Imbedded matrix Green's functions in atomic and molecular scattering theory

J. V. Lill

The James Franck Institute and The Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

T. G. Schmalz

Department of Marine Sciences, Texas A&M University, Galveston, Texas 77553

J. C. Light

The James Franck Institute and The Department of Chemistry, The University of Chicago, Chicago, Illinois 60637
(Received 20 October 1982; accepted 13 December 1982)

This paper presents a general, simple, and unified treatment of Green's function approaches to the solution of the sets of coupled second order differential equations encountered in the theory of inelastic and reactive scattering. The standard scalar theory of Sturm–Liouville problems is extended to systems of equations without recourse to spectral resolutions of the Green's operator. A nonstandard approach to invariant imbedding is then developed to yield the most general kind of recursion relation for Wigner $R$ matrices possible; the $R$-matrix propagation of Light and Walker and the variable interval-variable step algorithm of Parker, Schmalz, and Light are shown to be particularly simple examples of this more general scheme. Extensions and simplifications are offered. Also recurrence relations, stabilization of solutions, adiabatic and diabatic representations, and the use of nonorthogonal bases are all treated in a transparent manner.

I. INTRODUCTION

The quantum mechanical description of heavy particle scattering has long been a goal of theoretical chemistry. Indeed, accurate calculations for simple systems have been performed for more than a decade.¹ The size and complexity of the general problem, however, has stimulated much interest in the construction of rapid and efficient algorithms for the solution of the systems of coupled second order differential equations, which result from the most common approach to the exact nonrelativistic quantum theory. Rapid progress has been made in the past few years and several computer codes are now widely available.² The purpose of this article is to provide a powerful formalism for analysis of the scattering problem which is very general yet simply yields two of the fastest and most stable algorithms yet devised: i.e., $R$-matrix propagation³⁴ and the variable interval-variable step method.⁵ Extensions and simplifications, as well as discussion of such topics as recurrence relations, stabilization of solutions, adiabatic and diabatic representations, and the use of non-orthogonal bases in both inelastic and reactive problems, are easily made. Before proceeding, however, the notation to be used will be established.

Matrix notation will be employed because of its compactness and because it allows the clearest expression of the analogies between the matrix and scalar theories. Matrices will be labeled by two sets of discrete indices: subscripts (rows) will refer to the range space while superscripts (columns) will refer to the domain space. In general, matrices will also be functions of continuous variables. When confusion is possible variables in the range space will be listed first. Thus, an element of a matrix Green’s function will be written as [$G(R,R')^\hat{n}$], where $\hat{n}$ and $R$ refer to the range space and $R'$ to the domain space. (Here, $\hat{n}$ represents a set of discrete indices.) Then the typical equation

$$\phi(R) = \phi_0(R) + \int_{a}^{b} dR' G(R, R') W(R') \phi(R')$$

may be written as

$$\left[ \phi(R)^{\hat{n}} \right] = \left[ \phi_0(R)^{\hat{n}} \right]^{\hat{n}}$$
$$+ \sum_{\hat{n}_1 \hat{n}_2} \int_{a}^{b} dR' \left[ G(R,R') \right]^{\hat{n}_1 \hat{n}_2} \left[ W(R') \right]^{\hat{n}_2} \left[ \phi(R') \right]^{\hat{n}_1}.$$

This clearly shows that $[G(R,R')^\hat{n}]$ defines a mapping from $\hat{n}'$ to $\hat{n}$ and $R'$ to $R$. The more compact matrix notation will be used except when there is any possible confusion.

Also, it will be convenient to write sets of internal basis functions as row matrices such as $x^\hat{n}(RR')$. For example, a suitable set of internal basis functions for atom–rigid rotor collisions is provided by the product space of spherical harmonics⁶:

$$x^\hat{n}(RR') = \sum_{m} y_{m}^{\hat{n}}(\theta, \phi) y_{m}(\theta, \phi).$$

Here, the basis is independent of the scattering distance $R$, the internal coordinates $\hat{R}$ are the rotor and orbital angles $\{\theta, \phi\}$ and $\Theta, \Phi$, respectively, and the indices $\hat{\mu}$ are the rotor and orbital angular momentum quantum numbers, $j$ and $l$, and their space-fixed projections $m_j$ and $m_l$.

This notation will now be employed to study the transformational nature of the relation between the partial and coupled ordinary differential equations of quantum
mechanical scattering. In particular, self-adjoint operations and boundary conditions. Sturm–Liouville problems, and Green’s functions may all be formulated for systems of equations in a manner exactly analogous to the standard scalar developments.\textsuperscript{1,4}

\section{Partial and Coupled Ordinary Frames}

Partial and coupled ordinary differential equation representations for the scattering problem are important for the present discussion because they permit simple comparisons between the matrix approach taken here and more standard developments of the scalar Sturm–Liouville problem. More importantly, the analysis presented here will serve as the basis for the discrete variable-finite basis approach to quantum mechanical scattering as discussed in another article.

Begin by writing the partial differential Schrödinger equation as

\[ H(R,\hat{R}) \psi'(R,\hat{R}) = \left[ \frac{\hat{\mathbf{r}}^2}{2\mathbf{r}} + K^2(R,\hat{R}) - V(R,\hat{R}) \right] \psi'(R,\hat{R}) - \sigma. \]  

(II.1)

Here, \( \mathbf{r} \) is the distance between the colliding particles and \( \hat{\mathbf{r}} \) denotes all the internal variables including interparticle angles. The kinetic operator \( K^2(R,\hat{R}) \) is assumed to be separable in some orthonormal basis and the non-separable potential \( V(R,\hat{R}) \) is assumed to be real and to vanish asymptotically.\textsuperscript{9}

In general, we put into \( K^2 \) the separable (and soluble) portion of the Hamiltonian

\[ K^2(R,\hat{R}) = E - h(R,\hat{R}), \]  

(II.2)

where \( E \) is the scattering energy and \( h(R,\hat{R}) \) is the internal Hamiltonian. Since the operator \( h(R,\hat{R}) \) is assumed to be separable, the \( R \) dependence can at most be multiplicative. The \( R \)-independent basis in which Eq. (II.1) separates asymptotically, say \( \mathcal{E}(R) \), is a basis of energy eigenstates of the internal Hamiltonian and forms the set of quantum mechanical observables of the scattering system. Equation (II.1) has been scaled by \(-2\mu/\hbar^2\), where \( \mu \) is the reduced mass of the scattering system.

The scattering wave function \( \psi'(R,\hat{R}) \) is written as a row matrix, the columns of which are indexed by the quantum numbers \( \hat{\mathbf{m}} \); these refer to the asymptotically separable basis functions \( [\mathcal{E}(R)]^{\hat{\mathbf{m}}} \). Physically column \( \hat{\mathbf{m}} \) of \( \psi'(R,\hat{R}) \) is the scattering solution obtained by preparing the system in the initial state \( [\mathcal{E}(R)]^{\hat{\mathbf{m}}} \). Mathematically, the columns of \( \psi'(R,\hat{R}) \) correspond to the independent scattering solutions obtained by imposing boundary conditions on the internal degrees of freedom described by the basis functions \( \mathcal{E}(\hat{R}) \). These boundary conditions will be discussed shortly.

The most common treatment of the scattering problem—the close coupled method—expands \( \psi'(R,\hat{R}) \) in the basis \( \mathcal{E}(\hat{R}) \). A more general approach is taken here and the scattering wave function is expanded in the basis \( \chi'(R,\hat{R}) \)

\[ \psi'(R,\hat{R}) = \chi'(R,\hat{R}) \psi(R). \]  

(II.3)

In general, \( \chi'(R,\hat{R}) \) has a nonunit overlap matrix

\[
\Sigma(R) = \int d\hat{R} \chi'(R,\hat{R}) \chi'(R,\hat{R}).
\]

(II.4)

Thus, \( [\psi'(R)]^\dagger \) is seen to be the projection of \( [\Sigma^{-1}(\hat{R})] \chi'(R,\hat{R}) \) on the scattering solution characterized by the initial state \( [\mathcal{E}(\hat{R})]^\dagger \)

\[ \psi'(R) = \Sigma^{-1}(R) \int d\hat{R} \chi'(R,\hat{R}) \psi'(R,\hat{R}). \]  

(II.5)

Usually one views the basis functions \( \chi'(R,\hat{R}) \) as being the elements of a Hilbert space. The present approach is to view \( \chi'(R,\hat{R}) \) as a transformation connecting representations of the scattering solution in the partial and coupled ordinary frames, denoted by \( \{\psi'(R,\hat{R})\} \) and \( \{\psi(R)\} \), respectively. These dual spaces may easily be shown to be Hilbert spaces. The equations governing the transformation

\[ \int d\hat{R} \int d\hat{R}' \chi'(R,\hat{R}) \delta(\hat{R} - \hat{R}') \chi'(R,\hat{R}') = \Sigma(R), \]  

(II.6a)

\[ \chi'(R,\hat{R}) \Sigma^{-1}(R) \chi'(R,\hat{R}') = \delta(\hat{R} - \hat{R}'), \]  

(II.6b)

are seen to be of the general form of a transformation between Hilbert spaces with weight functions \( \Sigma(R) \) and \( \delta(\hat{R} - \hat{R}') \).

The set of all functions \( \{\psi'(R,\hat{R})\} \) and \( \{\psi(R)\} \) are easily seen to satisfy the elementary properties of vector spaces; the only real difficulty in establishing that the sets have inner products lies in the definition of an inner product. Following the standard scalar formulation define the conjugate bilinear matrix form:

\[ \int_a^b d\mathbf{r} \int d\hat{\mathbf{r}} \phi'(\mathbf{r},\hat{\mathbf{r}}) \psi'(\mathbf{r},\hat{\mathbf{r}}) = \int_a^b d\mathbf{r} \phi'(\mathbf{r}) \psi(\mathbf{r}), \]  

(II.7)

where \( \phi'(R,\hat{R}) \) and \( \phi(R) \) are elements of the dual partial and coupled ordinary spaces related by \( \phi'(R,\hat{R}) = \chi'(R,\hat{R}) \phi(R) \). The matrix generalization of the requirement that the scalar inner product be positive definite is simply that the matrix (II.7) be positive definite. This is assured by requiring the basis functions \( \chi'(R,\hat{R}) \) to be linearly independent. The only time Eq. (II.7) may vanish is then when \( \phi'(R,\hat{R}) = \sigma' \) or \( \phi(R) = 0 \) identically. As will be shown in the section on invariant imbedding, no loss of generality is involved in specifying the range of integration of the radial coordinate to be any arbitrary finite closed interval \([a, b]\).

Note that the transformation (II.6) can never be one-to-one, there being a denumerable infinity of functions and a nondenumerable infinity of points spanning the internal degrees of freedom. The transformation may be made one-to-one and handled with simple matrix algebra by replacing the integration over the internal coordinates with appropriate quadratures. This is the heart of the discrete variable-finite basis method.\textsuperscript{9} The present analysis is based on the resemblance of the right-hand side of Eq. (II.7) to standard scalar definitions of inner products as discussed in relation to self-adjoint operators.\textsuperscript{4} In the following section it will be shown how the standard scalar treatment of Sturm–Liouville problems may be extended to systems of equations, the positive semidefinite overlap matrix \( \Sigma(R) \) serving as the weight function.

J. Chem. Phys., Vol. 78, No. 7, 1 April 1983
III. THE MATRIX STURM– LIOUVILLE PROBLEM

Considering the partial differential equation as given above, and using the conventions for the inner product already described, the typical equations of scalar Sturm–Liouville theory may be seen to have exact analogs in the study of systems of equations obtained by expansion of the problem in the basis \( \chi'(R) \). Begin by noting that Eqs. (II.6) and (II.3) allow transformation of the partial differential Eq. (II.1) into the coupled ordinary form

\[
S^{-1}(R) H(R) \Psi(R) = 0 , \tag{III.1}
\]

where

\[
H(R) = \frac{d}{dR} S(R) \frac{d}{dR} + S'(R) \frac{d}{dR} + K^2(R) + V(R) . \tag{III.2}
\]

The physical boundary conditions are most easily applied in the coupled ordinary frame

\[
\lim_{R \to 0} \Psi(R) = 0 , \tag{III.3a}
\]

\[
\lim_{R \to \infty} \Psi(R) = \lim_{R \to \infty} \{ (R - 0) S \} , \tag{III.3b}
\]

Here the scattering wave function has been transformed so that \( \{ \Psi_s(R) \} \) gives the projection of \( \{ \chi'(R) \} \) on the solution characterized by the initial state \( \{ \chi'(R) \} \).

Then, \( \tau(R) \) and \( 0(R) \) are the diagonal matrices of incoming and outgoing solutions, respectively, and \( S \) is the scattering matrix.

Usually \( \Psi(R) \) is labeled by \( \hat{n} \) and \( \hat{n}' \). Often the partial differential equation is expanded in a basis of the form \( \chi'(R) \chi'(R) \), where \( \chi'(R) \) is some unitary transformation. This is considered later when diabatic and adiabatic representations are discussed. In some circumstances it may be more convenient to work with a basis which does not separate the problem asymptotically, an example being the use of harmonic oscillator functions instead of vibrational–rotational eigenfunctions. Finally, it is sometimes convenient to employ bases of functions centered on the colliding particles; such nonorthogonal bases may be easily included in the present formalism. In any case boundary conditions of the form of Eq. (III.3) may be imposed.

In keeping with the definition of the inner product in the partial and coupled ordinary representations it is convenient to define the matrix Sturm–Liouville problem on the finite closed radial interval \([a, b]\) with the equation

\[
S^{-1}(R) [H(R) + L_{ab}(R)] S^{-1}(R) G(R, R') = \delta(R - R') 1 , \tag{III.4}
\]

Here, \( L_{ab}(R) \) is a two-sided matrix Bloch operator—a simple generalization of the quantity defined by Bloch—and serves to impose boundary conditions on the Green's operator \( S^{-1}(R) G(R, R') \). These will be discussed shortly, but first note that Eq. (III.4) may be simplified by first writing the weight function as

\[
S(R) = \tau'(R) \tau(R) \tag{III.5}
\]

and then performing the similarity transformation

\[
\tau(R) [S^{-1}(R) [H(R) + L_{ab}(R)] S^{-1}(R)] \tau^{-1}(R')
\]

\[
= \delta(R - R') \tau(R) \tau^{-1}(R') \tag{III.6a}
\]

where

\[
H(R) = \tau'^{-1}(R) H(R) \tau^{-1}(R) , \tag{III.7a}
\]

\[
L_{ab}(R) = \tau'^{-1}(R) L_{ab}(R) \tau^{-1}(R) , \tag{III.7b}
\]

\[
G(R, R') = \tau'^{-1}(R) G(R, R') \tau^{-1}(R') . \tag{III.7c}
\]

Note that the transformations (III.7a) hold regardless of whether or not \( \tau(R) \) is unitary.

This matrix \( \tau(R) \) is uniquely defined by Eq. (III.5) up to an arbitrary constant unitary transformation. This will be discussed further when diabatic and adiabatic representations are described; for now, note that Eq. (III.6a) has the effect of performing the calculation in the symmetrically orthogonalized \( R \)-independent frame \( \chi'(R) \tau^{-1}(R) \). The Hamiltonian now becomes

\[
H(R) = \frac{d^2}{dR^2} + K^2(R) - V(R) . \tag{III.8}
\]

Letting \( \phi_s(R) \) and \( \phi_s(R) \) be arbitrary functions in the coupled ordinary space \( H(R) \) may be shown to be self-adjoint, i.e.,

\[
\int_a^b dR \phi_s^*(R) [H(R) \phi_s(R)]
\]

\[
= \int_a^b dR [H(R) \phi_s(R)]^* \phi_s(R) + W_{ab} \, , \tag{III.9}
\]

where the surface term \( W_{ab} \) is given by

\[
W_{ab} = \phi_s^*(R) \phi_s'(R) - \phi_s'(R) \phi_s(R) \tag{III.10}
\]

Quantum mechanically \( W_{ab} \) is an evaluation of the flux operator; here it will take the place of the Wronskian in determining an expression for \( G(R, R') \). If \( \phi_s(R) \) and \( \phi_s(R) \) are solutions to the homogeneous equations

\[
H(R) \phi_s(R) = H(R) \phi_s(R) = 0 \tag{III.11a}
\]

subject to the homogeneous boundary conditions

\[
\phi_s'(a) = \delta_s \phi_s(a) , \quad \phi_s'(b) = \delta_s \phi_s(b) \tag{III.11b}
\]

where \( \delta_s = \delta_s^* \) and \( \delta_s = \delta_s^* \) are arbitrary conjugate symmetric matrices, then \( W_{ab} \) is strictly constant and the following symmetry relation holds for \( \phi_s(R) \) and \( \phi_s(R) \)

\[
\phi_s'(R) \phi_s'(R) = [\phi_s'(R) \phi_s'(R)]^* , \quad c = a , b \tag{III.12}
\]

The Bloch operator \( L_{ab}(R) \) may now be defined so as to impose the same arbitrary boundary conditions on \( G(R, R') \)

\[
L_{ab}(R) = - \delta(R - b) \left[ \frac{d}{dR} - \delta_s \right]
\]

\[
+ \delta(R - a) \left[ \frac{d}{dR} - \delta_s \right] , \tag{III.13a}
\]

\[
= \frac{d}{dR} G(R, R') \big|_{a=\delta_s} \frac{d}{dR} G(R, R') \big|_{b=\delta_s} . \tag{III.13b}
\]

And the matrix Green's function may be constructed from the matrix homogeneous solutions just as in the scalar case.\(^{1,5,6}\) Begin by writing

\[
G(R, R') = \begin{cases} G'(R, R') = \phi_s(R) A(R') , & a \leq R \leq R' \leq b \\
G'(R, R') = \phi_s(R) B(R') , & a \leq R' \leq R \leq b , \end{cases} \tag{III.14}
\]

J. Chem. Phys., Vol. 78, No. 7, 1 April 1983
Obviously from Eq. (III.6b), \( \mathbf{G}(R, R') \) must be continuous at \( R = R' \) and \( (d/dR) \mathbf{G}(R, R') \) must be discontinuous at \( R = R' \) in order to provide the delta function on the right-hand side of the equation. [The singularities in \( \mathbf{L}_{\text{as}} \) are eliminated by the boundary conditions (III.13b).] Following the scalar argument\(^3\) one finds that \( \mathbf{G}^{(R, R')} - \mathbf{G}^{(R', R')} = 1 \), or in super matrix form

\[
\begin{pmatrix}
  -A & 0 \\
  B & 0
\end{pmatrix}
\begin{pmatrix}
  \phi_s & \phi_s^* \\
  \phi_s^* & \phi_s
\end{pmatrix}^{-1}
\begin{pmatrix}
  0 \\
  1
\end{pmatrix}.
\] (III.15)

The super matrix may be inverted in block form\(^{15}\) to yield:

\begin{align*}
\mathbf{A}(R') &= \mathbf{W}^{-1}_{\text{as}} \mathbf{G}^{(R', R')} \mathbf{W}^{1/2}_{\text{as}}, \quad \text{(III.16a)} \\
\mathbf{B}(R') &= \mathbf{W}^{-1/2}_{\text{as}} \mathbf{G}^{(R', R')} \mathbf{W}^{1/2}_{\text{as}}, \quad \text{(III.16b)}
\end{align*}

so the matrix Green's function becomes

\[
\mathbf{G}(R, R') = \mathbf{W}^{-1}_{\text{as}} \mathbf{G}^{(R', R')} \mathbf{W}^{1/2}_{\text{as}} 
\]

(III.17)

This completes the analysis of matrix Green's functions. It should be stressed that such functions must exist because of the duality discussed in Sec. II; the interesting feature of the present analysis is that all the standard formulas of the scalar Sturm–Liouville problem have simple matrix analogs. Similar constructions for matrix Green's functions have been developed independently by Huang and Rabitz\(^{16}\) in connection with sensitivity analysis, and by McLennan and Secretst to improve angular momentum coupling schemes.\(^{17}\) Basically, the approach taken here differs from those in that rigorous attention is paid to the self-adjointness of the operators. Note that definition of the matrix Wronskian \( \mathbf{W}_{\text{as}} \) as the surface term (III.10) guarantees the symmetry \( \mathbf{G}(R, R') = \mathbf{G}^{(R', R)} \) as demanded by the Sturm–Liouville problem. Further, the treatment of bases with nonunit weights will be seen to be of importance in the theory of discrete variable representations.\(^9\)

Matrix Green's functions have also been used in the study of atomic and molecular collisions before, e.g., in connection with optical potentials for elastic scattering,\(^{18}\) and in the solution of the equations for inelastic\(^{19}\) and reactive scattering.\(^{20}\) However, these methods are quite different from those presented here. The connection between the matrix Sturm–Liouville problem and the quantum mechanical scattering problem will now be made using ideas from the theory of invariant imbedding.

IV. INVARIANT IMBEDDING

Although the approach taken here is nonstandard, three basic features of invariant imbedding\(^{21}\) may be discerned. First the global problem of physical interest is viewed as a collection of smaller imbedded problems. Letting \( R_u \) be a value of the scattering distance large enough to warrant application of scattering boundary conditions, the scattering problem is seen to be in the form of a matrix Sturm–Liouville problem on \( [0, R_u] \). Formally, of course, the scattering problem is defined on \([0, \infty)\)  [or, \((-\infty, \infty)\) for reactive problems] but as will become obvious no difficulties arise from imbedding the Sturm–Liouville problems for finite radial intervals such as \([0, R_1], [R_1, R_2], \ldots [a, b], \ldots [R_{u-1}, R_u]\).

The second feature of invariant imbedding to be found in the present analysis is that the quantities of physical interest—the matrix Green's function—need only be evaluated on the surfaces of \([0, R_u]\), rather than actually constructed throughout the interval. This will be seen to save much work.

Finally, the third feature of invariant imbedding to be used here is that a two-point boundary condition problem [for \( \mathbf{G}(R, R') \)] may be replaced by two initial value problems [for \( \phi_s(R) \) and \( \phi_s^*(R) \)]. This will be considered explicitly in the following section on perturbation theory and will be shown to be of great benefit.

One difference between this analysis and more standard approaches to invariant imbedding\(^{21}\) lies in the treatment of the equation. In traditional imbedding of solutions of second order differential equations, the points at which boundary conditions are applied are treated as variables. Differentiation of the boundary conditions with respect to these variables then yields a set of nonlinear first order equations for the quantities of physical interest—refraction and transmission coefficients in transport problems, for example. Recently, Singer, Band, and Freed used this technique in connection with imbedding \( T \) matrices for a set of driven equations describing photodissociation.\(^{22}\) Sometimes physical arguments concerning flux on the surfaces of the problem may be used to derive the proper imbedding equations. Such an approach has been used by Secretst to derive the standard equations of \( R \)-matrix propagation.\(^{23}\)

In contrast the present analysis will only deal with the original linear second order differential equation, albeit with arbitrary boundary conditions imposed locally on intervals such as \([a, b]\). The numerical motivation for restricting attention to such Sturm–Liouville problems is that they may be easily solved by perturbation theory.

The basic imbedding procedure will now be presented. Begin with the Schrödinger equation in the \( R \)-independent orthonormalized frame

\[
\mathbf{H}(R) \psi(R) = 0.
\] (IV.1a)

Now simply add the Bloch operator \( \mathbf{L}_{\text{as}}(R) \) to each side to yield

\[
[\mathbf{H}(R) + \mathbf{L}_{\text{as}}(R)] \psi(R) = \mathbf{L}_{\text{as}}(R) \psi(R),
\] (IV.1b)

Note that this imposes no boundary conditions on the scattering wave function; \( \psi(R) \) is completely specified by boundary conditions of the form of Eq. (III.3). The point of Eq. (IV.1b) is that now the operator \([\mathbf{H}(R) + \mathbf{L}_{\text{as}}(R)] \) may be inverted using the Green's functions derived in the previous section

\[
\psi(R) = \int_a^b dR \mathbf{G}(R, R') \mathbf{L}_{\text{as}}(R') \psi(R')
\]

\[
= -\mathbf{G}(R, b) [\psi'(b) - \delta_s \psi(b)] + \mathbf{G}(R, a) [\psi'(a) - \delta_s \psi(a)].
\] (IV.2)

J. Chem. Phys., Vol. 78, No. 7, 1 April 1983
Equations (IV. 2) allow the matrix Sturm–Liouville problem discussed in Sec. III to be imbedded directly into the scattering problem. This results in the set of algebraic Eqs. (IV. 2) involving quantities evaluated on the surfaces of $[a, b]$. One connection with standard scattering theory may now be made by evaluating Eq. (IV. 2) with $\delta_\alpha = \delta_\alpha = 0$, and $a = 0$ and $b = R_R$

$$\begin{aligned}
\begin{pmatrix}
\phi(0) \\
\phi(R_R)
\end{pmatrix} &= -\begin{pmatrix}
G(0, 0) & G(0, R_R) \\
G(R_R, 0) & G(R_R, R_R)
\end{pmatrix} \begin{pmatrix}
-\phi'(0) \\
-\phi'(R_R)
\end{pmatrix} \\
&= \begin{pmatrix}
R_{11}(R_R) & R_{12}(R_R) \\
R_{21}(R_R) & R_{22}(R_R)
\end{pmatrix} \begin{pmatrix}
-\phi'(0) \\
-\phi'(R_R)
\end{pmatrix} \cdot \psi'(R) \cdot \phi'(R). 
\end{aligned} \quad (IV. 3)
$$

Here, $R_1$, $R_2$, $R_3$, and $R_4$ are the blocks of the Wigner $R$ matrix. They obviously have the symmetry relations $R_1 = R_2^*$, $R_2 = R_3^*$, and $R_3 = R_4^*$. Also it is obvious that the $R$ matrix is unique. For the $N$-channel problem, there are $4^N$ elements of the full $R$ matrix; since there must be two independent matrix solutions—say $\psi(R)$ and $\psi'(R)$—there is a total of $4^N$ equations such as in Eq. (IV. 3), thus uniquely specifying all the $R$-matrix elements.

The basic fact that the $R$ matrix is an evaluation of a Green's function on some surface has been known for a long time. More recently Bloch operators and Green's functions have been used in the analysis of $R$-matrix propagation methods. The novelty of the present approach lies in the generality of the boundary conditions considered and the simple form for the matrix Green's function which in particular involves no spectrual resolution.

Equation (IV. 3) may be used to generate the most general imbedding formula to evaluate $R$ matrices for the intervals $[0, R_1]$, $[0, R_2]$, $[0, a]$, $[0, b]$, $[0, R]$. First write the equations

$$\begin{aligned}
\phi(0) &= -R_{11}(a)\phi'(0) + R_{12}(a)\phi'(a) \quad (IV. 4a) \\
\phi(a) &= -R_{11}(a)\phi'(0) + R_{12}(a)\phi'(a) \quad (IV. 4b) \\
\phi(a) &= -G(a, b)\left[\phi'(b) - \delta_g\phi(b)\right] + G(a, a)\left[\phi'(a) - \delta_g\phi(a)\right] \quad (IV. 4c) \\
\phi(b) &= -G(b, b)\left[\phi'(b) - \delta_g\phi(b)\right] + G(a, a)\left[\phi'(a) - \delta_g\phi(a)\right] \quad (IV. 4d) \\
\phi(0) &= -R_{11}(b)\phi'(0) + R_{12}(b)\phi'(b) \quad (IV. 4e) \\
\phi(b) &= -R_{11}(b)\phi'(0) + R_{12}(b)\phi'(b) \quad (IV. 4f) 
\end{aligned}$$

The algebra involved in solving for the $R$ matrix at $R = b$ in terms of the $R$-matrix at $R = a$ and the matrix Green's function for $[a, b]$ is tedious but straightforward. The rather complicated results are shown below

$$\begin{aligned}
X &= 1 + G(a, a)\delta_g \quad (IV. 5a) \\
X &= 1 - \delta_g R_{11}(a) \quad (IV. 5b) \\
Z &= R_{11}(a) - (1 - G(a, a)\delta_g)^{-1} G(a, a) \quad (IV. 5c) \\
R_1(b) &= R_{11}(a) - R_{12}(a) Z^{-1}(1 + \delta_g)^{-1} G(b, b) \delta_g \\
&- G(b, a) Y Z^{-1} X^{-1} G(a, b) \delta_g \quad (IV. 5d) \\
R_2(b) &= -R_{12}(a) Z^{-1} X^{-1} G(a, b) \delta_g \\
&- G(b, a) Y Z^{-1} X^{-1} G(a, b) \delta_g \quad (IV. 5g)
\end{aligned}$$

These general equations are much too cumbersome to use with an arbitrary $\delta_g$ and $\delta_g$. Note, however, that because the $R$ matrix is unique it is invariant with respect to the boundary conditions of the imbedded Sturm–Liouville problem on $[a, b]$. This is the sense in which the imbedding technique is invariant. The practical value of Eq. (IV. 5) lies in the opportunity they offer to derive an optimal set of imbedding formulas which minimize the number of matrix operations required. Examination of Eq. (IV. 5) reveals that setting $\delta_g = 0$ results in a great simplification. This choice will be assumed in the following analysis.

One particularly simple choice would be to set $\delta_g = 0$ as well. The resulting formulas, displayed in Eq. (IV. 6), are seen to be the standard $R$-matrix recursion formulas of Light and Walker

$$\begin{aligned}
\delta_g &= \delta_g = 0 \quad (IV. 6a) \\
X &= Y = 1 \quad (IV. 6b) \\
Z &= R_{11}(a) - G(a, a) \quad (IV. 6c) \\
R_1(b) &= R_{11}(a) - R_{12}(a) Z^{-1} R_{11}(a) \quad (IV. 6d) \\
R_2(b) &= -R_{12}(a) Z^{-1} G(a, b) \quad (IV. 6e) \\
R_3(b) &= -G(b, a) Z^{-1} R_{11}(a) \quad (IV. 6f) \\
R_4(b) &= -R_{12}(a) G(a, b) \quad (IV. 6g)
\end{aligned}$$

A simpler set of imbedding formulas is obtained by setting $\delta_g = R_{11}^{-1}(a)$. These formulas are displayed in Eqs. (IV. 7)

$$\begin{aligned}
\delta_g &= R_{11}^{-1}(a) \quad (IV. 7a) \\
X &= Y = 1 + G(a, a) R_{11}^{-1}(a) \quad (IV. 7b) \\
Y &= 0 \quad (IV. 7c) \\
Z &= R_{11}(a) R_{11}(a) + G(a, a) \quad (IV. 7d) \\
R_1(b) &= R_{11}(a) - R_{12}(a) Z^{-1} R_{11}(a) \quad (IV. 7e) \\
R_2(b) &= -R_{12}(a) R_{11}^{-1}(a) G(a, b) \quad (IV. 7f) \\
R_3(b) &= -G(b, a) R_{11}^{-1}(a) R_{11}(a) \quad (IV. 7g) \\
R_4(b) &= -R_{12}(a) \quad (IV. 7h)
\end{aligned}$$

The simplicity of the expression for $R_4(b)$ is notable: use of the boundary conditions $\delta_g = R_{11}^{-1}(a)$ and $\delta_g = 0$ results in an imbedded Green's function whose value on the surface $R = b$ is the same as that of the global Green's function. This simplicity may be further exploited by the following trick which is more in keeping with the spirit of imbedding. Since all that is required are evaluations of $G(R, R')$ on the surfaces of $[a, b]$ the expression (III.17) may be simplified by noticing that because the Wronskian Eq. (III.10) is constant it may be evaluated at either $R = a$ [with $\delta_g = R_{11}^{-1}(a)$] or $R = b$ [with $\delta_g = 0$] to obtain:

J. Chem. Phys., Vol. 78, No. 1, 1 April 1983
\[ W_{a\bar{a}} = -\phi_{a}(b)\phi_{\bar{b}}(b) \]  
\[ = \phi_{a}(a)[\phi_{a}(a)\phi_{\bar{b}}(a) - R_{a}^{\dagger}(a)]\phi_{\bar{b}}(a). \]  

The appropriate evaluations of the matrix Green's function then become

\[ G(a, a) = [\phi_{a}(a)\phi_{\bar{b}}(a) - R_{a}^{\dagger}(a)]^{-1}, \]  
\[ G(a, b) = -\phi_{a}(a)\phi_{\bar{b}}(b), \]  
\[ G(b, a) = -[\phi_{a}(b)]^{-1}\phi_{\bar{b}}(a), \]  
\[ G(b, b) = -\phi_{a}(b)\phi_{\bar{b}}(b)^{-1}. \]  

The imbedding formulas of Eqs. (IV, 7) may now be simplified to yield

\[ R_{a}(b) = R_{a}(a) - R_{b}(a) R_{a}^{\dagger}(a) R_{a}(a) \]  
\[ + (\phi_{a}(a)\phi_{\bar{b}}(a) - R_{a}^{\dagger}(a)]^{-1} R_{a}^{\dagger}(a) R_{a}(a), \]  
\[ R_{b}(b) = R_{b}(a) R_{a}^{\dagger}(a) \phi_{a}(a)\phi_{\bar{b}}(b)^{-1}, \]  
\[ R_{b}(b) = [\phi_{a}(a)\phi_{\bar{b}}(b)]^{-1} R_{a}^{\dagger}(a) R_{a}(a), \]  
\[ R_{b}(b) = \phi_{a}(b)\phi_{\bar{b}}(b)^{-1}. \]  

These equations will be simplified a bit further whenurbation theory is discussed in the following section.

Equations (IV, 9) first show that much matrix work may be saved in bypassing the actual construction of \( G(R, R') \) over \([a, b]\). Secondly, they clearly demonstrate the relation between \( R \)-matrix integrators and “wave function” integrators. In fact, the boundary conditions imposed on \( \phi_{a}(R) \) are just those used in the variable interval-variable step algorithm. Equation (IV, 9d) in particular shows the evaluation of the matrix Green’s function subject to the proper boundary conditions to be the inverse of the so-called “logarithmic derivative” of Johnson. Thirdly, Eqs. (IV, 8) and (IV, 9) clearly show the stability of the method with respect to the propagation of closed channels, especially when it is remembered that a standard technique for the stabilization of matrix solutions is to multiply it by the inverse of its derivative. From Eq. (III.17) it is clear that \( G(R, R') \) is independent of the normalization of the solutions; instabilities due to propagation of closed channels can only occur in the construction of \( \phi_{a}(R) \) and \( \phi_{b}(R) \) over \([a, b]\). This will be explained in the following section. The only subject left to discuss here concerns algebraic considerations involving the transformations between the various imbedded problems.

In particular the similarity transformation (III, 6) combined with the imbedding analysis allows for a very simple discussion of diabatic and adiabatic representations. In the most general terms, an adiabatic representation uses a basis that is \( R \) dependent and a diabatic representation uses a basis that is independent of the scattering distance. Most commonly, an adiabatic frame is understood to be that basis in which the representations of the potential and kinetic operators are diagonal for all \( R \). As will become obvious in the following section there are advantages to working in a representation in which these operators are diagonal, or nearly so, but then the resulting expressions for the Schrödinger equation and Green’s function are not as simple as those used here. An approach that is perfectly suited to the imbedding method developed here is the use of a quasi-adiabatic basis which is independent of \( R \) within each interval such as \([a, b]\) but may be different in every interval.

The analysis is greatly facilitated by remembering that the matrix \( T(R) \) in Eq. (III, 5) is determined only up to an arbitrary unitary transformation. Thus, for some point \( R_{t} \) in \([a, b]\), \( a < R_{t} < b \), one can always write:

\[ T(R_{t}) = T^{*}(R_{t}) S^{1/2}(R_{t}) \]

where \( T(R_{t}) \) is unitary

\[ T^{*}(R_{t}) T(R_{t}) = 1. \]

Using Eq. (III, 6) the interaction in the transformed representation is

\[ T^{*}(R_{t}) [S^{1/2}(R_{t}) (K^{2}(R) - \mathbf{V}(R)) S^{1/2}(R_{t})] T(R_{t}) \]

The choice \( T(R_{t}) = 1 \) yields a diabatic representation, an adiabatic representation is obtained by choosing \( T(R_{t}) \) to diagonalize the expression in brackets in Eq. (IV, 11). The connection between the problems in adjoining intervals may be made by remembering that the transformed basis

\[ \chi_{t}(\tilde{R}) = \chi^{\ast}(R_{t}, \tilde{R}) \tau^{-1}(R_{t}) \]

is independent of \( R \). Then in the quasiadiabatic limit

\[ \chi^{\ast}(R_{t+1}, \tilde{R}) = \chi^{\ast}(R_{t}, \tilde{R}) \]

\[ = \chi_{t}(\tilde{R}) = \chi_{t-1}(\tilde{R}) \tau^{-1}(R_{t}). \]

Here, \( R_{t} \) in \([a, b]\) and \( R_{t+1} \) in the previous interval.

The full \( R \) matrix may then be written so that each block provides a map into the proper frame as follows:

\[ \tau_{t+1} = \tau(R_{t+1}) \tau^{-1}(R_{t}) \]

\[ = T^{*}(R_{t+1}) S^{1/2}(R_{t+1}) S^{-1/2}(R_{t}) T(R_{t}), \]

\[ R_{t}(a) = R_{t+1}^{\dagger}(a), \]

\[ R_{t}(a) = R_{t}^{\dagger}(a) \tau^{-1}_{t+1}, \]

\[ R_{t}(a) = \tau^{-1}_{t+1} R_{t+1}^{\dagger}(a), \]

\[ R_{t}(a) = \tau_{t+1}^{\dagger} R_{t+1}^{\dagger}(a) \tau_{t+1}. \]

Here, the superscripts on the \( R \) matrices indicate the interval in which the representation is defined. These equations hold whether or nor \( \tau \) is unitary. They were first derived by Stechel, Schmalz, and Light using operator arguments; the finite dimensional results given here follow from paying strict attention to the self-adjointness of the Green’s function and the transformation (III, 6).

The question of how to begin the imbedding procedure is determined by whether the problem is inelastic or reactive. In the former case consider the solution of the Sturm–Liouville problem in the first interval \([0, R_{1}]\), where \( R_{1} \) is some small value of the scattering distance. Because this problem is inelastic \( \phi(0) = 0 \), and hence \( R_{1}(R_{1}) \) and \( R_{0}(R_{1}) \) must also vanish since in general \( \phi'(R_{1}) \neq 0 \). By symmetry then \( R_{0}(R_{1}) \) must also vanish.
and thus only \( \mathbf{R}_t \) need be computed. Each of the specific imbedding schemes allows this to be done.

In the reactive problem the solution must be matched onto solutions from other reactive channels on some surface at small \( R \). Such a procedure is a problem in itself and is not studied here as the present article is concerned with only the integration of the equations. The actual construction of these solutions via perturbation theory is now considered.

V. PERTURBATION THEORY

The entire scattering problem has been reduced to solving a series of matrix Sturm–Liouville problems in intervals such as \([a, b]\). The analysis of imbedding methods has yielded a method that minimizes the amount of matrix work required. The computational goal is now obtained by solving the matrix Green’s function for the problem on \([a, b]\) in a manner that minimizes the number of matrix operations.

Begin by writing the Hamiltonian (III.8) as the sum of diagonal and off-diagonal parts

\[
\mathcal{H}(R) = \int \frac{d^2}{dR^2} + \Lambda^2(R) - \mathbf{W}(R) .
\]  

Here, \( \Lambda(R) \) is the diagonal part of \([k^2(R) - \mathbf{V}(R)]\) and \(-\mathbf{W}(R)\) is the off-diagonal part of \([k^2(R) - \mathbf{V}(R)]\). Write the zero-order Hamiltonian as

\[
\mathcal{H}_0(R) = \int \frac{d^2}{dR^2} + \Lambda^2(R) .
\]  

Because the normalization of the solutions \( \phi_a(R) \) and \( \phi_{sa}(R) \) is arbitrary, these functions may be defined by

\[
\phi_a(R) = \mathbf{R}_a(R), \quad \phi_{sa}(R) = 1 ,
\]  

\[
\mathcal{H}_0(R) \phi_a(R) = \mathbf{W}(R) \phi_a(R) ,
\]  

\[
\phi_a(b) = 0 ; \quad \phi_{sa}(b) = 1 .
\]  

and the zero-order solutions may be defined by

\[
\mathcal{H}_0(R) \phi_a(R) = \mathbf{R}_a(R),
\]  

\[
\phi_{sa}(b) = 0 ; \quad \phi_a(b) = 1 .
\]  

Hence

\[
\phi_a^0(R) = \phi_a(R) + \phi_{sa}(R) ,
\]  

\[
\phi_{sa}(R) = \phi_{sa}(R) .
\]  

Because \( \phi_a(R) \) and \( \phi_{sa}(R) \) satisfy initial value boundary conditions they may be written as solutions to Volterra equations whose resolvents satisfy arbitrary boundary conditions

\[
\phi_a(R) = \int_0^R dR' \mathbf{K}_a(R, R') \mathbf{W}(R') \phi_a(R') ,
\]  

\[
\phi_{sa}(R) = \int_0^R dR' \mathbf{K}_{sa}(R, R') \mathbf{W}(R') \phi_{sa}(R') .
\]  

The resolvents \( \mathbf{K}_a(R; R') \) may be determined just as in the scalar case \(^3\) using the techniques of Sec. III

\[
\mathbf{K}_a(R, R') \phi_a(R') = \phi_a(R) \phi_{sa}(R') - \phi_{sa}(R) \phi_a(R') ,
\]  

\[
\mathbf{K}_{sa}(R, R') \phi_{sa}(R') = \phi_{sa}(R) \phi_a(R') - \phi_a(R) \phi_{sa}(R') .
\]  

The sine- and cosine-like solutions as well as the following perturbation integrals must be determined numerically:

\[
\mathcal{I}_{sec} = \int_0^R dR' \phi_a^0(R) \mathbf{W}(R) \phi_{sa}(R') ,
\]  

\[
\mathcal{I}_{sec} = \int_0^R dR' \phi_a^0(R) \mathbf{W}(R) \phi_{sa}(R) ,
\]  

\[
\mathcal{I}_{sa} = \int_0^R dR' \phi_{sa}^0(R) \mathbf{W}(R) \phi_a(R) ,
\]  

\[
\mathcal{I}_{sa} = \int_0^R dR' \phi_{sa}^0(R) \mathbf{W}(R) \phi_{sa}(R) .
\]  

Evaluation of Eqs. (V.5a) and (V.5b) to first order then yields the following expressions for the sector solutions and their derivatives:

\[
\phi_a(b) = \phi_{sec}(b) [\mathbf{R}_a(a) - \mathbf{I}_{sec} \mathbf{R}_a(a) - \mathbf{I}_{sec}^{-1}] ,
\]  

\[
\phi_{sa}(b) = \phi_{sa}(b) [\mathbf{R}_a(a) - \mathbf{I}_{sec} \mathbf{R}_a(a) - \mathbf{I}_{sec}^{-1}] ,
\]  

\[
\phi_a^0(b) = \phi_{sa}(b) [\mathbf{R}_a(a) - \mathbf{I}_{sec} \mathbf{R}_a(a) - \mathbf{I}_{sec}^{-1}] .
\]  

The only matrix \( (N^2) \) operations required are the multiplications \( \mathbf{I}_{sec} \mathbf{R}_a(a) \) and \( \mathbf{I}_{sec} \mathbf{R}_a(a) \); these may be done only once in each interval.

The standard scalar analysis of the convergence of Volterra series also generalizes to the matrix case. In general, write

\[
\phi(R) = \sum_{n=1} \phi_n(R) + \phi_0(R) ,
\]  

where

\[
\phi_n(R) = \frac{\mathbf{R}_n(a)}{1 + \mathbf{I}_{sec} \mathbf{R}_n(a) + \mathbf{I}_{sec}^{-1}} .
\]  

J. Chem. Phys., Vol. 78, No. 7, 1 April 1983
\[ \phi_n(R) = \int_\varepsilon^\eta \, dR' \, K(R, R') \, \mathbf{W}(R') \, \phi_{n-1}(R) . \]  
\[ \text{(V. 8b)} \]

Comparing all matrices in an element by element fashion define the following upper bounds:

\[ |K(R, R')\mathbf{W}(R')| \leq M , \]
\[ \int_\varepsilon^\eta \, dR \, |\phi(R)| \leq N . \]

Then where \( h = b - a \) is the size of the interval one may show

\[ |\phi_n| \leq \frac{h^{n-1}}{(n-1)!} \, M^n N . \]  
\[ \text{(V. 8c)} \]

For any finite-dimensional problem the Volterra series (V. 8a) always converges because the factor of \((n-1)!\) in Eq. (V. 8c) will dominate any element in \( M^n N \) for some \( n \). Put another way, first order approximation to (V. 8a) provides sufficient accuracy. This argument is true regardless of the representation used, although as is obvious from (V. 8c) more diagonal representations may allow for a more efficient solution of the problem by using larger intervals.

VI. DISCUSSION

In summary, this paper has presented a very powerful but simple formalism for analysis of the coupled equations that are obtained in the study of quantum mechanical scattering. In particular, it has been shown that the standard scalar analysis of Sturm-Liouville problems may be extended to sets of coupled second order differential equations. All the standard scalar equations generalize to the matrix case and with the proper definition of the inner product, self-adjointness is guaranteed.

A nonstandard but very general approach to invariant imbedding using Bloch operators was then presented. The \( R \)-matrix propagation of Light and Walker\(^2\) and the variable interval-variable step algorithm of Parker, Schmalz, and Light\(^3\) were shown to be specific examples of the more general procedure. Extensions and simplifications were given. Adiabatic, diabatic, and quasiadiabatic representations—both orthogonal and nonorthogonal—were treated in a simple fashion.

Finally perturbation theory in the form of simple stable Volterra series may be employed exclusively, even in the reactive problems. This permits a great saving in matrix work, the only matrix operations being required each time a new interval is taken—i.e., each time a new matrix Sturm-Liouville problem is imbedded.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Dr. Charles Cerjan for his careful reading of the manuscript and his many useful suggestions. This material is based upon work supported by the National Science Foundation under Grants CHE-7808696 and CHE-8203453, and by The Robert Welch Foundation (T.G.S.).

\[ ^1 \text{W. A. Lester and R. B. Bernstein, J. Chem. Phys. 48, 4896 (1968).} \]
\[ ^2 \text{NRCC Proceedings No. 5, LBL-9501 (1979–1980), Vols. I and II.} \]
\[ ^4 \text{E. B. Stechel, R. B. Walker, and J. C. Light, J. Chem. Phys. 69, 3518 (1978).} \]
\[ ^5 \text{G. A. Parker, T. G. Schmalz, and J. C. Light, J. Chem. Phys. 73, 1757 (1980).} \]
\[ ^7 \text{F. W. Byron and R. W. Fuller, Mathematics of Classical and Quantum Physics (Addison-Wesley, Reading, Mass., 1969).} \]
\[ ^8 \text{G. Arfken, Mathematical Methods for Physicists (Academic, New York, 1970).} \]
\[ ^9 \text{V. Lill, G. A. Parker, and J. C. Light (to be published).} \]
\[ ^10 \text{J. R. Taylor, Scattering Theory (Wiley, New York, 1972).} \]
\[ ^11 \text{E. B. Stechel, T. G. Schmalz, and J. C. Light, J. Chem. Phys. 70, 5640 (1979).} \]
\[ ^12 \text{D. R. Halmos, Finite Dimensional Vector Spaces (Springer, Berlin, 1974).} \]
\[ ^13 \text{T. G. Schmalz, E. B. Stechel, and J. C. Light, J. Chem. Phys. 70, 5660 (1979).} \]
\[ ^14 \text{C. Bloch, Nucl. Phys. 4, 53 (1957).} \]
\[ ^15 \text{A. W. Joshi, Matrices and Tensors in Physics (Wiley, New York, 1975).} \]
\[ ^16 \text{M. T. Huang and H. Rabitz, J. Chem. Phys. 70, 4609 (1979).} \]
\[ ^17 \text{K. McLenithan and D. Secrest, J. Chem. Phys. 73, 2313 (1980).} \]
\[ ^18 \text{H. Zimmer, and J. F. George, Chem. Phys. 4, 315 (1979).} \]
\[ ^19 \text{G. Wolken, Chem. Phys. Lett. 14, 249 (1972).} \]
\[ ^20 \text{L. Shoemaker and R. E. Wyatt, J. Chem. Phys. 76, 1347 (1982).} \]
\[ ^21 \text{J. Casti and R. Kalaba, Imbedding Methods in Applied Mathematics (Addison-Wesley, Reading, Mass., 1973).} \]
\[ ^22 \text{S. Singer, Y. Band, and K. F. Freed, J. Chem. Phys. 77, 1942 (1982).} \]
\[ ^23 \text{D. Secrest, in Atom–Molecule Collision Theory, edited by R. B. Bernstein (Plenum, New York, 1979).} \]
\[ ^24 \text{A. M. Lane and R. G. Thomas, Rev. Mod. Phys. 30, 257 (1958).} \]
\[ ^25 \text{D. J. Ziviac and J. C. Light, Chem. Phys. 12, 237 (1976).} \]
\[ ^26 \text{B. L. Schneider and R. B. Walker, J. Chem. Phys. 70, 2466 (1979).} \]
\[ ^29 \text{M. J. Redmon and D. A. Micha, Chem. Phys. Lett. 28, 341 (1974).} \]
\[ ^30 \text{M. S. Child, Molecular Collision Theory (Academic, New York, 1974).} \]
\[ ^31 \text{N. H. Mullane and D. G. Truhlar, Chem. Phys. Lett. 58, 512 (1978).} \]
\[ ^32 \text{H. H. Mullane and D. G. Truhlar, Chem. Phys. 39, 91 (1979).} \]

J. Chem. Phys., Vol. 78, No. 7, 1 April 1983