0.0153	0.1723
40	0.0085	0.0004
45	0.0054	a

	$E = 7.2$ P_{01}		P_{02}		P_{03}	
N	NVP-F	KVP	NVP-F	KVP	NVP-F	KVP
30	0.0230	1.0	0.0224	1.0	0.6357	0.9991
35	0.0089	0.8429	0.0078	0.6351	0.0461	0.4221
40	0.0048	0.5207	0.0038	0.5232	0.0017	0.5352
45	0.0030	0.0059	0.0022	0.0559	0.0064	0.0544
50	0.0020	0.0002	0.0015	0.0002	0.0040	0.0002

	P_{12}		P_{13}		P_{23}	
N	NVP-F	KVP	NVP-F	KVP	NVP-F	KVP
30	0.0003	0.9903	0.0287	0.9891	0.0185	0.0071
35	0.0008	1.3700	0.0167	1.3499	0.0153	0.0100
40	0.0008	0.0162	0.0126	0.0102	0.0117	a
45	0.0006	0.0017	0.0095	0.0010	0.0089	a
50	0.0004	a	0.0072	a	0.0068	a

[a] Error is less than 5.0×10^{-5}.

from these one-dimensional potentials at eight different energies, using a Green's function defined at a fixed energy. In Sec. IV, we extended this approach to the multichannel case, and computed the transition probabilities for the Secrest–Johnson inelastic scattering problem,[13] using Green's functions defined with respect to a fixed energy in each vibrational channel. Further calculations showed that the method succeeds in achieving rapid convergence even when the energy range of interest includes channel thresholds.

The present approach is therefore, a practical method for scattering calculations at several different energies, having important advantages over the K matrix Schwinger and Newton methods. A consideration of the computational effort (CPU times) required for each stage of the calculations helps to bring this point into sharp focus. The times quoted below were obtained during a typical run for the Secrest–Johnson problem, using a total of five channels, on the CRAY X-MP/24 at the University of Texas Center for High Performance Computing. For $N = 35$, it takes 53.4 seconds to evaluate the half-integrated Green's functions for all 35 L^2 basis functions in the five channels. Evaluation of all the matrix elements required to set up matrices **A** and **B** requires another 2.1 s. (Although we are certain that considerable improvements can be achieved in these times with more efficient quadrature schemes,[9,10] we feel that this part of the calculation would still require relatively large amounts of CPU time.) However, once these matrix elements are evaluated, we are able to set up and solve the linear system $\mathbf{AC} = \mathbf{B}$ in only 0.7 s at each of the seven energies,[25] *without having to repeat the first two steps.* In effect, by going to the log-derivative formulation, we have avoided having to repeat the most time-consuming steps of the calculation at each energy.

The present method, however, does not compare well with the discrete representation of the log-derivative Kohn method,[12] as far as computational times are concerned. For the same basis size as above, i.e., $N = 35$, the setup time in the discrete representation of the log-derivative Kohn method is only 0.20 s. Even if one abandons the discrete representation and employs higher order quadratures to evaluate the matrix elements of **A** and **B** exactly, the setup time will still be much less than the times quoted above for the NVP, for the single reason that the lengthy step of evaluating the half-integrated Green's functions is completely absent in the Kohn method.

In spite of these comments, we believe that the present approach is a useful one. The faster convergence of the NVP compared to the Kohn method is likely to become a significant factor as the energy increases and more vibrational channels become open. Note that as the energy increases, the KVP requires larger and larger numbers of basis functions to converge the P_{ij}'s to 1% accuracy, while the convergence of the SVP and the NVP can certainly be enhanced by redefining the value of κ. This becomes an important consideration when larger problems such as the reactive collision of an atom A with a heteronuclear diatomic BC, are to be tackled. In such cases, the savings in memory offered by the rapid convergence of the present methods, coupled with the possibility of a further reduction in the basis size by the use of a distortion potential,[9,10] cannot be overlooked.

We conclude with a discussion of a further modification to the method presented in this paper. This has to do with the way the Green's functions are represented in the present work. Recall that the most time-consuming step of our calculations is the evaluation of the half-integrated Green's functions. The modification we discuss below effectively eliminates this step, and promises to make the method more competitive with the Kohn method. The essential idea behind this approach comes from the work of Miller and Jansen op de Haar,[5(a)] where they present an approximation to the Green's function. Our approach consists of writing the kernel of the Green's function as

$$G^0(R,R') = \sum_{k,l} \langle R|k\rangle (\langle k|\kappa^2 - H_0|l\rangle)^{-1} \langle l|R'\rangle, \tag{21}$$

where the $\{|k\rangle\}$ form *a complete set* of basis functions that satisfy the same boundary conditions imposed in the log-derivative Kohn method[12]: all $|k\rangle$ except one vanish at $R = 0$ and $R = a$; the one exception [labeled $u_0(R)$ in Ref. 12] vanishes at $R = 0$, but is equal to 1 at $R = a$. The Lobatto basis of Ref. 12 is an example of a class of functions that meet these requirements. Matrix elements of H_0 do not contain any discontinuities, nor do they have discontinuous derivatives, and hence can be rapidly evaluated either approximately by a discrete representation or exactly by higher order Gaussian quadratures. The advantage of this approach is that the matrix elements involving the Green's function can now be evaluated by simple matrix multiplications. For example, the matrix element $\langle u_I|G^0|u_J\rangle$ is now evaluated as

$$\langle u_I|G^0|u_J\rangle = \sum_{k,l} \langle u_I|k\rangle (\langle k|\kappa^2 - H_0|l\rangle)^{-1} \langle l|u_J\rangle,$$

where the $|u_I\rangle$ and $|u_J\rangle$ *need not belong to the same class of functions* as the $\{|k\rangle\}$. This has at least two important implications. One, in vector processing computers, matrix multiplications are executed much faster than the repeated quadratures necessary to evaluate the half-integrated Green's functions for each basis function no longer need be stored at each quadrature point. A distorted wave Green's function can be represented by simply including the distortion potential in H_0. These modifications are likely to cut down quite dramatically, the time required to evaluate the matrix elements that constitute matrices **A** and **B**, and thus make the log-derivative Schwinger and Newton methods more competitive with the Kohn method. We are at present, incorporating this treatment of the Green's function into the log-derviative Newton method, in an application to a reactive scattering problem.

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[1] W. Kohn, Phys. Rev. **74**, 1763 (1948).

[2] R. K. Nesbet, *Variational Methods in Electron-Atom Scattering* (Plenum, New York, 1980).

[3] J. Schwinger, Phys. Rev. **72**, 742 (1947).

[4] R. G. Newton, *Scattering Theory of Waves and Particles*, 2nd. ed. (Springer, Berlin, 1982).

[5] (a) W. H. Miller and B. M. D. D. Jansen op de Haar, J. Chem. Phys. **86**, 6213 (1987); (b) J. Z. H. Zhang and W. H. Miller, Chem. Phys. Lett. **140**, 329 (1987); (c) J. Z. H. Zhang, S.-I. Chu, and W. H. Miller, J. Chem. Phys. **88**, 6233 (1988).

[6] J. Z. H. Zhang and W. H. Miller, J. Chem. Phys. **88**, 4549 (1988).

[7] J. Z. H. Zhang and W. H. Miller, Chem. Phys. Lett. **153**, 465 (1988).

[8] J. E. Adams and W. H. Miller, J. Phys. Chem. **83**, 1505 (1979); M. R. Hermann and W. H. Miller, Chem. Phys. **109**, 163 (1986).

[9] (a) D. W. Schwenke, K. Haug, D. G. Truhlar, Y. Sun, J. Z. H. Zhang, and D. J. Kouri, J. Phys. Chem. **91**, 6080 (1987); (b) D. W. Schwenke, K. Haug, M. Zhao, D. R. Truhlar, Y. Sun, J. Z. H. Zhang, and D. J. Kouri, J. Phys. Chem. **92**, 3202 (1988); (c) M. Mladenovic, M. Zhao, D. G. Truhlar, D. W. Schwenke, Y. Sun, and D. J. Kouri, Chem. Phys. Lett. **146**, 358 (1988); (d) M. Zhao, M. Mladenovic, D. G. Truhlar, D. W. Schwenke, Y. Sun, D. J. Kouri, and N. C. Blais, J. Am. Chem. Soc. **111**, 852 (1989); (e) D. W. Schwenke, M. Mladenovic, M. Zhao, D. G. Truhlar, Y. Sun, and D. J. Kouri, in *Proceedings of the NATO Advanced Research Workshop on Supercomputer Algorithms for Reactivity, Dynamics, and Kinetics of Small Molecules*; NATO ASI Series, edited by A. Lagana (Riedel, Dordrecht, to be published).

[10] M. Mladenovic, M. Zhao, D. G. Truhlar, D. W. Schwenke, Y. Sun, and D. J. Kouri, J. Phys. Chem. **92**, 7035 (1988).

[11] K. Haug, D. W. Schwenke, Y. Shima, D. G. Truhlar, J. Zhang, and D. J. Kouri, J. Phys. Chem. **90**, 6757 (1986); J. Z. H. Zhang, D. J. Kouri, K. Haug, D. W. Schwenke, Y. Shima, and D. G. Truhlar, J. Chem. Phys. **88**, 2492 (1988); K. Haug, D. W. Schwenke, D. G. Truhlar, Y. Zhang, J. Z. H. Zhang, and D. J. Kouri, *ibid.* **87**, 1892 (1987); J. Z. H. Zhang, Y. Zhang, D. J. Kouri, B. C. Garrett, K. Haug, D. W. Schwenke, and D. G. Truhlar, Faraday Discuss. Chem. Soc. **84**, 371 (1987); Y. C. Zhang, J. Z. H. Zhang, D. J. Kouri, K. Haug, D. W. Schwenke, and D. G. Truhlar, Phys. Rev. Lett. **60**, 2367 (1988).

[12] D. E. Manalopoulos and R. E. Wyatt, Chem. Phys. Lett. **152**, 23 (1988).

[13] D. Secrest and B. R. Johnson, J. Chem. Phys. **45**, 4556 (1966).

[14] T. N. Rescigno and B. I. Schneider, Phys. Rev. A **37**, 1044 (1988); J. Z. H. Zhang and W. H. Miller, J. Chem. Phys. **89**, 4454 (1988).

[15] (a) B. Ramachandran, T.-G. Wei, and R. E. Wyatt, Chem. Phys. Lett. **151**, 540 (1988); (b) J. Chem. Phys. **89**, 6785 (1988). Reference 15(a) contains an error: the Green's function for the K matrix is given in Eq. (2) of this work, while the computations were done with the Green's function for the T matrix. Reference 13(b) contains the correct expression for the T matrix Green's function.

[16] Many comparisons of the various variational methods have been made, for one potential using one type of basis functions. See, for example, D. Thirumalai and D. G. Truhlar, Chem. Phys. Lett. **70**, 330 (1980); G. Staszewska and D. G. Truhlar *ibid.* **130**, 341 (1986); J. Chem. Phys. **86**, 2739 (1987). Also see Refs. 5(a) and 5(c).

[17] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953), Vol. 1, p. 351.

[18] D. E. Manolopoulos, Ph.D. thesis, Cambridge University, 1988.

[19] W. H. Miller, J. Chem. Phys. **50**, 407 (1969).

[20] I. P. Hamilton and J. C. Light, J. Chem. Phys. **84**, 306 (1986).

[21] For example, see M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972) (25.4.32).

[22] B. R. Johnson, J. Comp. Phys. **13**, 445 (1973).

[23] T. E. Sharp and D. Rapp, J. Chem. Phys. **43**, 1233 (1965).

[24] A. C. Peet and W. H. Miller, Chem. Phys. Lett. **149**, 257 (1988).

[25] We have used the NaG routine F04AEF to solve the system $\mathbf{AC}=\mathbf{B}$ for multiple right-hand sides.