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COMPUTATIONAL STRATEGIES AND IMPROVEMENTS IN THE LINEAR ALGEBRAIC VARIATIONAL APPROACH TO REARRANGEMENT SCATTERING

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ABSTRACT. We discuss the computational steps in calculating quantum mechanical reactive scattering amplitudes by the \mathcal{L}^2 generalized Newton variational principle with emphasis on computational strategies and recent improvements that make the calculations more efficient. We place special emphasis on quadrature techniques, storage management strategies, use of symmetry, and boundary conditions. We conclude that an efficient implementation of these procedures provides a powerful algorithm for the accurate solution of the Schroedinger equation for rearrangements.

1. Introduction

Rearrangement scattering is certainly one of the most difficult problems in few-body physics. The quantum mechanical theory of chemical reactions, as a subfield of the larger topic of rearrangement scattering, is similarly one of the most difficult subtopics in molecular collision theory. Successful and useful procedures for rearrangement scattering problems have been advanced from many different directions, including (references are perforce representative rather than exhaustive) the theory of compound nuclei and resonances,¹ formal many-body physics,² and multichannel inelastic scattering theory,³⁻⁵ and the theory will certainly continue to benefit from further progress in those fields in which it has its roots.

The approach discussed here has its origins in both many-body theory and multichannel scattering theory. From many-body theory it builds on the method called "configuration interaction" or "superposition of configurations" (SOC), especially as that method is viewed as a systematic way to enlarge multiconfiguration Hartree-Fock basis sets until convergence is reached. This approach has its roots in bound-state electronic structure theory,⁶ and applications to dynamics may be found in electron-atom scattering,^{3,7-9} electron-molecule scattering,¹⁰ and nuclear physics¹¹ (where it is sometimes called the "resonating group method"). In the work discussed here the SOC approach is used to expand the reactive amplitude density,¹²⁻¹⁵ rather than the scattering wave function,^{3,4,7-10,16-18} and the coefficients in the expansion are obtained variationally by a generalization^{19,20} of a variational principle due to Newton.²¹ Since the reactive amplitude density is vector of \mathcal{L}^2 (i.e., square integrable) functions in arrangement channel space, the configurations in our SOC may also be taken as \mathcal{L}^2 , and this simplification of the basis set is one of the desirable features of this approach which motivates our work.

Another important element in our work is the use of a distortion potential which defines a partially decoupled scattering problem whose solutions are obtained as the first step of the dynamics calculation. Distortion potentials appear as the first step of many inelastic and rearrangement scattering calculations,²²⁻²⁴ often in conjunction with a variational principle, a combination which is motivated by the expectation that as one increases the coupling in the distortion potential, the level of theory required to treat the remaining channel coupling accurately will be lower. We have recently²⁰ shown this to be true in our formalism, in particular as we increased the coupling in the distortion potential, the size of the basis set required to solve the full problem decreased. Our approach allows for *multichannel* single-arrangement distortion potentials, as applied previously²⁵⁻³⁰ to rearrangement problems in various contexts. We have shown, however, that the combination of this approach with the \mathcal{L}^2 generalized Newton variational principle (GNVP) is a particularly powerful method for treating chemical reactions,^{19,20,31,32} and it has allowed us to converge very large-scale problems, involving (so far) up to³³ 1035 coupled channels.

Our previous work relevant to this approach has been published in several papers. Our original calculations were based on an \mathcal{L}^2 SOC expansion of the reactive amplitude density with the coefficients obtained by the method of moments. We have published several applications,^{13-15,34-36} full details of the numerical procedures,¹⁴ a discussion of storage management,³⁷ and three derivations^{14,15,38} of the final equations. In more recent work we have obtained the coefficients of the expansion by the GNVP. We have carried out new applications,^{19,20,31-33,39} and we have presented full details of the method and its initial implementation.²⁰ The present paper presents a discussion of improved computational and storage management strategies for GNVP calculations, including recent improvements in the quadratures. We also give an overview of

the method, including a reformulation in terms of the scattering matrix and a discussion of symmetry decoupling, which subjects are also treated elsewhere.^{40,41}

2. Generalized Newton Variational Formalism

2.1. BASIC EQUATIONS

The theoretical developments leading up to the equations presented below are given in detail elsewhere,²⁰ thus only an overview of the formalism will be given, and the emphasis will be on selected details and improvements. Reference 20 plus the current paper should be considered as a pair; together they express the current state of our program.

Our methods are designed to be as efficient as possible for calculations at a single total energy on vector pipeline supercomputers. Thus quantities which are used only once or a few times for a single energy calculation are usually not saved but rather calculated when they are required, even if they are independent of energy. This strategy influences the choice of several computational details and will be discussed in more detail in Sect. 4.

We consider reactive scattering between different arrangements of the atoms A, B, and C. The label α specifies the asymptotic partitioning of the atoms: $\alpha = 1$ for A + BC, $\alpha = 2$ for B + CA, and $\alpha = 3$ for C + AB. We mass scale the Jacobi coordinates for each of the three arrangements to the single reduced mass μ defined by

$$\mu = [m_A m_B m_C / (m_A + m_B + m_C)]^{1/2} \quad (1)$$

where m_A is the mass of atom A, etc. For arrangement $\alpha = 1$, \hat{R}_α is the mass-scaled vector from the center of mass of BC to atom A, \hat{r}_α is the mass-scaled vector from atom B to atom C, and $\cos \gamma_\alpha = \hat{r}_\alpha \cdot \hat{R}_\alpha$. The coordinates of the other arrangements are defined by cyclic permutation of the three atoms. It will be also convenient to let x_α denote the collection of all coordinates except the scalar length R_α .

The Hamiltonian operator is partitioned into arrangement-dependent components as

$$H = H_\alpha^D + V_\alpha^C, \quad (2)$$

where H_α^D is the Hamiltonian for non-reactive scattering in arrangement channel α with the distortion potential V_α^D , and V_α^C is the coupling potential responsible for connecting the various distortion potential blocks and various arrangements. We

denote the Green's function corresponding to the potential H_α^D as G_α^D .

The index n is used to specify a particular α , v , j , ℓ channel where v , j , and ℓ are vibrational, rotational, and orbital quantum numbers; the index m is used to specify a particular transitional basis function, and β denotes a particular pair of n and m . Note that sometimes for clarity we will label quantities by both α and n although the specification of α is redundant. In addition we use $|\alpha_n n\rangle$ to denote a product of an Arthurs–Dalgarno rotational–orbital function (depending on j , ℓ , and J) and a vibrational function (depending on v and j) in channel n . We use α_n to denote the value of α for channel n . Then we may write

$$H_\alpha^D = T + V_\alpha^{\text{diat}} + \sum_n \sum_{n'} \delta_{\alpha_n \alpha_{n'}} \Delta_{nn'}^\alpha |\alpha_n, n'\rangle V^{\text{int}, \alpha} \langle \alpha_n n| \quad (2a)$$

where T is the total kinetic energy, V_α^{diat} is the diatomic potential in channel α ,

$$V^{\text{int}, \alpha} = V - V_\alpha^{\text{diat}}, \quad (2b)$$

V is the total potential, and $\Delta_{nn'}^\alpha$ is unity if channel n and channel n' belong to the same distortion potential block and zero otherwise.

The GNVP may be applied to calculate the reactance matrix K , the scattering matrix S , or the transition matrix, T , from any of which one may calculate all physical observables for the collision processes by standard^{42,43} formulas. In this section, as well as Sects. 3 and 4, we consider the application to the reactance matrix; in Sect. 5 we will consider the direct calculation of the scattering matrix. In all sections, we use a generalized reactance matrix with the form

$$K = \begin{bmatrix} K^{oo} & K^{oc} \\ K^{co} & K^{cc} \end{bmatrix} \quad (3)$$

where o stands for open and c for closed. Although the physical results depend only on K^{oo} , we retain the other parts in the calculation because it simplifies the code and adds negligibly to the computer time. (In addition we will use the closed channel parts to simplify the arithmetic in Sect. 5). In practice the channels are not actually stored in the order necessary to partition K as indicated in (3), but they are re-ordered this way prior to calculating eq. (53) below.

Using n to label the channels and β to label the basis functions, coupling the various arrangement components of the total system wave function by the Fock coupling scheme,^{4,5,7,16,44} expanding the Fock reactive amplitude density^{14,15} for each arrangement in an \mathcal{L}^2 basis set expressed in the coordinates of that arrangement, and solving for the coefficients by the GNVP, yields the following expression for the elements of the generalized full reactance matrix:²⁰

$$K_{nn_0} = \delta_{\alpha\alpha_0} {}^0K_{nn_0} + \mathcal{K}_{nn_0}, \quad (3a)$$

where 0K is the collection of all nonzero reactance matrix elements for the decoupled distortion blocks, and

$$\begin{aligned} \mathcal{K}_{nn_0} &\equiv \langle \alpha_n nE | \mathcal{K} | \alpha_0 n_0 E \rangle = \langle \alpha_n nE | \mathcal{U} | \alpha_0 n_0 E \rangle + \\ &+ \sum_{\beta} \sum_{\beta'} \langle \alpha_n nE | \mathcal{U} \mathcal{G} | \beta \rangle \langle \beta | \mathcal{G} - \\ &- \mathcal{G} \mathcal{U} \mathcal{G} \rangle^{-1} | \beta' \rangle \langle \beta' | \mathcal{G} \mathcal{U} | \alpha_0 n_0 E \rangle \end{aligned} \quad (4)$$

where $\alpha_0 (\equiv \alpha_{n_0})$ is the initial arrangement, $|\alpha_n nE\rangle$ is a regular standing-wave distorted-wave scattering state for the Hamiltonian $H_{\alpha_n}^D$,

$$\mathcal{U} = (-2\mu/\hbar^2)(H-E), \quad (5)$$

$$\mathcal{G} = \sum_{\alpha} G_{\alpha}^D \hat{P}_{\alpha}, \quad (5a)$$

$$\mathcal{G} \mathcal{U} \mathcal{G} = (-2\mu/\hbar^2) \sum_{\alpha'} \sum_{\alpha} \hat{P}_{\alpha'} G_{\alpha'}^D (H-H_{\alpha}^D) G_{\alpha}^D \hat{P}_{\alpha}, \quad (5b)$$

\hat{P}_{α} is a projector on arrangement α , and the basis set is taken to have the form

$$\begin{aligned} |\beta\rangle &= |\alpha_{\beta} n_{\beta} m_{\beta}\rangle \\ &= R_{\alpha\beta}^{-1} \phi_{n_{\beta}}^{\alpha\beta}(\mathbf{x}_{\alpha\beta}) t_{m_{\beta} n_{\beta}}(R_{\alpha\beta}). \end{aligned} \quad (6)$$

In Eq. (6), $t_{m_{\beta} n_{\beta}}$ is a translational basis function, and $\phi_{n_{\beta}}^{\alpha\beta}$ is a vibrational-rotational-orbital function given by

$$\phi_{n_{\beta}}^{\alpha}(\mathbf{x}_{\alpha}) = \chi_{\alpha v_{n_{\beta}} j_{n_{\beta}}}(\mathbf{r}_{\alpha}) \mathcal{Y}_{j_{n_{\beta}} \ell_{n_{\beta}}}^{JM}(\hat{\mathbf{r}}_{\alpha}, \hat{\mathbf{R}}_{\alpha}) \quad (6a)$$

where $\chi_{\alpha v_{n_{\beta}} j_{n_{\beta}}}$ is an asymptotic vibrational eigenfunction, $v_{n_{\beta}}$ is a vibrational quantum number, $j_{n_{\beta}}$ is a rotational quantum number, $\ell_{n_{\beta}}$ is an orbital angular momentum quantum number for relative translational motion, and $\mathcal{Y}_{j_{n_{\beta}} \ell_{n_{\beta}}}^{JM}$ is a laboratory-frame angular function⁷ coupled to total angular momentum quantum numbers J and M . All equations are decoupled in J and in parity P , given by

$$P = (-1)^{j+\ell}, \quad (6b)$$

so we treat each JP block independently and set $M = 0$. In the rest of this article it will be understood that all equations refer to a single JP block.

In what follows we write Eq. (4) as

$$\mathcal{K} = \mathcal{K}^B + \mathbf{B}^T \mathbf{C}^{-1} \mathbf{B} \quad (7)$$

where T denotes a matrix transpose, and \mathcal{K}^B is the distorted-wave Born approximation²²⁻³⁰ to the reactance matrix. In practice, Eq. (7) is replaced by

$$\mathcal{K} = \mathcal{K}^B + \mathbf{B}^T \mathbf{B} \quad (7a)$$

where

$$\mathbf{C} \mathbf{B} = \mathbf{B}. \quad (7b)$$

We note that \mathbf{C} is symmetric, which guarantees the symmetry of \mathcal{K} . The matrix elements diagonal in the arrangement label ($\alpha_n = \alpha_0 = \alpha$) are given by

$$\begin{aligned} \mathcal{K}_{nn_0}^B = & \sum_{n'} \Delta_{nn'}^\alpha \int dR_\alpha \overset{(r)}{f}_{n',n}^\alpha(R_\alpha) \sum_{n''} V_{n',n''}^\alpha(R_\alpha) \Delta_{n''n_0}^\alpha \times \\ & \times \overset{(r)}{f}_{n''n_0}^\alpha(R_\alpha), \end{aligned} \quad (8)$$

$$\begin{aligned} \mathbf{B}_{\beta n_0} = & \sum_{n'} \Delta_{n\beta n'}^{\alpha_0} \int dR_\alpha \overset{N}{g}_{n',\beta}^N(R_\alpha) \sum_{n''} V_{n',n''}^\alpha(R_\alpha) \Delta_{n''n_0}^\alpha \times \\ & \times \overset{(r)}{f}_{n''n_0}^\alpha(R_\alpha), \end{aligned} \quad (9)$$

and

$$\begin{aligned} \mathbf{C}_{\beta\beta'} = & \Delta_{n\beta n\beta'}^\alpha \int dR_\alpha \overset{N}{g}_{n\beta',\beta}^N(R_\alpha) t_{m\beta',n\beta'}^\alpha(R_\alpha) - \\ & - \sum_{n'} \Delta_{nn'}^\alpha \int dR_\alpha \overset{N}{g}_{n',\beta}^N(R_\alpha) \sum_{n''} \times \\ & \times U_{n',n''}^\alpha(R_\alpha) \Delta_{n''n\beta'}^\alpha \overset{N}{g}_{n''\beta'}^N(R_\alpha), \end{aligned} \quad (10)$$

while those off-diagonal in arrangement are given by

$$\begin{aligned} \mathcal{H}_{nn_0}^B = & \sum_{n'} \Delta_{nn'}^{\alpha_n} \int dR_{\alpha_n} \int dR_{\alpha_0} {}^{(r)}f_{n'n}^{\alpha_n}(R_{\alpha_n}) \times \\ & \times \sum_{n''} W_{n'n''}^{\alpha_n \alpha_0}(R_{\alpha_n}, R_{\alpha_0}) \Delta_{n''n_0}^{\alpha_0} {}^{(r)}f_{n''n_0}^{\alpha_0}(R_{\alpha_0}), \end{aligned} \quad (11)$$

$$\begin{aligned} B_{\beta n_0} = & \sum_{n'} \Delta_{n\beta n'}^{\alpha_\beta} \int dR_{\alpha_\beta} \int dR_{\alpha_0} g_{n'\beta}^N(R_{\alpha_\beta}) \sum_{n''} W_{n'n''}^{\alpha_\beta \alpha_0}(R_{\alpha_\beta}, R_{\alpha_0}) \times \\ & \times V \Delta_{n''n_0}^{\alpha_0} {}^{(r)}f_{n''n_0}^{\alpha_0}(R_{\alpha_0}), \end{aligned} \quad (12)$$

and

$$\begin{aligned} C_{\beta\beta'} = & \sum_{n'} \Delta_{n'n\beta}^{\alpha_\beta} \int dR_{\alpha_\beta} \int dR_{\alpha_{\beta'}} g_{n'\beta}^N(R_{\alpha_\beta}) \mathcal{E}_{n'n\beta'}^{\alpha_\beta \alpha_{\beta'}}(R_{\alpha_\beta}, R_{\alpha_{\beta'}}) \times \\ & \times t_{m\beta'n\beta'}^{\alpha_{\beta'}}(R_{\alpha_{\beta'}}) - \sum_{n'} \Delta_{n\beta n'}^{\alpha_\beta} \int dR_{\alpha_\beta} \int dR_{\alpha_{\beta'}} g_{n'\beta}^N(R_{\alpha_\beta}) \times \\ & \times \sum_{n''} W_{n'n''}^{\alpha_\beta \alpha_{\beta'}}(R_{\alpha_\beta}, R_{\alpha_{\beta'}}) \Delta_{n''n\beta'}^{\alpha_{\beta'}} g_{n''\beta'}^N(R_{\alpha_{\beta'}}), \end{aligned} \quad (13)$$

where ${}^{(r)}f_{nn'}^{\alpha}$ is a radial distorted wave function, $V_{nn'}^{\alpha}$ is an intra-arrangement matrix element of the coupling potential given by

$$V_{nn'}^{\alpha} = U_{nn'}^{\alpha} - U_{nn'}^{D\alpha}, \quad (14)$$

where

$$U_{nn'}^{D\alpha} = \Delta_{nn'}^{\alpha} U_{nn'}^{\alpha}, \quad (14a)$$

$$U_{nn'}^{\alpha} = (-2\mu/\hbar^2) \int dx_{\alpha} \phi_n^{\alpha*}(x_{\alpha}) V^{\text{int},\alpha}(R_{\alpha}, x_{\alpha}) \phi_{n'}^{\alpha}(x_{\alpha}), \quad (15)$$

and $V^{\text{int},\alpha}$ is the interaction potential for arrangement α . The function $g_{n\beta}^N$ is a half-integrated Green's function; $W_{nn_0}^{\alpha\alpha_0}$ is given by

$$W_{nn_0}^{\alpha\alpha_0} = \mathcal{E}_{nn_0}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) - \sum_{n_0'} \mathcal{E}_{nn_0'}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) U_{n_0'n_0}^{D\alpha_0}(R_{\alpha_0}), \quad (16)$$

where $\mathcal{E}_{nn_0}^{\alpha\alpha_0}$ is $-2\mu/\hbar^2$ times the inter-arrangement matrix element of the

interaction potential; and $\mathcal{K}_{nn_0}^{\alpha\alpha_0}$ is an inter-arrangement overlap matrix element.

Further details of all these quantities are given in Ref. 20.

2.2. COMPUTATIONAL STEPS

The organization of the computational steps is as follows. First the parameters which specify the calculation are initialized. These include masses, the total energy, basis set parameters, and various other numerical parameters. Next, commonly used quantities are pre-calculated and stored. These include vibrational wavefunctions and weights and nodes for the various quadratures used. After that, the radial distorted wave functions and the radial half-integrated Green's functions are calculated and the values of these functions at the radial quadrature points are stored, either in memory or on disk, depending on options. Then the integrations to obtain the $\mathcal{K}_{nn'}^B$, $B_{\beta n}$, and $C_{\beta\beta'}$ matrix elements are carried out. Next, the correction \mathcal{K} to the reactance matrix is evaluated by means of Eqs. (7a) and (7b). Using this matrix, the full reactance matrix is calculated from Eq. (3), followed by the evaluation of the scattering matrix and related quantities useful in the interpretation of the outcome of the collisions.

All of these computational steps involve special considerations in order that they and subsequent steps are performed as efficiently as possible. Thus we now discuss the steps in more detail.

2.2.1. Asymptotic channel states. We first consider the calculation of the vibrational functions and their associated eigenenergies. The vibrational functions $\chi_{\alpha v j}$ are expanded in terms of harmonic oscillator wave functions with coefficients

$B_{\gamma}^{\alpha v j}$. The matrix elements of the diatomic Hamiltonian are evaluated by

Gauss-Hermite quadrature, and the Rayleigh-Ritz variational principle is used to determine the expansion coefficients and eigenenergies. The harmonic basis for the vibrational eigenstates is chosen for computational convenience of later steps, namely the calculation of the inter-arrangement integrals. There the vibrational functions will have to be evaluated at many different bond lengths, and it is advantageous to avoid the necessity of interpolating a numerical wave function. As it is, the vibrational functions are evaluated by first recursively calculating the harmonic oscillator basis functions at many bond lengths simultaneously using vector operations and then transforming to the $\chi_{\alpha v j}$ by a call to the very efficient Cray matrix multiply library routine MXM or a new fast matrix multiplication routine⁴⁵ utilizing local memory and Strassen's⁴⁶ algorithm. In addition to these considerations, another reason for using analytic basis functions is that they provide a more compact representation than a numerical wave function, i.e., less storage space is required to save the expansion coefficients than would be required if one were to save the wave function on a grid.

One difficulty with using harmonic oscillator wave functions is that they behave in a non-physical manner as the bond length goes to zero. These functions go to zero in the limit as the bond length goes to minus infinity, rather than as the bond length goes to zero. However this is not a problem in practice because molecular potentials are very repulsive for small bond lengths, and so the

variational principle causes the wave function to be small in that region. It is sometimes necessary to modify the vibrational potentials near the origin or at negative r_α so that the integrals involved in the Rayleigh-Ritz variational principle are all finite; however the final results are not sensitive to the exact nature of this modification provided that the potential for small and non-physical values of the bond length are sufficiently repulsive. These considerations apply as well to the centrifugal potential $j(j+1)\hbar^2/2\mu r_\alpha^2$, which is singular at the origin.

We make this nonsingular by replacing r_α^2 with $r_\alpha^2 + r_0^2$, where r_0 is a small distance we have taken to be $1.0 \times 10^{-3} \alpha_0$.

The integrals $U_{nn'}^\alpha$, are computed by optimized quadratures⁴⁷ with weights $w_{\alpha v' j' v j}$.

2.2.2. *Distorted waves and Green's functions for nonreactive scattering.* Next we turn to the evaluation of the functions ${}^{(r)}f_{nn'}^\alpha$, and $g_{n\beta}^N$, where $\alpha_n = \alpha_\beta = \alpha$; these are respectively the scattering solution and half-integrated Green's functions governed by the last term in Eq. (2a). The distorted wave radial functions solve the homogeneous equations

$$\begin{aligned} [d^2/dR_\alpha^2 - \ell_n(\ell_n+1)/R_\alpha^2 + k_n^2] {}^{(r)}f_{nn'}^\alpha(R_\alpha) + \\ + \sum_{n'} U_{nn'}^{D\alpha}(R_\alpha) {}^{(r)}f_{n',n''}^\alpha(R_\alpha) = 0 \end{aligned} \quad (17)$$

subject to the boundary conditions

$${}^{(r)}f_{nn'}^\alpha \underset{R_\alpha \rightarrow 0}{\sim} 0, \quad (18)$$

$${}^{(r)}f_{nn'}^\alpha \underset{R_\alpha \rightarrow \infty}{\sim} \begin{cases} k_n^{-1/2} [\delta_{nn'} \sin(k_n R_\alpha - \ell_n \pi/2) + \\ + {}^0K_{nn'} \Delta_{nn'}^\alpha \cos(k_n R_\alpha - \ell_n \pi/2)] & k_n^2 > 0; \\ (2|k_n|)^{-1/2} \{ \delta_{nn'} \exp[|k_n|(R_\alpha - R_f)] + \\ + {}^0K_{nn'} \Delta_{nn'}^\alpha \exp[-|k_n|(R_\alpha - R_f)] \} & k_n^2 < 0, \end{cases} \quad (19)$$

where k_n is the wave vector for channel n , and R_f is a numerical parameter chosen to avoid overflow or underflow problems. In practice, we replace the sines and cosines in (19) by Ricatti-Bessel functions; these behave the same as $R_\alpha \rightarrow \infty$, but they allow the boundary condition to be applied at a smaller value of R_α . The

half-integrated Green's functions solve the inhomogeneous equations

$$\begin{aligned} & [d^2/dR_\alpha^2 - \ell_n(\ell_n + 1)/R_\alpha^2 + k_n^2] g_{n\beta}^N(R_\alpha) + \sum_{n'} U_{nn'}^{D\alpha}(R_\alpha) g_{n'\beta}^N(R_\alpha) \\ & = -\delta_{nn} t_{m\beta}^\alpha(R_\alpha) \end{aligned} \quad (20)$$

subject to the boundary conditions

$$g_{n\beta}^N \underset{R_\alpha \rightarrow 0}{\sim} 0, \quad (21)$$

$$g_{n\beta}^N \underset{R_\alpha \rightarrow \infty}{\sim} d_{\beta n}^\alpha \begin{cases} k_n^{-1/2} \cos(k_n R_\alpha - \ell_n \pi/2) & k_n^2 > 0 \\ (2|k_n|)^{-1/2} \exp[-|k_n|(R_\alpha - R_f)] & k_n^2 < 0, \end{cases} \quad (22)$$

where the matrix element in the boundary condition matrix is defined by

$$d_{\beta n}^\alpha = \Delta_{nn}^\alpha \int dR_\alpha^{(r)} f_{n\beta}^\alpha(R_\alpha) t_{m\beta}^\alpha(R_\alpha). \quad (23)$$

We solve equations (17) and (20) using the finite difference boundary value method (FDBVM)^{14,48,49} using a 9-point representation of the second derivative operator, with lower order approximations near the large- R_α edge of the grid in

order to conveniently¹⁴ impose the nonhomogeneous boundary condition. This numerical method is not the most efficient method to solve such coupled ODEs, but in the present context it offers many advantages over other methods. First of all we are concerned in this step with calculating the radial functions at all distances for use in integrals rather than just determining the asymptotic form of the radial functions as is done in standard close coupling calculations; the FDBVM yields the solutions at all R_α in a stable manner without requiring complicated

reorthogonalization⁵⁰ procedures. A second advantage is that there is no restriction as to the uniformity of the stepsizes used for the finite difference grid. We take advantage of this flexibility by evaluating the integrals over radial functions with efficient quadrature rules which do not have evenly spaced nodes while avoiding the interpolation of the radial functions by including the quadrature points used in the radial integrals in the finite difference grid. In particular we use repeated Gauss-Legendre quadrature to evaluate the R_α and R_{α_0} integrals in Eqs.

(8)-(13). This is important because in practice this allows the number, N_α^{QRS} , of radial quadrature points in the integration over R_α to be much less than the number, N_α^F , of points $\{R_{\alpha,j}^F\}$ in the finite difference grid in arrangement α . This

saves both in storage, because it is only necessary to store the radial functions which will be used later at the quadrature points (rather than saving all the values for interpolation), and it saves in the time required for the radial integrals, especially the inter-arrangement integrals which involve two R_α -type integrations, as shown in Eqs. (11)–(13). (The time savings result from avoiding the time for interpolation and by keeping the number of points in the quadrature down because the order is high.)

One aspect of the storage of the radial functions not yet addressed concerns the order in which they will be accessed during the integration steps. In the FDBVM, a given radial function is calculated at all grid points simultaneously before any other radial function is calculated, thus it may seem most advantageous to store them in the same manner. However when performing the integrations, it is more convenient to access all radial functions together at a single integration point. Since the inter-arrangement integrals require accessing the same radial function at a given quadrature point many times, it is more efficient to originally store the radial functions so that they are sequentially accessed in these later steps. This is especially important if the radial functions are stored on disk rather than in memory. When the radial functions are stored on disk, we accomplish this ordering by storing the radial functions using standard FORTRAN-77 direct access files with a fixed record length equal to the square of the maximum number of channels per distortion potential block. Then record 1 contains the function

$f_{nn}^{(r)1}$, for the first distortion potential block at the first quadrature point, records

2 through $N(G) + 1$ contains the functions $g_n^N \beta$ for the first distortion potential block at the first quadrature point, where $N(G)$ is the number of translational basis functions, record $N(G) + 2$ contains the function $f_{nn}^{(r)1}$, for the second distortion potential block at the first quadrature point, etc. When the radial functions are stored in memory, the same ordering is used except now a word rather than record addressing scheme is used to avoid wasting any space in memory caused by differing numbers of channels in the various distortion potential blocks.

The final advantage of the FDBVM is that once the distorted wave radial functions $f_{nn}^{(r)\alpha}$ have been calculated, the half-integrated Green's functions can be calculated relatively inexpensively. This is because the FDBVM equations take the form

$$\Lambda X = \beta, \quad (24)$$

where Λ is a banded matrix of half band width $4N_\delta$, where N_δ is the number of channels in the distortion potential block, and X is the vector of radial functions determined by the boundary condition/inhomogeneity vector β . It should be noted that the matrix Λ contains only the term on the left hand sides of Eqs. (17) and (20) and is therefore the same whether calculating the $f_{nn}^{(r)\alpha}$, or the $g_n^N \beta$. The computational work required to solve Eq. (24) can be broken down into the two steps of factoring the nonsymmetric matrix Λ into its LU form followed by back substitution and forward elimination to obtain the solution.⁵¹ The time to form

the LU decomposition is much larger than the time for the forward substitution and backward elimination steps and so many different solution vectors can be generated with relatively little extra effort once the LU decomposition is known. A detailed analysis of the operation count require to solve Eq. (24) is complicated by the possibility of pivoting; however, if we ignore this complication then the relative work of factoring and solving can be assessed. From Ref. 51 we see that the work to factor will be proportional to $16N_\alpha^F N(D)^3$ for large N_α^F and $N(D)$, while the substitution and elimination time is proportional to $8N_\alpha^F N(D)^2$ to obtain a single solution or $8N_\alpha^F N(D)^3$ to obtain the entire ${}^{(r)}f_{nn}^\alpha$ matrix for this distortion potential block. The time to solve for the $g_{n\beta}^N$ for a single translational basis function will be $8N_\alpha^F N(D)^3$ also, so one can obtain the half-integrated Green's functions for three basis functions for about the same cost as is required to just calculate the ${}^{(r)}f_{nn}^\alpha$. In addition, if the time to evaluate the potential coupling matrix $U_{nn}^{D\alpha}$ is significant, then the calculation of the $g_{n\beta}^N$ will be relatively even less expensive because the potential coupling matrix only appears in Λ . An additional point is that there exist efficient vectorized routines for the solution of standard forms of equation like (24). We use the LINPACK⁵² routines SGBFA to factor Λ and SGBSL to solve for the radial functions.

We now address some aspects of the calculation of the Λ matrix. First consider the finite difference coefficients which must be generated for unevenly spaced grid points. We generate these coefficients by requiring that

$$\left. \frac{d^2 F}{dR^2} \right|_{R=R_j} = \sum_{i=1}^N c_i^j F(R_{j+i-(N-1)/2-1}), \quad (25)$$

where F is a polynomial of order $N-1$, R_j is the j^{th} grid point, and the c_i^j are the finite difference coefficients. In particular, we write

$$F(R_k) = F(R_j) + \sum_{i=1}^{N-1} F^{(i)}(R_j) [(R_k - R_j)^i / i!],$$

$$k = j - (N-1)/2, \dots, j + (N+1)/2, \quad (26)$$

where $F^{(i)} = d^i F / dR^i$. We can write this in the form $\mathbf{A}\mathbf{c} = \mathbf{F}$, where \mathbf{A} is the matrix of $[(R_k - R_j)^i / i!]$, \mathbf{c} is the unknown vector of values of the derivatives $F^{(i)}$ and \mathbf{F} is the vector of functions at the neighboring grid points. Multiplying through by \mathbf{A}^{-1} , we then see that

$$F^{(i)}(R_j) = \sum_{k=1}^N (A^{-1})_{i+1,k} F(R_{j-(N-1)/2+k-1}), \quad (27)$$

thus the elements $(A^{-1})_{3k}$ are the coefficients we seek.

Now consider the evaluation of the intra-arrangement potential $U_{nn'}^\alpha$. This is evaluated by expanding the interaction potential as

$$V^{\text{int},\alpha} = \sum_{\lambda=0}^{\lambda_{\text{max}}} \nu_\lambda^{\text{int},\alpha}(R_\alpha, r_\alpha) P_\lambda(\cos \gamma_\alpha), \quad (28)$$

where $\nu_\lambda^{\text{int},\alpha}$ is an expansion coefficient, P_λ is a Legendre polynomial, and λ_{max} is a convergence parameter we take equal to the minimum of $N_{\alpha\alpha}^{\text{QA}}$ and $2j_{\text{max}} + 1$, where $N_{\alpha\alpha}^{\text{QA}}$ is the number of points in the Gauss-Legendre quadrature used for non-exchange angular integrals, and j_{max} is the maximum rotational quantum number. The expansion coefficients are determined by projection of the Legendre polynomials; the numerical quadrature involved in that process is written as a matrix multiply and evaluated using a fast matrix multiplication routine. Note that the potential expansion coefficients are independent of channel indices, although they do depend on the arrangement index. The matrix elements are then assembled using Percival-Seaton coefficients,⁵³

$$f_{nn'}^{J\lambda\alpha} = \int d\hat{R}_\alpha d\hat{r}_\alpha Y_{j_n \ell_n}^{JM*}(\hat{r}_\alpha, \hat{R}_\alpha) P_\lambda(\cos \gamma_\alpha) Y_{j_n \ell_n}^{JM}(\hat{r}_\alpha, \hat{R}_\alpha), \quad (29)$$

for the angular integrals and optimized vibrational quadrature for the r_α integral.

Finally we consider the imposition of the boundary conditions of Eq. (22). One way to impose these conditions is to calculate the $d_{\beta n}$ matrix elements and

include them times the proper matching functions in the vector β so that radial functions with the proper boundary conditions are automatically produced.

Another way is to use arbitrary boundary conditions in β to produce the function $\tilde{g}_{n\beta}^N$ which is related to the desired functions by

$$\tilde{g}_{n\beta}^N = g_{n\beta}^N(R_\alpha) + \sum_{n'}^{(r)} f_{nn'}^\alpha(R_\alpha) X_{n'\beta} \quad (30)$$

where the matrix element $X_{n\beta}$ can be determined numerically from the asymptotic form of $\tilde{g}_{n\beta}^N$. This equation can also be used when changing from real to complex

boundary conditions as described in Sect. 5. In our calculations we use the $d_{\beta n}$ matrix elements and the β vector to directly generate functions satisfying the proper boundary conditions.

2.2.3. *Angular exchange integrals.* We next consider the evaluation of the inter-arrangement integrals, $\mathcal{E}_{nn_0}^{\alpha\alpha_0}$ and $\mathcal{B}_{nn_0}^{\alpha\alpha_0}$. These take the form

$$\begin{aligned} \mathcal{E}_{nn_0}^{\alpha\alpha_0} = & 2\pi(\mathcal{M}^{\alpha\alpha_0})^3 R_{\alpha} R_{\alpha_0} [(2\ell_n + 1)(2\ell_{n_0} + 1)]^{\frac{1}{2}} (2J + 1)^{-1} \times \\ & \times \sum_{\Omega} \sum_{\Omega'} (j_n \ell_n \Omega | j_n \ell_n J \Omega) (j_{n_0} \ell_{n_0} \Omega' | j_{n_0} \ell_{n_0} J \Omega') \\ & \times \int d\cos\Delta_{\alpha\alpha_0} \frac{1}{r_{\alpha}} \chi_{\alpha v j_n} (r_{\alpha}) Y_{j_n \Omega} (\gamma_{\alpha}, 0) \times \\ & \times \left[\frac{-2\mu}{\hbar^2} V^{\text{int}, \alpha_0} (R_{\alpha_0}, x_{\alpha_0}) \right] \\ & \times \frac{1}{r_{\alpha_0}} \chi_{\alpha_0 v j_{n_0}} (r_{\alpha_0}) Y_{j_{n_0} \Omega'} (\gamma_{\alpha_0}, 0) d_{\Omega \Omega'}^J (\Delta_{\alpha\alpha_0}), \end{aligned} \quad (31)$$

where $\mathcal{M}^{\alpha\alpha_0}$ is a mass factor, J is the total angular momentum, $(\dots | \dots)$ is a Clebsch-Gordan coefficient, $\Delta_{\alpha\alpha_0}$ is the angle which rotates the coordinate system of one arrangement to the other, i.e., $\cos \Delta_{\alpha\alpha_0} = \hat{R}_{\alpha} \cdot \hat{R}_{\alpha_0}$, $Y_{j\Omega}$ is a spherical

harmonic, and $d_{\Omega \Omega'}^J$ is a reduced rotation matrix element. The equation for $\mathcal{B}_{nn_0}^{\alpha\alpha_0}$ is the same as Eq. (31) except the $-2\mu V^{\text{int}, \alpha_0} / \hbar^2$ factor is replaced by unity. The coordinates in the integrand are functions of R_{α} , R_{α_0} , and $\Delta_{\alpha\alpha_0}$, i.e.,

$$r_{\alpha} = \mathcal{M}^{\alpha\alpha_0} [R_{\alpha_0}^2 + (\overline{\mathcal{M}}^{\alpha\alpha_0} R_{\alpha})^2 + 2 \overline{\mathcal{M}}^{\alpha\alpha_0} R_{\alpha} R_{\alpha_0} \cos \Delta_{\alpha\alpha_0}]^{\frac{1}{2}} \quad (32)$$

$$r_{\alpha_0} = \mathcal{M}^{\alpha\alpha_0} [R_{\alpha}^2 + (\overline{\mathcal{M}}^{\alpha\alpha_0} R_{\alpha_0})^2 + 2 \overline{\mathcal{M}}^{\alpha\alpha_0} R_{\alpha} R_{\alpha_0} \cos \Delta_{\alpha\alpha_0}]^{\frac{1}{2}}, \quad (33)$$

$$\cos \gamma_{\alpha} = (-1)^{P_{\alpha\alpha_0}} \mathcal{M}^{\alpha\alpha_0} (\overline{\mathcal{M}}^{\alpha\alpha_0} R_{\alpha} + R_{\alpha_0} \cos \Delta_{\alpha\alpha_0}) / r_{\alpha} \quad (34)$$

$$\cos \gamma_{\alpha_0} = (-1)^{P_{\alpha_0\alpha}} \mathcal{M}^{\alpha\alpha_0} (\overline{\mathcal{M}}^{\alpha\alpha_0} R_{\alpha_0} + R_{\alpha} \cos \Delta_{\alpha\alpha_0}) / r_{\alpha_0} \quad (35)$$

where $\overline{\mathcal{M}}^{\alpha\alpha_0}$ is another mass factor and $P_{\alpha\alpha_0}$ is the parity of the permutation from (12) to $(\alpha\alpha_0)$. Both $\mathcal{M}^{\alpha\alpha_0}$ and $\overline{\mathcal{M}}^{\alpha\alpha_0}$ are symmetric with respect to α and α_0 .

We first simplify Eq. (31) by writing it in terms of the body-frame matrix elements which are labeled by the quantum numbers, v, j, Ω, J, P rather than the laboratory-frame quantum numbers v, j, ℓ, J . Here Ω is the projection of the total angular momentum on the diatom bond axis, and P is the parity, defined as $P = (-1)^{j+\ell}$. Equation (31) then becomes

$$\mathcal{E}_{nn_0}^{\alpha\alpha_0} = \sum_{\Omega \geq 0} \sum_{\Omega' \geq 0} T_{\Omega \ell_n}^{J j_n} T_{\Omega' \ell_{n_0}}^{J j_{n_0}} \mathcal{E}_{v_n j_n \Omega v_{n_0} j_{n_0} \Omega'}^{\alpha\alpha_0 JP}, \quad (36)$$

where the body-frame-to-space-frame transformation is

$$T_{\Omega \ell}^{J j} = \left[\frac{2}{1 + \delta_{\Omega 0}} \right]^{\frac{1}{2}} \left[\frac{2\ell + 1}{2J + 1} \right]^{\frac{1}{2}} (j \Omega \ell 0 | j J \Omega). \quad (37)$$

We note that if $P(-1)^J = -1$, then the Ω and $\Omega' = 0$ terms are not present in Eq. (36), and the sum runs over $\Omega \geq 1$ and $\Omega' \geq 1$. Also it should be noted that this transformation is independent of the vibrational quantum numbers so that if channel pairs which only differ by v_n and v_{n_0} are grouped together, they can be transformed using vector instructions.

The body-frame matrix elements are written as

$$\begin{aligned} \mathcal{E}_{v j \Omega v' j' \Omega'}^{\alpha\alpha_0 JP} &= \pi (\overline{\mathcal{M}}^{\alpha\alpha_0})^3 R_{\alpha} R_{\alpha_0} \int d\cos\Delta_{\alpha\alpha_0} \frac{1}{r_{\alpha}} \chi_{\alpha v j}(\mathbf{r}_{\alpha}) Y_{j \Omega}(\gamma_{\alpha}, \mathbf{0}) \times \\ &\times \left[\frac{-2\mu}{\hbar^2} V^{\text{int}, \alpha_0}(\mathbf{R}_{\alpha_0}, \mathbf{x}_{\alpha_0}) \right] \frac{1}{r_{\alpha_0}} \\ &\times \chi_{\alpha_0 v' j'}(\mathbf{r}_{\alpha_0}) Y_{j' \Omega'}(\gamma_{\alpha_0}, \mathbf{0}) \tilde{d}_{\Omega \Omega'}^{JP}(\Delta_{\alpha\alpha_0}), \end{aligned} \quad (38)$$

and the modified rotation matrix elements are given by

$$\begin{aligned} \tilde{d}_{\Omega \Omega'}^{JP} &= [(1 + \delta_{\Omega 0})(1 + \delta_{\Omega' 0})]^{-\frac{1}{2}} [d_{\Omega \Omega'}^J + (-1)^{\Omega + \Omega'} d_{-\Omega - \Omega'}^J + \\ &+ P(-1)^{J + \Omega} d_{-\Omega \Omega'}^J + P(-1)^{J + \Omega'} d_{\Omega - \Omega'}^J]. \end{aligned} \quad (39)$$

The body-frame matrix is then evaluated using Gauss-Legendre quadrature. In particular, we define the quantities

$$b_{\alpha v j \Omega i} = \frac{1}{r_{\alpha}(i)} \chi_{\alpha v j}[r_{\alpha}(i)] Y_{j \Omega}[\gamma_{\alpha}(i), 0], \quad (40)$$

where $r_{\alpha}(i)$ is r_{α} evaluated at the i^{th} quadrature point, etc.,

$$\mathcal{V}_i^{\text{JP}\Omega\Omega'} = \frac{-2\mu}{\hbar^2} V^{\text{int}, \alpha_0} [R_{\alpha_0, \mathbf{x}_{\alpha_0}}(i)] R_{\alpha} R_{\alpha_0} \pi(\mathcal{M}^{\alpha\alpha_0})^3 w_i \tilde{d}_{\Omega\Omega'}^{\text{JP}}[\Delta_{\alpha\alpha_0}(i)], \quad (41)$$

where w_i is the weight for the i^{th} quadrature point, and

$$\tilde{b}_{i \alpha v j}^{\text{JP}\Omega\Omega'} = b_{\alpha v j \Omega' i} \mathcal{V}_i^{\text{JP}\Omega\Omega'}, \quad (42)$$

so that the final result is a matrix multiply:

$$\mathcal{E}_{v j \Omega v' j' \Omega'}^{\alpha\alpha_0} = \sum_i b_{\alpha v j \Omega i} \tilde{b}_{i \alpha_0 v' j'}^{\text{JP}\Omega\Omega'}. \quad (43)$$

All of the quantities in Eqs. (39)–(42) are evaluated using vector instructions and the matrix multiply is evaluated using a fast matrix multiply routine. It should be noted that the coordinates specified by $\mathbf{x}_{\alpha}(i)$ and $\mathbf{x}_{\alpha_0}(i)$ all depend on R_{α} , R_{α_0} , and $\Delta_{\alpha\alpha_0}$ so that $b_{\alpha v j \Omega i}$ does also; however the $\tilde{d}_{\Omega\Omega'}^{\text{JP}}$ are independent of R_{α} and R_{α_0} .

An additional subtlety exists concerning the evaluation of the rotation matrix elements. This arises because the equations relating the \mathbf{x}_{α} to the R_{α} , R_{α_0} and $\Delta_{\alpha\alpha_0}$ only involve $\cos\Delta_{\alpha\alpha_0}$ and so we only store the cosine rather than the angle [see eqs. (32)–(35)]. The sign of the angle then is not specified and so it is necessary to keep track of the sense of the rotation based upon α and α_0 . In particular, in Eq. (38), $\Delta_{\alpha\alpha_0}$ will be a positive rotation if $\alpha_0 = \alpha + 1$ (modulo 3) and a negative rotation if $\alpha_0 = \alpha - 1$ (modulo 3). The rotation matrix elements at negative angles are obtained by exchanging the subscripts, i.e. $\tilde{d}_{\Omega\Omega'}^{\text{JP}}$ is replaced by $\tilde{d}_{\Omega'\Omega}^{\text{JP}}$.

The matrix elements $\mathcal{B}_{nn_0}^{\alpha\alpha_0}$ are calculated in an analogous manner except that the $-2\mu V^{\text{int}, \alpha_0} / \hbar^2$ factor is not included in Eq. (41).

We note in passing that the matrix elements $W_{nn_0}^{\alpha\alpha_0}$, $\mathcal{E}_{nn_0}^{\alpha\alpha_0}$, and $\mathcal{B}_{nn_0}^{\alpha\alpha_0}$ are

independent of energy, and the matrix elements $b_{\alpha\nu j\Omega i}$ used to calculate them are independent of J .

An alternative to the above procedure of evaluating the body-frame matrix elements and then transforming them into the space frame is to note that the entire calculation can be carried out in the body frame. This can lead to a sizeable reduction in operations because the transformation of Eq. (36), which needs to be performed inside of the integral over R_α and R_{α_0} , is eliminated if the body frame is used throughout. To perform the calculations in the body frame, it is necessary to apply the transformation $T_{\Omega\ell}^{Jj}$ to all quantities labeled by the ℓ quantum

number, namely the radial functions ${}^{(r)}f_{n'n}^\alpha$, and $g_{n'\beta}^N$, the distortion potential reactance matrix ${}^oK_{n'n'}$, and the intra-arrangement potential matrix elements

$V_{n'n}^\alpha$, and $U_{n'n}^{D\alpha}$. With these changes, one proceeds as before, except Eq. (36) is now eliminated and it is necessary to back transform the final reactance or scattering matrix before calculating physical observables.

The only limitation of using the body frame throughout the entire calculation concerns the choice of the distortion potential. It is necessary that a given distortion potential block include the channels with all values of ℓ allowed by total angular momentum and parity constraints for a given ν, j state. If this were not the case, the transformation $T_{\Omega\ell}^{Jj}$ will mix different distortion potential blocks and complicate the various computational steps. Two kinds of distortion potentials which do not allow the use of the body frame throughout are a single channel distortion potential and a distortion potential based on a centrifugal sudden decoupling index.⁵⁴

2.2.4. Radial integrals. We next consider the radial integrals. For computational purposes, it is convenient to rewrite these equations by defining the quantities

$$\mathcal{F}_{n'n_0} = \begin{cases} \sum_{n'} \Delta_{n'n'}^\alpha {}^{(r)}f_{n'n}^{\alpha_0}(R_{\alpha_0}) V_{n'n_0}^{\alpha_0}(R_{\alpha_0}), & \alpha_n = \alpha_0; \\ \int dR_\alpha \sum_{n'} \Delta_{n'n'}^\alpha {}^{(r)}f_{n'n}^\alpha(R_\alpha) W_{n'n_0}^{\alpha\alpha_0}(R_\alpha, R_{\alpha_0}), & \text{otherwise,} \end{cases} \quad (44)$$

$$\mathcal{G}_{\beta n_0} = \begin{cases} \sum_{n'} \Delta_{n'\beta n'}^\alpha g_{n'\beta}^N(R_{\alpha_0}) V_{n'n_0}^\alpha(R_{\alpha_0}) & \alpha_\beta = \alpha_0; \\ \int dR_{\alpha_\beta} \sum_{n'} \Delta_{n'\beta n'}^{\alpha_\beta} g_{n'\beta}^N(R_{\alpha_\beta}) W_{n'n_0}^{\alpha_\beta\alpha_0}(R_{\alpha_\beta}, R_{\alpha_0}), & \text{otherwise,} \end{cases} \quad (45)$$

and

$$\mathcal{H}_{\beta n_0} = \begin{cases} \Delta_{n\beta n_0}^{\alpha_0} g_{n'\beta}^N(R_{\alpha_0}), & \alpha_\beta = \alpha_0; \\ \int dR_{\alpha_\beta} \sum_{n'} \Delta_{n\beta n'}^{\alpha_\beta} g_{n'\beta}^N(R_{\alpha_\beta}) \mathcal{Z}_{n'n_0}^{\alpha_\beta \alpha_0}(R_{\alpha_\beta}, R_{\alpha_0}), & \text{otherwise.} \end{cases} \quad (46)$$

With these definitions, Eqs. (8)–(13) become

$$\mathcal{H}_{nn_0}^B = \int dR_{\alpha_0} \sum_n \Delta_{n'n_0}^{\alpha_0} \mathcal{F}_{nn'}(R_{\alpha_0}) {}^{(r)}f_{n'n_0}^{\alpha_0}(R_{\alpha_0}), \quad (47)$$

$$B_{\beta n_0} = \int dR_{\alpha_0} \sum_n \Delta_{n'n_0}^{\alpha_0} \mathcal{G}_{\beta n'}(R_{\alpha_0}) {}^{(r)}f_{n'n_0}^{\alpha_0}(R_{\alpha_0}), \quad (48)$$

and

$$\begin{aligned} C_{\beta\beta'} = & \int dR_{\alpha_{\beta'}} \mathcal{H}_{\beta n \beta'}(R_{\alpha_{\beta'}}) t_{m\beta' n \beta'}^{\alpha_{\beta'}}(R_{\alpha_{\beta'}}) - \\ & - \int dR_{\alpha_{\beta'}} \sum_{n'} \Delta_{n'n \beta'}^{\alpha_{\beta'}} \mathcal{G}_{\beta n'}(R_{\alpha_{\beta'}}) g_{n'\beta'}^N(R_{\alpha_{\beta'}}). \end{aligned} \quad (49)$$

Equations (47)–(49) take the form of a matrix multiply followed by integration, and we carry out the matrix multiplications using a fast matrix multiply routine.

In order to efficiently evaluate the sums over n and n' inside of the R_{α} integral in Eqs. (44)–(46), we proceed as follows. The basic operation to be performed is the multiplication of a full matrix (with elements $W_{n'n_0}^{\alpha\alpha_0}$ or $\mathcal{Z}_{n'n_0}^{\alpha\alpha_0}$) and a block diagonal matrix (${}^{(r)}f_{n'n}^{\alpha}$ or $g_{n'\beta}^N$), and it is most efficient to organize these steps so that multiplication from the right is by the block diagonal matrix. This maximizes the vector lengths involved in the multiplication process. This ordering is easily accomplished by transposing the matrix equations. For illustration, we consider an example where there are two distortion potential blocks, then the product we wish to form is

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} E & 0 \\ 0 & F \end{bmatrix} = \begin{bmatrix} G & H \\ I & J \end{bmatrix}, \quad (50)$$

where 0 is the null matrix, and this is evaluated as

$$\begin{bmatrix} A \\ C \end{bmatrix} \begin{bmatrix} E \\ F \end{bmatrix} = \begin{bmatrix} G \\ I \end{bmatrix}, \quad (51)$$

and

$$\begin{bmatrix} \mathbf{B} \\ \mathbf{D} \end{bmatrix} \begin{bmatrix} \mathbf{F} \end{bmatrix} = \begin{bmatrix} \mathbf{H} \\ \mathbf{J} \end{bmatrix}. \quad (52)$$

Equations (51)–(52) are each evaluated by a call to a fast matrix multiply routine.

The amount of work involved in the double radial integrals is substantial, so it is desirable to minimize it. We do this by two means. First of all, we use efficient Gaussian quadrature rules to evaluate the integrals; this minimizes the number of terms in the quadrature sums. Secondly we note that many values of R_α , R_{α_0} , and $\Delta_{\alpha\alpha_0}$ lead to geometries which have no physical importance so that

the $\mathcal{S}_{nn_0}^{\alpha\alpha_0}$ and $\mathcal{B}_{nn_0}^{\alpha\alpha_0}$ matrices will be negligible and not make any significant contributions to the quadrature sums. By detecting these geometries prior to the calculation of the $\mathcal{S}_{nn_0}^{\alpha\alpha_0}$ and $\mathcal{B}_{nn_0}^{\alpha\alpha_0}$ matrices, we can save a considerable amount of work. We do this by noting that the primary cause of the small values of these matrices are the non-classical values of the bond lengths r_α and r_{α_0} where the vibrational wavefunctions $\chi_{\alpha v j}$ are exponentially decaying to zero. Thus we specify limits on the bond lengths and if a particular combination of R_α , R_{α_0} , and $\Delta_{\alpha\alpha_0}$ produces values of r_α or r_{α_0} which lie outside of these limits, this point is omitted from the inner quadrature over $\cos\Delta_{\alpha\alpha_0}$. In practice, the limits are determined by comparing the vibrational wavefunctions to an input parameter and determining the distances where the absolute values of the $\chi_{\alpha v j}$ are less than this parameter. We always check that the results are converged with respect to decreasing this parameter.

The choice of which integration is carried out first, i.e., R_α or R_{α_0} , is important in determining the efficiency of the calculation of matrix elements between different arrangements. This is because Eq. (16) involves three parts, two of which depend explicitly on the two arrangements and one which depends only on the α_0 arrangement. Thus by performing the R_α integral first we avoid the inefficiency of repeatedly calculating the U_{nn}^α , or the storage problem of having to save them. Instead each matrix element is calculated as it is needed and then discarded. This is discussed in more detail in Sect. 4.

2.2.5. Final steps. Once all of the integrals have been evaluated, we solve for the reactance matrix by means of Eqs. (3), (3a), and (7). Then the scattering matrix is determined from

$$\mathbf{S} = (\mathbf{1} - i\mathbf{K}^{00})^{-1}(\mathbf{1} + i\mathbf{K}^{00}), \quad (53)$$

where $\mathbf{1}$ is the unit matrix, and $i = \sqrt{-1}$. For computational purposes, this is rewritten as

$$S = [1 + (K^{00})^2]^{-1} [1 - (K^{00})^2 + 2iK^{00}] \quad (54)$$

so that the real and imaginary parts of the scattering matrix are each determined using only real arithmetic.

3. Symmetry Decoupling

For systems with identical atoms, some numerical simplifications of the above equations are possible. First of all, some quantities, such as the vibrational wavefunctions and the radial functions, are common to more than one arrangement. Thus it is advantageous to calculate only the unique quantities. This applies to the integrals needed to construct the various matrices as well; because of the symmetry of the system, many matrix elements are either equal or related by a phase factor. Thus one can take advantage of this and only calculate the matrix elements that are unique by symmetry.

A second type of simplification present in systems having symmetry is that the diatom in at least one arrangement will be homonuclear. This can be exploited in several places. First of all, the work in the quadratures to determine the potential expansion coefficients of Eq. (28) can be cut in half because the interaction potential is an even function. This also means that only even values of λ occur in the Legendre expansion. Thus even and odd rotational quantum numbers are not coupled by the distortion potential and so the size of the distortion potential blocks decreases as does also the time to solve for the radial functions and the resources required to save them.

The final use of symmetry concerns the solution of Eq. (7) for the correction to the reactance matrix. So far in the discussion we have emphasized aspects of the calculation prior to this step, but when the basis set is large enough, most of the run time for a calculation will be spent in forming \mathbf{B} . We can use symmetry here also to save on computational resources. Thus we seek to exploit the symmetry of the \mathcal{K} , \mathcal{K}^B , \mathbf{B} , and \mathbf{C} matrices by introducing simple unitary transformations U_K and U_C into Eq. (7), i.e.

$$U_K^\dagger \mathcal{K} U_K = U_K^\dagger \mathcal{K}^B U_K + U_K^\dagger \mathbf{B}^\dagger U_C (U_C^\dagger \mathbf{C} U_C)^{-1} U_C^\dagger \mathbf{B} U_K, \quad (55)$$

where \dagger denotes Hermitian conjugate and U_K and U_C are chosen such that \mathcal{K} , \mathcal{K}^B , \mathbf{B} , and \mathbf{C} are block diagonalized. (In \mathbf{B} the blocks are rectangular.) Then each block can be solved separately at much reduced cost.

To discuss the transformations in detail we consider a generic matrix \mathbf{M} , which may be \mathcal{K}^B , \mathbf{B} , or \mathbf{C} . Let the dimensions of \mathbf{M} be $N_r \times N_c$. When \mathbf{M} represents \mathcal{K}^B , it has elements $\langle \alpha n E | \hat{M} | \alpha' n' E \rangle$ so $N_r = N_c = N$, the number of channels. When \mathbf{M} represents \mathbf{B} , it has elements $\langle \beta | \hat{M} | \alpha n E \rangle$ so $N_c = N$ and $N_r = M$, the number of basis functions. When \mathbf{M} represents \mathbf{C} , it has elements

$\langle \beta | M | \beta' \rangle$ so $N_r = N_c = M$. The order of the rows in B and of the rows and columns in C is such that all basis functions for a given distortion block occur consecutively.

In order to specify the transformations we now have to discuss in detail the form of the matrices for specific cases. We first consider the case where two atoms are the same and arrangement 1 is $A + B_2$; arrangements 2 and 3 both correspond to $AB + B$ in this case, but differ in which B atom is bound. In arrangement 1, the channels are ordered such that the N_{even} channels with even j appear before the N_{odd} channels having odd j . Arrangements 2 and 3 are indistinguishable and have N_{other} channels each, thus the total number of channels is $N = N_{\text{even}} + N_{\text{odd}} + 2N_{\text{other}}$. A generic matrix will have the form

$$M = \begin{bmatrix} A^e & 0 & C^e & C^e P' \\ 0 & A^o & C^o & -C^o P' \\ B^e & B^o & D & EP' \\ PB^e & -PB^o & PE & PDP' \end{bmatrix}, \quad (56)$$

where A^e is the submatrix containing elements between channels of arrangement 1 with even j , B^e is the submatrix containing elements between channels of arrangements 2 and channels of arrangement 1 with even j , etc. The phase matrices P (of dimension $N_r \times N_r$) and P' (of dimension $N_c \times N_c$) are diagonal

with elements equal to $(-1)^{j_n}$, where j_n is the rotational quantum number for the appropriate channel of arrangement 3. If the matrix M is symmetric, e.g., \mathcal{H}^B or C , then E is symmetric also, and C^e and C^o are transposes of B^e and B^o , respectively.

We now discuss the reasons for this structure. First consider the matrix elements which are diagonal in arrangement quantum number. In arrangement 1, the diatom is homonuclear and the potential is an even function of the $\cos \gamma_1$, thus there will be nonzero coupling only between channels which are either both even or both odd functions of $\cos \gamma_1$. As a result channels with even j will not be coupled to channels with odd j . This is the reason for the null matrices in Eq. (56). Now turn to arrangements 2 and 3. Even though they are physically indistinguishable, they do not have identical radial functions, as we have defined them. This is because the angles γ_2 and γ_3 , defined below Eq. (1), are related such that a geometry of arrangement 2 which is superimposable with a geometry of arrangement 3 will have

$$\gamma_2 = \pi - \gamma_3. \quad (57)$$

This causes a change in sign of the terms in the Legendre expansion of the potential which correspond to odd angular functions [see Eq. (28)]. This is

equivalent to a phase change of $(-1)^{j_n + j_{n'}}$ in the radial functions because the Percival-Seaton coefficients are zero if $(-1)^{j_n + j_{n'} + \lambda} \neq 1$. Thus the lower right

submatrix in Eq. (56) is PDP' rather than D .

Now consider the matrices connecting arrangement 3 and arrangement 1. These are obtained from the $\langle \text{arrangement 2} | \text{arrangement 1} \rangle$ matrices as follows.

First the radial functions of arrangement 2 are multiplied by $(-1)^{j_n + j_{n'}}$, where n and n' are arrangement 2 channel labels, to produce arrangement 3 radial functions. The next change occurs in Eqs. (34) and (35), where the sign on the angles changes because the parity of the $(\alpha\alpha') = (13)$ [or (31)] permutation is opposite of the (12) [or (21)] permutation—this is equivalent to a phase change of

$(-1)^{j_{n'} + j_{n''}}$, where n' is an arrangement 2 channel label, and n'' is an

arrangement 1 channel label. The two $(-1)^{j_{n'}}$ phases cancel to give PB^e and $-PB^o$. By the same argument, we see that the relation between $\langle \text{arrangement 1} | \text{arrangement 3} \rangle$ matrix elements and $\langle \text{arrangement 1} | \text{arrangement 2} \rangle$ matrix elements is similar, except now P' appears on the right because the arrangement 2 radial functions multiply from the right.

Finally consider $\langle \text{arrangement 3} | \text{arrangement 2} \rangle$ and $\langle \text{arrangement 2} | \text{arrangement 3} \rangle$ matrix elements. For concreteness we consider elements of $B_{\beta n}$, but the argument is the same for the other matrices. These matrix elements are written symbolically as

$$B_{32} = \iint g_3^T W^{32} f_2, \quad (58)$$

and

$$B_{23} = \iint g_2^T W^{23} f_3. \quad (59)$$

Introducing $g_3^T = P g_2^T P'$ and $f_3 = P' f_2 P'$ due to Eq. (57) and $W^{23} = P' W^{32} P'$ from Eqs. (34) and (35), we have

$$B_{32} = \iint P g_2^T P' W^{32} f_2, \quad (60)$$

and

$$B_{23} = \iint g_2^T P' W^{32} f_2 P', \quad (61)$$

or

$$B_{23} = P B_{32} P'. \quad (62)$$

Thus PE becomes EP' .

The final statement about Eq. (56) to be verified is that E is symmetric when M is the C matrix or the \mathcal{H}^B matrix. Consider the Born matrix for which Eq. (60) becomes

$$\mathcal{K}_{32}^B = \iint \text{Pf}_2^T \text{PW}^{32} f_2, \quad (63)$$

thus we must show that PW^{32} is "symmetric", i.e.

$$(-1)^{j_n} W_{nn'}^{32}(R_{\alpha'}, R_{\alpha_0}) = W_{n'n}^{32}(R_{\alpha_0}, R_{\alpha'}) (-1)^{j_{n'}}. \quad (64)$$

This follows from the sign change of the parity of the permutations in Eqs. (34) and (35). The same argument applies to the C matrix.

We are now ready to introduce the transformation U which we write as (see Ref. 4)

$$U = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & fP & 0 & fP \\ 0 & f1 & 0 & -f1 \end{bmatrix}, \quad (65)$$

where f is $1/\sqrt{2}$. Then we have

$$U^T M U = \begin{bmatrix} A^e & gC^eP & 0 & 0 \\ gPB^e & PDP+PEP & 0 & 0 \\ 0 & 0 & A^o & gC^oP \\ 0 & 0 & gPB^o & PDP-PEP \end{bmatrix}, \quad (66)$$

where g is $\sqrt{2}$. Thus if the transformation of Eq. (65) is applied to C, it decouples Eq. (7b) into two independent matrix equations of order $N_{\text{even}} + N_{\text{other}}$ and $N_{\text{odd}} + N_{\text{other}}$ rather than one set of equations of order $N_{\text{even}} + N_{\text{odd}} + 2N_{\text{other}}$. If $N_{\text{even}} = N_{\text{odd}}$, then this results in a CPU time savings of $2^3/(1^3 + 1^3) = 4$ for large enough N.

Now consider the case when all atoms are the same, $A + A_2$. Here all arrangements are indistinguishable. The diatoms are all homonuclear, so again we will order the channels in a given arrangement so the N_{even} basis functions with j even occur before the N_{odd} basis functions with odd j. The total number of channels is then $N = 3N_{\text{even}} + 3N_{\text{odd}}$. Then, if we group the channels in a given arrangement with even j before those with odd j, the generic matrix is

$$M = \begin{bmatrix} A^e & 0 & B^{ee} & B^{eo} & B^{ee} & -B^{eo} \\ 0 & A^o & -B^{oe} & B^{oo} & B^{oe} & B^{oo} \\ B^{ee} & -B^{eo} & A^e & 0 & B^{ee} & B^{eo} \\ B^{oe} & B^{oo} & 0 & A^o & -B^{oe} & B^{oo} \\ B^{ee} & B^{eo} & B^{ee} & -B^{eo} & A^e & 0 \\ -B^{oe} & B^{oo} & B^{oe} & B^{oo} & 0 & A^o \end{bmatrix}, \quad (67)$$

where **A** represents intra-arrangement coupling and **B** inter-arrangement coupling. When **M** is symmetric, then B^{ee} and B^{oo} are also symmetric and B^{eo} and B^{oe} are transposes. The signs in Eq. (67) follow from the discussion above, except here the radial functions are the same for all arrangements since the potential is an even function of $\cos\gamma_\alpha$. However, the pattern of **P** matrices remains because the **P**

which arises from Eqs. (34)–(35) commutes with the radial functions. In writing Eq. (67) we have explicitly replaced the **P** matrix with \pm signs.

In this case, the transformation matrix is complex, albeit unitary. In particular we have (see Ref. 4)

$$U = \begin{bmatrix} 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & i1 & 0 & -i1 \\ 1 & 0 & \epsilon^*1 & 0 & \epsilon1 & 0 \\ 0 & 1 & 0 & i\epsilon^*1 & 0 & -i\epsilon1 \\ 1 & 0 & \epsilon1 & 0 & \epsilon^*1 & 0 \\ 0 & 1 & 0 & i\epsilon1 & 0 & -i\epsilon^*1 \end{bmatrix}, \quad (68)$$

where i is $\sqrt{-1}$, ϵ is $\exp 2i\pi/3$, and $*$ denotes complex conjugation. Applying this transformation we have

$$U^\dagger M U = \begin{bmatrix} A^e + 2B^{ee} & 0 & 0 & 0 & 0 & 0 \\ 0 & A^o + 2B^{oo} & 0 & 0 & 0 & 0 \\ 0 & 0 & A^e - B^{ee} & hB^{eo} & 0 & 0 \\ 0 & 0 & hB^{oe} & A^o - B^{oo} & 0 & 0 \\ 0 & 0 & 0 & 0 & A^e - B^{ee} & hB^{eo} \\ 0 & 0 & 0 & 0 & hB^{oe} & A^o - B^{oo} \end{bmatrix}, \quad (69)$$

where h is $\sqrt{3}$. This transformation block diagonalizes the matrices into four blocks, two of which are the same. Thus, applying the transformation to **C** in (7b), rather than solving one set of matrix equations of order $N = 3N_{\text{even}} + 3N_{\text{odd}}$, we can solve three smaller sets of matrix equations of order N_{even} , N_{odd} , and $N_{\text{even}} + N_{\text{odd}}$. If $N_{\text{even}} = N_{\text{odd}}$, then the CPU time savings for large enough N will be

$$6^3/(1^3 + 1^3 + 2^3) = 21.6.$$

Further discussion of symmetry decoupling will be provided in a later publication.⁴¹

In addition to the CPU time savings discussed above, these block diagonalization procedures reduce the storage requirements for the calculations since the null blocks need not be stored.

4. Storage Management Strategies

4.1. GENERAL CONSIDERATIONS

It is a general principle of conventional programming practice that recalculation of quantities appearing more than once in an algorithm should be minimized. However this goal often comes into conflict with the physical limitations of the available computational resources. One is then faced with the choice of using more CPU resources and calculating the same quantity more than once or saving every quantity of potential later use and limiting the size of possible calculations because of finite memory or disk or slow input/output. Our strategy in the newest version of our code is to minimize the storage requirements subject to the constraint that excessive amounts of CPU resources will not be spent in recalculating expensive steps. We now discuss the choices we have made and give examples of the penalties incurred by not storing all quantities used two or more times. It should be emphasized that we are designing the present methodology for very large-scale calculations and to the extent that various parts of the calculation scale differently with the size of the problem, our methods will not be optimum for simple problems like the reaction of H with H₂ at low total energy and angular momentum.

One reusable set of quantities in our calculations are the intra-arrangement, intra-distortion-block potential matrix elements $U_{nn}^{D\alpha}$, defined by Eq. (14a). The intra-arrangement, inter-distortion-block matrix elements V_{nn}^{α} , defined by Eq. (14) are required only in the nonreactive radial integrals of Eqs. (44) and (45), and hence they may be calculated, used once, and discarded without penalty, but the matrix elements $U_{nn}^{D\alpha}$, appear at two steps of the calculations and require further consideration. The $U_{nn}^{D\alpha}$, matrix elements are needed at every finite difference point to construct the FDBVM matrix in order to calculate the radial functions [Eqs. (17) and (20)], and they are used in the construction of the inter-arrangement matrix $W_{nn_0}^{\alpha\alpha_0}$ [Eq. (16)]. Thus it would seem advantageous to store them. However they occupy considerable space and so we consider recalculating them.

There are three considerations which make the recalculation of the nonreactive potential matrix elements feasible. The first is that in the limit of a large number N of channels, the time required for the calculation of this matrix will scale as the square of the number of channels while the solution of Eq. (7b) will scale as the cube of the number of channels. Thus comparatively little time

will be spent calculating the matrix elements when N is large (see, however, Sect. 5). The second consideration concerns the calculation of the potential matrix itself — it is possible to calculate the matrix at a single distance independently of all other distances and still do it using vector instructions. The final point concerns the strategic way in which we have organized our calculations. On average each $U_{nn}^{D\alpha}$ matrix element is used at most about $4/3$ times. Most of this factor of $4/3$ comes from Eqs. (17) and (20) where each matrix element is required once at every *finite difference* grid point. The remaining part comes from the integrations of Eqs. (44) and (45) [see also Eq. (16)]. By performing the integration over R_α as indicated in the inter-arrangement parts of Eqs. (44) and (45), each matrix element is required once at each R_α quadrature point and by using repeated Gauss-Legendre quadrature, there are typically only about a third as many quadrature points as finite difference grid points. In addition, these quadratures are only calculated provided the $\mathcal{S}_{nn_0}^{\alpha\alpha_0}$ and/or $\mathcal{B}_{nn_0}^{\alpha\alpha_0}$ matrices are non-negligible. Thus recalculating the matrix elements will not incur a large increase in computation time. We see then that an important consideration making the recalculation of the potential matrix elements feasible is our use of an efficient quadrature scheme. (It also should be noted that the matrix elements $V_{nn'}^\alpha$ coupling different distortion potential blocks of the same arrangement are also required only at the quadrature points rather than at all of the finite difference grid points.)

The analysis of timings for calculations we have made using simple potentials indicates that only a very small fraction of the overall run time is spent calculating the intra-arrangement potential coupling matrix elements. However, calculations³¹⁻³³ using complicated potentials such as the accurate H_3 DMBE⁵⁵ potential spend a nontrivial amount of time on this task. In this case one can consider the slightly different strategy of recalculating the $U_{nn'}^\alpha$, but saving the potential expansion coefficients $\nu_\lambda^{int,\alpha}$. These potential expansion coefficients are independent of the number of channels, so that eventually their evaluation will become negligible; however this is complicated by the fact that we need to retrieve or re-calculate each expansion coefficient for each distortion block, and as the number of channels increases, the number of distortion blocks usually increases also.

We now turn to the question of performing calculations at several energies. The quantities $U_{nn'}^{D\alpha}$ and $W_{nn_0}^{\alpha\alpha_0}$ are independent of energy while the radial functions are not and must be calculated at each new energy. Thus it might seem desirable to save the $U_{nn'}^\alpha$ and $W_{nn_0}^{\alpha\alpha_0}$. However these matrices would require considerable storage, especially $W_{nn_0}^{\alpha\alpha_0}$, which is a function of two radial distances. On the other hand, timing analyses indicate that only a small fraction of the overall run time is spent evaluating these matrices. Thus in our formulation of

reactive scattering, there is no significant advantage in saving energy-independent quantities.

4.2. ARRAY REQUIREMENTS

The program is organized into eleven links performing the various steps of the calculation. When arrays are needed in only one link, they are stored in blank COMMON, which thereby becomes a scratch space overwritten by each link. The size of blank COMMON is therefore determined by the link with the largest temporary storage needs; this is link 10 which forms the C and B matrices. Arrays needed by more than one link are stored in labeled COMMON blocks.

The major array storage requirements for the GNVP calculations are listed below along with their sizes. The arrays are listed in the order they occur in the calculation, as discussed in Sect. 2.2. Only arrays in blank COMMON in link 10 or in labeled COMMON affect the memory requirements, and only these are considered. For simplicity the list has been prepared for a case with no symmetry; we will discuss the savings possible when symmetry is used at the end of this section. In addition, we assume for simplicity in tabulation that all the following parameters are independent of arrangement:

N_{α}^{HO}	the number of harmonic oscillator functions used to expand the diatomic wave functions for arrangement α .
N_{α}	the number of channels in arrangement α .
$N_{\alpha\alpha}^{\text{QV}}$	the number of nodes in the optimized vibrational quadratures for computing U_{nn}^{α} .
$N_{\alpha\alpha}^{\text{QA}}$	the number of nodes in the angular quadratures for computing U_{nn}^{α}
N_{α}^{QRS}	is defined below Eq. (23).
$\delta_{\text{max},\alpha}$	number of distortion potential blocks in arrangement α .
$N_{\text{rot},\delta}$	number of channels per distortion potential block.
N_{α}^{F}	number of finite difference grid points in arrangement α .
m_{δ}	number of translational basis functions per distortion block.

The largest arrays requiring storage and the leading terms in their dimensions are given in Table I. The quantity f^{NZ} is a user input parameter, which equals the fraction of Percival-Seaton coefficients that are nonzero. (Since this is not known, we use an estimate which must be greater than or equal to the true fraction. Even a cautious estimate though can save a significant amount of storage.)

For typical runs the last three arrays in the Table I account for about 90% of the storage. Thus the memory requirement scales approximately as the second power of the number of channels.

When symmetry is included, the storage needed for these N_{α}^2 arrays is

TABLE I
Storage requirements for largest arrays (case of no symmetry)

array	defined in Sect.	storage required
B_{γ}^{avj}	2.2.1	$3N_{\alpha}^2 N_{\alpha}^{HO}$
$w_{av'j'vj}$	2.2.1	$3N_{\alpha}^2 N_{\alpha}^{QV}$
$f_{nn'}^{J\lambda\alpha}$ and associated packed indices	2.2.2	$6 N_{\alpha}^{QA}, N_{\alpha}^{2f}, N_{\alpha}^{NZ}$
$t_{mn}(R_{\alpha,j}^R)$	2.1, 2.2.2	$3N_{\alpha}^F m_{\delta}^{\delta} \max, \alpha$
$(r) f_{nn'}^{\alpha}(R_{\alpha,j}^F)$	2.2.2	$3N_{\alpha}^{QRS} N_{\text{rot}, \delta} N_{\alpha}$
$g_{m\beta}^N(R_{\alpha,j}^F)$	2.2.2	$3N_{\alpha}^{QRS} N_{\text{rot}, \delta} N_{\alpha} m_{\delta}$
$\mathcal{F}_{nn_0}(R_{\alpha,j}^F)$	2.2.4	N_{α}^2
$\mathcal{G}_{\beta n_0}(R_{\alpha,j}^F)$	2.2.4	$m_{\delta} N_{\alpha}^2$
$\mathcal{H}_{\beta n_0}(R_{\alpha,j}^F)$	2.2.4	$m_{\delta} N_{\alpha}^2$
$\mathcal{K}_{nn_0}^B$	2.1	$9N_{\alpha}^2$
$B_{\beta n}$	2.1	$9N_{\alpha}^2 m_{\delta}$
$C_{\beta\beta'}$	2.1	$9N_{\alpha}^2 m_{\delta}^2$

decreased by a factor of 1/2 for the $A + B_2$ case and by a factor of 1/6 for the A_3 case.

5. Scattering Matrix Formulation

5.1. THEORY

We now discuss using complex rather than real boundary conditions to directly calculate the scattering matrix. This can have several advantages. First of all, the use of complex boundary conditions eliminates the possibility of spurious singularities in the final inversion step. Second, if iterative methods are used to solve the complex analog of Eq. (7b), it is possible to solve for a column of the scattering matrix corresponding to a particular initial state without having to solve for the other initial states; this can convert the final N^3 step to an N^2 one. An

additional possible advantage is that fewer channels and gaussians may be required to converge an individual column of the transition matrix than to converge the whole reactance matrix.

A re-derivation of the GNVP equations in terms of scattering matrix boundary conditions shows that few of the equations presented in Sect. 2 are modified. The ones that change are Eq. (3), which becomes

$$S_{nn_0} = \delta_{\alpha\alpha_0} {}^0S_{nn_0} + \mathcal{S}_{nn_0}, \quad (70)$$

and Eqs. (4) and (7), which become

$$\mathcal{S} = \mathcal{S}^B + \mathbf{B}^T \mathbf{C}^{-1} \mathbf{B}, \quad (71)$$

where ${}^0S_{nn_0}$ is the scattering matrix due to the distortion potential, and the quantities \mathcal{S}^B , \mathbf{B} , and \mathbf{C} are given by the same equations as those for \mathcal{S}^B , \mathbf{B} , and \mathbf{C} in Sect. 2 except that the radial functions ${}^{(r)}f_{nn_0}^\alpha$ and $g_{n\beta}^N$, with $\alpha_n = \alpha_\beta = \alpha$, are replaced by the complex functions ${}^{(r)}\tilde{f}_{nn_0}^\alpha$ and $\tilde{g}_{n\beta}^N$ which satisfy the large- R_α boundary conditions

$$\tilde{f}_{nn'}^\alpha, R_\alpha \xrightarrow{\sim} \infty \begin{cases} \left(\frac{1}{2i}\right)^{\frac{1}{2}} k_n^{-\frac{1}{2}} \{ \delta_{nn'}, \exp[-i(k_n R_\alpha - \ell_n \pi/2)] - \\ - {}^0S_{nn'}, \Delta_{nn'}^\alpha \exp[i(k_n R_\alpha - \ell_n \pi/2)] \}, & k_n^2 > 0; \\ i(2|k_n|)^{-\frac{1}{2}} \{ \delta_{nn'}, \exp[|k_n| (R_\alpha - R_f)] - \\ - {}^0S_{nn'}, \Delta_{nn'}^\alpha \exp[-|k_n| (R_\alpha - R_f)] \}, & k_n^2 < 0, \end{cases} \quad (72)$$

and

$$\tilde{g}_{n\beta}^N, R_\alpha \xrightarrow{\sim} \infty \tilde{d}_{\beta n}^\alpha \begin{cases} \left(\frac{1}{2i}\right)^{\frac{1}{2}} k_n^{-\frac{1}{2}} \exp[i(k_n R_\alpha - \ell_n \pi/2)], & k_n^2 > 0 \\ i(2|k_n|)^{-\frac{1}{2}} \exp[-k_n | (R_\alpha - R_f)], & k_n^2 < 0, \end{cases} \quad (73)$$

where the new boundary condition matrix $\tilde{d}_{\beta n}^\alpha$ is given by Eq. (23) with the complex radial function ${}^{(r)}\tilde{f}_{n\beta}^\alpha$ substituted for the real one. It should be noted

that the form of the matching functions in Eqs. (72) and (73) is required for the simple form of Eqs. (70) and (71) to be valid.

The matrices required for Eq. (71) can be calculated in two ways. First of all one can modify the boundary conditions used when solving the FDBVM equations

to directly yield the complex radial functions and then proceed as with the real case. The second way of calculating the required matrices is to note that they can be constructed from the corresponding real matrices. This should be the more efficient method since the increased work of complex arithmetic is avoided until the end. In addition, the storage requirements should be less since real quantities require half the storage of complex ones. Thus we adopted this strategy.

In order to give the relations between the real and complex quantities, it is desirable to partition matrices into parts corresponding to open (i.e., energetically allowed) and closed (i.e., classically forbidden) channels. This is because of the different boundary conditions for these cases. Thus distortion potential block δ has a reactance matrix which we write, similarly to Eq. (3), as

$${}^o\mathbf{K}_\delta = \begin{bmatrix} {}^o\mathbf{K}_\delta^{OO} & {}^o\mathbf{K}_\delta^{OC} \\ {}^o\mathbf{K}_\delta^{CO} & {}^o\mathbf{K}_\delta^{CC} \end{bmatrix}, \quad (74)$$

where o again stands for open and c stands for closed. Then the distortion potential scattering matrices ${}^o\mathbf{S}_\delta$ are given by

$${}^o\mathbf{S}_\delta = (1 - i{}^o\mathbf{K}_\delta^{OO})^{-1}(1 + i{}^o\mathbf{K}_\delta^{OO}). \quad (75)$$

We will transform the distorted wave radial functions for distortion blocked δ by

$${}^{(r)}\mathbf{r}_\delta^\alpha = {}^{(r)}\mathbf{f}_\delta^\alpha \mathbf{A}_\delta, \quad (76)$$

where the transformation matrix \mathbf{A}_δ is given by

$$\mathbf{A}_\delta = \begin{bmatrix} -(2i)^{\frac{1}{2}}(1 - i{}^o\mathbf{K}_\delta^{OO})^{-1} & -(1 - i{}^o\mathbf{K}_\delta^{OO})^{-1} {}^o\mathbf{K}_\delta^{OC} \\ \mathbf{0} & i\mathbf{1} \end{bmatrix}. \quad (77)$$

This also means that the boundary condition matrix for distortion block δ is given by

$$\mathbf{d}_\delta^T = \mathbf{d}_\delta^T \mathbf{A}_\delta. \quad (78)$$

Finally we use Eq. (30) to generate the half integrated Green's functions which satisfy Eq. (73), and for distortion block δ , the transformation matrix \mathbf{X}_δ is given by

$$\mathbf{X}_\delta = \begin{bmatrix} -\frac{1}{2}(1+i)\mathbf{d}_\delta^{\text{oo}T} & -\frac{1}{2}(1+i)\mathbf{d}_\delta^{\text{oc}T} \\ \mathbf{0} & \mathbf{0} \end{bmatrix}. \quad (79)$$

For the following equations, we define \mathbf{A} and \mathbf{X} to be the block diagonal matrices with diagonal blocks equal to \mathbf{A}_δ and \mathbf{X}_δ , respectively.

With these definitions, the matrices we require are

$$\mathcal{S}^B = \mathbf{A}^T \mathcal{K}^{B_{00}} \mathbf{A}, \quad (80)$$

$$\mathbf{B} = (\mathbf{B} + \mathbf{X}^T \mathcal{S}^B) \mathbf{A}, \quad (81)$$

and

$$\mathbf{C} = \mathbf{C} + \mathbf{X}^T \mathcal{D} - \mathbf{B}\mathbf{X} - \mathbf{X}^T \mathbf{B} - \mathbf{X}^T \mathcal{K}^B \mathbf{X}, \quad (82)$$

where the elements of \mathcal{D} are given by

$$\mathcal{D}_{n\beta_0} = \int dR_{\alpha_0} \mathcal{F}_{nn\beta_0}^{\alpha_0}(R_{\alpha_0}) t_{m\beta_0 n\beta_0}^{\alpha_0}(R_{\alpha_0}) \quad (83)$$

with

$$\mathcal{F}_{nn_0} = \begin{cases} \Delta_{nn_0}^{\alpha_0} \quad {}^{(r)}f_{n_0 n}^{\alpha_0}(R_{\alpha_0}), & \alpha_n = \alpha_0; \\ \int dR_{\alpha_n} \Sigma_{\Delta_{nn'}^{\alpha_n}} \quad {}^{(r)}f_{n' n}^{\alpha_n}(R_{\alpha_n}) \mathcal{B}_{n' n_0}^{\alpha_n \alpha_0}(R_{\alpha_n}, R_{\alpha_0}), & \text{otherwise,} \end{cases} \quad (84)$$

and

$$\mathcal{B}_{n\beta_0} = \int dR_{\alpha_0} \Sigma_{\Delta_{n' n}^{\alpha_0}} \mathcal{F}_{nn'}(R_{\alpha_0}) g_{n' \beta_0}^N(R_{\alpha_0}). \quad (85)$$

Thus it is necessary to compute the additional two matrices \mathcal{B} and \mathcal{D} when complex boundary conditions are used. However, by virtue of their smaller dimensions, the extra work required will be small compared to the work required to generate the \mathbf{C} matrix.

The symmetry decoupling procedures of the previous section apply here as well without change.

Another treatment of complex boundary conditions is provided in Ref. 40.

Equation (71) may be solved iteratively by extending iterative techniques developed already⁵⁶ for solving eq. (7). With iterative methods the computational effort for these steps scales with the number of channels as M^2 , as compared to M^3 for direct methods. Thus it becomes more imperative to optimize the other M^2 steps in the calculation, as discussed in detail in Sect. 2.

5.2. EXAMPLES

As an example of the convergence properties for runs with employing symmetry decoupling and real and complex boundary conditions we consider the reaction $D + H_2 \rightarrow HD + H$ on the DMBE⁵⁵ potential energy surface. The $A + B_2$ symmetry was used in the same way for both sets of boundary conditions. We considered a total energy E of 0.98337 eV. For both of the arrangements, $D + H_2$ ($\alpha = 1$) and $H + HD$ ($\alpha = 2$), the number of harmonic functions used to expand the vibrational eigenstates is 78. The number of nodes in the optimized vibrational quadratures⁴⁷ employed for U_{nn}^α , is 14. The number of nodes $N_{\alpha\alpha}^{QA}$ in the angular quadratures for non-exchange integrals is 30. The finite difference grid extends from $R_\alpha = 0.80 a_0$ to $20.0 a_0$ for $D + H_2$ and from $0.40 a_0$ to $15.0 a_0$ for $HD + H$; in both cases the number N_α^F of grid points is 596.

For the exchange integrals the number $N_{\alpha\alpha}^{QA}$, of angular quadrature points is 60, and the radial integrals are carried out with 16 repetitions of 12-point Gauss-Legendre quadrature ($N_\alpha^{QGL} = 16$, $N_\alpha^{QR} = 12$, $N_\alpha^{QRS} = N_\alpha^{QGL} N_\alpha^{QR}$). The maximum and minimum bond distances for which any vibrational wave

TABLE II
Parameters of the gaussian basis sets

	m=3	m=5	m=7	m=16
$\alpha = 1$ ($D + H_2$)				
$R_{\alpha,1}^G$ (a_0)	2.50	2.20	2.20	2.20
$\Delta(G)$ (a_0)	0.50	0.40	0.31	0.30
$R_{\alpha,m}^G$ (a_0)	3.50	3.80	4.06	6.70
$\alpha = 2,3$ ($HD + H$)				
$R_{\alpha,1}^G$ (a_0)	2.50	2.20	2.20	2.20
$\Delta(G)$ (a_0)	0.50	0.40	0.33	0.30
$R_{\alpha,m}^G$ (a_0)	3.50	3.80	4.18	6.70

function exceeds 10^{-9} were determined, and angles corresponding to distances outside this range were excluded from the inner (angular) quadrature loop in all exchange integrals.

We will compare four gaussian basis sets with complex boundary conditions and three with real boundary conditions. In all cases the gaussian width parameter⁵⁷ c , which determines the overlap of neighboring gaussians, was set equal to 1.4. The other parameters of the runs are given in Table II. The notation is as follows: m is the number of gaussians per channel, $R_{\alpha,1}^G$ is the center of the innermost gaussian, $\Delta(G)$ is the spacing between gaussians, and $R_{\alpha,m}^G$ is the center of the outermost gaussian.

Five vibrational levels with maximum rotational quantum numbers of 16, 15, 14, 13, and 12 were used in each arrangement. Thus the total number of channels for $J = 0$ is 225, and 55 of these are open. For $J = 1$, this vibrational-rotational basis yields 210 channels with 49 open for parity $P = 1$, and it yields 435 channels with 104 open for parity $P = -1$.

Reaction probabilities for $D + H_2(v,j,\ell) \rightarrow H + HD$ are defined by

$$P_{vj\ell} = \sum_{\alpha'=2}^3 \sum_{v'} \sum_{j'} \sum_{\ell'} P_{1vj\ell \rightarrow \alpha'v'j'\ell'} \quad (86)$$

where

$$P_{\alpha_n v_n j_n \ell_n \rightarrow \alpha_{n'} v_{n'} j_{n'} \ell_{n'}} = |S_{nn'}|^2, \quad n \neq n'. \quad (87)$$

In separate runs we determined that the values $P_{vj\ell}$ in the run with complex boundary conditions and $m = 16$ are well converged with respect to changing all numerical and basis parameters. (In fact, some of the parameters are overly cautious. For example, except for the very small probabilities, very good convergence is achieved for both real and complex boundary conditions by $m = 11$.) Thus we define the percentage deviation for other runs by

$$\text{per. dev.} = \frac{|P_{vj\ell}^{(m, R \text{ or } C)} - P_{vj\ell}^{(m=16, C)}|}{P_{vj\ell}^{(m=16, C)}} \times 100\% \quad (88)$$

where R and C denote real and complex boundary conditions, respectively. Selected results for $J = 0$ are given in Table III, and Tables IV and V give selected results for the two parity blocks of $J = 1$. We see that real and complex boundary conditions converge to the same reaction probabilities. Furthermore, we see that many reaction probabilities are converged to better than 1% with $m = 3$, and almost all the reaction probabilities are converged to better than 1% with $m = 7$. For the reaction probabilities shown, the average deviation of the $m = 7$, C run from the $m = 16$, C run is 0.2%.

A few of the results for $m = 5$ show surprisingly large deviations. Additional calculations with all m in the range $m = 3-11$ and with both real and complex boundary conditions showed such instabilities only for $m = 5$ and—to a lesser

TABLE III
Convergence checks for $D + H_2 \rightarrow HD + H, J = 0$

$v j \ell$	$P_{v j \ell}$	percentage deviation					
		$m=16,C$	$m=3,R$	$m=5,R$	$m=7,R$	$m=3,C$	$m=5,C$
0 0 0	6.14(-1)	0.30	1.0	0.034	1.1	0.29	0.0073
0 1 1	9.05(-1)	1.3	0.71	0.21	1.3	0.34	0.0053
0 2 2	5.57(-1)	0.19	0.18	0.081	1.3	0.0067	0.093
0 3 3	6.77(-1)	0.56	0.44	0.0015	0.67	0.29	0.043
0 4 4	7.08(-1)	0.073	0.16	0.036	0.66	0.30	0.014
0 5 5	4.62(-1)	0.90	1.1	0.11	0.85	0.85	0.12
0 6 6	2.21(-1)	0.79	0.12	0.22	1.2	0.44	0.22
0 7 7	5.39(-2)	3.9	0.51	0.077	1.5	0.10	0.059
1 0 0	2.96(-1)	7.8	22.	0.64	1.3	1.6	1.0
1 1 1	4.08(-1)	7.4	0.26	0.42	2.2	1.0	0.89
1 2 2	1.20(-1)	17.	36.	0.0095	5.8	0.89	0.40
1 3 3	8.65(-3)	13.	5.8	1.0	14.	6.4	1.4

TABLE IV
Convergence checks for $D + H_2 \rightarrow HD + H, J = 1, P = +1$

$v j \ell$	$P_{v j \ell}$	percentage deviation					
		$m=16,C$	$m=3,R$	$m=5,R$	$m=7,R$	$m=3,C$	$m=5,C$
0 1 1	4.70(-1)	0.43	1.8	0.17	0.14	0.023	0.11
0 2 2	8.61(-1)	0.26	0.18	0.089	0.085	0.076	0.051
0 3 3	6.23(-1)	0.17	2.9	0.039	1.1	0.0096	0.062
0 4 4	5.79(-1)	0.16	0.16	0.0065	0.22	0.24	0.021
0 5 5	6.06(-1)	0.022	0.61	0.040	0.040	0.31	0.046
0 6 6	3.24(-1)	1.4	0.12	0.22	1.3	0.23	0.21
0 7 7	6.54(-2)	3.3	12.	0.045	2.7	0.27	0.047
1 1 1	5.50(-3)	16.	3.4	0.089	7.4	0.73	0.11
1 2 2	6.70(-3)	25.	3.2	0.41	7.8	0.86	0.29
1 3 3	1.49(-3)	19.	592.	0.23	11.	2.2	0.93

TABLE V
Convergence checks for $D + H_2$, $HD + H$, $J = 1$, $P = -1$

v j ℓ	$P_{v j \ell}$ m=16,C	percentage deviation					
		m=3,R	m=5,R	m=7,R	m=3,C	m=5,C	m=7,C
0 0 1	6.14(-1)	2.3	0.15	0.15	0.99	0.29	0.046
0 1 2	7.62(-1)	0.024	0.016	0.086	0.85	0.24	0.0063
0 2 3	6.74(-1)	1.2	0.31	0.16	0.60	0.082	0.000088
0 3 4	6.50(-1)	0.083	0.24	0.017	0.45	0.15	0.050
0 4 5	6.40(-1)	0.48	0.20	0.10	0.27	0.33	0.031
0 5 6	4.89(-1)	0.25	0.41	0.044	0.45	0.59	0.061
0 6 7	2.25(-1)	1.2	0.22	0.17	1.2	0.32	0.18
0 7 8	4.33(-2)	3.1	0.19	0.047	2.2	0.15	0.031
0 9 8	4.56(-5)	1.5	1.5	0.54	2.4	1.4	0.43
1 1 0	1.55(-1)	5.2	0.52	0.26	3.1	0.99	0.66
1 2 1	6.27(-2)	1.1	1.1	0.16	6.0	0.67	0.41
1 3 2	6.07(-3)	15.	4.7	1.2	14.	5.0	0.42

extent—for $m = 10$ and only for the real boundary conditions. No such instabilities have been observed in calculations with complex boundary conditions.

6. Concluding Remarks

With sufficient attention to algorithmic efficiency, it has become possible to solve very large-scale problems in quantum mechanical reaction dynamics. Section 5.2 discusses calculations on the reaction $D + H_2(v=0,1) \rightarrow HD + H$ both for $J = 0$ (see also Refs. 13, 14, and 36) and $J \neq 0$, and, in previous work using the techniques described here, as well as earlier nonvariational and variational algorithms for \mathcal{L}^2 expansions of the reactive amplitude density, we and coworkers have performed converged calculations of several other reactive processes, including, for $J = 0$, $H + H_2(v=0-2) \rightarrow H_2(v'=0-2) + H$,^{19,20,31-33,39} $O + H_2(v=0,1) \rightarrow OH(v'=0,1) + H$,^{15,34,36} $H + HBr(v=0) \rightarrow H_2(v'=0,1,2) + Br$,^{35,39} and $Cl + H_2(v=0) \rightarrow HCl(v'=0) + H$.⁵⁸ We have also obtained accurate results for $H + H_2(v=0,1) \rightarrow H_2(v'=0,1) + H$ for $J = 0-20$,³³ and accurate results have been obtained for $O + HD(v=0) \rightarrow OH(v'=0) + D$ and $OD(v'=0) + H$ for $J = 0-2$.³⁹ We anticipate further improvements in several areas, e.g., more efficient strategies for the Green's functions, better basis sets, and physical or decoupling approximations as initial guesses for iterative techniques. These improvements should allow even more progress in the future.

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