Kohn variational principle for a general finite-range scattering functional

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The Kohn variational principle (KVP) has been used to compute both the \( R \) and the log-derivative matrices, which are formally inverses of one another. We show that the KVP for these matrices are special cases of a KVP for a more general functional which can be derived by imposing more general boundary conditions on the trial function space. This more general matrix, which we denote \( Z \), can then be used to compute the \( S \)-matrix in a procedure analogous to that for \( R \) and \( Y \). This approach is demonstrated for the Eckart barrier problem. Our studies suggest that within the framework presented, the log derivative case presents some computational advantage.

I. INTRODUCTION

The \( R \) matrix and the log derivative matrix \( Y \) have desirable features which make them popular tools for scattering studies.1,2,3 Both are real symmetric matrices if real bases are used in their calculation, and the \( S \)-matrix can be expressed in terms of both matrices in such a way that it is manifestly both unitary and symmetric. Both are computable by means of the Kohn variational principle (KVP) and other variational principles,4 which allows the use of well-established linear algebraic algorithms for their computation; yet, unlike the \( K \)-matrix, the \( R \) and log derivative matrices do not appear to be plagued by the infamous Kohn anomalies.5

Early variational \( R \)-matrix computations suffered from slow convergence with respect to basis size, resulting in the need for the application of various correction schemes.6,7 The problem was recognized more than two decades ago to be a result of an unnecessary restriction on the basis sets which were commonly imposed at the time.8 Although the \( R \)-matrix KVP without these restrictions has occasionally appeared in the chemical physics literature,9,10 it does not appear to have recovered its former respectability. On the other hand, a Kohn variational principle for the log derivative matrix, which is the formal inverse of the \( R \)-matrix, was derived by Manolopoulos and co-workers.3 Their use of unrestricted basis functions in their formalism led to a very efficient algorithm for the computation of the log derivative matrix and thus of the \( S \)-matrix.

The \( R \)- and log derivative matrices map wave functions and their derivatives with respect to the scattering coordinate onto one another at finite values of the scattering coordinate, and are expressed in the KVP as functionals of the scattering wave functions. For these reasons, we call them finite-range scattering functionals. In this paper we will define a generalization, which we will denote \( Z \), of the \( R \)- and log derivative matrices. We will then determine the cases in which a Kohn variational principle for \( Z \) can be derived. A general variational expression for \( Z \) will then be given in terms of basis sets satisfying certain conditions (or, rather, failing to satisfy certain conditions) as discussed by Nesbet,5 for example. Our intentions are largely pedagogical. First, we wish to make concrete the remark by Manolopoulos et al. that “variational \( R \)-matrix theory and the log derivative Kohn variational principle are essentially the same” by deriving them within a common framework. Our approach is similar to that of Nesbet,11 who derived parallel variational expressions for the \( R \)- and log derivative matrices for scattering from cells of arbitrary geometry,11 but we extend this approach to a larger class of finite-range scattering functionals. Second, we wish to give a simple expression for these functionals which is applicable to a wide range of basis functions. That said, the general \( Z \)-matrix formalism has not appeared in the literature as far as we are aware.

In Sec. II, the generalized theory will be presented. The theory is strictly analogous to that presented by Manolopoulos and co-workers, and our expression for the log derivative matrix will be shown to be essentially equivalent to theirs. On the other hand, our result for the \( R \)-matrix is somewhat different from the related expressions.8,11 Section III presents transmission coefficients for the Eckart potential as calculated via three cases of the generalized functional, including the \( R \)- and log derivative matrices. Section IV concludes with a brief discussion.

II. THEORY

We consider a scattering problem which can be described in terms of coordinates \((s,q)\), where \( s \) describes the separation of the scattering particles and \( q \) collectively describes their internal degrees of freedom. It is assumed that the coordinates \( q \) are orthogonal to \( s \). When rearrangements take place, it may be convenient to consider several such coordinate systems; generalization to such systems should be straightforward and will not be discussed here.

The Hamiltonian for such a system is assumed to be of the form

\[
H = \frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial s^2} + \nabla_q^2 \right) + V(s,q),
\]

where \( \lim_{|s| \to \infty} V(s,q) = V_0(q) \). Some factorization of the wave functions involved may be required to bring the Hamil-
tonian into this form. The separated reactants are described by the eigenfunctions $\phi_n$ of an internal state Hamiltonian such that
\[ h_0 \phi_n = -\frac{\hbar^2}{2\mu} \nabla^2 \phi_n + V_0(q) \phi_n = \epsilon_n \phi_n. \] (2)

The log derivative and R matrix formalisms are based on the same approach to scattering theory. Briefly, this approach is to partition configuration space into an internal region, in which the scattering particles interact strongly, and an external region in which the scattered particles interact weakly or not at all. At the boundary between these regions, which we will take to be a surface $s_b$ of constant $s$, the R-matrix effects the mapping
\[ R \Psi'(s_b) = \Psi(s_b), \] (3)
while the log derivative matrix $Y$ effects the inverse mapping
\[ Y \Psi(s_b) = \Psi'(-s_b), \] (4)
where $\Psi$ is a matrix representation of the degenerate scattering wave functions at the scattering energy $E$ evaluated at $s = s_b$ and $\Psi'$ is the matrix representation of the derivatives with respect to $s$ of these wave functions at $s = s_b$. Let us define the matrix $Z$ to effect the mapping
\[ Z(a \Psi + b \Psi') = d \Psi + e \Psi', \] (5)
where $a$, $b$, $d$, and $e$ are real parameters.

Of particular importance is the case for which the wave functions obey the scattering boundary conditions
\[ \lim_{s \to \pm \infty} \psi_n(s) = e^{-ik_n s} \phi_n(q), \] (6)
where $\hbar k_n = \sqrt{2\mu(E - \epsilon_n)}$ is the norm of the asymptotic momentum for state $\phi_n(q)$. We define $\Psi_{mn} = \int dq \phi_m(q) \phi_n^*(q, s_b)$, so that $\Psi$ takes the familiar form
\[ \Psi = (1 - OS), \] (7)
where $I_{mn} = \int dq e^{-ik_m q} \delta_{mn}$ and $O_{mn} = \int dq e^{ik_m q} \delta_{mn}$. Since at finite $s$ the closed channel contributions to the scattering wave functions cannot be assumed negligible, the definitions of $k_n$ for closed channels are chosen such that the outgoing waves are exponentially decaying while the incoming ones are exponentially increasing. The matrix $\Psi$ then takes the form
\[ \Psi = \begin{pmatrix} \Psi_{oo} & \Psi_{oc} \\ \Psi_{co} & \Psi_{cc} \end{pmatrix}, \] (8)
where the $o$ and $c$ subscripts label open and closed channels, respectively. Plugging Eq. (7) into Eq. (5) allows us to solve for the augmented $S$-matrix in terms of $Z$,
\[ S = [Z(a \Omega + b \Omega') - (d \Omega + e \Omega')]^{-1} \times [Z(a \Gamma + b \Gamma') - (d \Gamma + e \Gamma')]. \] (9)

This is the analog of the $S$-matrix in terms of the $R$-matrix and the log derivative matrix. As in these special cases, the physical $S$-matrix is the open-open subblock of the augmented $S$-matrix (9).

We note that the log derivative matrix $Y$ and the $R$-matrix $R$ are special cases of $Z$. For the former quantity, $b = d = 0$, and $e = a = 1$; for the latter, $a = e = 0$ and $d = b = 1$. We now determine the values of $a$, $b$, $d$, and $e$ for which a Kohn variational principle can be derived.

A. Definition of the variational trial functions

Hamiltonian eigenfunctions obey the Schrödinger equation
\[ (H - E) \psi = 0 \] (10)
and are determined by the imposition of boundary conditions at some value (possibly infinite) of $s$, along with the requirement that the wave function be regular everywhere in configuration space. To determine the appropriate variational functionals, we begin by setting the boundary conditions on the multichannel trial functions and their variations. Let us define the partial inner product
\[ \langle \phi | \psi(s) \rangle = \int dq \phi^*(q) \psi(q, s). \] (11)

We choose to define the trial functions $\psi_n$ and their variations $\delta \psi_n$ by the boundary conditions
\[ a(\phi_m | \tilde{\psi}_n(s_b)) + b(\phi_m | \tilde{\psi}'_n(s_b)) = 0, \] (12a)
\[ a(\phi_m | \delta \tilde{\psi}_n(s_b)) + b(\phi_m | \delta \tilde{\psi}'_n(s_b)) = 0, \] (12b)
where $\tilde{\psi}_n(s_b)$ is the partial derivative of $\psi_n$ with respect to $s$ evaluated at $s = s_b$, at which point it is assumed that $V(s, q) \approx V_0(q)$. We will not consider the partial inner product at any point other than $s_b$, so the explicit dependence on $s_b$ will be suppressed in the remainder of the paper. We now consider the nonstationary functional
\[ i_{mn} = \langle \tilde{\psi}_m | (H - E) | \tilde{\psi}_n \rangle, \] (13)
where in this case the inner product is defined by integration over the entire range of $q$, but only the range $(0, s_b)$ of $s$. If $\tilde{\psi}_m$ and $\tilde{\psi}_n$ are exact eigenfunctions of the Hamiltonian subject to boundary conditions (12), then $i_{mn}$ is identically zero. The first variation of $i_{mn}$ with respect to variations in $\psi_m$ and $\psi_n$ is
\[ \delta i_{mn} = \langle \delta \tilde{\psi}_m | (H - E) | \tilde{\psi}_n \rangle + \langle \tilde{\psi}_m | (H - E) | \delta \tilde{\psi}_n \rangle + \langle \delta \tilde{\psi}_m | (H - E) | \tilde{\psi}_n \rangle + \langle \tilde{\psi}_m | (H - E) | \delta \tilde{\psi}_n \rangle = 0. \] (14)

Integrating the last equality by parts twice yields
\[ \delta i_{mn} = -\frac{\hbar^2}{2\mu} \int dq \left[ \frac{\partial}{\partial s} \tilde{\psi}_m^*(q, s_b) \delta \tilde{\psi}_n(q, s_b) - \frac{\partial}{\partial s} \tilde{\psi}_m(q, s_b) \delta \tilde{\psi}_n^*(q, s_b) \right]. \] (15)

Inserting the unit operator on the internal state space yields
\[ \delta i_{mn} = -\frac{\hbar^2}{2\mu} \sum_l \left[ \langle \tilde{\psi}_m | \phi_l \rangle \delta \tilde{\psi}_n^l \right] \]

\[ -\langle \delta \tilde{\psi}_m | \phi_l \rangle \langle \phi_l | \tilde{\psi}_m^l \rangle, \tag{16} \]

where \( N_a \) is the number of internal states \( \phi_l \) included in the expansion. Formally this number should be infinite, but in practice it will include all channels open at energy \( E \) plus a few closed channels. By employing boundary conditions (12), we find that Eq. (16) gives

\[ \delta i_{mn} = -\frac{\hbar^2}{2\mu} \left[ \langle \tilde{\psi}_m | \phi_l \rangle (\phi_l | \tilde{\psi}_m^l) \right]. \tag{17} \]

We now add to \( i_{mn} \) a variational correction \( z_{mn}^v \) which cancels this first variation. This correction is

\[ z_{mn}^v = -\frac{\hbar^2}{2\mu} \left( a(\tilde{\psi}_m | \phi_l) + b(\tilde{\psi}_m | \phi_l) \right) (d \phi_l | \tilde{\psi}_n) + e(\phi_l | \tilde{\psi}_n) \]. \tag{18} \]

Variation of this quantity gives

\[ \frac{-2\mu}{\hbar^2} \delta z_{mn}^v = \left( a(\tilde{\psi}_m | \phi_l) + b(\tilde{\psi}_m | \phi_l) \right) (d \phi_l | \tilde{\psi}_n) + e(\phi_l | \tilde{\psi}_n) \times \left( d(\phi_l | \delta \tilde{\psi}_n) + e(\phi_l | \delta \tilde{\psi}_n) \right). \tag{19} \]

The first term in Eq. (19) is zero due to boundary condition (12b). To evaluate the second term, we again use boundary condition (12b) to find that

\[ a d(\tilde{\psi}_m | \phi_l) (\phi_l | \delta \tilde{\psi}_n) + b e(\tilde{\psi}_m | \phi_l) (\phi_l | \delta \tilde{\psi}_n) \]

\[ = -bd(\tilde{\psi}_m | \phi_l) (\phi_l | \delta \tilde{\psi}_n) - ae(\tilde{\psi}_m | \phi_l) (\phi_l | \delta \tilde{\psi}_n) \]. \tag{20} \]

Thus, the variation of \( z_{mn}^v \) is

\[ \delta z_{mn}^v = -\frac{\hbar^2}{2\mu} \left( ae - bd \right) \left[ (\tilde{\psi}_m | \phi_l) (\phi_l | \delta \tilde{\psi}_n) \right] \]

\[ -\langle \delta \tilde{\psi}_m^l | \phi_l \rangle (\phi_l | \tilde{\psi}_m^l \rangle). \tag{21} \]

If we choose

\[ ae - bd = -1, \tag{22} \]

then this variation cancels the variation in \( i_{mn} \), and the functional

\[ i_{mn} = z_{mn}^v + i_{mn} \tag{23} \]

is stationary with respect to variations in \( \tilde{\psi}_m \) and \( \tilde{\psi}_n \). The values \( i_{mn} \) form an \( N_a \times N_a \) matrix. When the wave functions \( \tilde{\psi}_n \) are the exact Hamiltonian eigenstates subject to the boundary conditions (12), then the matrix \( Z \) whose elements are \( Z_{mn} = -\left( 1/c^2 \right) (2\mu/\hbar^2) I_{mn} \) obeys the matrix equation,

\[ Z(a \tilde{\Psi} + b \tilde{\Psi}') = d \tilde{\Psi} + \tilde{\Psi}', \tag{24} \]

where the matrix \( \tilde{\Psi} \) is the matrix representation of the scattering eigenstates obeying boundary conditions (12). The \( N_a \) degenerate scattering eigenstates represented in Eq. (7) can be superposed to yield functions which obey boundary conditions (12), a process which amounts to the multiplication on the right of the matrices \( \Psi \) and \( \Psi' \) by an invertible transformation matrix; the transformed matrices can then satisfy Eq. (24). This transformation matrix can then in turn be canceled on the right from Eq. (24), which demonstrates that the variational \( Z \) matrix can be used in Eq. (9) to solve for the \( S \) matrix.

### B. Implementation

In order to apply this algorithm, we need a suitable basis in which to expand the trial functions, i.e.,

\[ \psi_{m,n} = \sum_l \xi_{m,n}^l \omega_l (s, q), \tag{25} \]

where \( l \) may be interpreted as a collective index representing any set of numbers needed to specify the basis functions. In decades past, there was a tendency among practitioners of variational R-matrix theory to choose bases which obeyed homogeneous boundary conditions at \( s = s_b \) in the sense that

\[ \alpha(\phi_m | \omega_l) + \beta(\phi_m | \omega_l) = 0 \]

for some \( \alpha \) and \( \beta \). The difficulty with such a choice is that only those functions which obey the same homogeneous boundary conditions can be expanded in such a basis. When the Hamiltonian eigenfunctions did not obey these boundary conditions, this choice led to the notoriously slow convergence of the \( R \) matrix results and therefore to the necessity for Buttle corrections and other such modifications to accelerate convergence.\(^6\)\(^7\)

We assume that our basis \( \omega_l \) consists of \( N \) functions chosen in such a way that the quantities \( (\phi_m | \omega_l) \) do not obey homogeneous boundary conditions at \( s = s_b \). We will also take the basis to be real, but this restriction is not necessary. The words “symmetric” and “transpose” can be replaced by the words “Hermitian” and “adjoint,” respectively, in the following discussion if need be. The total trial function (25) must obey the boundary conditions (12a); these boundary conditions on the trial function are imposed by means of a constraint on the stationary functional. In order to render the notation more compact, we introduce several new matrices (boldface quantities) and vectors (underlined quantities),

\[ (u^m) = a(\phi_m | \omega_l) + b(\phi_m | \omega_l), \tag{27a} \]

\[ (v^m) = d(\phi_m | \omega_l) + e(\phi_m | \omega_l), \tag{27b} \]

\[ [z^m]_l = -\frac{\hbar^2}{2\mu} [u^m v^m^T]_l, \tag{27c} \]

\[ U_{lm} = (u^m)_l, \tag{27d} \]

\[ [H - E]_l = |l - H - E|_l, \tag{27e} \]

\[ (\xi^m) = \xi_l^m, \tag{27f} \]

\[ (\lambda^m)_l = \lambda_{lm}^m, \tag{27g} \]

\[ (1^m)_l = \delta_{lm}^m. \tag{27h} \]

The vectors \( \xi^m \), \( u^m \), and \( v^m \) have dimension \( N \times 1 \), and there are \( N_a \) of each set. The elements of the vectors \( \lambda^m \) are the
Lagrange multipliers for the $N_a$ constraints on $\psi_m$; there are therefore $N_a$ of these vectors as well. The vector $1^n$ is the $n^{th}$ column of the $N_a \times N_a$ unit matrix. The $N \times N_a$ matrix $\Pi$ is the matrix whose columns are the vectors $u^n$.

Using these definitions, the variational functional subject to the boundary conditions constraints can then be written in matrix form as

$$-c^2 \frac{\hbar^2}{2\mu} Z_{mn} = \xi^m + \lambda^m \left( c 1^n - U^T \xi^m \right) + \lambda^m (c 1^n - U^T \xi^m).$$

Differentiating with respect to the coefficients $\xi^m$ gives coupled equations for the coefficients $\lambda^m$ and the Lagrange multipliers $\lambda_{np}$,

$$(z^m + H - E) \xi^m + U \lambda^m = 0.$$  

where $0$ is the zero vector, while differentiation with respect to the Lagrange multipliers $\lambda_{np}$ yield the constraints for the coefficients $\xi^m$,

$$u^T \lambda^m = c \delta_{pn}.$$  

All these equations can be written as a single matrix-vector equation as

$$\begin{pmatrix} M & U \\ U^T & 0 \end{pmatrix} \begin{pmatrix} \xi \\ \lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},$$

where $M = z^m + H - E$ and $0$ is the $N \times N_a$ matrix whose elements are all zero. All elements of the vector $b^m$ are zero except for that corresponding to the constraint that $a(\phi_m | \psi_n) + b(\phi_m | \psi'_n) = c$; that element is equal to $c$.

Since our basis does not obey homogeneous boundary conditions, the matrix $H$ is not symmetric since the surface terms $(\omega_i | \phi_m) (\phi_i | \omega_n)$ which result from the integration by parts of Eq. (13) have both symmetric and antisymmetric parts. It turns out, however, that the antisymmetric parts of $z^m$ and $-(\hbar^2/2\mu)(\omega_i | \phi_m) (\phi_m | \omega_i')$ cancel. $M$ can therefore be symmetrized by adding the appropriate multiples of the columns of the matrix $U$ to the columns of $M$. This operation is equivalent to the insertion of the $(N + N_a) \times (N + N_a)$ unit matrix $\mathcal{F}^T \mathcal{F}$ between the matrix and vector on the left-hand side of Eq. (31), where $\mathcal{F}$ is the nonorthogonal transformation matrix

$$\mathcal{F} = \begin{pmatrix} 1_{1^n} & 0_{1^n} \\ T & 1_{1^n} \end{pmatrix},$$

where $1_{1^n}$ and $1_{1^n}$ are the $N \times N$ and $N_a \times N_a$ unit matrices, respectively, $0_{1^n}$ is the $N \times N_a$ zero matrix, and

$$T_{mp} = -\frac{\hbar^2}{2\mu} \left[ d(\phi_m | \omega_i) + e(\phi_m | \omega_i') \right](1 - \delta_{mp}).$$

The operation $\mathcal{F}^{-1}$ on the solution vector transforms the Lagrange multipliers into linear combinations of multipliers and coefficients but leaves the vector $\xi$ unchanged.

Likewise, differentiation of the functional with respect to $\xi^m$ and $\lambda_{np}$ yields coupled equations for the coefficients $\xi^m$ and Lagrange multipliers $\lambda_{np}$, respectively. The resulting matrix equation can be symmetrized in a manner analogous to that outlined in the preceding paragraph. The result of these operations is that the equations defining both the coefficient vectors $\xi^m$ and $\lambda^m$ can be written as

$$\begin{pmatrix} M & U \\ U^T & 0 \end{pmatrix} \begin{pmatrix} \xi \\ \lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},$$

where

$$M_S = \sum_{r=1}^{N_a} \frac{1}{2} \left( z^r + z^r^T \right) + \frac{1}{2} \left( H - E + H^T - E^T \right) = \mathcal{F}M_S \mathcal{F}^T,$$

since the matrix $E$ is always symmetric. From these equations the constraint vector $\lambda$ can be eliminated, yielding

$$\xi = M_S^{-1}U(U^T M_S^{-1}U)^{-1}b.$$  

It is easy to show that the operator $H - E + z^m$ which appears in the functional Eq. (29) can be replaced with $M_S$. We need only note that the addition of the matrices $z^m$ leaves the functional unchanged since by construction $\xi^m \lambda_{np}^m = 0$. The antisymmetric parts of the sum of the $z^m$ matrices and the Hamiltonian matrix cancel, leaving $M_S$. The result, then is

$$-c^2 \frac{\hbar^2}{2\mu} Z_{mn} = b^m + U^T M_S^{-1} U^{-1} b^m,$$

so that

$$Z_{mn} = -\frac{\mu}{\hbar^2} \left( (U^T M_S^{-1} U)^{-1} \right)_{mn}.$$  

Note that the parameter $c$ has dropped out of the equation.

III. EXAMPLE

To test this formalism, we computed transmission coefficients for the Eckart barrier problem, the exact values of which are known. For all energies this problem has two open channels corresponding to the possibilities of approaching the barrier from the left or the right. There are no closed channels, so $N_a$ is always 2. The Hamiltonian for this problem is

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + V_0 \operatorname{sech}^2(x).$$

Our values for the parameters were those of Park and Light in their study of the rate constant for this system; $\hbar = 1$, $\mu = 1834$ a.u., and $V_0 = 1.14 \times 10^{-2}$ a.u. The distances are also in atomic units. To construct the required matrices, we used a set of normalized Legendre polynomials $\{P_n(la)^{1/2} \} = \{\psi_i\}$, and $x_{\text{max}}$ is chosen to cover the range over which the Eckart potential is nonzero. We used $x_{\text{max}} = 3$ a.u. Using the equations,

$$P_n(1) = 1,$$

$$P_n(-1) = (-1)^n,$$  

and

we constructed the symmetrized kinetic energy matrix and surface terms. The potential matrix elements were computed with an \(N\)-point Gauss-Legendre quadrature, where \(N\) is the basis size. Since we wished to compute the \(Z\)-matrices at many energies, we then diagonalized the matrix \(H\). In the resulting (orthogonal) basis, the matrix \(E\) is just the energy \(E\) times the unit matrix, and the inverse matrix elements \((H - E)^{-1}\) are just \((E - E)^{-1} \delta_{ij}\), where \(E\) is the \(i\)th eigenvalue of \(H\).

We computed the \(S\)-matrix in terms of the \(Z\) matrix for the cases \(a = -e = 1\), \(b = d = 0\) (log derivative); \(a = e = 0\), \(b = d = 1\) (\(R\)-matrix); and \(a = b = 1\), \(d = 8\), and \(e = 7\), which we will refer to as the \(Z\)-matrix. From these results, we computed the transmission coefficients \(T_Y\), \(T_R\), and \(T_Z\) as the square modulus of the off-diagonal elements of the corresponding \(S\) matrices. These quantities were computed at 123 values of the energy on the range \((5.8 \times 10^{-3}, 1.5 \times 10^{-2})\) over which the transmission coefficient ranges from low to practically unity. For each \(Z\)-matrix, energy \(E\), and basis size \(N\), we computed the percent difference from the exact transmission coefficient as

\[
\Delta_\varepsilon(E) = 100 \times \frac{T_{\text{exact}} - T_{\text{computed}}}{T_{\text{exact}}},
\]

where \(\varepsilon = Y, R,\) or \(Z\). Using these values, we also examined the errors

\[
\Delta_{\text{max}} = \sqrt{\frac{1}{N} \sum_i \Delta_i^2(E_i)},
\]

and

\[
\delta_{\varepsilon_1 \varepsilon_2}(E_i) = |\Delta_{\varepsilon_1}(E_i) - \Delta_{\varepsilon_2}(E_i)|;
\]

the former quantity measures the average error over the entire energy range while the latter measures the convergence of the computed transmission coefficients with respect to one another. In Table 1 we present the largest of these errors as functions of basis size and, where appropriate, the energies and \(Z\)-matrices for which they occur. In all cases, the largest discrepancies \(\delta\) between the computed transmission coefficients are between those for the \(R\)- and log derivative matrices. We mention two observations. First, the \(R\)-matrix results usually yield the largest of the reported errors, but the differences in accuracy of the three computed transmission coefficients are really very slight. Note that the maximum \(\delta\) value is always considerably smaller than the maximum deviations from the exact transmission coefficient values; in other words, the computed results converge to one another more rapidly than they converge to the right answer. Second, there is a persistent (maximum) error of about 2% at the energy \(E_{\text{max}} = 6.26 \times 10^{-3}\) a.u. We believe that this error results from the fact that at such low energies, plane waves are an inadequate representation of the wave function at \(x = \pm x_{\text{max}}\). This supposition is supported by the fact that the error is suppressed when the basis range \((i.e., \text{the parameter } x_{\text{max}})\) is increased.

Due to this source of error, the parameters \(\delta\) are a better measure of the convergence properties. The results are all practically converged at a basis size of \(N = 25\), as shown in Fig. 1.

**IV. DISCUSSION**

The results show that the same information can be extracted using any of an infinite number of matrices which map one set of boundary conditions of the scattering wave functions at a finite value of the scattering coordinate onto a linearly independent set of boundary conditions, and that these matrices may be computed via the Kohn variational principle.
principle. The variational principles differ only in the boundary conditions imposed on the trial function space.

The symmetrization of the matrix $M$ described in Sec. II leaves symmetrized surface terms in the expression. In the log derivative case, it turns out that all surface terms cancel with the matrices $Z$ so that

$$M_{S} = \frac{\hbar^{2}}{2\mu} \int_{0}^{R_{b}} dR \int d\mathbf{q} \frac{\partial}{\partial R} \omega_{i} \frac{\partial}{\partial R} \omega_{i} + \int_{0}^{R_{b}} dR \int d\mathbf{q} (V - E) \omega_{i} \omega_{i} .$$

(This was proved in Ref. 3.) Neglecting an unimportant constant (including a sign) in the definitions of our functional, the matrix result for the log derivative given by Manolopoulos, D'Mello, and Wyatt is a special case of our own result for the log derivative case of Eq. (38). On the other hand, our $R$-matrix has a different form than other variational results. The derivation of Oberoi and Nesbet, for example, is similar to ours, but their constraints were chosen to impose continuity of each internal component of the wave function at the boundary $s = s_{b}$, whereas our boundary conditions are imposed upon the derivatives of the wave functions. Later, Nesbet derived a somewhat different variational principle for the $R$-matrix in which the boundary conditions were imposed upon the normal derivative at the boundary; his result is essentially the matrix inverse of the log derivative matrix as computed from Eq. (38). Numerical tests on the $R$ and log derivative matrices as computed by our formalism show that these two matrices do converge to inverses of one another.

We also note that our treatment implies three matrix inverses in the computation of the $S$-matrix; the inversion of $M_{S}$ in the full basis, the inversion of the $N_{a} \times N_{a}$ matrix $U^{T} M_{S}^{-1} U$, and the matrix inverse of $Z(a \mathbf{O} + b \mathbf{O}') - (d \mathbf{O} + e \mathbf{O}')$ in Eq. (9). The second inversion is unnecessary; by inserting $Z Z^{-1}$ between the two bracketed matrices in Eq. (9), the $S$ matrix can be expressed equally conveniently in terms of $Z^{-1}$.

The performance of the three cases studied in this paper suggest that there is no advantage or disadvantage of any functional over another in terms of the size of the inversion required. The log derivative matrix and, more generally, the $Z$ matrices for which $b = 0$—have one advantage over the other cases: the symmetric part of the surface term in the integration by parts of the Hamiltonian matrix elements with respect to $R$ vanishes along with the antisymmetric part. If this fact is taken into account explicitly, only the matrix elements $\langle \phi_{i} | \omega_{j} \rangle$ are required; in the other cases, the matrix elements $\langle \phi_{i} | \omega_{j} \rangle$ are needed as well. Thus, within the framework presented in this paper, there is some advantage to the use of the log derivative matrix—rather than an anticlimax after all that trouble.

We have shown that the $R$-matrix and log derivative matrix are special cases of a more general finite-range functional to which the Kohn variational principle can be applied. We believe that the general computational treatment will be of value. We hope that someday other researchers will find some use for the more general functional expressions as well.

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