

Localized Basis Functions and Other Computational Improvements in Variational Nonorthogonal Basis Function Methods for Quantum Mechanical Scattering Problems Involving Chemical Reactions*

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Abstract. In this paper we very briefly review the Generalized Newton Variational Principle for 3-dimensional quantum mechanical reactive scattering. Then three techniques are described which improve the efficiency of the computations. First we use the fact that the Hamiltonian is Hermitian to reduce the number of integrals computed, and then we exploit the properties of localized basis functions in order to eliminate redundant work in the integral evaluation. In addition we suggest a new type of localized basis function with desirable properties. Finally we show how partitioned matrices can be used with localized basis functions to reduce the amount of work required to handle the complex boundary conditions. The new techniques do not introduce any approximations into the calculations, so they may be used to obtain converged solutions of the Schrödinger equation.

1. Introduction.

There are many approaches to solving multidimensional quantum mechanical scattering problems. The most widely studied practical methods in physical chemistry are based on writing the solution of the time-independent Schrödinger equation with nonhomogeneous boundary conditions as an expansion over products of unknown non-square-integrable radial relative translational functions and known square-integrable internal-orbital functions [1,2]. This leads in the case of nonreactive collisions to coupled ordinary differential equations for the radial functions, and these are usually solved by propagation along the radial scattering coordinate

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[3]. In atomic and chemical physics this is usually called the close coupling method. Each internal-orbital state function is called a channel, and the number of coupled equations equals the number of coupled channels. In 1979 a workshop [4] was held comparing most of the available specialized techniques for solving these equations. In addition they were compared to a widely used, state-of-the-art, general-purpose variable-order, variable-stepsize predictor-corrector (PC) algorithm [5]. Interestingly, adding the computer times to solve four test cases shows that the PC algorithm rated 15th out of 15 schemes tested, with a computer time 19 times greater than the best specialized scheme. This showed the great utility of special methods and the great progress achieved in developing highly accurate specialized techniques for atomic and molecular collisions.

The four trial problems used to compare algorithms in the 1979 workshop involved 15–22 coupled channels [4]. With supercomputers and efficient vectorization [6] and storage management [7] strategies, much larger single-arrangement problems have been treated successfully, *e.g.*, a four-body problem with a realistic potential function and 1358 coupled channels has been solved [8] by the technique discussed above of propagation along a scattering coordinate, and a model problem involving the scattering of a diatom by a corrugated crystal surface with 18711 channels has been treated successfully [9] by a time propagation algorithm [10].

Rearrangement collisions, however, pose special difficulties. For example, we will consider a rearrangement collision consisting of the reaction of an atom *A* with a diatom *BC*: *A* scatters onto *BC*, a rearrangement (chemical reaction) occurs, and *AB* scatters away from *C*, or *AC* scatters away from *B*; the solution also contains terms and boundary conditions corresponding to *A* scattering nonreactively off *BC*. To define a single propagation coordinate, we must either introduce special coordinates that complicate the differential operators and the boundary conditions [11–19], or one must introduce nonlocal potential operators that convert the differential equations into integrodifferential equations [20–22]. Alternatively one can propagate nonreactive-type equations in coordinates of each of the arrangements and then match the subsolutions on internal boundaries [23,24]. Non-propagative methods for rearrangement scattering have been developed to avoid these problems [10,25–36]. In physical chemistry these have been especially widely employed for electron scattering (*e.g.*, electron-helium scattering in which the incident electron may exchange with either bound electron of helium). Because of the essentially infinite ratio of nuclear and electronic masses and the simplicity of the coulomb potential, the coordinates and nonlocal potential operators both become particularly simple for electron scattering. A variety of basis set techniques—which may be viewed as nonorthogonal spectral methods, although not having “exponential convergence”—has been developed and successfully applied to such problems [26–28,30–32,35,36].

Chemical reactions are harder to treat than electron scattering not only because the coordinate transformations and potential functions are more complicated (potential functions for chemical reactions typically involve hundreds of lines of code as contrasted to the simple coulomb potential that completely suffices for electron-atom scattering in nonrelativistic problems), but also because the de Broglie wavelengths are smaller, *i.e.*, there is more structure in the solutions. In the last few years we and our collaborators have developed a variational nonorthogonal spectral method for chemical reactions [37,38], and we have applied it to obtain converged solutions to the time-independent Schrödinger equation with rearrangement scattering boundary conditions and up to 844 coupled channels [39]. Our method involves a generalization of a variational principle [40–50] due originally to Newton, and it involves expanding the reactive amplitude density [10,51,52] in a nonorthogonal

basis set. Other basis set variational methods [38,53-60] based on the Schwinger [35,38,53,61] or Kohn [27,30-32,54,58,62] variational principles and sharing many attractive features in common with our approach have also been proposed recently. All these approaches, as well as new nonvariational basis set techniques [10,63-66], are very encouraging for improving the computational efficiency of nonorthogonal spectral methods for the quantum dynamics of reactive scattering. The present paper is concerned only with the approach based on the generalized Newton variational principle (GNVP). The theoretical formulation of the method [38] and some computational improvements [67,68] are presented elsewhere. The present paper, after a brief overview of the working equations, describes three additional computational improvements, including improved use of inherent symmetries and a new more localized basis set.

The final variational equations in the method described here may be obtained in several ways. They were originally derived by applying the GNVP to the problem posed as a set of coupled Fredholm integral equations of the second kind [10,38,64]. (They can also be obtained from the formulation of the problem as coupled integrodifferential equations [20,21,65] or with a scattered wave or outgoing wave variational principle [69-72] based directly on the Schrödinger equation with nonhomogeneous boundary conditions.) There are many general techniques for solving Fredholm integral equations of the second kind in a single variable [73]. Just as the specialized techniques developed in physical chemistry for single-arrangement scattering are much more efficient than general-purpose predictor-corrector algorithms for coupled ordinary differential equations, we believe that the specialized techniques developed for solving the coupled equations describing reactive scattering are also more efficient than general techniques developed previously for solving coupled integral equations.

Spectral techniques are now widely employed for solutions of problems in fluid dynamics [74-79]. The choice of basis functions in these applications is very critical, and the same is true for treating reactive scattering. One possibility is to choose basis functions to minimize the number of nonzero weights in the quadratures leading to a given matrix element; this kind of consideration leads to using, *e.g.*, Lobatto functions [58]. Another possibility is to choose the basis functions to allow more efficient quadratures by using fast Fourier transforms or fast cosine transforms; the latter can be accomplished, *e.g.*, by using Chebyshev basis functions [79]. A third possibility is to use basis functions that reduce the number of integrals and the time to solve the final coupled linear equations; this has been our philosophy so far. In the present work we discuss a new consideration, namely a choice of basis function that minimizes the computational effort in obtaining the half-integrated Green's functions that enter the GNVP and in integrating over these functions.

2. Theory.

First we outline the formalism of the basic calculations, and then the improvements are described in detail.

2.1 General Equations.

We consider atom-diatom reactive scattering with three arrangements: $\alpha = 1$ denoting $A + BC$, $\alpha = 2$ denoting $B + AC$, and $\alpha = 3$ denoting $C + AB$. The formalism and notation are the same as used previously [38,67]. The Schrödinger equation is

$$(H - E)\Psi^{n_0} = 0 \quad (1)$$

where H is the Hamiltonian, E is the total energy, and Ψ^{n_0} is the wave function with complex nonhomogeneous boundary conditions corresponding to an incoming

wave in channel n_o and outgoing waves in all open channels. The wave function determines the scattering matrix, a complex matrix of scattering amplitudes from which all physical observables of the scattering process may be calculated. Although the boundary conditions on the final solution are complex, to correspond to the physical conditions, we form the solution to the problem in such a way that most of the computations involve real quantities. The channel label n is a collective index denoting arrangement α and internal quantum numbers specifying a channel in that arrangement. The initial channel and initial arrangement (or—sometimes below—any special channel and its corresponding arrangement) are denoted n_o and α_o , respectively. We use conservation of total angular momentum J , parity, and arrangement symmetry, if present, to block diagonalize the problem, and all further considerations refer to a single block of N coupled channels.

Equation (1) is rewritten in three different ways ($\alpha = 1, 2, 3$) as

$$(H_\alpha^D + V_\alpha^C - E)\Psi^{n_o} = 0 \quad (2)$$

where H_α^D is called the distortion Hamiltonian. It contains the kinetic energy and a part of the potential that only couples channels in the same arrangement (with subblocks called distortion blocks), and V_α^C contains the rest of the potential. First we define the regular solutions ψ^{n_o} of

$$(H_\alpha^D - E)\psi^{n_o} = 0 \quad (3)$$

for various possible initial channels n_o and initial arrangements α_o , and we define the principal value Green's functions by

$$G_\alpha^D = -\hbar^2 \mathcal{P}[2\mu(E - H_\alpha^D)]^{-1} \quad (4)$$

for all three arrangements. These are called the distorted waves and the distorted wave Green's functions, respectively. Then we apply the GNVP to solve for the remaining coupling due to the V_α^C potentials. This is accomplished by expanding the reactive amplitude density [38,64] in a square-integrable (\mathcal{L}^2) basis of functions Φ_β , with $\beta = 1, 2, \dots, M$. Each basis function is a product of a radial translational function $t_{m_\beta n_\beta}^{\alpha_\beta}(R_{\alpha_\beta})$, where R_{α_β} is the radial translational coordinate in arrangement α_β , and an internal-orbital function $\phi_{n_\beta}^{\alpha_\beta}$ corresponding to channel n_β in this arrangement. The GNVP then leads to a matrix equation for the scattering matrix in which the matrix elements are integrals over V_α^C , G_α^D , and $G_\alpha^D V_\alpha^C G_\alpha^D$, sandwiched between the various ψ^n and Φ_β .

An important computational aspect of the resulting equations is that every Green's function always appears in an integrand multiplied by a basis function in the same arrangement. Thus we never compute the Green's functions themselves, but only a set of functions representing the effect of integrating the Green's functions with the various basis functions. These integrals are called half-integrated Green's functions (HIGFs). The radial distorted waves and radial HIGFs are computed by a finite difference boundary value method (FDBVM) [64,80], using an irregular mesh that contains Gauss-Legendre quadrature nodes for all further quadratures of these quantities as a sub-mesh [38]. This avoids the difficulties [81,82] of integrating over functions with discontinuous slopes.

Then the scattering matrix is given by [67]

$$S_{nn_0} = \delta_{\alpha_n \alpha_0} {}^{\circ}S_{nn_0} + \underline{S}_{nn_0}, \quad (5)$$

where ${}^{\circ}S$ is the scattering matrix for the distortion potential, \underline{S} is the correction produced by the remainder of the potential, and α_n is the arrangement associated with channel n . (We ignore the notational complications due to the presence of closed channels, for these details play no important role in the subsequent discussion.) The correction to the scattering matrix due to the coupling potential is given by

$$\underline{S} = \underline{S}^B + \tilde{B}^T \tilde{C}^{-1} \tilde{B}, \quad (6)$$

where the matrices in Eq. (6) are given by

$$\underline{S}^B = \mathbf{A}^T \underline{\mathcal{K}}^B \mathbf{A}, \quad (7)$$

$$\tilde{B} = (\mathbf{B} + \mathbf{X}^T \underline{\mathcal{K}}^B) \mathbf{A}, \quad (8)$$

and

$$\tilde{C} = \mathbf{C} - \mathbf{B}\mathbf{X} - \mathbf{X}^T \tilde{B} + \mathbf{X}^T \underline{\mathcal{D}} - \mathbf{X}^T \underline{\mathcal{K}}^B \mathbf{X}. \quad (9)$$

Note that matrices are denoted by bold for Roman letters and by double underlines for calligraphic letters. \underline{S}^B and $\underline{\mathcal{K}}^B$ are distorted-wave Born-type [83] contributions of the coupling potential to the scattering and reactance matrices, respectively; \mathbf{A} is the transformation which takes the regular distorted waves from real standing wave boundary conditions to complex scattering matrix boundary conditions; \mathbf{X} is the transformation required to form the outgoing wave HIGF given the real function; and

$$\mathcal{K}_{nn_0}^B = \int dR_{\alpha_0} \sum_{n'} \Delta_{n'n_0}^{\alpha_0} \mathcal{F}_{nn'}(R_{\alpha_0}) {}^{(r)}f_{n'n_0}^{\alpha_0}(R_{\alpha_0}), \quad (10)$$

$$B_{\beta n_0} = \int dR_{\alpha_0} \sum_{n'} \Delta_{n'n_0}^{\alpha_0} \mathcal{G}_{\beta n'}(R_{\alpha_0}) {}^{(r)}f_{n'n_0}^{\alpha_0}(R_{\alpha_0}), \quad (11)$$

$$\mathcal{D}_{n\beta_0} = \int dR_{\alpha_0} \tilde{T}_{nn\beta_0}(R_{\alpha_0}) t_{m\beta_0, n\beta_0}^{\alpha_0}(R_{\alpha_0}), \quad (12)$$

$$\tilde{B}_{n\beta_0} = \int dR_{\alpha_0} \sum_{n'} \Delta_{n'n_0}^{\alpha_0} \mathcal{F}_{nn'}(R_{\alpha_0}) \dot{g}_{n'\beta_0}^N(R_{\alpha_0}), \quad (13)$$

and

$$\begin{aligned} C_{\beta\beta_0} = & \int dR_{\alpha_0} \mathcal{T}_{\beta n\beta_0}(R_{\alpha_0}) t_{m\beta_0, n\beta_0}^{\alpha_0}(R_{\alpha_0}) \\ & - \int dR_{\alpha_0} \sum_{n'} \Delta_{n'n_0}^{\alpha_0} \mathcal{G}_{\beta n'}(R_{\alpha_0}) \dot{g}_{n'\beta_0}^N(R_{\alpha_0}). \end{aligned} \quad (14)$$

A three-body system involves three internal coordinates, and these equations involve the final (third) integration of the three-dimensional quadrature over these

coordinates. The matrix element $\Delta_{nn_o}^{\alpha_o}$ is one if channel n and channel n_o are both members of the same distortion block of arrangement α_o and are zero otherwise, $(^r)f_{nn_o}^{\alpha_o}$ is the regular radial function for the distortion potential defined by n and n_o and satisfying real boundary conditions (*i.e.*, it is one of the radial relative translational functions obtained by solving a set of close coupling equations for ψ^{n_o}), β_o is a specific basis function associated with arrangement α_o , and $\dot{g}_{n\beta}^N$ is the radial part of the real HIGF associated with the distortion block containing n and basis function β . The HIGF can be expressed as [38]

$$\dot{g}_{n\beta}^N(R_\alpha) = \int dR'_\alpha g_{nn\beta}(R_\alpha, R'_\alpha) t_{m_\beta n_\beta}^\alpha(R'_\alpha), \quad (15)$$

where n and β are both associated with the same arrangement α , and the radial Green's function is defined as

$$g_{nn'}(R_\alpha, R'_\alpha) = \sum_{n''} \Delta_{nn''}^\alpha \Delta_{n'n''}^\alpha \begin{cases} (^r)f_{nn''}^\alpha(R_\alpha) (^i)f_{n'n''}^\alpha(R'_\alpha) & R_\alpha < R'_\alpha \\ (^i)f_{nn''}^\alpha(R_\alpha) (^r)f_{n'n''}^\alpha(R'_\alpha) & R_\alpha > R'_\alpha \end{cases}, \quad (16)$$

where $(^i)f_{nn''}^\alpha$ is the irregular analog of $(^r)f_{nn''}^\alpha$. In addition the integrals \mathcal{F}_{nn_o} , $\mathcal{G}_{\beta n_o}$, $\tilde{\mathcal{T}}_{nn_o}$, and $\mathcal{T}_{\beta n_o}$ are given by the expressions

$$\mathcal{F}_{nn_o} = \begin{cases} \sum_{n'} \Delta_{nn'}^{\alpha_o} (^r)f_{n'n}^{\alpha_o}(R_{\alpha_o}) e_{n'n_o}(R_{\alpha_o}), & \alpha = \alpha_o; \\ \int dR_\alpha \sum_{n'} \Delta_{nn'}^\alpha (^r)f_{n'n}^\alpha(R_\alpha) W_{n'n_o}^{\alpha\alpha_o}(R_\alpha, R_{\alpha_o}), & \text{otherwise,} \end{cases} \quad (17)$$

$$\mathcal{G}_{\beta n_o} = \begin{cases} \sum_{n'} \Delta_{n\beta n'}^{\alpha_o} \dot{g}_{n'\beta}^N(R_{\alpha_o}) e_{n'n_o}(R_{\alpha_o}), & \alpha = \alpha_o; \\ \int dR_\alpha \sum_{n'} \Delta_{n\beta n'}^\alpha \dot{g}_{n'\beta}^N(R_\alpha) W_{n'n_o}^{\alpha\alpha_o}(R_\alpha, R_{\alpha_o}), & \text{otherwise,} \end{cases} \quad (18)$$

$$\tilde{\mathcal{T}}_{nn_o} = \begin{cases} \Delta_{nn_o}^{\alpha_o} (^r)f_{n_o n}^{\alpha_o}(R_{\alpha_o}), & \alpha = \alpha_o; \\ \int dR_\alpha \sum_{n'} \Delta_{nn'}^\alpha (^r)f_{n'n}^\alpha(R_\alpha) \mathcal{B}_{n'n_o}^{\alpha\alpha_o}(R_\alpha, R_{\alpha_o}), & \text{otherwise,} \end{cases} \quad (19)$$

and

$$\mathcal{T}_{\beta n_o} = \begin{cases} \Delta_{n\beta n_o}^{\alpha_o} \dot{g}_{n_o\beta}^N(R_{\alpha_o}), & \alpha = \alpha_o; \\ \int dR_\alpha \sum_{n'} \Delta_{n\beta n'}^\alpha \dot{g}_{n'\beta}^N(R_\alpha) \mathcal{B}_{n'n_o}^{\alpha\alpha_o}(R_\alpha, R_{\alpha_o}), & \text{otherwise.} \end{cases} \quad (20)$$

The integrals (17–20) contain the inner two quadratures of the three-dimensional integration mentioned above. For integrations over functions defined in two different arrangements, say α and α_o , the quadratures are carried out in a coordinate system consisting of R_α , R_{α_o} , and the angle $\Delta_{\alpha\alpha_o}$ between the vector from the atom to the diatom in arrangement α and the analogous vector in α_o . The inner loop involves integration over $\Delta_{\alpha\alpha_o}$ and yields $\mathcal{B}_{n'n_o}^{\alpha\alpha_o}$ or $\mathcal{C}_{n'n_o}^{\alpha\alpha_o}$, from which we calculate $W_{n'n_o}^{\alpha\alpha_o}$ [38]. The various middle loops are given in Eqs. (17–20), and the various outer loops are indicated in Eqs. (10–14). Similarly $e_{n'n_o}(R_{\alpha_o})$ is defined as a two-dimensional integral over internal coordinates orthogonal to R_{α_o} when all functions in the integrand are associated with the same arrangement α_o . Further details of

the quantities in Eqs. (1-20) are not necessary for the discussion in this paper—see Refs. [38,67] for full details.

2.2 Hermitian Property of the Hamiltonian Operator.

Let us consider the integrals given by Eqs. (17-20) for a triatomic system where all arrangements are different. Now the matrices $\underline{\underline{K}}^B$ and $\underline{\underline{C}}$ are symmetric while $\underline{\underline{B}}$, $\underline{\underline{\tilde{B}}}$, and $\underline{\underline{D}}$ are rectangular. For the symmetric matrices it is necessary to just compute the lower triangle, *i.e.*, we can restrict $\alpha \leq \alpha_0$; thus only 3 of the 6 possible reactive arrangement pairs are required. However at first glance it may seem that for the rectangular matrices it will be necessary to use all 6 of the reactive arrangement pairs, but we now show that this is not so. That is, the rectangular matrices can also be assembled from only the 3 reactive arrangement pairs required for the symmetric matrices.

To derive the relation we require, it is useful to express the matrix elements of the rectangular matrices in Dirac notation [38]:

$$B_{\beta n_0} = \langle \Phi_\beta | G_\alpha^D U_{\alpha\alpha_0} | \psi^{n_0} \rangle = \langle \Phi_\beta | G_\alpha^D U^{\alpha_0} | \psi^{n_0} \rangle, \quad (21)$$

$$\tilde{B}_{n\beta_0} = \langle \psi^n | U^{\alpha_0} G_{\alpha_0}^D | \Phi_{\beta_0} \rangle, \quad (22)$$

and

$$D_{n\beta_0} = \langle \psi^n | \Phi_{\beta_0} \rangle, \quad (23)$$

where

$$U_{\alpha\alpha_0} = -(2\mu/\hbar^2)[H - E + \delta_{\alpha\alpha_0}(E - H_\alpha^D)], \quad (24)$$

$$U^{\alpha_0} = -(2\mu/\hbar^2)[H - H_{\alpha_0}^D], \quad (25)$$

and μ is the reduced mass. Now for inter-arrangement integrals, $U_{\alpha\alpha_0}$ is just $-(2\mu/\hbar^2)(H - E)$, which is Hermitian in Eq. (21) since the surface terms vanish; thus since $B_{\beta n_0}$ is real it can be written as

$$B_{\beta n_0} = \langle \psi^{n_0} | U_{\alpha_0\alpha} G_\alpha^D | \Phi_\beta \rangle. \quad (26)$$

Now we also know that [38]

$$U_{\alpha_0\alpha} G_\alpha^D = U^\alpha G_\alpha^D - 1 + \delta_{\alpha_0\alpha}, \quad (27)$$

thus for inter-arrangement matrix elements,

$$B_{\beta n_0} = \langle \psi^{n_0} | U^\alpha G_\alpha^D | \Phi_\beta \rangle - \langle \psi^{n_0} | \Phi_\beta \rangle, \quad (28)$$

or

$$B_{\beta n_0} = \tilde{B}_{n_0\beta} - D_{n_0\beta}. \quad (29)$$

This has two consequences. First of all Eq. (9) can be rewritten as

$$\tilde{\underline{\underline{C}}} = \underline{\underline{C}} - \underline{\underline{B}}\underline{\underline{X}} - \underline{\underline{X}}^T \underline{\underline{B}}^T + \underline{\underline{X}}^T \underline{\underline{\tilde{D}}} - \underline{\underline{X}}^T \underline{\underline{K}}^B \underline{\underline{X}}, \quad (30)$$

where $\underline{\underline{D}}$ is zero unless an intra-arrangement integral is involved, in which case it is equal to \underline{D} (see also Ref. [68]). Thus there is no need to compute and store the additional matrices $\underline{\underline{B}}$ and \underline{D} . This means that there are no integrals required for the complex scattering matrix boundary conditions which are not also needed for calculations which employ real reactance matrix boundary conditions. However this is not the only advantage. If in calculating the integrals given by Eqs. (17-20), the restriction $\alpha < \alpha_0$ is made, then there is enough information to calculate $B_{\beta n_0}$ for $\alpha < \alpha_0$ and the matrix elements $\tilde{B}_{n\beta_0}$ and $\mathcal{D}_{n\beta_0}$ for $\alpha < \alpha_0$. Then by using Eq. (29), one can obtain $B_{\beta n_0}$ for $\alpha > \alpha_0$.

Thus it is not necessary to evaluate the integrals (17-20) for $\alpha > \alpha_0$. This is an important simplification because the calculation of these integrals of Eqs. (11-14) usually requires a substantial fraction of the whole time taken up by the integral calculation. Thus for systems having no symmetry, this amounts to almost a factor of 2 decrease in the work involved, since only 3 out of the 6 possible reactive arrangement pairs are required. For systems having identical atoms this factor is smaller; for systems of the type $A + B_2$, i.e., where B is the same kind of atom as C , it is necessary only to perform 2 of the possible 3 unique reactive arrangement pairs, while for $A + A_2$ collisions, no savings above those already achieved by using arrangement symmetry [67] are possible from this technique.

2.3 Localized Basis Functions.

In this section we show how the calculations simplify if $t_{mn}^\alpha(R_\alpha)$ is a localized function. Although it is convenient numerically to bypass the calculation of the irregular function in Eq. (16) and solve for the HIGFs directly, it is necessary to consider the expressions (15-16) for the HIGF in terms of the regular and irregular distorted waves and the basis functions in order to see the effect of localization.

In particular suppose that the basis function $t_{m\beta n\beta}^\alpha$ is zero for $R'_\alpha < R_\beta^S$ and $R'_\alpha > R_\beta^L$. Then the limits on the integral in Eq. (15) reduce from original 0 to ∞ to the computationally more attractive R_β^S to R_β^L . Thus if $R_\alpha < R_\beta^S$, then in the integral of Eq. (15) we will have $R_\alpha < R'_\alpha$ for all R'_α , and the HIGF will be equal to a linear combination of the columns of the regular function. Similarly if $R_\alpha > R_\beta^L$, the HIGF will be equal to a linear combination of the columns of the irregular function. Now because of numerical difficulties, we wish to avoid calculating the irregular function; however this is not difficult since we only need to know the form of this function at large distances. Since the large R_α boundary conditions of the irregular function are known [38], one could generate this information by inward integration, stopping before the solution becomes unreliable, or alternatively one could use any other function which has the same large R_α boundary conditions and solves the same differential equations for $R_\alpha > R_\beta^L$ for all β . Such an alternative function can be constructed from the HIGFs for one basis function, and that is what we do. We will order the basis functions so that $\beta = 1, \dots, N$ correspond to the basis functions which have the smallest values of R_β^L for each n_β . Note: N , the number of channels, is less than M , the number of basis functions. Thus we can write

$$\dot{g}_{n\beta_0}^N(R_\alpha) = \begin{cases} \sum_{n'} {}^{(r)}f_{nn'}^\alpha(R_\alpha) d_{n'\beta_0}^{\alpha S} \Delta_{n'n\beta_0}^\alpha & R_\alpha < R_{\beta_0}^S \\ \sum_{n'} \dot{g}_{nn'}^N(R_\alpha) d_{n'\beta_0}^{\alpha L} \Delta_{n'n\beta_0}^\alpha & R_\alpha > R_{\beta_0}^L \\ \dot{g}_{n\beta_0}^N(R_\alpha) & \text{otherwise,} \end{cases} \quad (31)$$

where $d_{n'\beta_0}^{\alpha S}$ and $d_{n'\beta_0}^{\alpha L}$ are proportionality constants, $\dot{g}_{nn'}^N$ is the HIGF having the smallest value for R_β^L , and $\dot{g}_{n\beta_0}^N$ is the numerically generated function. The proportionality constants for small R_α can be evaluated via

$$d_{n\beta}^{\alpha S} = \Delta_{n\beta n}^\alpha \int dR_\alpha {}^{(i)}f_{n\beta n}^\alpha(R_\alpha) t_{m\beta n\beta}^\alpha(R_\alpha) \quad (32)$$

if the irregular function is known, or more practically by forming the ratio of the numerically determined HIGF and the regular distorted wave. We form the average of the radial functions over several distances immediately prior to R_β^S and then form the ratio to obtain $d_{n\beta}^{\alpha S}$. One difficulty with this procedure arises when distortion potential blocks contain both open and closed channels. In this case, some of the columns of ${}^{(r)}f_\alpha$ are so small near the origin that it is not possible to obtain an accurate inverse; then the procedure fails. This problem can be avoided by decoupling the open and closed channels in the distortion potential.

The proportionality constant for large R_α can be determined by a numerical ratio in a similar manner to the procedure for $d_{n\beta}^{\alpha S}$ or by solving

$$d_{\beta n}^\alpha = \sum_{n'} d_{n'n}^\alpha d_{n\beta}^{\alpha L}, \quad (33)$$

where

$$d_{\beta n}^\alpha = \Delta_{n\beta n}^\alpha \int dR_\alpha {}^{(r)}f_{n\beta n}^\alpha(R_\alpha) t_{m\beta n\beta}^\alpha(R_\alpha), \quad (34)$$

and $d_{n'n}^\alpha$ corresponds to the integral for the basis function having the smallest value for R_β^L . The integrals in Eq. (34) are also required for the large- R_α boundary conditions for the HIGFs [38].

Equation (31) has several consequences. First of all, it is clear that once ${}^{(r)}f_{n\beta n}^\alpha$ and $\dot{g}_{nn'}^N$ are known, it is only necessary to calculate and store the remaining HIGFs in the ranges R_β^S to R_β^L . In practice since we determine the $\dot{g}_{n\beta_0}^N$ by solving an inhomogeneous form of the finite difference boundary value method [38,67] (FDBVM), we can reduce the finite difference grid used for the regular function and the first HIGF, which goes from $R_{\alpha,1}^F$ to $R_{\alpha,N(F)}^F$, to a grid which goes from $R_{\alpha,1}^F$ to just beyond the maximum value of R_β^L . Because $R_{\alpha,N(F)}^F$ is determined by the distance where the potential becomes negligible, whereas the maximum value of R_β^L is determined by the distance where the difference between the potential and the distortion potential becomes negligible, this can result in a considerable savings. The most important consequence of Eq. (31) however, arises from applying it to the integrals in Sect. 2.1.

There are two classes of integrals to consider. First of all there are the radial integrals with one HIGF and no basis functions, which we will approximate by a quadrature sum:

$$I_{\beta n}^{(1)} = \sum_{i=1}^{N^R Q} M_{\beta n}^g(i), \quad (35)$$

where

$$M_{\beta n}^g = w_i^\alpha \sum_{n'} \Delta_{n'n_\beta}^\alpha \dot{g}_{n'\beta}^N(R_{\alpha i}) M_{n'n}(R_{\alpha i}), \quad (36)$$

w_i^α being a quadrature weight and $M_{nn'}$ some matrix function. The integrals falling in this case are $\mathcal{G}_{\beta n_\alpha}$, $\mathcal{T}_{\beta n_\alpha}$, $\tilde{\mathcal{B}}_{n_\alpha\beta}$ (for which the transpose of Eq. (35) and following are used), the intra-arrangement parts of $B_{\beta n_\alpha}$, and the inter-arrangement parts of $C_{\beta\beta_\alpha}$. It is useful to define a quantity analogous to $M_{\beta n}^g$, called $M_{nn'}^f$, which differs by replacing the HIGF with the regular function. Then applying Eq. (31), the integral becomes

$$\begin{aligned} I_{\beta n}^{(1)} = & \sum_{n'} \Delta_{n'n_\beta}^\alpha d_{n'\beta}^{\alpha S} \left[\sum_{i=1}^{i_\beta^S} M_{n'n}^f(i) \right] + \sum_{i=i_\beta^S+1}^{i_\beta^L} M_{\beta n}^g(i) \\ & + \sum_{n'} \Delta_{n'n_\beta}^\alpha d_{n'\beta}^{\alpha L} \left[\sum_{i=i_\beta^L+1}^{N^{RQ}} M_{n'n}^g(i) \right], \end{aligned} \quad (37)$$

where $R_{\alpha i_\beta^S}$ is the largest quadrature point less than R_β^S and $R_{\alpha i_\beta^L}$ is the largest quadrature point less than R_β^L . (For the HIGF with the smallest R_β^L , we set i_β^L equal to N^{RQ} .) It should be noted that the quantities in the first sum must be calculated anyway—for the list of integrals mentioned after Eq. (36), these correspond to \mathcal{F}_{nn_α} , $\tilde{\mathcal{T}}_{nn_\alpha}$, $\mathcal{K}_{n_\alpha n}^B$, $\mathcal{K}_{nn_\alpha}^B$, and $B_{\beta n_\alpha}$, respectively. Thus we see that the radial quadrature points fall into three regions: those less than all i_β^S where only quantities involving the regular function need be accumulated, those greater than all R_β^L where only quantities involving the regular function and the HIGFs with the smallest value of i_β^L need to be accumulated, and points in the intermediate region where the sums will include some number of HIGFs less than the full set.

Now consider the case when there are two HIGFs. Here the integral can be written

$$I_{\beta\beta_\alpha}^{(2)} = \sum_{i=1}^{N^{RQ}} M_{\beta\beta_\alpha}^{gg}(i), \quad (38)$$

where

$$M_{\beta\beta_\alpha}^{gg} = w_i^\alpha \sum_{n'n''} \Delta_{n'n_\beta}^\alpha \Delta_{n''n_\beta_\alpha}^\alpha \dot{g}_{n'\beta}^N(R_{\alpha i}) M_{n'n''}(R_{\alpha i}) \dot{g}_{n''\beta_\alpha}^N(R_{\alpha i}). \quad (39)$$

The integrals falling in this case are the intra-arrangement parts of C. The presence of two HIGFs greatly complicates this case compared to Eq. (37). There are now six cases to consider: nonoverlapping basis functions, one basis function contained within the other, and other overlapping basis functions, with the bra or ket starting

first. However it can be shown that the result of using Eq. (31) is

$$\begin{aligned}
 I_{\beta\beta_0}^{(2)} = & \left\{ \sum_{n'} \Delta_{n'n\beta_0}^\alpha I_{\beta n'}^{(1)}(i_{\beta_0}^S) d_{n'\beta}^{\alpha S} \quad i_{\beta_0}^S > i_\beta^S \right. \\
 & \left. + \sum_{i=\max(i_\beta^S, i_{\beta_0}^S)}^{\min(i_\beta^S, i_{\beta_0}^S)} M_{\beta\beta_0}^{gg}(i) \right. \\
 & \left. + \left\{ \sum_{n'} \Delta_{n'n\beta_0}^\alpha [I_{\beta n'}^{(2)}(N^{RQ}) - I_{\beta n'}^{(2)}(\max(i_{\beta_0}^L, i_\beta^S, i_{\beta_0}^S))] d_{n'\beta}^{\alpha L} \quad i_\beta^L > i_{\beta_0}^L \right. \right. \\
 & \left. \left. + \left\{ \sum_{n'} \Delta_{n'n\beta}^\alpha d_{n'\beta}^{\alpha L} [I_{n'\beta}^{(2)}(N^{RQ}) - I_{n'\beta}^{(2)}(\max(i_\beta^L, i_\beta^S, i_{\beta_0}^S))] \quad i_\beta^L > i_{\beta_0}^L \right\} \right. \right.
 \end{aligned} \tag{40}$$

In this equation, $I_{\beta n}^{(1)}$ corresponds to B , and an argument of i is interpreted as the sum up to the i^{th} quadrature point. It should be noted that for nonoverlapping basis functions, the middle sum will have no contribution. In addition, this formula applies as well to matrix elements consisting of one HIGF and one translational basis function. In this case, $d_{n\beta}^{\alpha S}$ and $d_{n\beta}^{\alpha L}$ for the translational basis function are zero and $I_{\beta n}^{(1)}$ corresponds to \bar{D} . Since the number of terms in the middle sum is much less than the number of radial quadrature points, N^{RQ} , using Eq. (40) greatly reduces the work required for evaluating the integrals. It should be noted that care needs be taken to avoid excessive roundoff error when evaluating the last subtraction in Eq. (40). Optimally one would separately store the contributions from the various intervals between $\min(i_\beta^S, i_{\beta_0}^S)$ and $\max(i_{\beta_0}^L, i_\beta^S, i_{\beta_0}^S)$ or $\max(i_\beta^L, i_\beta^S, i_{\beta_0}^S)$, since in this way no explicit subtraction is required.

Another way to exploit Eq. (31) is to take linear combinations of the HIGFs and use these as basis functions. Consider the HIGF labeled by β . We can form the combination

$$\dot{g}_{n\beta}^{\mathcal{L}}(R_\alpha) = \dot{g}_{n\beta}^N(R_\alpha) - \sum_{n'} \dot{g}_{nn'}^N(R_\alpha) d_{n'\beta}^{\alpha L} \Delta_{n'n\beta}^\alpha, \tag{41}$$

in which case the analog of Eq. (31) for $\dot{g}_{n\beta}^{\mathcal{L}}$ becomes

$$\dot{g}_{n\beta}^{\mathcal{L}}(R_\alpha) = \begin{cases} \sum_{n'} {}^{(r)}f_{nn'}^\alpha(R_\alpha) d_{n'\beta}^{\alpha S\mathcal{L}} \Delta_{n'n\beta}^\alpha & R_\alpha < R^S \\ 0 & R_\alpha > R_\beta^L \\ \dot{g}_{n\beta}^{\mathcal{L}}(R_\alpha) & \text{otherwise,} \end{cases} \tag{42}$$

where R^S is the smallest value of $R_{n'}^S$, and $d_{n'\beta}^{\alpha S\mathcal{L}}$ is the new small R_α proportionality constant. There are two advantages of this formulation. First of all, when using the $\dot{g}_{n\beta}^{\mathcal{L}}$, Eqs. (37) and (40) simplify, because now only the first two terms are present. This is especially important for Eq. (40), because one now avoids the final subtraction, which is complicated to implement in a manner which avoids roundoff error. The second advantage arises when transforming to complex boundary conditions. This will be discussed in the next section.

One disadvantage of using the $\dot{g}_{n\beta}^{\mathcal{L}}$ is that while previously the first sum in Eqs. (37) and (40) went from 1 to i_β^S or $\min(i_\beta^S, i_{\beta_0}^S)$, it now goes from 1 to i^S , where

$R_{\alpha i^S}$ is the largest quadrature point less than R^S . Since i^S will be smaller than i_{β}^S or $\min(i_{\beta}^S, i_{\beta_0}^S)$, the overall efficiency is not as great. However, one can diminish this effect by not using in Eq. (41) the $\dot{g}_{n\beta}^N$, which are the HIGFs based on the basis functions with the smallest values for R_{β}^L , but rather using HIGFs which are based on basis functions having as large R_{β}^S as possible subject to the constraint that their R_{β}^L is not larger than the R_{β}^L for the β in Eq. (41). This will maximize i^S .

We now consider the effect on the matrix elements when the $\dot{g}_{n\beta}^{\mathcal{L}}$ are substituted for the $\dot{g}_{n\beta}^N$ in Eqs. (10-14) and (17-20). Since Eq. (41) can be written as

$$\dot{\mathbf{g}}^{\mathcal{L}} = \dot{\mathbf{g}}^N \mathbf{L}, \quad (43)$$

where the matrix elements of \mathbf{L} are the constant factors in Eq. (41), we see that provided we combine the $t_{n_{\beta} n_{\beta}}^{\alpha}$ in Eq. (14) using the same rule as was used to produce the $\dot{g}_{n\beta}^{\mathcal{L}}$, then we obtain

$$\mathbf{B}^{\mathcal{L}} = \mathbf{L}^T \mathbf{B} \quad (44)$$

and

$$\mathbf{C}^{\mathcal{L}} = \mathbf{L}^T \mathbf{C} \mathbf{L} \quad (45)$$

when using the $\dot{g}_{n\beta}^{\mathcal{L}}$. Provided that \mathbf{L}^{-1} exists, it is easy to see that

$$\mathbf{B}^{\mathcal{L}^T} \mathbf{C}^{\mathcal{L}^{-1}} \mathbf{B}^{\mathcal{L}} = \mathbf{B}^T \mathbf{C}^{-1} \mathbf{B}, \quad (46)$$

thus it is not necessary to transform back to the $\dot{g}_{n\beta}^N$. In order to ensure that \mathbf{L}^{-1} exists, it is necessary to retain at least one $\dot{g}_{n\beta}^N$ per channel.

Now consider the transformation from real to complex boundary conditions, Eqs. (7), (8), and (30). Since the $\dot{g}_{n\beta}^{\mathcal{L}}$ are strictly zero beyond the distance where the associated localized basis functions are zero, they will be independent of the boundary conditions. That is, the subblock of \mathbf{X} associated with $\dot{g}_{n\beta}^{\mathcal{L}}$ will be the unit matrix, the subblock of $\tilde{\mathbf{D}}$ will be the zero matrix, and the portions of $\tilde{\mathbf{C}}^{\mathcal{L}}$ which are associated with two of the $\dot{g}_{n\beta}^{\mathcal{L}}$ will be real and the same as $\mathbf{C}^{\mathcal{L}}$. In the next section, we will show how this can be exploited to save work in evaluating Eq. (6).

Thus we see that substantial work can be saved in evaluating the integrals when localized basis functions are used. We now consider the choice of such functions. In our previous work using variational methods, we have used distributed Gaussian functions [37-39,53,63-65,67,68,84-98], linear combinations of distributed Gaussians[99], or sine-type functions [38] as a basis. Strictly speaking, the Gaussian functions are not local, since they are zero only asymptotically; however for practical purposes they differ significantly from zero only in a narrow region. Thus one procedure to use would be to set the Gaussian to zero whenever it falls below some fraction of its maximum, say 10^{-14} . However this procedure introduces discontinuities into the integrands which can cause slow convergence of the numerical

integrals. Thus we seek a localized function which is continuous and has continuous derivatives. The function we will use is inspired by the cutoff function of Ref. [100], and is given by

$$t = \begin{cases} \exp[-\frac{a}{1-(x/b)^2}] & |x| < b \\ 0 & |x| \geq b \end{cases} \quad (47)$$

We call this function a "cut off Gaussian" (COG). It has the property that for small x/b , it behaves like $\exp[-a(x/b)^2]$, so can be made similar to our previous basis functions, yet it is localized within b of its center. It should be noted that as $a \rightarrow \infty$ with fixed a/b^2 , the COG becomes a Gaussian.

2.4 Partitioned Matrices.

We will partition the matrices into blocks consisting either of functions which are localized (the $g_{n\beta}^{\mathcal{L}}$) or those which are delocalized. Thus we write

$$\mathbf{B}^{\mathcal{L}} = \begin{pmatrix} \mathbf{B}_c \\ \mathbf{B}_{\mathcal{L}} \end{pmatrix}, \quad (48)$$

and

$$\mathbf{C}^{\mathcal{L}} = \begin{pmatrix} \mathbf{C}_{cc} & \mathbf{C}_{\mathcal{L}c}^T \\ \mathbf{C}_{\mathcal{L}c} & \mathbf{C}_{\mathcal{L}\mathcal{L}} \end{pmatrix}, \quad (49)$$

where the subscript \mathcal{L} means localized and c delocalized. If we solve the matrix equation

$$\underline{\underline{\mathbf{K}}} = \underline{\underline{\mathbf{K}}}^B + \mathbf{B}^{\mathcal{L}T} \mathbf{C}^{\mathcal{L}-1} \mathbf{B}^{\mathcal{L}}, \quad (50)$$

by blocks, we obtain

$$\underline{\underline{\mathbf{K}}} = \underline{\underline{\mathbf{K}}}^{Bf} + \mathbf{B}^{fT} \mathbf{C}^{f-1} \mathbf{B}^f, \quad (51)$$

where the folded matrices are given by

$$\underline{\underline{\mathbf{K}}}^{Bf} = \underline{\underline{\mathbf{K}}}^B - \mathbf{B}_{\mathcal{L}}^T \mathbf{C}_{\mathcal{L}\mathcal{L}}^{-1} \mathbf{B}_{\mathcal{L}}, \quad (52)$$

$$\mathbf{B}^f = \mathbf{B}_c - \mathbf{C}_{\mathcal{L}c}^T \mathbf{C}_{\mathcal{L}\mathcal{L}}^{-1} \mathbf{B}_{\mathcal{L}}, \quad (53)$$

and

$$\mathbf{C}^f = \mathbf{C}_{cc} - \mathbf{C}_{\mathcal{L}c}^T \mathbf{C}_{\mathcal{L}\mathcal{L}}^{-1} \mathbf{C}_{\mathcal{L}c}. \quad (54)$$

Now consider solving Eq. (6) by the same procedure. The result is

$$\underline{\underline{\mathbf{S}}} = \underline{\underline{\mathbf{S}}}^{Bf} + \bar{\mathbf{B}}^{fT} \bar{\mathbf{C}}^{f-1} \bar{\mathbf{B}}^f, \quad (55)$$

where the complex folded matrices are obtained from Eqs. (7), (8), and (30) using the real folded matrices of Eqs. (52-54). Similar procedures have been employed in the context of the Kohn variational principle [54,56,60].

Several things should be noted concerning the above procedure as it affects the GNVP calculations. First of all, if the number of localized functions is considerably larger than the number of delocalized functions, as may often be the case, the work to produce the folded matrices will be greater than the work to evaluate Eq. (55).

This means that the computational effort involved in a calculation with complex boundary conditions will be very similar to what would have been required if real boundary conditions had been used. Also the memory requirements will be similar, because it will not be necessary to store the imaginary part of \bar{C} .

3 Applications and Directions for Future Work.

The techniques presented here and previously provide an efficient method for large-scale quantum mechanical calculations of chemical reaction dynamics based on the generalized Newton variational principle. Some applications that have been made include the calculation of converged cross sections for the $H + H_2$ [89] and $D + H_2$ [39,97] reactions and converged state-selected reactive transition probabilities for these reactions [37,38,67,68,87,88,91,92,95] and for the $O + H_2$ [68,98] and $O + HD$ [68,93] reactions. We have also presented converged reactive transition probabilities for the $F + H_2$ reaction with total angular momentum $J = 0-2$ [90,94,96,99]. We have calculated converged collisional delay times, which require very stable (numerically differentiable) solutions as a function of energy, for $H + H_2$ with $J = 0, 1$, and 4 [95], for $D + H_2$ with $J = 0$ [91], and for $F + H_2$ with $J = 0$ and 1 [94,96]. An earlier nonvariational version of the method was used to obtain converged transition probabilities for the $H + H_2$ [64], $D + H_2$ [63,64], $O + H_2$ [65,84], $H + OH$ [65], and $H + HBr$ [85] reactions.

For $O + H_2$ we have obtained very well converged results with an average of as few as three Gaussians per channel [98]. A recent study of basis set requirements for $F + H_2$ showed that excellent convergence can be achieved with 10 Gaussians per channel in the $F + H_2$ arrangement and 18 Gaussians per channel in the $H + HF$ arrangement [99]. Further efficiencies can be achieved by using better basis sets, *e.g.*, by basis set contraction [38,99,101,102] or the use of localized basis sets as described in the present paper. Another promising approach is based on the reinterpretation of the GNVP using a scattered wave variational principle [69-72]. This allows for hybrid basis sets which effectively convert some of the integrals over $G_{\alpha}^D U^{\alpha} G_{\alpha}^D$, as in $C_{\beta\beta\alpha}$, into simpler energy-independent integrals. All these approaches are being explored for further applications.

4 Summary.

We have introduced new techniques to reduce the work required in applying the generalized Newton variational principle to three-dimensional reactive scattering calculations. The underlying idea behind these developments is to minimize redundant work as much as possible. This is accomplished in two ways. First of all the fact that the Hamiltonian is Hermitian is used to decrease the number of inter-arrangement integrals which must be calculated. Even for a system with no symmetry, *e.g.*, $O + HD$, this reduces by half the number of two dimensional integrals which are performed before the final integration of the three-dimensional exchange integrals. Secondly we introduce a localized translational basis set which need not differ significantly from our previous basis functions and then exploit the effect this has on the half-integrated Green's functions to reduce the amount of work required to calculate these functions, the amount of storage required to save these functions, the amount of work required for the integrals over these functions, and the work required for the final linear-equations step when complex boundary conditions are used.

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