

## LINEAR ALGEBRAIC FORMULATION OF REACTIVE SCATTERING WITH GENERAL BASIS FUNCTIONS

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### ABSTRACT

This chapter provides a self-contained description of the formulation and computational implementation of the outgoing wave variational principle for inelastic and reactive scattering. In particular, we present extensions that allow the treatment of multiple electronic surfaces and the use of basis functions that are not eigenfunctions of the noninteracting (asymptotic) Hamiltonian. The choice of a diabatic electronic representation is used to simplify the treatment of multiple electronic states. The chapter presents the details of the matrix elements required when half-integrated Green's functions, asymptotic eigenfunctions, and general square-integrable basis functions are simultaneously included in a multiple-arrangement, multiple-electronic-state basis.

### 1. INTRODUCTION

The calculation of converged quantum dynamics for atom-diatom reactions on realistic potential energy surfaces was solved for colinear collisions around 1970 [1,2] and for coplanar [3] and three-dimensional [4-6] collisions around 1975. The first accurate three-dimensional calculations involved the H + H<sub>2</sub> reaction at low energies and were converged for total angular momentum zero. About ten years later accurate calculations were available for heavier atoms and higher energies [7,8], nonzero total angular momentum [9], and nonsymmetric reactions (both initial and final diatomic heteronuclear) [10,11]. Now there are several

groups applying accurate quantum dynamics to a variety of atom-diatom reactions [12].

Although there are many new results in the literature, and many more problems could be treated by existing methods, there is still plenty of room for improving efficiency, for example, by improving the basis functions. One class of atom-diatom reactions for which converged three-dimensional quantum dynamics calculations are still unavailable is the class of reactions involving two or more electronic states, or—equivalently—two or more coupled potential energy surfaces. Reactions involving two electronic states are the prototype for “photochemical” reactions in organic chemistry, and their accurate treatment, which will require efficient basis sets, may be expected to yield qualitatively new insights into chemical reactivity.

In the present paper we present a formalism for treating reactions with very general basis functions including electronically excited states. Our formalism is based on the generalized Newton [13–18], scattered wave [19–21], and outgoing wave [20,22] variational principles that we have used previously for reactive collisions on a single potential energy surface (for recent applications see Refs. [23–29]), and it incorporates three new features:

1. The basis functions include electronic degrees of freedom [30] as required to treat reactions involving electronic excitation and two or more coupled potential energy surfaces.
2. The primitive electronic basis is assumed to be diabatic [31], and we do not assume that it diagonalizes the electronic Hamiltonian even asymptotically.
3. Contracted basis functions for vibrational–rotational–orbital degrees of freedom are included in a very general way, similar to previous prescriptions for locally adiabatic functions [32] in various quantum scattering algorithms.

We also allow for contracted translational basis functions as treated previously [18,33,34].

Since the description of the algorithms used and numerical techniques involved in our current single-surface quantal reactive dynamics codes is spread out over several different references [8,18,22,27,35,36], each of which presents new aspects developed since the previous paper without repeating most of the previous material, it is becoming somewhat inconvenient for a new researcher to understand how all the parts

fit together, except by reading the papers in chronological order. One goal of the present paper, therefore, is to summarize the equations and methods that have evolved in a more logically organized way. Since our single-surface methods are a special case of the multiple-surface formalism, the present paper provides an opportunity to do this, and we will indeed capitalize on this opportunity. Thus the present paper summarizes the current status of our code, including all the most useful options but omitting some older variants of the numerical methods that appear less useful in the present context.

Section 2 reviews the variational principles and presents the notation for the variational trial function. Section 3 presents a special case of the new formalism for single-arrangement scattering. Section 4 provides the equations for the case of multiple-arrangement scattering. Section 5 summarizes our current numerical algorithms for all the steps of the calculation. Section 6 offers an analysis of the memory resources needed to implement the algorithms discussed in Section 5. Section 7 gives conclusions.

## 2. VARIATIONAL PRINCIPLES

### 2.1. Partitioning the Hamiltonian

The technique we are developing for converged quantum dynamics calculations in the present paper is the outgoing wave variational principle [20,22] (OWVP), which is a generalization of the Newton variational principle [13–18] and which is identical to the scattered wave variational principle [19–21] except that  $S$ -matrix boundary conditions are used instead of  $T$ -matrix boundary conditions. This linear algebraic variational method involves several steps:

1. The full Hamiltonian  $H$  is split into a distortion Hamiltonian, which contains the distortion potential  $V^D$ , and a coupling potential  $V^C$ . We employ a combination of rotationally coupled multichannel distortion potentials for low rotational states and single-state or single-channel distortion potentials for high rotational states.
2. The regular solution,  $\psi^{\text{reg}}$ , of the distorted-wave equation is determined by the finite difference boundary value method (FDBVM). The distorted-wave scattering matrix and the auxiliary functions

involving the distorted-wave Green's functions are also computed by this method.

3. The outgoing wave,  $\Psi_{ow}$ , is expanded in basis functions  $\tilde{\Gamma}_\beta$  and matrix elements of the form  $\langle \tilde{\Gamma}_\beta | V^C | \Psi^{in} \rangle$  and  $\langle \tilde{\Gamma}_\beta | (E - H) | \tilde{\Gamma}_\beta \rangle$  are computed.
4. Using a stationary functional for the scattering matrix and solving a linear algebraic problem involving the matrix elements of step (3), we can calculate all the desired state-to-state transition probabilities, which are functions of the scattering matrix elements.

The great advantage of this method is its efficiency in terms of basis set requirements. The basis functions  $\tilde{\Gamma}_\beta$  are taken to be of the form:

$$\tilde{\Gamma}_\beta(R_{\alpha\beta}, \mathbf{x}_{\alpha\beta}) = R_{\alpha\beta}^{-1} \sum_{\gamma=1}^{\delta_\beta} \tilde{c}_{\beta\gamma} \tilde{q}_{\beta\gamma}(R_{\alpha\beta}) \tilde{\varphi}_{\beta\gamma}(\mathbf{x}_{\alpha\beta}), \quad (2.1)$$

where  $R_{\alpha\beta}$  is a mass-scaled relative radial translational coordinate in arrangement  $\alpha_\beta$ ,  $\mathbf{x}_{\alpha\beta}$  is a collection of all other coordinates,  $\tilde{c}_{\beta\gamma}$  is a contraction coefficient,  $\tilde{q}_{\beta\gamma}$  is a general radial function,  $\tilde{\varphi}_{\beta\gamma}$  is a general internal electronic-vibrational-rotational-orbital function, and  $\gamma$  labels a term in this very general basis function. Equation (2.1) introduces a convention that we will follow throughout this paper, that is, complex quantities have tildes, unless they have a (+) or (-) superscript, which automatically denotes complex as well, and except for the various scattering matrices, which are also complex by definition. In applications carried out so far,  $\tilde{\varphi}_{\beta\gamma}$  has been chosen to be an asymptotic electronic-vibrational-rotational-orbital function  $\tilde{\varphi}_{n_r}$ . Since this is built from electronic functions times a linear combination of primitive harmonic oscillator vibrational functions times rotational-orbital angular functions, it may be called a contracted internal function. When the  $\tilde{\Gamma}_\beta$  basis is chosen in a special way, discussed below, the OWVP can be shown [20] to be equivalent to the generalized Newton variational principle (GNVP) [17,18,35,36].

In the present paper we make two important changes in the basis functions as compared to previous GNVP and OWVP calculations—one change in the primitive vibrational basis and one change in the way the contracted internal function  $\tilde{\Gamma}_\beta$  is defined. The new variational formulation, like the previous one, is based on the simultaneous use of three Hamiltonian partitionings [37]

$$H = H_\alpha^D + V_\alpha^C, \quad \alpha = 1, 2, 3, \quad (2.2)$$

where  $\alpha$  denotes the chemical arrangement ( $\alpha = 1$  for A + BC,  $\alpha = 2$  for B + AC, and  $\alpha = 3$  for C + AB),  $H_\alpha^D$  is a distortion Hamiltonian that includes no interarrangement coupling but an appreciable part of (or all of) the intra-arrangement coupling in arrangement  $\alpha$ , and  $V_\alpha^C$  is a coupling potential which includes the rest of the intra-arrangement coupling and all of the interarrangement coupling. The ability to treat multiarrangement reactive scattering is a critical element of the whole formulation, but many of the differences of the new formulation in terms of general basis functions from our earlier formulations involving [10,18,35,36] an asymptotic eigenstate basis are clear for single-arrangement scattering so we present the detailed equations first for that case. In particular we set  $\alpha = 1$  and suppress the  $\alpha$  index in the notation until Section 4 (thus, e.g., the radial translational coordinate  $R_\alpha$  becomes  $R$  and the collection of all other coordinates  $\mathbf{x}_\alpha$  becomes  $\mathbf{x}$ , and so on). We note that although the scattered wave variational principle [19–21] (SWVP) for the transition ( $T$ ) matrix and the outgoing wave variational principle [20,22] for the scattering ( $S$ ) matrix differ in their boundary conditions, they yield equivalent results. Our code uses the OWVP, and so we will present the equations in that form.

The boundary conditions used to define the scattering matrix we wish to calculate are expressed in a space-fixed coordinate frame (sometimes called a laboratory-fixed frame). Nevertheless, we can use basis functions defined either in the space frame or in a body-fixed coordinate frame (sometimes called a molecule-fixed frame). This choice determines whether we apply the variational principle in the space or body frame; if the latter, the scattering matrix is transformed to the space frame after the variational calculation. In either case cross sections are calculated using a space-frame scattering matrix [9c,35]. Even when space-frame basis functions are used, the angular part of the exchange integrals (i.e., those involving functions expressed in two different sets of arrangement coordinates) is carried out in the body frame. The best choice of frame for the basis set depends on the specific problem to be solved. Our algorithms can take advantage of either choice, and the frame-dependent aspects of the formalism itself are slight. The initial presentation in this paper will, for the purpose of clarity, consider only the space frame for the basis functions. The differences in the calculation when body-frame basis functions are used are given in Sections 5.2, 5.4, 5.5, and 5.10.

We will use diabatic electronic basis functions, which we will denote by  $X_\chi(\mathbf{x}_e; R, \omega)$ . In this paper we assume that the electronic functions are real, and we neglect electronic angular momentum.  $X_\chi$  is a function of

the electronic coordinates,  $\mathbf{x}_e$ , and it depends parametrically on the nuclear coordinates,  $R$  and  $\omega$ . Notice that the full collection of coordinates consists of  $R$ ,  $\omega$ , and  $\mathbf{x}_e$ . The collective coordinate  $\mathbf{x}$  introduced below Eq. (2.2) denotes the union of the  $\omega$  and  $\mathbf{x}_e$  coordinate sets. Since the electronic functions are diabatic, there are no derivative couplings; effectively:

$$\mathbf{p}X_\chi(\mathbf{x}_e; R, \omega) = 0, \quad (2.3)$$

where  $\mathbf{p}$  is a nuclear momentum (defined more precisely below); however, the potential matrix for nuclear motion is nondiagonal in the diabatic quantum number  $\chi$  [31].

Bras and kets in the electronic space are denoted by  $\{\chi|$  and  $|\chi\rangle$ , respectively, such that

$$\langle \mathbf{x}_e | \chi \rangle = X_\chi(\mathbf{x}_e; R, \omega) \quad (2.4)$$

and

$$\langle \chi | \mathbf{x}_e \rangle = X_\chi(\mathbf{x}_e; R, \omega). \quad (2.5)$$

Note that the metric scalar product in the diabatic basis is

$$\int d\mathbf{x}_e X_\chi(\mathbf{x}_e; R, \omega) X_\chi(\mathbf{x}_e; R, \omega) = \delta_{\chi\chi'}, \quad (2.6)$$

and the multiple-electronic-state scattering problem in the electronic-plus-nuclear space is equivalent to a multiple-electronic-surface scattering problem in the nuclear coordinates, where the potential is

$$V = \sum_{\chi} \sum_{\chi'} |\chi\rangle V_{\chi\chi'}(R, \omega) \langle \chi'|, \quad (2.7)$$

where

$$V_{\chi\chi'}(R, \omega) = \int d\mathbf{x}_e X_\chi(\mathbf{x}_e; R, \omega) \hat{H}^{EN} X_{\chi'}(\mathbf{x}_e; R, \omega), \quad (2.8)$$

and  $\hat{H}^{EN}$  is the sum of the electronic Hamiltonian and the nuclear repulsion. We note that

$$V_{\chi\chi'} = V_{\chi'\chi}. \quad (2.9)$$

As a consequence of Eqs. (2.3) and (2.7), all electronic integrals reduce to the one simple integral (2.6), and we do not have to work with the electronic wavefunctions.

In order to express the boundary conditions, we will also need to define an adiabatic basis. Let  $\bar{\chi}$  be an adiabatic [31] electronic quantum

number. The adiabatic basis is related to the diabatic basis via the transformation,

$$X_{\bar{\chi}} = \sum_{\chi} X_\chi(\mathbf{x}_e; R, \omega) U_{\chi\bar{\chi}}(R, \omega), \quad (2.10)$$

where  $U$  is an orthogonal matrix chosen such that

$$\langle \bar{\chi} | V | \bar{\chi}' \rangle = \delta_{\bar{\chi}\bar{\chi}'} \bar{V}_{\bar{\chi}\bar{\chi}'}(R, \omega), \quad (2.11)$$

and  $\bar{V}$  is an adiabatic potential energy surface. For single-surface scattering, there is only one  $\chi$  and one  $\bar{\chi}$  so  $V = V_{11} = \bar{V}_{11}$ .

We now consider nonreactive atom-diatom collisions of an atom  $A$  with a diatomic molecule  $BC$ . In this case the Hamiltonian is given by

$$H = T + V, \quad (2.12)$$

where  $T$  is the nuclear kinetic energy operator, and  $V$  is the potential energy defined by Eq. (2.7).  $T$  is given by

$$T = \frac{1}{2\mu} \mathbf{p} \cdot \mathbf{p}, \quad (2.13)$$

where  $\mu$  is the symmetrized reduced mass given by [38]

$$\mu = \left( \frac{m_A m_B m_C}{m_A + m_B + m_C} \right)^{1/2}, \quad (2.14)$$

and  $m_X$  is the mass of atom  $X$ . The 6-dimensional nuclear momentum in the center-of-mass frame is

$$\mathbf{p} = -i\hbar \begin{pmatrix} \nabla_R \\ \nabla_r \end{pmatrix}, \quad (2.15)$$

where

$$\mathbf{R} = M\mathbf{S}, \quad (2.16)$$

$$\mathbf{r} = M^{-1}\mathbf{s}, \quad (2.17)$$

$$M = \left( \frac{m_A(m_B + m_C)^2}{m_B m_C(m_A + m_B + m_C)} \right)^{1/4}, \quad (2.18)$$

$\mathbf{S}$  is the vector from the diatom mass center to the lone atom,  $A$ , and  $\mathbf{s}$  is the vector directed from  $B$  to  $C$ .

We next proceed by partitioning the Hamiltonian as

$$H = T + V^{\text{vib}} + V^{\text{int}}, \quad (2.19)$$

where  $V^{\text{int}}$  is the interaction potential, the vibrational potential is given by

$$V^{\text{vib}} = \lim_{R \rightarrow \infty} V, \quad (2.20)$$

and the interaction potential is given by

$$V^{\text{int}} = V - V^{\text{vib}}. \quad (2.21)$$

The asymptotic Hamiltonian is

$$H^A = T + V^{\text{vib}}. \quad (2.22)$$

The asymptotic eigenfunctions  $\tilde{\phi}_n$  must satisfy

$$H^A \tilde{\phi}_n(\mathbf{x}) = \epsilon_n \tilde{\phi}_n(\mathbf{x}), \quad (2.23)$$

where  $n$  is a channel index, and  $\epsilon_n$  is a diatomic eigenvalue. The channel index,  $n$ , represents the set of quantum numbers  $\chi, \nu, j$ , and  $l$ , where  $\chi$  is an adiabatic electronic quantum number,  $\nu$  is the vibrational quantum number,  $j$  is the rotational quantum number, and  $l$  is the orbital quantum number (i.e., the angular momentum quantum number associated with the angular part of  $\mathbf{R}$ ). Notice that  $\mathbf{x}$  includes the angular part of the relative translational motion, and so in general there is more than one channel associated with a given asymptotic eigenstate. Although we do not need this property until Section 3 we note here that in this chapter, the space-frame functions,  $\tilde{\phi}_n$ , are also assumed to be eigenstates of the square of the orbital angular momentum operator  $\hat{L}^2$  for relative translational motion of A with respect to BC. In particular the channel eigenstates,  $\tilde{\phi}_n$ , are taken to be a product of an Arthurs–Dalgarno rotational–orbital function [39] (which depends on  $j, l$ , the total angular momentum quantum number  $J$ , and the quantum number  $M$  for the projection of the total angular momentum) and an adiabatic electronic–vibrational function (which is labeled by  $\chi, \nu$ , and  $j$ ).

Now we partition the interaction potential into a distortion potential and a coupling potential

$$V^{\text{int}} = V^D + V^C. \quad (2.24)$$

The distortion potential is defined by partitioning the channels into disjoint sets called distortion blocks. Then if  $\Delta_{nn'}$  is a coupling parameter which is unity if channels  $n$  and  $n'$  are in the same distortion block and zero otherwise, we define the distortion potential as

$$V^D(R) = \sum_n \sum_{n'} \Delta_{nn'} | \tilde{\phi}_n \rangle V_{nn'}^{\text{int}}(R) \langle \tilde{\phi}_{n'} |, \quad (2.25)$$

where

$$V_{nn'}^{\text{int}}(R) = \int d\mathbf{x} \tilde{\phi}_n^*(\mathbf{x}) V^{\text{int}} \tilde{\phi}_{n'}(\mathbf{x}). \quad (2.26)$$

The coupling potential is given by

$$V^C = V^{\text{int}} - V^D, \quad (2.27)$$

and the distorted-wave Hamiltonian is defined by

$$H^D = T + V^{\text{vib}} + V^D \quad (2.28)$$

in terms of which the full Hamiltonian is written as

$$H = H^D + V^C. \quad (2.29)$$

The Schrödinger equation for the wavefunction which satisfies outgoing wave scattering boundary conditions is

$$(H^D + V^C)\Psi^{(+n_0)} = E\Psi^{(+n_0)}, \quad (2.30)$$

where  $n_0$  denotes the initial channel. This wavefunction satisfies the Lippmann–Schwinger [40] integral equation

$$\Psi^{(+n_0)} = \psi^{(+n_0)} + G^{D(+)} \mathcal{U} \Psi^{(+n_0)}, \quad (2.31)$$

where  $G^{D(\pm)}$  is the distorted-wave Green's operator defined by

$$G^{D(\pm)} = \lim_{\epsilon \rightarrow 0^+} -\frac{\hbar^2}{2\mu} \left( E - H^D \pm i\epsilon \right)^{-1}, \quad (2.32)$$

the coupling operator,  $\mathcal{U}$ , is given by

$$\mathcal{U} = -\frac{2\mu}{\hbar^2} V^C, \quad (2.33)$$

and  $\psi^{(+n_0)}$  is a regular distorted wave, i.e., a solution of

$$(H^D + E)\psi^{(+n_0)} = 0. \quad (2.34)$$

The regular distorted waves have the form

$$\psi^{(+n_0)}(R, \mathbf{x}) = \frac{1}{R} \sum_n \Delta_{nn_0} {}^{(r)}f_{\hbar n_0}^{(+)}(R) \tilde{\phi}_n(\mathbf{x}), \quad (2.35)$$

where  ${}^{(r)}f_{\hbar n_0}^{(+)}$  is a regular distorted-wave radial function,  $n_0$  is the initial channel, and  $n$  is the final channel.

If we left multiply Eq. (2.34) by  $(-2\mu R/\hbar^2)\tilde{\phi}_n^*(\mathbf{x})$ , substitute Eq. (2.35) into that result, and then integrate over the coordinates  $\mathbf{x}$ , we obtain the set of coupled differential equations for the regular radial functions

$$\left\{ \frac{d^2}{dR^2} - \frac{l_n(l_n + 1)}{R^2} + k_n^2 \right\} {}^{(r)}f_{n_0}^{(+)}(R) = -\sum_{n'} \Delta_{n'n} U_{n'n}(R) {}^{(r)}f_{n_0}^{(+)}(R), \quad (2.36)$$

which are subject to the boundary conditions

$${}^{(r)}f_{n_0}^{(+)}(R) \sim 0 \quad R \rightarrow 0 \quad (2.37)$$

and

$${}^{(r)}f_{n_0}^{(+)}(R) \sim \begin{cases} \left( \frac{1}{2ik_n} \right)^{1/2} \left\{ \begin{array}{l} \delta_{nn_0} \exp[-i(k_n R - l_n \pi/2)] \\ -{}^0S_{nn_0} \Delta_{nn_0} \exp[i(k_n R - l_n \pi/2)] \end{array} \right\}, & k_n^2 > 0, \\ i \left( \frac{1}{2|k_n|} \right)^{1/2} \left\{ \begin{array}{l} \delta_{nn_0} \exp[|k_n|(R - R_f)] \\ -{}^0S_{nn_0} \Delta_{nn_0} \exp[-|(k_n| R - R_f)] \end{array} \right\}, & k_n^2 < 0, \end{cases} \quad (2.38)$$

Here the channel wavenumber,  $k_n$ , is defined by

$$k_n = \frac{[2\mu(E - \epsilon_n)]^{1/2}}{\hbar}, \quad (2.39)$$

${}^0S_{nn_0}$  is an element of the extended scattering matrix for the distorted-wave problem,  $R_f$  is arbitrary, and

$$U_{n'n}(R) = -\frac{2\mu}{\hbar^2} V_{n'n}^{\text{int}}(R). \quad (2.40)$$

The extended scattering matrix is defined over the range of all channel indices such that the submatrix corresponding to both matrix indices being open channels is the scattering matrix, and the rest of the matrix is a generalization of the scattering matrix to closed channels.

The scattering matrix for the full problem is calculated from

$$S_{nn_0} = {}^0S_{nn_0} + \mathcal{S}_{nn_0}, \quad (2.41)$$

where  $n$  and  $n_0$  are the final and initial channels, respectively,  ${}^0S_{nn_0}$  is the contribution to the scattering matrix element due to the distortion potential, that is, it is a distorted-wave scattering matrix element, and  $\mathcal{S}_{nn_0}$  is the contribution to the scattering matrix element due to the coupling potential which is given by

$$\mathcal{S}_{nn_0} = \langle \Psi^{(-)n} | \mathcal{U} | \Psi^{(+n_0)} \rangle, \quad (2.42)$$

where  $\Psi^{(-)n}$  is a distorted wave with incoming boundary conditions. We obtain the distorted-wave scattering matrix from the large- $R$  behavior of the distorted wave using Eq. (2.38). The contribution to the scattering matrix due to the coupling potential, however, is obtained variationally, as discussed next.

## 2.2. Generalized Newton Variational Principle for $\mathcal{S}_{nn_0}$

We start by defining the amplitude density [41] as

$$\zeta^{(\pm)n_0} = \mathcal{U} \Psi^{(\pm)n_0}, \quad (2.43)$$

in terms of which the Lippmann-Schwinger equation is written

$$\zeta^{(+n_0)} = \mathcal{U} \Psi^{(+n_0)} + \mathcal{U} G^{D(+)} \zeta^{(+n_0)} \quad (2.44)$$

and the scattering matrix due to the coupling potential is written as

$$\mathcal{S}_{nn_0} = \langle \Psi^{(-)n} | \zeta^{(+n_0)} \rangle, \quad (2.45)$$

where the scalar product  $\langle \cdot |$  represents integration over all the coordinates  $R$  and  $\mathbf{x}$ . Substituting Eq. (2.44) into Eq. (2.45), we obtain

$$\mathcal{S}_{nn_0} = \langle \Psi^{(-)n} | \mathcal{U} | \Psi^{(+n_0)} \rangle + \langle \Psi^{(-)n} | \mathcal{U} G^{D(+)} | \zeta^{(+n_0)} \rangle. \quad (2.46)$$

Then from Eqs. (2.44) and (2.46) we obtain [21]

$$\begin{aligned} \mathcal{S}_{nn_0} = & \langle \Psi^{(-)n} | \mathcal{U} | \Psi^{(+n_0)} \rangle + \langle \Psi^{(-)n} | \mathcal{U} G^{D(+)} | \zeta^{(+n_0)} \rangle + \langle \zeta^{(-)n} | G^{D(+)} \mathcal{U} | \Psi^{(+n_0)} \rangle \\ & - \langle \zeta^{(-)n} | G^{D(+)} | \zeta^{(+n_0)} \rangle + \langle \zeta^{(-)n} | G^{D(+)} \mathcal{U} G^{D(+)} | \zeta^{(+n_0)} \rangle, \end{aligned} \quad (2.47)$$

which is the GNVP for the scattering matrix in terms of the amplitude density.

Expression (2.47) is more useful than (2.45) because it can be shown that (2.47) is correct to second order in the error of the amplitude density [21]. Thus for good estimates of the amplitude density the error in the scattering matrix will be small.

## 2.3. Outgoing Wave Variational Principle for $\mathcal{S}_{nn_0}$

We define the outgoing wave as

$$\Psi_{\text{OW}}^{(+n_0)} = G^{D(+)} \zeta^{(+n_0)}, \quad (2.48)$$

which is the second term of the Lippmann–Schwinger Eq. (2.31). When Eq. (2.48) is substituted into Eq. (2.47), we obtain

$$\begin{aligned} \mathcal{S}_{n_0} = & \langle \psi^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle + \langle \psi^{(-)n} | \mathcal{U} | \Psi_{\text{OW}}^{(+n_0)} \rangle + \langle \Psi_{\text{OW}}^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle \\ & - \langle \zeta^{(-)n} | \Psi_{\text{OW}}^{(+n_0)} \rangle + \langle \Psi_{\text{OW}}^{(-)n} | \mathcal{U} | \Psi_{\text{OW}}^{(+n_0)} \rangle. \end{aligned} \quad (2.49)$$

Now we insert  $G^{D(+)}(G^{D(+)}-1)^{-1}$  into the fourth term on the right-hand side of Eq. (2.49) to obtain

$$\langle \zeta^{(-)n} | \Psi_{\text{OW}}^{(+n_0)} \rangle = \langle \zeta^{(-)n} | G^{D(+)}(G^{D(+)}-1)^{-1} | \Psi_{\text{OW}}^{(+n_0)} \rangle \quad (2.50)$$

and by using Eq. (2.48) we obtain

$$\langle \zeta^{(-)n} | \Psi_{\text{OW}}^{(+n_0)} \rangle = \langle \Psi_{\text{OW}}^{(-)n} | (G^{D(+)}-1)^{-1} | \Psi_{\text{OW}}^{(+n_0)} \rangle. \quad (2.51)$$

Putting Eq. (2.51) back into Eq. (2.49) and using Eqs. (2.29), (2.32), and (2.33), we obtain

$$\begin{aligned} \mathcal{S}_{n_0} = & \langle \psi^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle + \langle \psi^{(-)n} | \mathcal{U} | \Psi_{\text{OW}}^{(+n_0)} \rangle + \langle \Psi_{\text{OW}}^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle \\ & - \langle \Psi_{\text{OW}}^{(-)n_0} | \frac{2\mu}{\hbar^2} (H - E) | \Psi_{\text{OW}}^{(+n_0)} \rangle, \end{aligned} \quad (2.52)$$

which is the OWVP for the scattering matrix. As with the GNVP for the scattering matrix, it can be shown that Eq. (2.52) is correct to second order in the error of the outgoing wave. (The proof is entirely analogous to that for the SWVP in Ref. [21].) Thus for good estimates of the outgoing wave, the error in the scattering matrix will be small.

#### 2.4. Relationship of the GNVP to the OWVP

In previous work we considered a trial amplitude density that is expanded in  $\mathcal{L}^2$  basis functions as follows:

$$\zeta^{(+n)}(R, \mathbf{x}) = \sum_{\beta} \tilde{A}_{\beta n} \tilde{\Phi}_{\beta}(R, \mathbf{x}). \quad (2.53)$$

Here  $\tilde{\Phi}_{\beta}$  is a product basis function, which has the form

$$\tilde{\Phi}_{\beta}(R, \mathbf{x}) = \frac{1}{R} t_{m_{\beta} n_{\beta}}(R) \tilde{\Phi}_{n_{\beta}}(\mathbf{x}), \quad (2.54)$$

where  $t_{m_{\beta} n_{\beta}}$  is the translational part of the basis function, and  $\tilde{\Phi}_{n_{\beta}}(\mathbf{x})$  is a particular channel eigenstate. Throughout the paper  $\beta$  is a collective index that specifies a basis function. For a basis function like the one in

Eq. (2.54) it specifies the set of quantum numbers  $\bar{\chi}_{\beta}$ ,  $\nu_{\beta}$ ,  $j_{\beta}$ ,  $l_{\beta}$ , and the parameter  $m_{\beta}$  that labels translational radial basis functions; therefore,  $\beta$  specifies an  $n, m$  pair which is conveniently denoted  $n_{\beta}, m_{\beta}$ . In Eq. (2.53)  $\beta$  ranges from 1 to the total number of basis functions included in the expansion. When (2.53) and its adjoint are substituted into (2.47) we obtain

$$\begin{aligned} \mathcal{S}_{n_0} = & \langle \psi^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle + \sum_{\beta} \tilde{A}_{\beta n_0} \langle \psi^{(-)n} | \mathcal{U} G^{D(+)} | \tilde{\Phi}_{\beta} \rangle \\ & + \sum_{\beta} \tilde{A}_{\beta n} \langle \tilde{\Phi}_{\beta} | G^{D(+)} \mathcal{U} | \psi^{(+n_0)} \rangle \\ & - \sum_{\beta\beta'} \tilde{A}_{\beta n_0} \tilde{A}_{\beta' n} \langle \tilde{\Phi}_{\beta} | G^{D(+)} - G^{D(+)} \mathcal{U} G^{D(+)} | \tilde{\Phi}_{\beta'} \rangle. \end{aligned} \quad (2.55)$$

We next introduce a convenient notation [21] for the complex non- $\mathcal{L}^2$  function defined by

$$\hat{g}_{\beta}^{(+)} = G^{D(+)} \tilde{\Phi}_{\beta} \quad (2.56)$$

and its adjoint

$$\hat{g}_{\beta}^{(-)} = \tilde{\Phi}_{\beta}^* G^{D(+)} \quad (2.57)$$

These functions will be called half-integrated Green's functions (HIGFs). From Eqs. (2.32) and (2.56) we obtain the following nonhomogeneous differential equation for the half-integrated Green's function

$$\frac{2\mu}{\hbar^2} (H^D - E) \hat{g}_{\beta}^{(+)} = \tilde{\Phi}_{\beta}. \quad (2.58)$$

With this new notation, Eq. (2.55) may be written

$$\begin{aligned} \mathcal{S}_{n_0} = & \langle \psi^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle + \sum_{\beta} \tilde{A}_{\beta n_0} \langle \psi^{(-)n} | \mathcal{U} | \hat{g}_{\beta}^{(+)} \rangle \\ & + \sum_{\beta} \tilde{A}_{\beta n} \langle \hat{g}_{\beta}^{(-)} | \mathcal{U} | \psi^{(+n_0)} \rangle \\ & - \sum_{\beta\beta'} \tilde{A}_{\beta n_0} \tilde{A}_{\beta' n} \langle \hat{g}_{\beta}^{(-)} | \frac{2\mu}{\hbar^2} (H - E) | \hat{g}_{\beta'}^{(+)} \rangle. \end{aligned} \quad (2.59)$$

This bilinear form of the variational functional may be used to obtain the variationally correct scattering matrix as discussed below.

We can also obtain Eq. (2.59) from the OWVP. To do this we expand the outgoing wave in an HIGF basis

$$\Psi_{\text{OW}}^{(+n)} = \sum_{\beta} \tilde{A}_{\beta} \hat{\beta}^{(+)} \quad (2.60)$$

and use (2.52). Thus the GNVP expression and the OWVP expression for the scattering matrix are identical if one expands the amplitude density in an  $\mathcal{L}^2$  product basis in the GNVP case, and one expands the outgoing wave in a derived non- $\mathcal{L}^2$  HIGF basis in the OWVP case. The OWVP, though, may also be used with more general basis functions, of which Eq. (2.60) is a special case.

In the present paper we will expand the outgoing wave in a set of general basis functions

$$\Psi_{\text{OW}}^{(+n)} = \sum_{\beta} \tilde{A}_{\beta n} \tilde{\Gamma}_{\beta} \quad (2.61)$$

where the  $\tilde{\Gamma}_{\beta}$  are defined in Eq. (2.1).

## 2.5. Obtaining the Expansion Coefficients and Scattering Matrix

Substituting Eq. (2.61) into Eq. (2.52), we obtain

$$\begin{aligned} \mathcal{S}_{n n_0} = & \mathcal{S}_{n n_0}^B + \sum_{\beta} \langle \Psi^{(-n)} | \mathcal{U} | \tilde{\Gamma}_{\beta} \rangle \tilde{A}_{\beta n_0} + \sum_{\beta} \tilde{A}_{\beta n} \langle \tilde{\Gamma}_{\beta} | \mathcal{U} | \Psi^{(+n_0)} \rangle \\ & - \sum_{\beta \beta'} \tilde{A}_{\beta n} \langle \tilde{\Gamma}_{\beta} | \frac{2\mu}{\hbar^2} (H - E) | \tilde{\Gamma}_{\beta'} \rangle \tilde{A}_{\beta' n_0} \end{aligned} \quad (2.62)$$

or in matrix form

$$\mathcal{S} = \mathcal{S}^B + \tilde{\mathbf{B}}^T \tilde{\mathbf{A}} + \tilde{\mathbf{A}}^T \tilde{\mathbf{C}} - \tilde{\mathbf{A}}^T \tilde{\mathbf{C}} \tilde{\mathbf{A}}, \quad (2.63)$$

where  $\mathcal{S}^B$  is the distorted-wave Born approximation to the scattering matrix with matrix elements given by

$$\mathcal{S}_{n n_0}^B = \langle \Psi^{(-n)} | \mathcal{U} | \Psi^{(+n_0)} \rangle \quad (2.64)$$

and the matrix elements of  $\tilde{\mathbf{B}}$  and  $\tilde{\mathbf{C}}$  are given by

$$\tilde{B}_{\beta n_0} = \langle \tilde{\Gamma}_{\beta} | \mathcal{U} | \Psi^{(+n_0)} \rangle, \quad (2.65)$$

and

$$\tilde{C}_{\beta \beta'} = \langle \tilde{\Gamma}_{\beta} | \frac{2\mu}{\hbar^2} (H - E) | \tilde{\Gamma}_{\beta'} \rangle, \quad (2.66)$$

respectively. By virtue of Eqs. (2.29), (2.33), and (2.34) we can rewrite  $\mathcal{S}^B$  and  $\tilde{\mathbf{B}}$  as

$$\mathcal{S}_{n n_0}^B = \langle \Psi^{(-n)} | \frac{2\mu}{\hbar^2} (E - H) | \Psi^{(+n_0)} \rangle \quad (2.67)$$

and

$$\tilde{B}_{\beta n_0} = \langle \tilde{\Gamma}_{\beta} | \frac{2\mu}{\hbar^2} (E - H) | \Psi^{(+n_0)} \rangle. \quad (2.68)$$

Now we require that  $\mathcal{S}_{n n_0}$  be stationary with respect to changes in the coefficients,  $\tilde{A}_{\beta n}$ , that is,

$$\frac{\partial \mathcal{S}_{n n_0}}{\partial \tilde{A}_{\beta n'}} = 0; \quad n' = n_0 \text{ or } n; \quad \text{all } n, n_0, \beta. \quad (2.69)$$

This yields

$$\tilde{\mathbf{A}} = \tilde{\mathbf{C}}^{-1} \tilde{\mathbf{B}}, \quad (2.70)$$

and putting this into Eq. (2.63), we obtain

$$\mathcal{S} = \mathcal{S}^B + \tilde{\mathbf{B}}^T \tilde{\mathbf{C}}^{-1} \tilde{\mathbf{B}}, \quad (2.71)$$

which is the scattering matrix due to the coupling potential. The full scattering matrix is given by

$$\mathbf{S} = {}^0\mathbf{S} + \mathcal{S}^B + \tilde{\mathbf{B}}^T \tilde{\mathbf{C}}^{-1} \tilde{\mathbf{B}}. \quad (2.72)$$

In summary, we must calculate the distorted waves and  ${}^0\mathbf{S}$ , evaluate the matrix elements in Eqs. (2.66)–(2.68), solve the linear Eqs. (2.70), and finally form the  $\mathbf{S}$  matrix as in (2.72). Next we consider the evaluation of the matrix elements in more detail.

## 3. CALCULATION OF THE $\mathcal{S}^B$ , $\tilde{\mathbf{B}}$ , AND $\tilde{\mathbf{C}}$ MATRIX ELEMENTS AND CONSTRUCTION OF THE FULL SCATTERING MATRIX IN TERMS OF PARTITIONED MATRICES

### 3.1. Basis Functions

Equations (2.1) and (2.61) are very flexible. For example they include the asymptotic eigenstate functions of Eq. (2.54). However, because we use multichannel distorted waves, (2.54) is not flexible enough to



represent the basis functions we use in the OWVP, but (2.1) with  $\tilde{\varphi}_{\beta\gamma} = \tilde{\phi}_n$  is general enough for this purpose. To see this note that the HIGFs of Eq. (2.56) have the form

$$\tilde{\xi}_{\beta}^{(+)}(R, \mathbf{x}) = \frac{1}{R} \sum_{n'} \Delta_{n'm_{\beta}} \tilde{\xi}_{n'm_{\beta}}^{(+)}(R) \tilde{\phi}_{n'}(\mathbf{x}), \quad (3.1)$$

where the  $\tilde{\xi}_{n'm_{\beta}}^{(+)}$  is a radial HIGF.

We will use the flexibility of (2.1) not only to include multichannel dynamically adapted basis functions but also to include functions obtained by associating a set of  $\tilde{\varphi}_{\beta\gamma}$  functions with each of a subset of  $\tilde{q}_{\beta\gamma}$  functions. Our basis will include  $\tilde{\varphi}_{\beta\gamma}$  functions that are not associated with channels, and it will not be restricted to a direct product.

The special case of Eqs. (2.1) and (2.61) that we actually propose to use is

$$\begin{aligned} \Psi_{\text{OW}}^{(+)}(R, \mathbf{x}) = & \frac{1}{R} \sum_{n=1}^{N_g} \sum_{m=1}^{m_n} \tilde{A}_{\beta n m}^g \sum_{n'=1}^N \Delta_{n'n} \tilde{\xi}_{n'n m}^{(+)}(R) \tilde{\phi}_{n'}(\mathbf{x}) \\ & + \frac{1}{R} \sum_{n=1}^{N_e} \sum_{m=1}^{v_n} \tilde{A}_{\beta n m}^e \iota_{nm}(R) \tilde{\phi}_n(\mathbf{x}) \\ & + \frac{1}{R} \sum_{\beta=1}^{M_a} \tilde{A}_{\beta n_0}^a \sum_{\gamma=1}^{\delta_{\beta}} \tilde{c}_{\beta\gamma} \tilde{q}_{\beta\gamma}(R) \tilde{\varphi}_{\beta\gamma}(\mathbf{x}), \end{aligned} \quad (3.2)$$

where  $\tilde{\phi}_n$  and  $\tilde{\varphi}_{\beta\gamma}$  themselves are linear combinations of "primitive" basis functions,  $m_n$ ,  $u_n$ ,  $v_n$ , and  $\delta_{\beta}$ , are new parameters that specify the ranges involved in the various sums,  $N$  is the total number of channels defined for the problem,  $N_g$  is the number of channels summed over to form the linear combination of HIGFs,  $N_e$  is the number of channels summed over to form the linear combination of eigenstate functions,  $M_a$  is the total number of basis functions of the third form in Eq. (3.2), and  $\tilde{A}_{\beta n m}^g$ ,  $\tilde{A}_{\beta n_0}^e$ , and  $\tilde{A}_{\beta n_0}^a$  are special cases of the coefficients  $\tilde{A}_{\beta n m}$ .

Another way to specify the basis is to specify the three types of basis functions that occur in (3.2) in terms of the general notation of (2.1). We will label these three types of basis functions with a  $g$ , an  $e$ , or an  $a$  to denote, respectively, the HIGFs in the first summation of (3.2), the asymptotic eigenstates in the second summation, or the arbitrary basis functions in the third. Arbitrary basis functions have the form (2.1) with

the only further restrictions that  $\tilde{c}_{\beta\gamma}$ ,  $\tilde{q}_{\beta\gamma}$ , and  $\tilde{\varphi}_{\beta\gamma}$  are real and henceforth the tildes will be removed from these quantities.

Type  $e$  basis functions have the form of (2.54) where  $\phi_{n_0}$  is assumed to be real, to satisfy (2.23), and to be an eigenstate of the  $\hat{L}^2$  operator for the square of the orbital angular momentum of relative translation. In this case  $\delta_{\beta} = \tilde{c}_{\beta\gamma} = 1$ ,  $\tilde{q}_{\beta\gamma} = \iota_{m_{\beta} n_{\beta}}$ , and  $\varphi_{\beta\gamma} = \phi_{n_0}$  in (2.1).

Finally, a  $g$  type basis function has the form of (2.56), where the  $\tilde{\phi}_n$  are real, they satisfy (2.23), and are also eigenstates of  $\hat{L}^2$ . In this case  $\tilde{c}_{\beta\gamma} = 1$ , the sum over  $\gamma$  becomes a sum over  $n'$ ,  $\tilde{\varphi}_{\beta\gamma}$  is set to  $\phi_{n'}$ , and  $\tilde{q}_{\beta\gamma}$  is set equal to  $\tilde{\xi}_{n'n m_{\beta}}^{(+)}$  in (2.1).

The basis that we have defined above is more general than that which we have used previously because of the presence of the type  $a$  functions. Previously our basis sets consisted of type  $g$  and/or type  $e$  functions, and these proved to be sufficient to obtain converged quantum dynamics for a variety of electronically adiabatic atom-diatom reactions. However, electronically nonadiabatic reactions involve one or more electronic excited state surfaces. Quantum dynamics on excited state surfaces can be more difficult to converge than dynamics on typical ground state surfaces. This is true because the excited state surfaces can involve higher occupancies of antibonding orbitals with the result that the internuclear separation of the nuclei in the diatom may be much larger than its asymptotic value. Hence an expansion in asymptotic eigenstates and HIGFs generated by asymptotic eigenstates may not be the best choice for spanning the coordinates of the diatomic. The arbitrary functions are included in our formulation to allow us complete freedom in defining basis functions that will be suitable for electronically nonadiabatic problems.

To define the radial HIGFs more precisely we first left multiply Eq. (2.58) by  $(-2\mu R/\hbar^2)\phi_n(\mathbf{x})$ , then we substitute Eq. (3.1) into the resulting equation and integrate over the coordinates  $\mathbf{x}$ . This yields the following set of differential equations for the radial part of the HIGFs:

$$\left\{ \frac{d^2}{dR^2} - \frac{l_n(l_n+1)}{R^2} + k_n^2 \right\} \tilde{\xi}_{n'm_{\beta}}^{(+)}(R) + \sum_{n'} \Delta_{nn'} U_{nn'}(R) \tilde{\xi}_{n'm_{\beta}}^{(+)}(R) = -\delta_{n'n m_{\beta}} \quad (3.3)$$

with the boundary conditions

$$\tilde{\xi}_{n'm_{\beta}}^{(+)}(R) \sim 0, \quad R \rightarrow 0 \quad (3.4)$$

and

$$g_{n\beta m\beta}^{(+)}(R) \sim \bar{d}_{n\beta m\beta}^{(+)} \begin{cases} (1/2ik_n)^{1/2} \exp\left[i(k_n R - \frac{t_{n\beta} \pi}{2})\right], & k_n^2 > 0, \\ i(2|k_n|)^{-1/2} \exp[-|k_n|(R - R_f)], & k_n^2 < 0, \end{cases} \quad (3.5)$$

where for the large- $R$  form of the HIGF

$$\bar{d}_{n\beta m\beta}^{(+)} = \int dR \Delta_{n\beta n} f_{n\beta n}^{(+)}(R) t_{m\beta n\beta}(R). \quad (3.6)$$

Next we discuss the calculation of the matrix elements of Section 2.5 in terms of this particular set of basis functions. These matrix elements are not calculated directly; rather the matrix elements are computed from the real analogues of  $\mathcal{S}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  that occur in the SWVP for the reactance ( $K$ ) matrix [22]. Note that application of the SWVP for the  $K$  matrix would yield different results from either the SWVP for the  $T$  matrix or the OWVP for the  $S$  matrix, but in the method discussed in the present paper (and used previously) we do not complete the calculation with  $K$  matrix boundary conditions. Instead we use these real-valued matrices until as late in the calculation as possible to avoid the extra cost and storage of working with complex matrices. We do eventually require the solution of the complex linear system in Eq. (2.70), but we can arrange matters so that only a relatively small submatrix of  $\mathbf{C}$  is complex, thus permitting most of the calculation to be done in real arithmetic.

### 3.2. Transformation of the Non- $\mathcal{L}^2$ Basis Functions

In order to make most of the algebra real, as just discussed, we form the complex basis  $\bar{\Gamma}_\beta$ , the complex distorted functions,  $\psi^{(+n)}$ , and the complex HIGFs,  $\bar{g}_{n\beta m\beta}^{(+)}$ , by transformation from their real analogues. First we calculate the functions  $\bar{g}_{n\beta m\beta}^{(N)}$  that satisfy Eqs. (3.3) and (3.4) but with the large- $R$  boundary conditions [10,18]

$$\bar{g}_{n\beta m\beta}^{(N)} \sim \begin{cases} -d_{n\beta m\beta} k_n^{1/2} R n_{i_c}(k_n R), & k_n^2 > 0, \\ d_{n\beta m\beta} (2|k_n|)^{1/2} \exp[-|k_n|(R - R_f)], & k_n^2 < 0, \end{cases} \quad (3.7)$$

where

$$d_{n\beta m\beta} = \int dR \Delta_{n\beta n} {}^{(r)}f_{n\beta n}(R) t_{m\beta n\beta}(R). \quad (3.8)$$

We also calculate  ${}^{(r)}f_{n\beta n}$ , which is a real regular radial function that solves (2.36) with the boundary condition (2.37) and

$${}^{(r)}f_{n\beta n} \sim \begin{cases} k_n^{1/2} R [\delta_{nn} j_{l_c}(k_n R) - \Delta_{nn} {}^0 K_{nn} n_{l_c}(k_n R)], & k_n^2 > 0, \\ (2|k_n|)^{-1/2} [\delta_{nn} \exp[|k_n|(R - R_f)] \\ + \Delta_{nn} {}^0 K_{nn} \exp[-|k_n|(R - R_f)]], & k_n^2 < 0, \end{cases} \quad (3.9)$$

where  ${}^0\mathbf{K}$  is the extended reactance matrix, defined such that the submatrix with two open-channel indices is the ordinary reactance matrix. In Eqs. (3.7) and (3.9),  $j_{l_c}$  and  $n_{l_c}$  are spherical Bessel and Neumann functions, respectively, and  $R_f$  is an arbitrary numerical parameter.

We define the following real analogues of the matrices in (2.66)–(2.68):

$$\mathcal{X}_{m\beta 0}^B = \langle \psi^n | \frac{2\mu}{\hbar^2} (E - H) | \psi^{n_0} \rangle, \quad (3.10)$$

$$B_{\beta n_0} = \langle \Gamma_\beta | \frac{2\mu}{\hbar^2} (E - H) | \psi^{n_0} \rangle, \quad (3.11)$$

and

$$C_{\beta\beta'} = \langle \Gamma_\beta | \frac{2\mu}{\hbar^2} (H - E) | \Gamma_{\beta'} \rangle, \quad (3.12)$$

where the distorted-wave radial function with  $K$  matrix boundary conditions is

$$\psi^{n_0}(R, \mathbf{x}) = \frac{1}{R} \sum_n \Delta_{n n_0} {}^{(r)}f_{n n_0}(R) \phi_n(\mathbf{x}), \quad (3.13)$$

and the real basis function,  $\Gamma_\beta$ , is given by

$$\Gamma_\beta(R, \mathbf{x}) = \frac{1}{R} \sum_{\gamma=1}^{\delta_\beta} c_{\beta\gamma} q_{\beta\gamma}(R) \varphi_{\beta\gamma}(\mathbf{x}). \quad (3.14)$$

### Transforming HIGFs to $\mathcal{L}^2$ Functions

By taking linear combinations of the HIGFs it is possible to transform a subset of them to localized functions. This has two significant benefits — it reduces the space over which the quadratures must be performed — and it also permits a larger fraction of the solution of the linear system required in (2.70) to be done with real arithmetic.

We start by considering the formal expression for the HIGFs [18]

$$\mathcal{G}_{m\beta m\beta}^N(R) = \int dR' \mathcal{G}_{nn\beta}(R, R') t_{m\beta n\beta}(R'), \quad (3.15)$$

where

$$\mathcal{G}_{nn'}(R, R') = \sum_{n''} \Delta_{nn''} \Delta_{n''n'} \begin{cases} {}^{(r)}f_{nn''}(R) {}^{(l)}f_{n''n'}(R'), & R < R', \\ {}^{(l)}f_{nn''}(R) {}^{(r)}f_{n''n'}(R'), & R > R', \end{cases} \quad (3.16)$$

and the  ${}^{(l)}f_{nn'}$  solve

$$(H^D - E) \frac{1}{R} \sum_n \Delta_{nn'} {}^{(l)}f_{nn'}(R) \phi_n(\mathbf{x}) = 0 \quad (3.17)$$

together with the boundary conditions

$${}^{(l)}f_{nn'}(R) \sim \begin{cases} -\delta_{nn'} k_n^{1/2} R n_{\beta} I_n(k_n R), & k_n^2 > 0, \\ \delta_{nn'} (2|k_n|)^{1/2} \exp[-|k_n|(R - R_{\beta}^L)], & k_n^2 < 0. \end{cases} \quad (3.18)$$

If we set the  $t_{m\beta n\beta}$  equal to zero outside the region  $R_{\beta}^S < R < R_{\beta}^L$ , then (3.15) yields

$$\mathcal{G}_{m\beta m\beta}^N(R) = \begin{cases} \sum_{n'} \Delta_{nn'} {}^{(r)}f_{nn'}(R) d_{n'n\beta}^S t_{m\beta n\beta}(R), & R < R_{\beta}^S, \\ \mathcal{G}_{nn\beta}^N(R) & R_{\beta}^S \leq R \leq R_{\beta}^L, \\ \sum_{n'} \Delta_{nn'} {}^{(l)}f_{nn'}(R) d_{n'n\beta}^L t_{m\beta n\beta}(R), & R > R_{\beta}^L, \end{cases} \quad (3.19)$$

where

$$d_{m\beta m\beta}^S = \Delta_{m\beta} \int dR {}^{(l)}f_{n\beta n}(R) t_{m\beta n\beta}(R) \quad (3.20)$$

and

$$d_{m\beta m\beta} = \Delta_{m\beta} \int dR {}^{(r)}f_{n\beta n}(R) t_{m\beta n\beta}(R). \quad (3.21)$$

We can then form the set of localized functions,  $\mathcal{G}_{m\beta m\beta}^{\mathcal{L}}$  by

$$\mathcal{G}_{m\beta m\beta}^{\mathcal{L}}(R) = \mathcal{G}_{m\beta m\beta}^N(R) - \sum_{n'} \Delta_{nn'} \mathcal{G}_{nn'm_0}^N(R) d_{n'n\beta}^L t_{m\beta n\beta}, \quad m\beta \neq m_0, \quad (3.22)$$

where  $m = m_0$  denotes the HIGF with the smallest value of  $R_{\beta}^L$  for each value of  $n'$ , and the  $d_{nn'm\beta}^L$  solve

$$d_{nn'm\beta} = \sum_{n''} d_{n''m_0}^L d_{n''n\beta}^L. \quad (3.23)$$

We then have

$$\mathcal{G}_{nn'm\beta}^{\mathcal{L}}(R) = 0, \quad R > R_{\beta}^L, \quad m\beta \neq m_0, \quad (3.24)$$

so we can reduce the number of non- $\mathcal{L}^2$  functions to one per open channel.

It is also possible to express the small- $R$  portion of the  $\mathcal{G}_{m\beta m\beta}^{\mathcal{L}}$  in terms of the regular radial functions and thereby reduce the quadrature costs [36], but the additional savings is not large, and we have not implemented this option. Since the set of functions obtained after the transformation (3.22) spans the same space as the original set, the solution of the variational calculation is unchanged.

In the actual calculation of the  $B$  and  $C$  matrix elements, certain of the formulas involve the  $t_{m\beta n\beta}$  associated with a given HIGF, and these must be transformed as well using

$$t_{m\beta n\beta}^{\mathcal{L}}(R) = t_{m\beta n\beta}(R) - \sum_{n'} \Delta_{n'n\beta} t_{m_0 n'}(R) d_{n'n\beta}^L t_{m\beta n\beta}, \quad m\beta \neq m_0. \quad (3.25)$$

One complication with using (3.22) is that when a distortion block contains some closed channels, the linear system that must be solved in (3.23) is ill conditioned, and therefore we do not use (3.22) in these situations.

### Transformation to Complex Boundary Conditions

The  $\Gamma_{\beta}$  and  $\tilde{\Gamma}_{\beta}$  bases differ only in the non- $\mathcal{L}^2$  basis functions. Thus it is convenient to denote the  $\mathcal{L}^2$  basis functions as  $\Gamma_{\beta}^{\mathcal{L}}$  and the non- $\mathcal{L}^2$  basis functions as  $\Gamma_{\beta}$ . The  $\mathcal{L}^2$  subspace is composed of type  $e$  functions, type  $a$  functions, and square integrable linear combinations of HIGFs defined in Eq. (3.22). The  $c$  subspace is composed of continuum functions, in particular the remaining HIGFs. With these designations, we may partition the  $B$ ,  $C$ ,  $\tilde{B}$ , and  $\tilde{C}$  matrices as

$$\mathbf{B} = \begin{pmatrix} \mathbf{B}^c \\ \mathbf{B}^{\mathcal{L}} \end{pmatrix}, \quad (3.26)$$

$$\tilde{\mathbf{B}} = \begin{pmatrix} \tilde{\mathbf{B}}^c \\ \tilde{\mathbf{B}}^{\mathcal{L}} \end{pmatrix}, \quad (3.27)$$

$$\mathbf{C} = \begin{pmatrix} \mathbf{C}^{cc} & \mathbf{C}^{c\mathcal{L}} \\ \mathbf{C}^{\mathcal{L}c} & \mathbf{C}^{\mathcal{L}\mathcal{L}} \end{pmatrix}, \quad (3.28)$$

and

$$\tilde{\mathbf{C}} = \begin{pmatrix} \tilde{\mathbf{C}}^{cc} & \tilde{\mathbf{C}}^{c\mathcal{L}} \\ \tilde{\mathbf{C}}^{\mathcal{L}c} & \tilde{\mathbf{C}}^{\mathcal{L}\mathcal{L}} \end{pmatrix}. \quad (3.29)$$

Then the transformations may be written [35,36]

$$\tilde{\mathbf{B}}^c = (\mathbf{B}^c + \tilde{\mathbf{X}}^T \mathcal{A}^{\mathcal{L}}) \tilde{\mathbf{A}}, \quad (3.30)$$

$$\tilde{\mathbf{B}}^{\mathcal{L}} = \mathbf{B}^{\mathcal{L}} \tilde{\mathbf{A}}, \quad (3.31)$$

$$\tilde{\mathbf{C}}^{cc} = \mathbf{C}^{cc} - \mathbf{B}^c \tilde{\mathbf{X}}^T - \tilde{\mathbf{X}}^T \mathbf{B}^{cT} + \tilde{\mathbf{X}}^T \mathcal{A}^{\mathcal{L}} - \tilde{\mathbf{X}}^T \mathcal{A}^{\mathcal{L}} \tilde{\mathbf{X}}, \quad (3.32)$$

$$\tilde{\mathbf{C}}^{c\mathcal{L}} = \mathbf{C}^{c\mathcal{L}} - \tilde{\mathbf{X}}^T \mathbf{B}^{\mathcal{L}T}, \quad (3.33)$$

$$\tilde{\mathbf{C}}^{\mathcal{L}c} = \mathbf{C}^{\mathcal{L}c} - \mathbf{B}^{\mathcal{L}} \tilde{\mathbf{X}}, \quad (3.34)$$

$$\tilde{\mathbf{C}}^{c\mathcal{L}} = (\tilde{\mathbf{C}}^{\mathcal{L}c})^T, \quad (3.35)$$

and

$$\tilde{\mathbf{C}}^{\mathcal{L}\mathcal{L}} = \mathbf{C}^{\mathcal{L}\mathcal{L}}, \quad (3.36)$$

where

$$\mathcal{A}_{n\beta}^c = \int dR \Delta_{n\beta} n^{(r)} f_{n\beta} n(R) I_{m\beta n\beta}(R). \quad (3.37)$$

The transformation matrix,  $\tilde{\mathbf{A}}$ , is required [35] to obtain the complex  ${}^{(r)}f_{n\beta}^{(c)}$  from the real  ${}^{(r)}f_{n\beta}$ , and the transformation matrix,  $\tilde{\mathbf{X}}$ , is required [35] to obtain the complex  $\tilde{g}_{n\beta}^{(c)}$  from the real regular functions and the  $\tilde{g}_{n\beta}^{(N)}$ . These matrices are most conveniently given when we partition the problem into open and closed channels. These matrices for distortion block  $\delta$  are

$$\tilde{\mathbf{A}}_{\delta} = \begin{pmatrix} -(2i)^{1/2} (1 - i^0 \mathbf{K}_{\delta}^{oo})^{-1} & -(1 - i^0 \mathbf{K}_{\delta}^{oo})^{-1} i^0 \mathbf{K}_{\delta}^{oc} \\ \mathbf{0} & i\mathbf{1} \end{pmatrix}, \quad (3.38)$$

and

$$\tilde{\mathbf{X}}_{\delta} = \begin{pmatrix} -\frac{1}{2}(1+i)\tilde{\mathbf{d}}_{\delta}^{ooT} & -\frac{1}{2}(1+i)\tilde{\mathbf{d}}_{\delta}^{ocT} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}, \quad (3.39)$$

where

$$\tilde{\mathbf{d}}_{\delta} = \tilde{\mathbf{A}}_{\delta} \mathbf{d}_{\delta}, \quad (3.40)$$

$o$  stands for open, and  $c$  in this context stands for closed.

The reactance matrix due to the distortion potential for distortion block  $\delta$  is

$${}^0\mathbf{K}_{\delta} = \begin{pmatrix} {}^0\mathbf{K}_{\delta}^{oo} & {}^0\mathbf{K}_{\delta}^{oc} \\ {}^0\mathbf{K}_{\delta}^{co} & {}^0\mathbf{K}_{\delta}^{cc} \end{pmatrix}, \quad (3.41)$$

the distorted-wave scattering matrices for the individual distortion blocks are given by

$${}^0\mathbf{S}_{\delta}^{oo} = (1 - i^0\mathbf{K}_{\delta}^{oo})^{-1} (1 + i^0\mathbf{K}_{\delta}^{oo}), \quad (3.42)$$

and the distorted-wave Born approximation to the scattering matrix is given by

$$\mathcal{A}^{\mathcal{B}} = \tilde{\mathbf{A}}^{ooT} \mathcal{R}^{\mathcal{B}oo} \tilde{\mathbf{A}}^{oo}. \quad (3.43)$$

With these equations, in particular (3.30)–(3.43) we can calculate all the quantities needed for (2.72) from real matrix elements.

Alternately, it is possible to solve (2.72) using a partitioned matrix scheme [36] that permits most of the work to be performed in real arithmetic. In this scheme [36]

$$\mathcal{A}^{\mathcal{B}f} = \mathcal{A}^{\mathcal{B}} + \mathbf{B}^{\mathcal{B}T} \mathbf{C}^{\mathcal{L}\mathcal{L}^{-1}} \mathbf{B}^{\mathcal{L}}, \quad (3.44)$$

$$\mathbf{B}^f = \mathbf{B}^c - \mathbf{C}^{\mathcal{L}cT} \mathbf{C}^{\mathcal{L}\mathcal{L}^{-1}} \mathbf{B}^{\mathcal{L}}, \quad (3.45)$$

$$\mathbf{C}^f = \mathbf{C}^{cc} - \mathbf{C}^{\mathcal{L}cT} \mathbf{C}^{\mathcal{L}\mathcal{L}^{-1}} \mathbf{C}^{\mathcal{L}c}, \quad (3.46)$$

$$\tilde{\mathbf{A}}_{\delta}^f = -(2i)^{1/2} (1 - i^0 \mathbf{K}_{\delta}^{oo})^{-1}, \quad (3.47)$$

and

$$\tilde{\mathbf{X}}_{\delta}^f = -\frac{1}{2} (1+i) \tilde{\mathbf{d}}_{\delta}^{ooT}, \quad (3.48)$$

where the superscript  $f$  designates a matrix over the  $c$  space in which the contribution of the  $\mathcal{L}$  space is "folded in" using partitioned matrices [36].

Once these folded matrices are constructed, the transformations to complex boundary conditions are

$$\mathcal{S}^{Bf} = \tilde{\mathbf{A}}^f \mathcal{F}^B \tilde{\mathbf{A}}^f, \quad (3.49)$$

$$\tilde{\mathbf{B}}^f = (\mathbf{B}^f + \tilde{\mathbf{X}}^f \mathcal{F}^B) \tilde{\mathbf{A}}^f, \quad (3.50)$$

$$\tilde{\mathbf{C}}^f = \mathbf{C}^f - \mathbf{B}^f \tilde{\mathbf{X}}^f - \tilde{\mathbf{X}}^f \mathbf{B}^{f\dagger} + \tilde{\mathbf{X}}^f \mathcal{C}^f - \tilde{\mathbf{X}}^f \mathcal{F}^B \tilde{\mathbf{X}}^f, \quad (3.51)$$

and the full scattering matrix is given by

$$\mathbf{S} = {}^0\mathbf{S} + \mathcal{S}^{Bf} + \tilde{\mathbf{B}}^f \tilde{\mathbf{C}}^{f\dagger} \tilde{\mathbf{B}}^f, \quad (3.52)$$

In summary, the  $S$  matrix is calculated from (3.52). The matrix elements needed for (3.52) are obtained from the real  ${}^0K$ ,  $\mathcal{F}^B$ ,  $B$ , and  $C$  matrices in two steps. In the first step we construct the folded matrices  $\mathcal{F}^{Bf}$ ,  $\mathbf{B}^f$ ,  $\mathbf{C}^f$ ,  $\tilde{\mathbf{A}}_6^f$ , and  $\tilde{\mathbf{X}}_8^f$ , that is, (3.44)–(3.48). Then we transform the folded matrices to their complex analogues by application of (3.49)–(3.51).

### 3.3. Real Matrix Elements

The equations for the  $\mathcal{F}^B$ ,  $B$ , and  $C$  matrices, (3.10)–(3.12), all have the same general form: they are matrix elements of  $(2\mu/\hbar^2)(H - E)$ . The functions involved can be type  $e$ ,  $a$ , or  $g$  basis functions, as defined above, or distorted waves. When we consider all possible pairs of functions, we obtain the supermatrix of tableau 1:

Tableau 1

$$\begin{array}{cccc} \langle f | \frac{2\mu}{\hbar^2} (E - H) | f \rangle & \langle f | \frac{2\mu}{\hbar^2} (E - H) | g \rangle & \langle f | \frac{2\mu}{\hbar^2} (E - H) | e \rangle & \langle f | \frac{2\mu}{\hbar^2} (E - H) | a \rangle \\ \langle g | \frac{2\mu}{\hbar^2} (E - H) | f \rangle & \langle g | \frac{2\mu}{\hbar^2} (E - H) | g \rangle & \langle g | \frac{2\mu}{\hbar^2} (E - H) | e \rangle & \langle g | \frac{2\mu}{\hbar^2} (E - H) | a \rangle \\ \langle e | \frac{2\mu}{\hbar^2} (E - H) | f \rangle & \langle e | \frac{2\mu}{\hbar^2} (E - H) | g \rangle & \langle e | \frac{2\mu}{\hbar^2} (E - H) | e \rangle & \langle e | \frac{2\mu}{\hbar^2} (E - H) | a \rangle \\ \langle a | \frac{2\mu}{\hbar^2} (E - H) | f \rangle & \langle a | \frac{2\mu}{\hbar^2} (E - H) | g \rangle & \langle a | \frac{2\mu}{\hbar^2} (E - H) | e \rangle & \langle a | \frac{2\mu}{\hbar^2} (E - H) | a \rangle \end{array}$$

where we have used the letter  $f$  to designate a distorted wave. In this scheme the upper left  $1 \times 1$  submatrix is the distorted-wave Born approximation to the reactance matrix, the lower left  $3 \times 1$  submatrix is the  $B$  matrix, the upper right  $1 \times 3$  submatrix is  $\mathbf{B}^T$ , and the lower right  $3 \times 3$  submatrix is the  $C$  matrix. The upper left  $2 \times 2$  submatrix involving only  $f$  type and  $g$  type functions represents those matrix elements that are used in the GNVP formalism. All sixteen types of matrix elements are used in the OWVP formalism.

### Matrix Elements of $\mathcal{F}^B$

The matrix elements of the  $\mathcal{F}^B$  matrix for initial channel  $n_0$  and final channel  $n$  are

$$\mathcal{F}_{nn_0}^B = \int dR \sum_n \mathcal{F}_{nn'}(R) \Delta_{n'n_0}(R) f_{n'n_0}(R), \quad (3.53)$$

where

$$\mathcal{F}_{nn'}(R) = \sum_{n''} \Delta_{n''n'}(R) f_{n''n}(R) e_{n''n'}(R), \quad (3.54)$$

$$e_{n'n}(R) = -\frac{2\mu}{\hbar^2} V_{n'n}^{\text{int}}(R) (1 - \Delta_{n'n}), \quad (3.55)$$

and

$$V_{n'n}^{\text{int}}(R) = \int d\mathbf{x} \phi_{n'}(\mathbf{x}) V^{\text{int}}(R, \mathbf{x}) \phi_n(\mathbf{x}). \quad (3.56)$$

### Matrix Elements of $B$

There are three types of  $B$  matrix elements, and they are represented by the second, third, and fourth rows in the first column of tableau 1. These entries will be referred to as  $\mathbf{B}^x$  where  $x = a$  for arbitrary functions,  $x = g$  for HIGFs, and  $x = e$  for eigenstate functions.  $\mathbf{B}^x$  is given by

$$B_{\beta n_0}^x = \int dR \sum_n \mathcal{G}_{\beta n}^x(R) \Delta_{nn_0}(R) f_{n n_0}(R), \quad (3.57)$$

and for  $x = a$ ,  $g$ , or  $e$  we have

$$\mathcal{G}_{\beta n}^a(R) = \sum_{\gamma} c_{\beta\gamma} q_{\beta\gamma}(R) e_{\beta\gamma n}(R), \quad (3.58)$$

$$\mathcal{G}_{\beta n}^e(R) = \sum_{n'} \Delta_{n'n\beta} \delta_{n'n\beta}^N m_{\beta} (R) e_{n'n}(R), \quad (3.59)$$

$$\mathcal{G}_{\beta n}^e(R) = t_{m_{\beta n}}(R) e_{n\beta n}(R), \quad (3.60)$$

$$e_{\beta\gamma, n}(R) = -\frac{2\mu}{\hbar^2} \left[ \int d\mathbf{x} \varphi_{\beta\gamma}(\mathbf{x}) V^{\text{int}}(R, \mathbf{x}) \phi_n(\mathbf{x}) - \sum_{n'} \Delta_{n'n} C_{\beta\gamma, n'} V_{n'n}^{\text{int}}(R) \right], \quad (3.61)$$

and

$$C_{\beta\gamma, n} = \int d\mathbf{x} \varphi_{\beta\gamma}(\mathbf{x}) \phi_n(\mathbf{x}). \quad (3.62)$$

### Matrix Elements of $C$

There are nine types of  $C$  matrix elements and they are represented by the second, third, and fourth rows in columns 2–4 of tableau 1. These entries will be referred to as  $C^{x'}$  where  $x = a, g, \text{ or } e$  and  $x' = a, g, \text{ or } e$ . If  $x = x' = a$  then

$$C_{\beta\beta}^{aa} = \int dR dx \sum_{\gamma} c_{\beta\gamma} q_{\beta\gamma}(R) \varphi_{\beta\gamma}(\mathbf{x}) \frac{2\mu}{\hbar^2} (H - E) \sum_{\gamma'} c_{\beta\gamma'} q_{\beta\gamma'}(R) \varphi_{\beta\gamma'}(\mathbf{x}). \quad (3.63)$$

First we write the operator in the coordinate representation:

$$\frac{2\mu}{\hbar^2} (H - E) = -\frac{1}{R} \frac{\partial^2}{\partial R^2} R - \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hat{J}^2}{r^2} + \frac{2\mu}{\hbar^2} [V^{\text{diat}} - E + V^{\text{int}}] + \frac{\hat{J}^2}{R^2}, \quad (3.64)$$

where  $R$  is the mass-scaled atom-diatom separation defined as the magnitude of the vector in Eq. (2.16),  $r$  is the mass-scaled diatomic distance defined as the magnitude of the vector in Eq. (2.17), and the operators  $\hat{J}$  and  $\hat{J}^2$  contain derivatives with respect to nuclear angular coordinates. We can write (3.64) as

$$\frac{2\mu}{\hbar^2} (H - E) = -\frac{1}{R} \frac{\partial^2}{\partial R^2} R - \hat{\tau} - U^{\text{eff}}(R, \mathbf{x}), \quad (3.65)$$

where

$$\hat{\tau} = \frac{2\mu}{\hbar^2} (E - V^{\text{diat}}) + \left\{ \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{\hat{J}^2}{r^2} \right\}, \quad (3.66)$$

and

$$U^{\text{eff}}(R, \mathbf{x}) = -\frac{2\mu}{\hbar^2} V^{\text{int}}(R, \mathbf{x}) - \frac{\hat{J}^2}{R^2}. \quad (3.67)$$

Putting (3.65) back into (3.63) and rearranging yields

$$\begin{aligned} C_{\beta\beta}^{aa} &= \int dR \sum_{\gamma} \sum_{\gamma'} c_{\beta\gamma} q_{\beta\gamma}(R) \\ &\times \left\{ -\int d\mathbf{x} \varphi_{\beta\gamma}(\mathbf{x}) \phi_{\beta\gamma'}(\mathbf{x}) \frac{\partial^2}{\partial R^2} - \int d\mathbf{x} \varphi_{\beta\gamma}(\mathbf{x}) \hat{\tau} \varphi_{\beta\gamma'}(\mathbf{x}) \right\} c_{\beta\gamma'} q_{\beta\gamma'}(R) \\ &- \int dR \sum_{\gamma} \sum_{\gamma'} c_{\beta\gamma} q_{\beta\gamma}(R) \int d\mathbf{x} \varphi_{\beta\gamma}(\mathbf{x}) U^{\text{eff}}(R, \mathbf{x}) \phi_{\beta\gamma'}(\mathbf{x}) c_{\beta\gamma'} q_{\beta\gamma'}(R). \end{aligned} \quad (3.68)$$

We now make the following definitions

$$O_{\beta\gamma, \beta'\gamma'} = \int d\mathbf{x} \varphi_{\beta\gamma}(\mathbf{x}) \varphi_{\beta'\gamma'}(\mathbf{x}), \quad (3.69)$$

$$\tau_{\beta\gamma, \beta'\gamma'} = \int d\mathbf{x} \varphi_{\beta\gamma}(\mathbf{x}) \hat{\tau} \varphi_{\beta'\gamma'}(\mathbf{x}), \quad (3.70)$$

$$U_{\beta\gamma, \beta'\gamma'}^{\text{eff}}(R) = \int d\mathbf{x} \varphi_{\beta\gamma}(\mathbf{x}) U^{\text{eff}}(R, \mathbf{x}) \varphi_{\beta'\gamma'}(\mathbf{x}), \quad (3.71)$$

$$\mathcal{G}_{\beta, \beta'\gamma'}^{a(\text{eff})}(R) = \sum_{\gamma} c_{\beta\gamma} q_{\beta\gamma}(R) U_{\beta\gamma, \beta'\gamma'}^{\text{eff}}(R), \quad (3.72)$$

after which we write (3.68) as

$$\begin{aligned} C_{\beta\beta}^{aa} &= \int dR \sum_{\gamma} \sum_{\gamma'} c_{\beta\gamma} q_{\beta\gamma}(R) \left\{ -O_{\beta\gamma, \beta'\gamma'} \frac{\partial^2}{\partial R^2} - \tau_{\beta\gamma, \beta'\gamma'} \right\} c_{\beta\gamma'} q_{\beta\gamma'}(R) \\ &- \int dR \sum_{\gamma'} \mathcal{G}_{\beta, \beta'\gamma'}^{a(\text{eff})}(R) c_{\beta\gamma'} q_{\beta\gamma'}(R), \end{aligned} \quad (3.73)$$

which is the expression for a  $C$  matrix element in terms of general basis functions.

For the case where  $x = g$  and  $x' = a$ , the  $C$  matrix element becomes

$$\begin{aligned} C_{\beta\beta}^{ga} &= \int dR \sum_n \Delta_{n\beta} \delta_{n\beta}^N m_{\beta} (R) \sum_{\gamma'} \left\{ -O_{n, \beta\gamma'} \frac{\partial^2}{\partial R^2} - \tau_{n, \beta\gamma'} \right\} c_{\beta\gamma'} q_{\beta\gamma'}(R) \\ &- \int dR \sum_{\gamma'} \mathcal{G}_{\beta, \beta'\gamma'}^{g(\text{eff})}(R) c_{\beta\gamma'} q_{\beta\gamma'}(R), \end{aligned} \quad (3.74)$$

where

$$\mathcal{G}_{\beta\beta'\gamma'}^{g(\text{eff})} = \sum_n \Delta_{n\eta_\beta} \delta_{n\eta_{\beta'}\eta_\gamma}^N(R) U_{n,\beta'\gamma'}^{\text{eff}}(R), \quad (3.75)$$

$$\tau_{n,\beta\gamma} = \int d\mathbf{x} \phi_n(\mathbf{x}) \hat{\tau}(\varphi_{\beta\gamma}(\mathbf{x})), \quad (3.76)$$

and

$$U_{n,\beta\gamma}^{(\text{eff})}(R) = \int d\mathbf{x} \phi_n(\mathbf{x}) U^{\text{eff}}(R, \mathbf{x}) \varphi_{\beta\gamma}(\mathbf{x}). \quad (3.77)$$

For the case where  $x = e$  and  $x' = a$  the  $C$  matrix element becomes

$$C_{\beta\beta'\gamma'}^{ea} = \int dR t_{m\eta_\beta\eta_\gamma}(R) \sum_{\gamma'} \left\{ -O_{\eta_\beta,\beta'\gamma'} \frac{\partial^2}{\partial R^2} - \tau_{\eta_\beta,\beta'\gamma'} \right\} c_{\beta'\gamma'q\beta'\gamma'}(R) - \int dR \sum_{\gamma'} \mathcal{G}_{\beta\beta'\gamma'}^{e(\text{eff})}(R) c_{\beta'\gamma'q\beta'\gamma'}(R), \quad (3.78)$$

where

$$\mathcal{G}_{\beta\beta'\gamma'}^{e(\text{eff})}(R) = t_{m\eta_\beta\eta_\gamma}(R) U_{n\eta_\beta,\beta'\gamma'}^{\text{eff}}(R). \quad (3.79)$$

For those cases of  $C$  where  $x' = e$ , the  $C$  matrix element can be written in the general form

$$C_{\beta\beta'\gamma'}^xe = \int dR T_{\beta\eta_\beta}^x(R) \left\{ -\frac{\partial^2}{\partial R^2} - k_{\eta_\beta}^2 \right\} t_{m\eta_\beta\eta_\beta}(R) - \int dR \mathcal{G}_{\beta\eta_\beta}^{x(\text{eff})}(R) t_{m\eta_\beta\eta_\beta}(R), \quad (3.80)$$

and for  $x = a, g$ , or  $e$  we have

$$T_{\beta\eta_\beta}^a(R) = \sum_\gamma c_{\beta\gamma} q_{\beta\gamma}(R) O_{\beta\gamma,\eta_\beta}, \quad (3.81)$$

$$T_{\beta\eta_\beta}^g(R) = \Delta_{n\eta_\beta} \delta_{n\eta_\beta\eta_\beta}^N(R), \quad (3.82)$$

$$T_{\beta\eta_\beta}^e(R) = t_{m\eta_\beta\eta_\beta}(R) \delta_{n\eta_\beta}, \quad (3.83)$$

$$\mathcal{G}_{\beta\eta_\beta}^{a(\text{eff})}(R) = \sum_\gamma c_{\beta\gamma} q_{\beta\gamma}(R) U_{\beta\gamma,\eta_\beta}^{\text{eff}}(R), \quad (3.84)$$

$$\mathcal{G}_{\beta\eta_\beta}^{g(\text{eff})}(R) = \sum_{n'} \Delta_{n'\eta_\beta} \delta_{n'\eta_\beta\eta_\beta}^N(R) U_{n',\eta_\beta}^{\text{eff}}(R), \quad (3.85)$$

$$\mathcal{G}_{\beta\eta_\beta}^{e(\text{eff})}(R) = t_{m\eta_\beta\eta_\beta}(R) U_{n\eta_\beta}^{\text{eff}}(R), \quad (3.86)$$

$$U_{\beta\gamma,\eta_\beta}^{\text{eff}}(R) = \int d\mathbf{x} \varphi_{\beta\gamma}(\mathbf{x}) U^{\text{eff}}(R, \mathbf{x}) \phi_n(\mathbf{x}), \quad (3.87)$$

and

$$U_{n\eta_\beta}^{\text{eff}}(R) = \int d\mathbf{x} \phi_n(\mathbf{x}) U^{\text{eff}}(R, \mathbf{x}) \phi_n(\mathbf{x}). \quad (3.88)$$

Note that  $\mathcal{G}_{\beta\eta_\beta}^{g(\text{eff})}$  and  $\mathcal{G}_{\beta\eta_\beta}^{e(\text{eff})}$  are called  $\mathcal{V}_{\beta\eta_\beta}$  in Ref. [22].

For those cases of  $C$  where  $x' = g$ , the  $C$  matrix element can be written in the general form

$$C_{\beta\beta'\gamma'}^{xg} = \int dR T_{\beta\eta_\beta}^x t_{m\eta_\beta\eta_\beta}(R) - \int dR \sum_n \mathcal{G}_{\beta\eta_\beta}^x(R) \Delta_{n\eta_\beta} \delta_{n\eta_\beta\eta_\beta}^N(R), \quad (3.89)$$

where the auxiliary matrices,  $T^x$ , are given by (3.81)–(3.83) and the auxiliary matrices,  $\mathcal{G}^x$ , are given by (3.58)–(3.60) respectively.

## 4. REACTIVE SCATTERING

### 4.1. Basis Functions and the General Form of the Matrix Elements

In this section we extend the theory presented in Sections 2 and 3 to reactive collisions. The new element in this extension is the presence of more than one chemical arrangement. As mentioned below Eq. (2.2), each chemical arrangement will be denoted by an arrangement quantum number  $\alpha$ ; for the case of atom–diatom scattering,  $\alpha = 1$  represents A + BC,  $\alpha = 2$  represents B + CA, and  $\alpha = 3$  represents C + AB. Each of these arrangements will have its own set of operators; in particular,  $V^{\text{int}}$ ,  $V^{\text{vib}}$ ,  $V^D$ ,  $V^C$ , and  $H^D$  will each have an  $\alpha$  as a subscript identifying the operator with the appropriate arrangement. Each arrangement also has its own set of coordinates  $R_\alpha$  and  $\mathbf{x}_\alpha$ , where  $R_\alpha$  is the mass-scaled radial separation between the atom and the center of mass of the diatom for arrangement  $\alpha$ , and  $\mathbf{x}_\alpha$  is the collection of all other coordinates. Because

the coordinates are different for each arrangement, Eq. (2.16) is generalized to

$$\mathbf{R}_\alpha = M_\alpha \mathbf{S}_\alpha, \quad (4.1)$$

where  $\mathbf{S}_\alpha$  is the vector from the diatom mass center to the lone atom in arrangement  $\alpha$ ,

$$M_\alpha = \left( \frac{m_\alpha(m_{\alpha'} + m_{\alpha'})^2}{m_{\alpha'}m_{\alpha'}(m_\alpha + m_{\alpha'} + m_{\alpha'})} \right)^{1/4}, \quad (4.2)$$

$m_\alpha$  is the mass of the lone atom in arrangement  $\alpha$ , and  $m_{\alpha'}$  and  $m_{\alpha''}$  are the masses of the other two atoms. Note that  $R_\alpha$  is the magnitude of  $\mathbf{R}_\alpha$ .

The Hamiltonian may be still written as in Eq. (2.12), but now the kinetic energy  $T$  may be expressed in any of the three mass-scaled Jacobi coordinate systems associated with any of the arrangements. Thus

$$T = \frac{1}{2\mu} \mathbf{p}_\alpha \cdot \mathbf{p}_\alpha \quad (4.3)$$

where  $\mu$  is still the same as in Eq. (2.14); and the 6-dimensional nuclear momentum in the center-of-mass frame is

$$\mathbf{p}_\alpha = -i\hbar \begin{pmatrix} \nabla_{R_\alpha} \\ \nabla_{r_\alpha} \end{pmatrix}, \quad (4.4)$$

where

$$\mathbf{r}_\alpha = M_\alpha^{-1} \mathbf{s}_\alpha, \quad (4.5)$$

and  $\mathbf{s}_\alpha$  is the vector directed from B to C for  $\alpha = 1$ , from C to A for  $\alpha = 2$ , and from A to B for  $\alpha = 3$ .

The coordinate  $\mathbf{x}_\alpha$  consists of nuclear components,  $\omega_\alpha$ , and electronic components,  $\mathbf{x}_e$ . The nuclear components in turn consist of the angular part of  $\mathbf{R}_\alpha$  and all of  $\mathbf{r}_\alpha$ .

The diabatic electronic functions are denoted by  $X_\chi(\mathbf{x}_e; R_\alpha, \omega_\alpha)$ ; they are functions of the electronic coordinates,  $\mathbf{x}_e$ , and they depend parametrically on the nuclear coordinates,  $R_\alpha$  and  $\omega_\alpha$ . Note that a given electronic function can be written as  $X_\chi(\mathbf{x}_e; R_\alpha, \omega_\alpha)$  or  $X_\chi(\mathbf{x}_e; R_{\alpha'}, \omega_{\alpha'})$  for any  $\alpha$  or  $\alpha'$  or even as  $X_\chi(\mathbf{x}_e; R, \omega)$  since  $R \equiv R_1$  and  $\omega \equiv \omega_1$ ; that is, we can use whichever nuclear coordinates are most convenient in any given context. Since the electronic functions are diabatic,

$$\mathbf{p}_\alpha X_\chi(\mathbf{x}_e; R_\alpha, \omega_\alpha) = 0. \quad (4.6)$$

The bras and kets in the electronic space are denoted by (2.4) and (2.5), and they are orthogonal, as indicated in Eq. (2.6).

The potential is given by

$$V = \sum_{\chi} \sum_{\chi'} |\chi\rangle V_{\chi\chi'}(R_\alpha, \omega_\alpha) \langle\chi'|, \quad (4.7)$$

where

$$V_{\chi\chi'}(R_\alpha, \omega_\alpha) = \int d\mathbf{x}_e X_\chi(\mathbf{x}_e; R_\alpha, \omega_\alpha) \hat{H}^{EN} X_{\chi'}(\mathbf{x}_e; R_\alpha, \omega_\alpha), \quad (4.8)$$

$\hat{H}^{EN}$  is the sum of the electronic Hamiltonian and the nuclear repulsion, and, just as for  $X_\chi(\mathbf{x}_e; R_\alpha, \omega_\alpha)$ , the potential surfaces  $V_{\chi\chi'}$  may be written in any of the  $R_\alpha, \omega_\alpha$  coordinate systems or even in the  $R, \omega$  notation, as convenient. We note that Eq. (2.9) still holds in the multiarrangement case. Again, as a consequence of Eqs. (4.6) and (4.7), all electronic integrals reduce to the one simple integral (2.6), and we do not have to work with the electronic wavefunctions.

We next proceed as in Section 2 by partitioning the Hamiltonian as

$$H = T + V_\alpha^{\text{vib}} + V_\alpha^{\text{int}}, \quad (4.9)$$

where  $V_\alpha^{\text{vib}}$  is the vibrational potential of the diatom of arrangement  $\alpha$ , and  $V_\alpha^{\text{int}}$  is the interaction potential between the atom and the diatom of arrangement  $\alpha$ , the vibrational potential is given by

$$V_\alpha^{\text{vib}} = \lim_{R_\alpha \rightarrow \infty} V, \quad (4.10)$$

and the interaction potential is given by

$$V_\alpha^{\text{int}} = V - V_\alpha^{\text{vib}}. \quad (4.11)$$

The channel wave number for arrangement  $\alpha$  is defined as in Eq. (2.39) but with  $k_{\alpha n}$  replacing  $k$ , and  $\epsilon_{\alpha n}$  replacing  $\epsilon_n$ .

The asymptotic Hamiltonian is

$$H_\alpha^A = T + V_\alpha^{\text{vib}} \quad (4.12)$$

and the asymptotic eigenfunctions,  $\tilde{\phi}_{\alpha n}$ , must satisfy

$$H_\alpha^A \tilde{\phi}_{\alpha n}(\mathbf{x}_\alpha) = \epsilon_{\alpha n} \tilde{\phi}_{\alpha n}(\mathbf{x}_\alpha), \quad (4.13)$$

where  $n$  is the channel index for arrangement  $\alpha$ . The channel index represents the set of quantum numbers  $\alpha, \chi, v, j$ , and  $l$  and the  $\tilde{\phi}_{\alpha n}$  are the arrangement-dependent channel eigenstate functions which were



described in Section 2.1. Note that we systematically include  $\alpha$  explicitly in many of the function labels, even though its value is implied by  $n$ , because it plays an important role in the *form* of the equations.

We proceed by partitioning the interaction potential into a distorted part and a coupling part

$$V_{\alpha}^{\text{int}} = V_{\alpha}^D + V_{\alpha}^C, \quad (4.14)$$

where the distortion potential is restricted to a single arrangement, that is,

$$\Delta_{nn'} = \delta_{\alpha, \alpha_n} \Delta_{nn'}^{\alpha}, \quad (4.15)$$

with  $\Delta_{nn'}$  defined above Eq. (2.25) and

$$V_{\alpha}^D = \sum_n \sum_{n'} \Delta_{nn'}^{\alpha} |\phi_{\alpha n'}\rangle V_{nn'}^{\text{int}, \alpha} \langle \phi_{\alpha n'}| \quad (4.16)$$

where

$$V_{nn'}^{\text{int}, \alpha} = \int d\mathbf{x}_{\alpha} \tilde{\phi}_{\alpha n'}^*(\mathbf{x}_{\alpha}) V_{\alpha}^{\text{int}}(R_{\alpha}, \mathbf{x}_{\alpha}) \tilde{\phi}_{\alpha n'}(\mathbf{x}_{\alpha}). \quad (4.17)$$

The coupling potential is given by

$$V_{\alpha}^C = V_{\alpha}^{\text{int}} - V_{\alpha}^D, \quad (4.18)$$

and the distorted-wave Hamiltonian is given by

$$H_{\alpha}^D = T + V_{\alpha}^{\text{ib}} + V_{\alpha}^D, \quad (4.19)$$

in terms of which the full Hamiltonian is

$$H = H_{\alpha}^D + V_{\alpha}^C. \quad (4.20)$$

The Schrödinger equation for the wavefunction that satisfies outgoing scattering boundary conditions is

$$(H_{\alpha}^D + V_{\alpha}^C) \Psi_{\alpha}^{(+)\alpha_0 n_0} = E \Psi_{\alpha}^{(+)\alpha_0 n_0}, \quad (4.21)$$

where  $n_0$  denotes the initial channel, and  $\alpha_0$  denotes the initial arrangement. We expand the full wave function for initial arrangement  $\alpha_0$  and initial channel  $n_0$  as

$$\Psi_{\alpha}^{(+)\alpha_0 n_0} = \sum_{\alpha} \Psi_{\alpha}^{(+)\alpha_0 n_0}, \quad (4.22)$$

where  $\Psi_{\alpha}^{(+)\alpha_0 n_0}$  is a particular arrangement component of  $\Psi^{(+)\alpha_0 n_0}$ . The Schrödinger equation can now be written as

$$(E - H_{\alpha}^D) \Psi_{\alpha}^{(+)\alpha_0 n_0} = -\frac{\hbar^2}{2\mu} \sum_{\alpha'} U_{\alpha\alpha'} \Psi_{\alpha'}^{(+)\alpha_0 n_0}, \quad (4.23)$$

where the coupling operator,  $U_{\alpha\alpha'}$ , is given by [42]

$$U_{\alpha\alpha'} = -\frac{2\mu}{\hbar^2} [H - E + \delta_{\alpha\alpha'}(E - H_{\alpha}^D)]. \quad (4.24)$$

This is identical to the scheme conventionally used to couple arrangement components corresponding to electronic exchange in Hartree–Fock theory and electron scattering [43,44], and it is called the Fock scheme. Other schemes are possible [45]. In the Fock scheme the arrangement component wavefunction,  $\Psi_{\alpha}^{(+)\alpha_0 n_0}$ , satisfies the coupled set of generalized Lippmann–Schwinger integral equations [8,46]:

$$\Psi_{\alpha}^{(+)\alpha_0 n_0} = \delta_{\alpha\alpha_0} \Psi^{(+)\alpha_0 n_0} + G_{\alpha}^{D(+)} \sum_{\alpha'} U_{\alpha\alpha'} \Psi_{\alpha'}^{(+)\alpha_0 n_0}, \quad (4.25)$$

where the distorted wave,  $\Psi^{(+)\alpha_0 n_0}$ , is a solution of

$$(H_{\alpha_0}^D - E) \Psi^{(+)\alpha_0 n_0} = 0. \quad (4.26)$$

The distorted waves have a form similar to (2.35); however, they are now dependent on arrangement,

$$\Psi^{(+)\alpha n}(R_{\alpha}, \mathbf{x}_{\alpha}) = \frac{1}{R_{\alpha}} \sum_{n'} \Delta_{n'n}^{\alpha} f_{n'n}^{(+)}(R_{\alpha}) \tilde{\phi}_{\alpha n'}(\mathbf{x}_{\alpha}). \quad (4.27)$$

The radial part of the distorted waves obey the set of differential equations (2.36) and are subject to the boundary conditions (2.37) and (2.38). The distorted-wave Green's operator  $G_{\alpha}^{D(+)}$  is given by

$$G_{\alpha}^{D(+)} = \lim_{\epsilon \rightarrow 0^+} -\frac{\hbar^2}{2\mu} (E - H_{\alpha}^D + i\epsilon)^{-1}, \quad (4.28)$$

and the full scattering matrix is given by

$$S_{nn_0} = \delta_{\alpha\alpha_0} {}^0S_{nn_0}^{\alpha} + \mathcal{S}_{nn_0}, \quad (4.29)$$

where  ${}^0S^{\alpha}$  is the distorted-wave scattering matrix which is determined from the boundary condition of the form (2.38), and  $\mathcal{S}$  is the scattering matrix due to the coupling potential and is determined variationally.

As discussed in Section 2, the variational part of the scattering matrix is given by Eq. (2.71). For reactive scattering the distorted-wave Born approximation to the scattering matrix is given by

$$\mathcal{S}_{m\alpha}^B = \langle \psi^{(-)\alpha n} | \frac{2\mu}{\hbar^2} (E - H) | \psi^{(+)\alpha_0 m_0} \rangle, \quad (4.30)$$

$\tilde{B}_{\beta m_0}$  is given by

$$\tilde{B}_{\beta m_0} = \langle \tilde{\Gamma}_\beta | \frac{2\mu}{\hbar^2} (E - H) | \psi^{(+)\alpha_0 m_0} \rangle, \quad (4.31)$$

$\tilde{C}_{\beta\beta'}$  is given by

$$\tilde{C}_{\beta\beta'} = \langle \tilde{\Gamma}_\beta | \frac{2\mu}{\hbar^2} (H - E) | \tilde{\Gamma}_{\beta'} \rangle, \quad (4.32)$$

and the coupling operator is

$$U^{\alpha_0} = -\frac{2\mu}{\hbar^2} V_{\alpha_0}^C. \quad (4.33)$$

The general basis functions,  $\tilde{\Gamma}_\beta$ , in each arrangement are the same as described in Section 3, and they are again designated as type  $g$ ,  $e$ , and  $a$  to denote HIGFs, eigenstate functions, and arbitrary functions, respectively. All the restrictions on basis functions that are described in Section 3.1 apply here as well.

In the multiple-surface reactive case we calculate the scattering matrix from the real analogues of  ${}^0\mathbf{S}$ ,  $\mathcal{S}^B$ ,  $\tilde{\mathbf{B}}$ , and  $\tilde{\mathbf{C}}$ ; these are called  ${}^0\mathbf{K}$ ,  $\mathcal{H}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$ , respectively. These real valued matrices are used until as late in the calculation as possible to avoid the extra effort of dealing with complex matrices. Equations (2.36), (3.3), (3.7), (3.9), and (3.14) hold for the determination of the real analogues of the distorted waves, the HIGFs, and the general functions; and Eqs. (3.10)–(3.12) become

$$\mathcal{H}_{m\alpha}^B = \langle \psi^{\alpha n} | \frac{2\mu}{\hbar^2} (E - H) | \psi^{\alpha_0 m_0} \rangle, \quad (4.34)$$

$$B_{\beta m_0} = \langle \Gamma_\beta | \frac{2\mu}{\hbar^2} (E - H) | \psi^{\alpha_0 m_0} \rangle, \quad (4.35)$$

and

$$C_{\beta\beta'} = \langle \Gamma_\beta | \frac{2\mu}{\hbar^2} (H - E) | \Gamma_{\beta'} \rangle. \quad (4.36)$$

The  $\tilde{\mathcal{C}}$  matrix defined by Eq. (3.37) is zero in the reactive case, that is,  $\alpha_\beta \neq \alpha_n$  because  $\tilde{\mathcal{C}}$  is block diagonal by distortion block, and the distur-

tion blocks do not couple together channels for more than one arrangement.

The forms for the  $\mathcal{H}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  matrices for reactive scattering are more general than for the single arrangement case in that some of them now contain functions written in the coordinates of two different arrangements, that is, exchange integrals. These manifest themselves in the appearance of the  $\mathcal{B}$ ,  $\mathcal{W}$ , and  $C^{\text{eff}}$  matrices, which are analogous to the  $\mathcal{O}$ ,  $e$ , and  $U^{\text{eff}}$  matrices of the nonreactive formalism.

## 4.2. Real Reactive Matrix Elements

The real matrix elements that we need to calculate for Eqs. (3.44)–(3.52) are the elements of  $\mathcal{H}^B$ ,  $\mathbf{B}^g$ ,  $\mathbf{B}^e$ ,  $\mathbf{C}^{\mathcal{L}\mathcal{L}}$ ,  $\mathbf{C}^{\mathcal{L}c}$ ,  $\mathbf{C}^{c\mathcal{L}}$ , and  $\mathbf{C}^{cc}$ . The superscript  $\mathcal{L}$  represents the  $\mathcal{L}^2$  subspace of basis functions which contains type  $e$  and type  $a$  functions and the  $\mathcal{L}^2$  HIGFs. The superscript  $c$  represents the non- $\mathcal{L}^2$  subspace of basis functions, which contains the remaining HIGFs. In addition to these functions we need the non- $\mathcal{L}^2$  distorted waves to calculate  $\mathcal{H}^B$ . The most general forms of the  $\mathcal{H}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  matrices are given by (4.34)–(4.36). However, when one distinguishes among the various types of basis functions that are used, and when one considers the distorted waves, 16 specific forms for the  $\mathcal{H}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  matrices result, and these are given in tableau 1 of Section 3.3. To obtain a particular entry in tableau 1 for the reactive case, one substitutes the appropriate basis function of type  $g$ ,  $e$ , or  $a$  or the appropriate distorted-wave function, operates to the right with  $H - E$ , and rearranges the resulting expression so that the radial integrals over  $R_\alpha$  and  $R_{\alpha_0}$  are outermost, and the integrals over the rest of the coordinates used to span the full coordinate space are innermost. The label  $\alpha_0$  is associated with the bra for a particular matrix element in tableau 1 of Section 3.3, and the label  $\alpha$  is associated with the ket.

### Coordinate Systems

The forms of the matrix elements that we need to calculate depend on the coordinate system used. As mentioned in Section 2.1, some parts of the calculations are most conveniently carried out in a body-frame coordinate system. The coordinates used in the space frame are  $\mathbf{x}_\alpha$  and  $\omega_\alpha$ , where  $\omega_\alpha$  is the collection of nuclear coordinates  $R_\alpha$ ,  $r_\alpha$ ,  $\Theta_\alpha$ ,  $\Phi_\alpha$  (here  $\Phi_\alpha$  is an angle, *not* a basis function),  $\theta_\alpha$ ,  $\phi_\alpha$ . When  $\alpha = 1$ , the coordinate  $R_\alpha$  is the magnitude of the vector given by Eq. (4.1) and is the mass-scaled distance from the center of mass of BC to atom A,  $r_\alpha$  is the

magnitude of the vector defined in Eq. (4.6) and is the mass-scaled distance from atom B to atom C,  $\Theta_\alpha$  and  $\Phi_\alpha$  are the colatitude and longitude of  $\mathbf{R}_\alpha$ , and  $\theta_\alpha$  and  $\phi_\alpha$  are the colatitude and longitude of  $\mathbf{r}_\alpha$  [8]. The nuclear coordinates of the other arrangements are defined by cyclic permutation of the three atoms.

In the body frame, which is related to the space frame by a rotation, the nuclear coordinates of interest are  $R_\alpha$ ,  $r_\alpha$ ,  $\gamma_\alpha$ ,  $\Phi_\alpha$ ,  $\Theta_\alpha$ , and  $\chi_\alpha$  ( $\chi_\alpha$  here is an angle, *not* an electronic quantum number), where  $\gamma_\alpha$  is the angle between  $\mathbf{r}_\alpha$  and  $\mathbf{R}_\alpha$ , and  $\Phi_\alpha$ ,  $\Theta_\alpha$ , and  $\chi_\alpha$ , are the Euler angles which relate the space frame to the body frame. For computational reasons it is convenient to transform the three internal nuclear coordinates from  $R_\alpha$ ,  $r_\alpha$ , and  $\gamma_\alpha$  to  $R_{\alpha_0}$ ,  $R_{\alpha_0}$ , and  $\Delta_{\alpha_0}$ , where  $\Delta_{\alpha_0}$  is the angle between  $\mathbf{R}_\alpha$  and  $\mathbf{R}_{\alpha_0}$ . Transformation between the two sets of nuclear coordinates is accomplished by the equations [18,47,48]

$$r_\alpha = \mathcal{M}^{\alpha\alpha_0} [R_{\alpha_0}^2 + (\overline{\mathcal{M}}^{\alpha\alpha_0} R_\alpha)^2 + 2\overline{\mathcal{M}}^{\alpha\alpha_0} R_\alpha R_{\alpha_0} \cos \Delta_{\alpha_0}]^{1/2}, \quad (4.37)$$

$$\cos \gamma_\alpha = (-1)^{P_{\alpha\alpha_0}} \mathcal{M}^{\alpha\alpha_0} (\overline{\mathcal{M}}^{\alpha\alpha_0} R_\alpha + R_{\alpha_0} \cos \Delta_{\alpha_0}) / r_\alpha, \quad (4.38)$$

$$r_{\alpha_0} = \mathcal{M}^{\alpha\alpha_0} [R_\alpha^2 + (\overline{\mathcal{M}}^{\alpha\alpha_0} R_{\alpha_0})^2 + 2\overline{\mathcal{M}}^{\alpha\alpha_0} R_\alpha R_{\alpha_0} \cos \Delta_{\alpha_0}]^{1/2}, \quad (4.39)$$

$$\cos \gamma_{\alpha_0} = (-1)^{P_{\alpha\alpha_0}} \mathcal{M}^{\alpha\alpha_0} (\overline{\mathcal{M}}^{\alpha\alpha_0} R_{\alpha_0} + R_\alpha \cos \Delta_{\alpha_0}) / r_{\alpha_0}, \quad (4.40)$$

$$\mathcal{M}^{\alpha\alpha_0} = [(M - m_\alpha)(M - m_{\alpha_0}) / (M - m_\alpha - m_{\alpha_0}) M]^{1/2}, \quad (4.41)$$

and

$$\overline{\mathcal{M}}^{\alpha\alpha_0} = [m_\alpha m_{\alpha_0} / (M - m_\alpha)(M - m_{\alpha_0})]^{1/2}, \quad (4.42)$$

where  $P_{\alpha\alpha_0}$  is the parity of the permutation from (12) to  $(\alpha\alpha_0)$ ,  $M$  here is the total mass of the three atoms, and, as before,  $m_\alpha$  is the mass of the lone atom in arrangement  $\alpha$ .

After this transformation, the set of nuclear coordinates consists of  $R_\alpha$ ,  $R_{\alpha_0}$ ,  $\Delta_{\alpha_0}$ ,  $\Phi_\alpha$ ,  $\Theta_\alpha$ , and  $\chi_\alpha$ . The volume element for the six-dimensional integration over these coordinates is [18,48]

$$(\mathcal{M}^{\alpha\alpha_0})^3 R_\alpha^2 dR_\alpha R_{\alpha_0}^2 dR_{\alpha_0} d\cos \Delta_{\alpha_0} d\chi_\alpha \sin \Theta_\alpha d\Phi_\alpha d\Theta_\alpha. \quad (4.43)$$

We define the collection of Euler angles as  $\boldsymbol{\varepsilon}_\alpha$  and the volume element over the Euler angles as

$$d\varepsilon_\alpha = d\chi_\alpha \sin \Theta_\alpha d\Phi_\alpha d\Theta_\alpha; \quad (4.44)$$

hence the total volume element becomes

$$(\mathcal{M}^{\alpha\alpha_0})^3 R_\alpha^2 dR_\alpha R_{\alpha_0}^2 dR_{\alpha_0} d\cos \Delta_{\alpha_0} d\varepsilon_\alpha d\mathbf{x}_e. \quad (4.45)$$

The basis functions depend on  $\mathbf{x}_e$ ,  $R_\alpha$ ,  $R_{\alpha_0}$ ,  $\Delta_{\alpha_0}$ , and  $\boldsymbol{\varepsilon}_\alpha$ , but the potential only depends on  $R_\alpha$ ,  $R_{\alpha_0}$ , and  $\Delta_{\alpha_0}$ . Since the potential is independent of the Euler angles, the integration over  $\boldsymbol{\varepsilon}_\alpha$  can be done analytically, which reduces the dimensionality of the numerical quadratures to 3. However, at this stage of our formulation we do not remove the Euler angle dependence by analytical integration because it would complicate the presentation of the rest of this section; a detailed description of the integration over the Euler angles in Eq. (4.45) is given in Appendix A of Ref. [8].

### Exchange Matrix Element of $\mathcal{H}^B$

The matrix element for  $\mathcal{H}^B$  for initial channel  $n_0$  and final channel  $n$  is

$$\mathcal{H}_{nn_0}^B = \int dR_{\alpha_0} \sum_{n'} \mathcal{F}_{nn'}(R_{\alpha_0}) \Delta_{n'n_0}^{\alpha_0} {}^{(r)} f_{n'n_0}(R_{\alpha_0}), \quad (4.46)$$

where

$$\mathcal{F}_{nn'}(R_{\alpha_0}) = \int dR_\alpha \sum_{n''} \Delta_{n''n}^\alpha {}^{(r)} f_{n''n}(R_\alpha) W_{n''n''}^{\alpha\alpha_0}(R_\alpha, R_{\alpha_0}), \quad (4.47)$$

and

$$W_{n''n''}^{\alpha\alpha_0}(R_\alpha, R_{\alpha_0}) = R_\alpha R_{\alpha_0} (\mathcal{M}^{\alpha\alpha_0})^3 \int d \cos \Delta_{\alpha_0} d\varepsilon_\alpha d\mathbf{x}_e \phi_{\alpha n''}(R_\alpha, R_{\alpha_0}, \Delta_{\alpha_0}, \boldsymbol{\varepsilon}_\alpha, \mathbf{x}_e) \\ \times \mathcal{U}^{\alpha_0}(R_\alpha, R_{\alpha_0}, \Delta_{\alpha_0}) \phi_{\alpha n''}(R_\alpha, R_{\alpha_0}, \Delta_{\alpha_0}, \boldsymbol{\varepsilon}_\alpha, \mathbf{x}_e). \quad (4.48)$$

### Exchange Matrix Elements of $B$

There are three types of  $B$  matrix elements and they are represented by the second, third, and fourth rows in the first column of tableau 1 in Section 3.3. These entries will be referred to as  $B^x$  where  $x = a$  for arbitrary functions,  $x = g$  for HIGFs, and  $x = e$  for eigenstate functions.  $B^x$  is given by

$$B_{\beta n_0}^x = \int dR_{\alpha_0} \sum_n \mathcal{G}_{\beta n}^x(R_{\alpha_0}) \Delta_{n n_0}^{\alpha_0} {}^{(r)} f_{n n_0}(R_{\alpha_0}), \quad (4.49)$$

and for  $x = a, g$ , or  $e$  we have

$$\mathcal{G}_{\beta n}^a(R_{\alpha_0}) = \int dR_\alpha \sum_\gamma c_{\beta\gamma} q_{\beta\gamma}(R_\alpha) W_{\beta\gamma n}^{\alpha\alpha_0}(R_\alpha, R_{\alpha_0}), \quad (4.50)$$

$$\mathcal{G}_{\beta n}^e(R_{\alpha_0}) = \int dR_{\alpha} \sum_{n'} \Delta_{n'n_0}^{\alpha} \delta_{n'n_0 m_{\beta}}^N(R_{\alpha}) W_{n'n}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}), \quad (4.51)$$

$$\mathcal{G}_{\beta n}^e(R_{\alpha_0}) = \int dR_{\alpha} t_{m_{\beta} n_{\beta}}(R_{\alpha}) W_{n'n}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}), \quad (4.52)$$

where

$$W_{n'n}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) = R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha\alpha_0})^3 \int d \cos \Delta_{\alpha\alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \phi_{\alpha n'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ \times \mathcal{U}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}) \phi_{\alpha n}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}). \quad (4.53)$$

We will also use alternate forms of the  $B$  matrix elements [36] for reasons which will be given in "Radial Quadratures" in Section 5.10. For functions of type  $a$ ,  $g$ , and  $e$ , these forms are given by

$$B_{\beta n_0}^a = \int dR_{\alpha} \int dR_{\alpha_0} \sum_n \Delta_{n n_0}^{\alpha} {}^{(r)}f_{n n_0}(R_{\alpha}) \\ \times \sum_{\gamma} \left\{ \mathcal{B}_{\beta n, \beta' \gamma}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) \frac{\partial^2}{\partial R^2} + T_{n, \beta' \gamma}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) \right\} c_{\beta' \gamma} q_{\beta' \gamma}(R_{\alpha}) \\ + \int dR_{\alpha} \sum_{\gamma} \mathcal{F}_{\alpha_0, \beta' \gamma}^{\text{eff}}(R_{\alpha}) c_{\beta' \gamma} q_{\beta' \gamma}(R_{\alpha}), \quad (4.54)$$

$$\tilde{B}_{\beta n_0}^e = \int dR_{\alpha} \sum_{n'} \mathcal{F}_{n_0 n'}(R_{\alpha}) \Delta_{n' n_0}^{\alpha} \delta_{n' n_0 m_{\beta}}^N(R_{\alpha}) - \int dR_{\alpha} \tilde{T}_{n_0 n_{\beta}}(R_{\alpha}) t_{m_{\beta} n_{\beta}}(R_{\alpha}), \quad (4.55)$$

and

$$B_{\beta n_0}^e = \int dR_{\alpha} \tilde{T}_{n_0 n_{\beta}}(R_{\alpha}) \left( \frac{\partial^2}{\partial R^2} + \hat{\tau}_{\alpha} \right) t_{m_{\beta} n_{\beta}}(R_{\alpha}) + \int dR_{\alpha} \mathcal{F}_{n_0 n_{\beta}}^{\text{eff}}(R_{\alpha}) t_{m_{\beta} n_{\beta}}(R_{\alpha}), \quad (4.56)$$

where

$$\mathcal{B}_{n, \beta' \gamma}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) = R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha\alpha_0})^3 \int d \cos \Delta_{\alpha\alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \phi_{\alpha n'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ \times \phi_{\alpha_0, \beta' \gamma}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}), \quad (4.57)$$

$$T_{n, \beta' \gamma}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) = R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha\alpha_0})^3 \int d \cos \Delta_{\alpha\alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \phi_{\alpha n'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ \times \hat{\tau}_{\alpha_0} \phi_{\alpha_0, \beta' \gamma}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}), \quad (4.58)$$

$$\mathcal{F}_{n_0, \beta' \gamma}^{\text{eff}}(R_{\alpha}) = \int dR_{\alpha_0} \sum_n \Delta_{n n_0}^{\alpha} {}^{(r)}f_{n n_0}(R_{\alpha_0}) C_{n, \beta' \gamma}^{\alpha\alpha_0, \text{eff}}(R_{\alpha}, R_{\alpha_0}), \quad (4.59)$$

$$\mathcal{F}_{n_0 n'}(R_{\alpha}) = \int dR_{\alpha_0} \sum_n \Delta_{n n_0}^{\alpha} {}^{(r)}f_{n n_0}(R_{\alpha_0}) W_{n n'}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}), \quad (4.60)$$

$$\tilde{T}_{n_0 n'}(R_{\alpha}) = \int dR_{\alpha_0} \sum_n \Delta_{n n_0}^{\alpha} {}^{(r)}f_{n n_0}(R_{\alpha_0}) \mathcal{T}_{n n'}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}), \quad (4.61)$$

$$\mathcal{F}_{n_0 n'}^{\text{eff}}(R_{\alpha}) = \int dR_{\alpha_0} \sum_n \Delta_{n n_0}^{\alpha} {}^{(r)}f_{n n_0}(R_{\alpha_0}) C_{n n'}^{\alpha\alpha_0, \text{eff}}(R_{\alpha}, R_{\alpha_0}), \quad (4.62)$$

$$\hat{\tau}_{\alpha_0} = \frac{2\mu}{\hbar^2} (E - V_{\alpha_0}^{\text{diat}}) + \left\{ \frac{1}{r_{\alpha_0}} \frac{\partial^2 r_{\alpha_0}}{\partial r_{\alpha_0}^2} - \frac{j_{\alpha_0}^2}{r_{\alpha_0}^2} \right\}, \quad (4.63)$$

$$C_{n, \beta' \gamma}^{\alpha\alpha_0, \text{eff}}(R_{\alpha}, R_{\alpha_0}) = R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha\alpha_0})^3 \int d \cos \Delta_{\alpha\alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \phi_{\alpha n'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ \times U_{\alpha_0}^{\text{eff}}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}) \phi_{\alpha_0, \beta' \gamma}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}), \quad (4.64)$$

$$\mathcal{B}_{n, n'}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) = R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha\alpha_0})^3 \int d \cos \Delta_{\alpha\alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \phi_{\alpha n'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ \times \phi_{\alpha n'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}), \quad (4.65)$$

$$C_{m m'}^{\alpha\alpha_0, \text{eff}}(R_{\alpha}, R_{\alpha_0}) = R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha\alpha_0})^3 \int d \cos \Delta_{\alpha\alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \phi_{\alpha m'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ \times U_{\alpha_0}^{\text{eff}}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}) \phi_{\alpha m'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}), \quad (4.66)$$

and

$$U_{\alpha_0}^{\text{eff}}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}) = -\frac{2\mu}{\hbar^2} V_{\alpha_0}^{\text{int}}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha\alpha_0}) - \frac{j_{\alpha_0}^2}{R_{\alpha_0}^2}. \quad (4.67)$$

### Exchange Matrix Elements of $C$

There are nine types of  $C$  matrix elements and they are represented by the second, third, and fourth rows in columns 2–4 of tableau 1 of Section 3.3. These entries will be referred to as  $C^{xx}$  where  $x = a, g, \text{ or } e$  and  $x' = a, g, \text{ or } e$ . If  $x = x' = a$  then

$$C_{\beta\beta'}^{aa} = \int dR_{\alpha_0} dR_{\alpha} \sum_{\gamma} \sum_{\gamma'} c_{\beta\gamma} q_{\beta\gamma}(R_{\alpha}) \\ \times \left\{ -\mathcal{B}_{\beta\gamma, \beta'\gamma'}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) \frac{\partial^2}{\partial R_{\alpha_0}^2} - T_{\beta\gamma, \beta'\gamma'}^{\alpha\alpha_0}(R_{\alpha}, R_{\alpha_0}) \right\} c_{\beta'\gamma'} q_{\beta'\gamma'}(R_{\alpha_0})$$

$$- \int dR_{\alpha_0} \sum_{\Upsilon} \mathcal{G}_{\beta, \beta' \gamma'}^{a(\text{eff})}(R_{\alpha_0}) c_{\beta' \gamma' q \beta \gamma}(R_{\alpha_0}), \quad (4.68)$$

where

$$\begin{aligned} \mathcal{B}_{\beta \gamma, \beta' \gamma'}^{\alpha \alpha_0}(R_{\alpha}, R_{\alpha_0}) &= R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha \alpha_0})^3 \int d\cos\Delta_{\alpha \alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \Phi_{\alpha, \beta \gamma}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ &\quad \times \varphi_{\alpha_0, \beta' \gamma'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}), \end{aligned} \quad (4.69)$$

$$\begin{aligned} T_{\beta \gamma, \beta' \gamma'}^{\alpha \alpha_0}(R_{\alpha}, R_{\alpha_0}) &= R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha \alpha_0})^3 \int d\cos\Delta_{\alpha \alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \Phi_{\alpha, \beta \gamma}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ &\quad \times \hat{\tau}_{\alpha_0} \varphi_{\alpha_0, \beta' \gamma'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}), \end{aligned} \quad (4.70)$$

$$\mathcal{G}_{\beta, \beta' \gamma'}^{a(\text{eff})}(R_{\alpha}, R_{\alpha_0}) = \int dR_{\alpha} c_{\beta \gamma q \beta' \gamma'}(R_{\alpha}) C_{\beta \gamma, \beta' \gamma'}^{\alpha \alpha_0(\text{eff})}(R_{\alpha}, R_{\alpha_0}), \quad (4.71)$$

and

$$\begin{aligned} C_{\beta \gamma, \beta' \gamma'}^{\alpha \alpha_0(\text{eff})}(R_{\alpha}, R_{\alpha_0}) &= R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha \alpha_0})^3 \int d\cos\Delta_{\alpha \alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \Phi_{\alpha, \beta \gamma}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ &\quad \times U_{\alpha_0}^{\text{eff}}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}) \varphi_{\alpha_0, \beta' \gamma'}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}). \end{aligned} \quad (4.72)$$

For the case where  $x = g$  and  $x' = a$ , the  $C$  matrix element becomes

$$\begin{aligned} C_{\beta \beta'}^g &= \int dR_{\alpha} dR_{\alpha'} \sum_{n'} \Delta_{n' n}^{\alpha} \delta_{n' n, n_p m_p}^N(R_{\alpha}) \\ &\quad \times \sum_{\Upsilon'} \left\{ -\mathcal{B}_{n', \beta' \gamma'}^{\alpha \alpha_0}(R_{\alpha}, R_{\alpha'}) \frac{\partial^2}{\partial R_{\alpha_0}^2} - T_{n', \beta' \gamma'}^{\alpha \alpha_0} \right\} c_{\beta \gamma q \beta' \gamma'}(R_{\alpha_0}) \\ &\quad - \int dR_{\alpha_0} \sum_{\Upsilon'} \mathcal{G}_{\beta, \beta' \gamma'}^{g(\text{eff})}(R_{\alpha_0}) c_{\beta \gamma q \beta' \gamma'}(R_{\alpha_0}), \end{aligned} \quad (4.73)$$

where

$$\mathcal{G}_{\beta, \beta' \gamma'}^{g(\text{eff})}(R_{\alpha_0}) = \int dR_{\alpha} \sum_{n'} \Delta_{n' n}^{\alpha} \delta_{n' n, n_p m_p}^N(R_{\alpha}) C_{n', \beta' \gamma'}^{\alpha \alpha_0(\text{eff})}(R_{\alpha}, R_{\alpha_0}). \quad (4.74)$$

For the case where  $x = e$  and  $x' = a$ , the  $C$  matrix element becomes

$$\begin{aligned} C_{\beta \beta'}^{ea} &= \int dR_{\alpha_0} dR_{\alpha} t_{m_p n_p}(R_{\alpha}) \sum_{\Upsilon'} \left\{ -\mathcal{B}_{n_p, \beta' \gamma'}^{\alpha \alpha_0}(R_{\alpha}, R_{\alpha_0}) \frac{\partial^2}{\partial R_{\alpha_0}^2} - T_{n_p, \beta' \gamma'}^{\alpha \alpha_0} \right\} c_{\beta \gamma q \beta' \gamma'}(R_{\alpha_0}) \\ &\quad - \int dR_{\alpha_0} \sum_{\Upsilon'} \mathcal{G}_{\beta, \beta' \gamma'}^{e(\text{eff})}(R_{\alpha_0}) c_{\beta \gamma q \beta' \gamma'}(R_{\alpha_0}), \end{aligned} \quad (4.75)$$

where

$$\mathcal{G}_{\beta, \beta' \gamma'}^{e(\text{eff})}(R_{\alpha_0}) = \int dR_{\alpha} t_{m_p n_p}(R_{\alpha}) C_{n_p, \beta' \gamma'}^{\alpha \alpha_0(\text{eff})}(R_{\alpha}, R_{\alpha_0}). \quad (4.76)$$

For those cases of  $C$  where  $x' = e$ , the  $C$  matrix element can be written in the general form

$$\begin{aligned} C_{\beta \beta'}^{xe} &= \int dR_{\alpha_0} T_{n_p}^x(R_{\alpha_0}) \left\{ -\frac{\partial^2}{\partial R_{\alpha_0}^2} - \hat{\tau}_{\alpha_0} \right\} t_{m_p n_p}(R_{\alpha_0}) \\ &\quad - \int dR_{\alpha_0} \mathcal{G}_{\beta \beta'}^{x(\text{eff})}(R_{\alpha_0}) t_{m_p n_p}(R_{\alpha_0}) \end{aligned} \quad (4.77)$$

and for  $x = a, g$ , or  $e$ , we have

$$T_{\beta n}^a(R_{\alpha_0}) = \sum_{\Upsilon} \int dR_{\alpha} c_{\beta \gamma q \beta' \gamma'}(R_{\alpha}) \mathcal{B}_{\beta \gamma, n}^{\alpha \alpha_0}(R_{\alpha}, R_{\alpha_0}), \quad (4.78)$$

$$T_{\beta n}^g(R_{\alpha_0}) = \sum_{n'} \int dR_{\alpha} \Delta_{n' n}^{\alpha} \delta_{n' n, n_p m_p}^N(R_{\alpha}) \mathcal{B}_{n' n}^{\alpha \alpha_0}(R_{\alpha}, R_{\alpha_0}), \quad (4.79)$$

$$T_{\beta n}^e(R_{\alpha_0}) = \int dR_{\alpha} t_{m_p n_p}(R_{\alpha}) \mathcal{B}_{n_p n}^{\alpha \alpha_0}(R_{\alpha}, R_{\alpha_0}), \quad (4.80)$$

$$\mathcal{G}_{\beta n}^{a(\text{eff})}(R_{\alpha_0}) = \sum_{\Upsilon} \int dR_{\alpha} c_{\beta \gamma q \beta' \gamma'}(R_{\alpha}) C_{\beta \gamma, n}^{\alpha \alpha_0(\text{eff})}(R_{\alpha}, R_{\alpha_0}), \quad (4.81)$$

$$\mathcal{G}_{\beta n}^{g(\text{eff})}(R_{\alpha_0}) = \sum_{n'} \int dR_{\alpha} \Delta_{n' n}^{\alpha} \delta_{n' n, n_p m_p}^N(R_{\alpha}) C_{n' n}^{\alpha \alpha_0(\text{eff})}(R_{\alpha}, R_{\alpha_0}), \quad (4.82)$$

$$\mathcal{G}_{\beta n}^{e(\text{eff})}(R_{\alpha_0}) = \int dR_{\alpha} t_{m_p n_p}(R_{\alpha}) C_{n_p n}^{\alpha \alpha_0(\text{eff})}(R_{\alpha}, R_{\alpha_0}), \quad (4.83)$$

$$\begin{aligned} \mathcal{B}_{\beta \gamma, n}^{\alpha \alpha_0}(R_{\alpha}, R_{\alpha_0}) &= R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha \alpha_0})^3 \int d\cos\Delta_{\alpha \alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \Phi_{\alpha, \beta \gamma}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ &\quad \times \Phi_{\alpha_0, n}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}), \end{aligned} \quad (4.84)$$

and

$$\begin{aligned} C_{\beta \gamma, n}^{\alpha \alpha_0(\text{eff})}(R_{\alpha}, R_{\alpha_0}) &= R_{\alpha} R_{\alpha_0} (\mathcal{M}^{\alpha \alpha_0})^3 \int d\cos\Delta_{\alpha \alpha_0} d\epsilon_{\alpha} d\mathbf{x}_{\epsilon} \Phi_{\alpha, \beta \gamma}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}) \\ &\quad \times U_{\alpha_0}^{\text{eff}}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}) \Phi_{\alpha_0, n}(R_{\alpha}, R_{\alpha_0}, \Delta_{\alpha \alpha_0}, \epsilon_{\alpha}, \mathbf{x}_{\epsilon}). \end{aligned} \quad (4.85)$$

Note that  $\mathcal{G}_{\beta n}^{g(\text{eff})}$  and  $\mathcal{G}_{\beta n}^{e(\text{eff})}$  are called  $\mathcal{V}_{\beta n}$  in Ref. [22].

For those cases of  $\mathbf{C}$  where  $x' = g$ , the  $C$  matrix element can be written in the general form

$$C_{\beta\beta'}^{xg} = \int dR_{\alpha_0} \mathcal{T}_{\beta n_{\alpha_0}}^x(R_{\alpha_0}) t_{m_{\alpha_0} n_{\alpha_0}}(R_{\alpha_0}) - \int dR_{\alpha_0} \sum_n \mathcal{G}_{\beta n}^x(R_{\alpha_0}) \Delta_{n_{\alpha_0}}^{\alpha_0} \mathcal{E}_{n_{\alpha_0} m_{\alpha_0}}^N(R_{\alpha_0}), \quad (4.86)$$

where the auxiliary matrices,  $\mathcal{T}$ , are given by Eqs. (4.78)–(4.80), and the auxiliary matrices,  $\mathcal{G}^x$ , are given by Eqs. (4.50)–(4.52), respectively.

## 5. COMPUTATIONAL CONSIDERATIONS

In this section we specify in detail our current computational methods and discuss the factors that weighed in their selection.

### 5.1. Basis Functions

In the previous sections we have specified the basis functions in a very general way to allow future flexibility. In actual computations performed so far we have imposed further restrictions on our basis, in part so that the matrix elements may be efficiently calculated. We now specify the more restricted basis to be considered in the rest of this paper.

No further restrictions were imposed on the HIGFs. For the  $\mathcal{B}^2$  basis functions, we restrict discussion, until Section 5.12, to the case where  $\delta_{\beta}$  in Eq. (3.2) is 1, so we now suppress the  $\gamma$  index in the last sum of this equation. This leads to type a basis functions of the form

$$\Gamma_{\beta} = R_{\alpha_{\beta}}^{-1} \varphi_{\beta}(R_{\alpha_{\beta}}) \varphi_{\beta}(x_{\alpha_{\beta}}), \quad (5.1)$$

where the precise form of  $\varphi_{\beta}$  depends on the frame in which the calculations are done; this will be discussed further in Section 5.2. Section 5.12 discusses contraction schemes by which matrix elements involving more general basis functions of the form of (3.14) may be calculated from the matrix elements of  $\mathbf{B}$  and  $\mathbf{C}$  in the primitive basis of (5.1).

All the equations are decoupled in the total angular momentum quantum number  $J$ , in the parity  $P = (-1)^{M_l}$ , and in the  $z$ -component,  $M_l$ , of the total angular momentum, where  $z$  is the initial momentum direction in a space-fixed coordinate system.[39] The results have no dependence on  $M_l$ . For systems with two or more identical atoms, the equations further decouple into 2 or 4 symmetry subblocks labeled by their symmetry  $S$ .[35] Each JP block is solved separately, and we may

solve each JPS block separately as well. However, computation of all  $S$  blocks in a single run is often desirable since some of the work is common to all symmetry subblocks and may be performed only once if storage is available for intermediate quantities.

The whole calculation involves three computationally intensive parts. These are the solutions of the distorted-wave problems, the quadratures to form the matrix elements of  $\mathcal{H}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$ , and the solution of the linear variational system. The relative cost and memory requirements of these steps vary markedly depending on the problem to be solved and on the basis set and numerical options selected.

### 5.2. Space and Body Frames

When we use space-frame basis functions we calculate the matrix elements of the variational functional (i.e., the matrix elements of  $\mathcal{H}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$ ) directly in the space frame, and when we use body-frame basis functions we calculate these matrices in the body frame and obtain a body-frame  $S$  matrix, which is transformed to a space-frame  $S$  matrix in an extra step. We have implemented both options.

When we use space-frame basis functions, we restrict them such that

$$\phi_n = r_{\alpha_n}^{-1} \chi_{\alpha_n, j_n}(r_{\alpha_n}) \mathcal{Y}_{j_n \ell_n}^{JM}(\hat{\mathbf{r}}_{\alpha_n}, \hat{\mathbf{R}}_{\alpha_n}) X_{\bar{\alpha}_n}(x_e; R_{\alpha_n}, \omega_{\alpha_n}) \quad (5.2)$$

and

$$\varphi_{\beta} = r_{\alpha_{\beta}}^{-1} \chi_{\beta}(r_{\alpha_{\beta}}) \mathcal{Y}_{j_{\beta} \ell_{\beta}}^{JM}(\hat{\mathbf{r}}_{\alpha_{\beta}}, \hat{\mathbf{R}}_{\alpha_{\beta}}) X_{\alpha_{\beta}}(x_e; R_{\alpha_{\beta}}, \omega_{\alpha_{\beta}}), \quad (5.3)$$

where  $\chi_{\alpha_n, j_n}$  is an asymptotic vibrational function for arrangement  $\alpha$ ,  $\chi_{\beta}$  is an unrestricted vibrational basis function (to be chosen for rapid convergence of the solution of the 3-body problem), and the rotational-orbital functions  $\mathcal{Y}_{j \ell}^{JM}$  are given in terms of spherical harmonics by [39]

$$\mathcal{Y}_{j \ell}^{JM}(\hat{\mathbf{r}}, \hat{\mathbf{R}}) = \sum_{m_j m_{\ell}} \langle j m_j m_{\ell} | j M J \rangle \bar{Y}_{j m_j}(\hat{\mathbf{r}}) \bar{Y}_{\ell m_{\ell}}(\hat{\mathbf{R}}). \quad (5.4)$$

The index  $n$  will indicate a specific choice of  $\alpha$ ,  $\bar{\alpha}$ ,  $v$ ,  $j$ , and  $\ell$ , while  $\beta$  is associated with a specific choice of  $\alpha$ ,  $\chi$ ,  $j$ ,  $\ell$ , and  $\chi_{\beta}$ . Notice the two distinct notational uses of  $\chi$ : as a vibrational function and as an electronic quantum number.

If space-frame basis functions are used, the allowed values of  $\ell$  for a given JP block and a given basis function with rotational angular momentum quantum number  $j$  are

$$|j - J| \leq \ell \leq j + J, \quad (5.5)$$

subject to the constraint on  $l$  that

$$(-1)^{l+j} = P. \quad (5.6)$$

At high  $J$  it is often possible to obtain well-converged results while retaining only the lowest few allowed values of  $l$  in the basis because the centrifugal potential makes the contribution of high  $l$  functions negligible. We employ one of two rules guiding the set of  $l$  values retained in the calculation. We either retain

$$|j - J| \leq l \leq \min[l_\alpha^{\max}, |j + J|] \quad (5.7)$$

or we retain

$$|j - J| \leq l \leq \min[\max(0, (l_\alpha^{\max} - j)), |j + J|], \quad (5.8)$$

where  $l_\alpha^{\max}$  is a parameter that is increased until convergence is attained.

When we use body-frame basis functions, we restrict them such that

$$\phi_n = r_{\alpha n}^{-1} \chi_{\alpha n \nu j n}(r_{\alpha n}) \tilde{Z}_{j\Omega}^{JM, P}(\hat{\mathbf{r}}_{\alpha n}, \hat{\mathbf{R}}_{\alpha n}) X_{\chi n}(\mathbf{x}_e; R_{\alpha n}, \omega_{\alpha n}) \quad (5.9)$$

and

$$\varphi_\beta = r_{\alpha\beta}^{-1} \chi_\beta(r_{\alpha\beta}) \tilde{Z}_{j\Omega}^{JM, P}(\hat{\mathbf{r}}_{\alpha\beta}, \hat{\mathbf{R}}_{\alpha\beta}) X_{\chi\beta}(\mathbf{x}_e; R_{\alpha\beta}, \omega_{\alpha\beta}), \quad (5.10)$$

where  $\chi_{\alpha\nu j}$  and  $\chi_\beta$  are as above.  $\tilde{Z}_{j\Omega}^{JM, P}(\hat{\mathbf{r}}_{\alpha}, \hat{\mathbf{R}}_{\alpha})$  is given by [8,47,49,50]

$$\begin{aligned} \tilde{Z}_{j\Omega}^{JM, P}(\hat{\mathbf{r}}_{\alpha}, \hat{\mathbf{R}}_{\alpha}) &= \sqrt{\frac{2J+1}{8\pi(1+\delta_{\Omega 0})}} [D_{-M, -\Omega}^{J*}(\Phi_\alpha, \Theta_\alpha, \chi_\alpha) \\ &+ (-1)^{J+\Omega} P D_{-M, \Omega}^{J*}(\Phi_\alpha, \Theta_\alpha, \chi_\alpha)] Y_{j\Omega}[\gamma_\alpha, 0], \end{aligned} \quad (5.11)$$

where  $D_{M, \Omega}^J$  is a rotation matrix element [51] having Euler angles  $\Phi_\alpha$ ,  $\Theta_\alpha$ , and  $\chi_\alpha$ ;  $\gamma_\alpha$  is the angle given by

$$\gamma_\alpha = \arccos(\hat{\mathbf{r}}_\alpha \cdot \hat{\mathbf{R}}_\alpha), \quad (5.12)$$

and  $\Omega$  is the magnitude of the projection of  $j$  (or  $J$ ) on the atom-to-diatom axis. In this case the index  $n$  denotes a specific choice of  $\alpha$ ,  $\bar{\chi}$ ,  $\nu$ ,  $j$ , and  $\beta$  denotes a specific choice of  $\alpha$ ,  $\chi$ ,  $j$ ,  $\Omega$ , and  $\chi_\beta$ .

The operation of  $\hat{L}^2$  on the body-frame functions  $\tilde{Z}_{j\Omega}^{JM, P}$  leads to [47,50]

$$\begin{aligned} \int d\hat{\mathbf{R}}_\alpha d\hat{\mathbf{r}}_\alpha \tilde{Z}_{j\Omega}^{JM, P*}(\hat{\mathbf{r}}_\alpha, \hat{\mathbf{R}}_\alpha) \hat{L}^2 \tilde{Z}_{j\Omega}^{JM, P}(\hat{\mathbf{r}}_\alpha, \hat{\mathbf{R}}_\alpha) &= \delta_{j'j} \{ [J(J+1) + j(j+1) - 2\Omega^2] \delta_{\Omega'\Omega} \\ &- \lambda_+(J, \Omega) \lambda_+(j, \Omega) \delta_{\Omega', \Omega+1} \sqrt{1 + \delta_{\Omega 0}} \\ &- \lambda_-(J, \Omega) \lambda_-(j, \Omega) \delta_{\Omega', \Omega-1} \sqrt{1 + \delta_{\Omega 1}} \}, \end{aligned} \quad (5.13)$$

where

$$\lambda_\pm(J, \Omega) = \sqrt{J(J+1) - \Omega(\Omega \pm 1)}. \quad (5.14)$$

If body-frame basis functions are used the allowed values of  $\Omega$  for a given basis function having rotational quantum number  $j$  are given by

$$0 \leq \Omega \leq \min(J, j) \quad \text{if} \quad P = (-1)^j, \quad (5.15)$$

or

$$1 \leq \Omega \leq \min(J, j) \quad \text{if} \quad P = (-1)^{j+1}. \quad (5.16)$$

We have found that well-converged results may often be attained while retaining only the lowest few  $\Omega$ , which is consistent with recent work by other workers [52,53].

The transformation from the body frame to the space frame is accomplished using the body-frame-to-space-frame transformation, which is given by the orthogonal matrix

$$T_{\Omega l}^{JP} = \left[ \frac{(2 - \delta_{\Omega 0})(2l+1)}{2J+1} \right]^{1/2} \langle j\Omega l 0 | jJ l \Omega \rangle \left[ \frac{1 + P(-1)^{j+l}}{2} \right]. \quad (5.17)$$

### 5.3. Asymptotic Vibrational Functions

The asymptotic vibrational wavefunctions  $\chi_{\alpha\nu j}$  solve the eigenvalue equation

$$\left[ -\frac{\hbar^2}{2\mu} \frac{1}{r_\alpha} \frac{\partial^2}{\partial r_\alpha^2} r_\alpha + \frac{j(j+1)\hbar^2}{2\mu r_\alpha^2} + V_{\alpha}^{\text{vb}}(r_\alpha) - \epsilon_{\alpha\nu j} \right] \chi_{\alpha\nu j}(r_\alpha) = 0, \quad (5.18)$$

where  $V_{\alpha}^{\text{vb}}$  is given by Eq. (4.10). The wavefunction and associated eigenenergies are obtained by the Rayleigh–Ritz variational principle. For single-surface problems we use a basis of  $N_\alpha(\text{HO})$  harmonic oscillator eigenfunctions. For multiple-surface problems we need basis functions on each surface, and if  $V_{\alpha\alpha'}$  does not become diagonal in  $\chi$  at large  $R_\alpha$ , the asymptotic eigenfunctions are mixtures of the two diabatic components. Here we consider the case where the vibrational problem corresponds to single surface. The Hamiltonian matrix elements are calculated using Gauss–Hermite quadrature of order  $N_\alpha(\text{HO}) + 14$ . Since the harmonic oscillator wavefunctions are defined on the region

$(-\infty, \infty)$  and thus do not have the desired  $r_\alpha = 0$  boundary conditions, their use requires some special handling. First we reset all quadrature nodes for  $r_\alpha < \delta$  to  $r = \delta$ , where  $\delta$  is a parameter that typically ranges from  $10^{-5} a_0$  to  $10^{-1} a_0$ . Second, the elements proportional to  $1/r_\alpha^2$  are made nonsingular by replacing  $r_\alpha^2$  in the denominator by  $r_\alpha^2 + r_0^2$ , where we take  $r_0$  typically to be about  $10^{-3} a_0$ . For sufficiently repulsive potentials the calculation is quite insensitive to the exact values of  $\delta$  and  $r_0$ ; thus no practical problems are encountered by ignoring the formal  $r_\alpha = 0$  boundary condition. (In the unlikely event that this procedure ever encounters difficulty, it would be a simple modification to change to basis functions of the proper form [54]).

#### 5.4. Distortion Potentials

By partitioning the interaction potential into a distortion potential and a coupling potential, the scattering matrix is split into associated terms as indicated in Eq. (2.72). Only the contributions to the  $S$  matrix due to the coupling potential are treated variationally (the contributions due to the distortion potential are calculated numerically), and thus our basis set requirements are determined principally by the coupling potential. As the coupling in the distortion potential is made more extensive, both the density and spatial extent of the basis functions needed to represent the residual coupling are diminished, and this permits substantial reductions in the size of the translational basis [18]. However, as more coupling is added to the distortion potential, the effort involved in the calculation of the radial functions increases, and the computation of the matrix elements of  $\mathcal{H}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  becomes more expensive. An optimal strategy must strike a balance between these competing considerations.

We consider distortion potentials of the form given by Eqs. (4.15) and (4.16). The distortion potential has a block diagonal form, and the resulting calculation for the distorted-wave problem decouples into several smaller problems.

The most elaborate distortion potentials we have used involved "full intra-arrangement coupling" [17]. This means that all channels within a given arrangement are coupled:

$$\Delta_{mm'}^\alpha = 1. \quad (5.19)$$

For some problems that use this coupling scheme, even the distorted-wave Born approximation yields converged results [55], and thus *no* translational basis functions are required. The resulting distorted-wave

problems are, however, so costly for most applications that this is not an efficient choice. At the other extreme we have the "single-channel" distortion potential (which we only use in the space frame), for which

$$\Delta_{mm'}^\alpha = \delta_{mm'}. \quad (5.20)$$

A slightly less extreme choice is the single-state distortion potential (which we use only in the body frame); this corresponds to

$$\Delta_{mm'}^\alpha = \delta_{\bar{\nu}, \bar{\nu}'} \delta_{v, v'} \delta_{j, j'}. \quad (5.21)$$

In the single-channel and single-state schemes the solution of the distorted-wave problems involves very little work, but a larger translational basis is required to achieve converged results for the final  $S$  matrix.

The "full rotational coupling" scheme is defined by

$$\Delta_{mm'}^\alpha = \delta_{\bar{\nu}, \bar{\nu}'} \delta_{v, v'}. \quad (5.22)$$

and it was used in many of our prior studies. The motivation for this scheme is that channels within a given  $\nu$  level tend to be the most strongly coupled. For problems requiring many high- $j$  states, though, this scheme can be unnecessarily expensive, so more recent calculations [22,27,28] have used more optimal schemes which couple only the lowest, most important rotational states within a given vibrational level (all  $j < j_{\nu}^d$ , where  $j_{\nu}^d$  is an input parameter) and which treat the remaining channels as either single-state or single-channel blocks depending on the frame. For calculations at high total angular momentum, the last few rotational states are responsible for a significant fraction of the total number of channels, so decoupling these states can result in vast savings without appreciable impact on the size of the basis set required for good convergence.

The reason we do not use single channel distortion potentials when calculations are carried out in the body frame has to do with the computation of the scattering boundary condition matching functions. These are formed using the space-frame matching functions [see, e.g., (3.9)] and the space-frame-to-body-frame transformation given by Eq. (5.17). This yields functions which have nonzero coupling between different values of  $\Omega$ . If the variational functional is to be formed in the space frame, no special restrictions are needed, and we make use of single-channel distortion blocks for channels in states that have weak coupling. Thus the space frame permits smaller distortion blocks than can be used in the body frame. Additionally, if high- $l$  channels are to be omitted from the basis, they may be culled prior to any computation,



whereas in the body frame, we require that all possible open- $\Omega$  channels be retained to satisfy the boundary conditions.

### 5.5. Solving the Distorted-Wave Problems

In the space frame, the distorted-wave radial functions solve the set of homogeneous Eqs. (2.36) subject to the boundary conditions (2.37) and (3.9). In Eq. (3.9),  $R_f$  is a numerical parameter chosen to avoid overflow or underflow problems; in practice we take  $R_f = R_{N_\alpha(F)+1}^{FD}$ , which is the outer finite difference boundary condition point for arrangement  $\alpha$ . Equation (3.9) is equivalent to (2.38) along with

$${}^0\mathbf{S} = (1 - i^0\mathbf{K})^{-1}(1 + i^0\mathbf{K}), \quad (5.23)$$

but the use of (3.9) allows the boundary conditions to be imposed at a smaller value of  $R_\alpha$ .

The half-integrated Green's functions  $\hat{g}_{n',nm}^N$  solve the inhomogeneous Eqs. (3.3) subject to the boundary conditions (3.4) and (3.7). We solve Eqs. (2.36) and (3.3) using the finite difference boundary value method [2,8,22,56] with an  $N_\alpha^{FD}$ -point representation of the second derivative operator except near the large- $R_\alpha$  edge of the grid, where lower-order approximations are used to conveniently impose the nonhomogeneous boundary conditions. The calculations are done one distortion block at a time. In matrix form (2.36) is written

$$\left[ \frac{d^2}{dR^2} \mathbf{I} + \mathbf{D}(R) \right] \mathbf{f}(R) = \mathbf{0}, \quad (5.24)$$

where

$$D_{nn'} = \delta_{nn'} k_n^2 + \Delta_{nn'}^\alpha U_{nn'}^\alpha(\text{eff})(R). \quad (5.25)$$

The finite difference approximation converts this to the set of equations

$$\sum_{v=-v_{L,i}}^{v_{U,i}} c_v^i \mathbf{f}(R_{i+v}) + \mathbf{D}(R_i) \mathbf{f}(R_i) = \mathbf{0}, \quad (5.26)$$

where  $c_v^i$  is a finite difference coefficient used to represent the second derivative operator at point  $i$  in terms of data at the points  $i - v_{L,i}$ ;  $i - v_{L,i} + 1$ ;  $\dots$ ;  $i + v_{U,i}$ . At large  $R_\alpha$  we specify conditions at one point beyond the edge of the grid, and we have used two different schemes for treating the finite difference approximation at the last few points. In the first scheme, we require the use of an equal number of

points before and after the point for which the derivative is to be evaluated. Then we have

$$v_{L,i} = v_{U,i} = \min[(N_\alpha^{FD} - 1)/2, N_\alpha(F) + 1 - i], \quad (5.27)$$

where  $N_\alpha(F)$  is the number of finite difference grid points. This results in only a 3-point formula at the last grid point. In the second scheme, we remove this restriction and use as many points as possible without increasing the bandwidth of the resulting linear equations. For this case we have

$$v_{L,i} = (N_\alpha^{FD} - 1)/2 \quad (5.28)$$

and

$$v_{U,i} = \min[(N_\alpha^{FD} - 1)/2, N_\alpha(F) + 1 - i]. \quad (5.29)$$

This results in a  $(N_\alpha^{FD} + 3)/2$ -point formula at the last grid point. In recent calculations we have usually used the latter approach.

Equation (5.26) together with the boundary conditions

$$\mathbf{f}(R_i) = \mathbf{0}, \quad i \leq 0, \quad (5.30)$$

and

$$\mathbf{f}(R_{N_\alpha(F)+1}) = \mathbf{I}, \quad (5.31)$$

where  $\mathbf{I}$  is the unit matrix, can be written as a supermatrix equation

$$\mathbf{A}\mathbf{F} = \beta_0, \quad (5.32)$$

where

$$\mathbf{F} = \begin{pmatrix} \mathbf{f}(R_1) \\ \mathbf{f}(R_2) \\ \vdots \\ \mathbf{f}(R_{N_\alpha(F)}) \end{pmatrix}, \quad (5.33)$$

$$\beta_0 = \begin{pmatrix} \mathbf{0} \\ \mathbf{0} \\ \vdots \\ \mathbf{0} \\ -c_{(N_\alpha^{FD}-1)/2}^{N_\alpha(F)-(N_\alpha^{FD}-1)/2+1} \mathbf{I} \\ \vdots \\ -c_1^{N_\alpha(F)} \mathbf{I} \end{pmatrix}, \quad (5.34)$$

and

$$\Lambda = \begin{pmatrix} D(R_1) + c_0^1 \mathbf{I} & c_1^1 \mathbf{I} & \dots & c_{\nu_{u,1}}^1 \mathbf{I} \\ c_2^1 \mathbf{I} & D(R_2) + c_0^2 \mathbf{I} & \dots & c_{\nu_{u,2}}^2 \mathbf{I} \\ & & \ddots & \\ & & & c_{\nu_{u,N_\alpha}}^{N_\alpha} \mathbf{I} \\ & & & c_{\nu_{l,N_\alpha}}^{N_\alpha} \mathbf{I} \dots c_{\nu_{l,N_\alpha}}^{N_\alpha} \mathbf{I} & D(R_{N_\alpha(F)}) + c_0^{N_\alpha(F)} \mathbf{I} \end{pmatrix} \quad (5.35)$$

Thus  $\Lambda$  is a real, nonsymmetric, banded matrix with upper and lower bandwidths both equal to  $N_\delta(N_\alpha^{FD} - 1)/2$ , where  $N_\delta$  is the number of channels in the distortion block under consideration. We solve (5.32) by LU factorization of  $\Lambda$  using the LINPACK routine SGBFA [57] and then performing  $N_\delta$  backsubstitutions and forward eliminations using the LINPACK routine SGBSL [57]. The work involved in the LU factorizations is proportional to  $1/4(N_\alpha^{FD} - 1)^2 N_\delta^3 N_\alpha(F)$ , and the work to then obtain the radial functions is proportional to  $1/2(N_\alpha^{FD} - 1)N_\delta^3 N_\alpha(F)$  [57].

For a given translational basis function,  $t_{m_p}$ , the radial HIGFs solve a supermatrix equation

$$\Lambda \mathbf{G}_m = \boldsymbol{\beta}_m \quad (5.36)$$

together with the boundary conditions

$$\mathbf{g}_m(R_i) = \mathbf{0}, \quad i \leq 0, \quad (5.37)$$

$$\mathbf{g}_m(R_{N_\alpha(F)+1}) = \mathbf{g}_m^{BC}, \quad (5.38)$$

where

$$\mathbf{G}_m = \begin{pmatrix} \mathbf{g}_m(R_1) \\ \mathbf{g}_m(R_2) \\ \vdots \\ \mathbf{g}_m(R_{N_\alpha(F)}) \end{pmatrix}, \quad (5.39)$$

$$\boldsymbol{\beta}_m = \begin{pmatrix} t_{m_p}(R_1) \mathbf{I} \\ t_{m_p}(R_2) \mathbf{I} \\ \vdots \\ t_{m_p}(R_{N_\alpha(F) - (N_\alpha^{FD} - 1)/2 - 1}) \mathbf{I} \\ t_{m_p}(R_{N_\alpha(F) - (N_\alpha^{FD} - 1)/2}) \mathbf{I} - c_{\nu_{l,N_\alpha}}^{N_\alpha(F) - (N_\alpha^{FD} - 1)/2 + 1} \mathbf{g}_m^{BC} \\ \vdots \\ t_{m_p}(R_{N_\alpha(F)}) \mathbf{I} - c_{\nu_{l,N_\alpha}}^{N_\alpha(F)} \mathbf{g}_m^{BC} \end{pmatrix}, \quad (5.40)$$

$\Lambda$  is the same as in (5.35),

$$[\mathbf{g}_m(R_i)]_{n'n} = \delta_{n'm}^N(R_i), \quad (5.41)$$

and the elements of the boundary condition matrix  $\mathbf{g}_m^{BC}$  are obtained by evaluating the right hand side of (3.7). Since  $\Lambda$  is the same for the calculation of all the radial HIGFs as well as the regular radial functions, we need to do only one LU decomposition per distortion block, and, as a consequence, the total work for calculating all the radial functions is proportional to

$$N_\alpha(F)N_\delta^3 \left[ \frac{1}{4}(N_\alpha^{FD} - 1)^2 + \frac{3}{2}(m_\delta + 1)(N_\alpha^{FD} - 1) \right], \quad (5.42)$$

where  $m_\delta$  is the number of distinct  $t_m$  radial functions used to define the HIGFs in distortion block  $\delta$ .

Calculations in the body frame proceed in essentially the same manner as discussed above except that we now calculate matrix elements of the  $\Lambda$  matrix, Eq. (5.35), *directly* in the body frame. The only complication is that the boundary condition matrices  $\mathbf{g}_m^{BC}$  of Eq. (5.38) are initially formed in the space frame and then transformed to the body frame using (5.17).

## 5.6. Generation of the Finite Difference Grid

A central element in our computational strategy is that a subset of the finite difference grid points is used as a quadrature grid for the evaluation of the matrix elements of  $\mathcal{A}^{\mathcal{C}^B}$ ,  $\mathbf{B}$ , and  $\mathbf{C}$ . This means that the numerically computed radial functions never need to be interpolated to carry out the quadratures. Evenly spaced grids are easier to implement in the finite difference methods, but the quadratures over  $R_\alpha$  are computationally intensive, so we use Gaussian quadrature nodes to increase their efficiency. The foundation of the grid is established by dividing the region to be covered into  $N^\sigma$  segments  $\sigma$  and then laying  $N_\alpha^{QS}(\sigma)$  repetitions of  $N_\alpha^{QGS}(\sigma)$ -point Gauss-Legendre quadrature nodes on each segment. This yields the  $N_\alpha^{QRS}$  quadrature points that are used in the integration over  $R_\alpha$ , where

$$N_\alpha^{QRS} = \sum_{\sigma=1}^{N^\sigma} N_\alpha^{QS}(\sigma) N_\alpha^{QGL}(\sigma). \quad (5.43)$$

We then use one of three "grid spacing schemes," denoted  $GSS_\alpha(\sigma)$  with  $\sigma = 0, 1, \text{ or } 2$ , to make the grid more uniform. In the "none scheme" [ $GSS_\alpha(\sigma) = 0$ ], no additional points are added. In the "truncate scheme"

[GSS $_{\alpha}(\sigma) = 1$ ], we add several additional, evenly spaced, points between successive quadrature points according to the rule

$$n_i = \text{INT} \left[ \frac{[R_{i+1} - R_i]}{h_S(\sigma)} \right] - 1, \quad (5.44)$$

where the  $R_i$  are quadrature nodes,  $n_i$  is the number of points added between the nodes at  $R_i$  and  $R_{i+1}$ ,  $h_S(\sigma)$  is the minimum spacing between successive quadrature points in segment  $\sigma$ , that is,

$$h_S(\sigma) = \min_{R_i, R_{i+1} \subseteq \text{segment } \sigma} (R_{i+1} - R_i), \quad (5.45)$$

and  $\text{INT}[x]$  denotes the integer part of  $x$ . In the "round scheme" [GSS $_{\alpha}(\sigma) = 2$ ], we instead calculate the number of evenly spaced points to be added by the rule

$$n_i = \text{INT} \left[ \frac{R_{i+1} - R_i}{h_S(\sigma)} + \frac{1}{2} \right] - 1. \quad (5.46)$$

In the next step we add  $n_{\alpha}^{FR}(\sigma)$  additional evenly spaced points between each consecutive pair of grid points in segment  $\sigma$ . Finally, the large- $R_{\alpha}$  edge of the grid is further augmented by  $N_{\alpha}^{SD}$  points that have a geometrically decreasing stepsize determined by the decrease factor  $f_{\alpha}^{SD}$ . The initial spacing of these  $N_{\alpha}^{SD}$  points is chosen to be  $h_S(N^{\sigma})$ . This procedure is used to decrease the spacing between the final few points and thus decrease the error associated with the requirement that lower order finite difference approximations are used at the far edge of the grid. In tabulations of the parameter sets, we usually give the region over which the grid extends by specifying the values of  $R_{\alpha,0}^F$  and  $R_{\alpha,N_{\alpha}(F)+1}^F$  at which the boundary conditions are specified. These points are positioned such that

$$R_{N_{\alpha}(F)+1} - R_{N_{\alpha}(F)} = R_{N_{\alpha}(F)} - R_{N_{\alpha}(F)-1}, \quad (5.47)$$

and

$$R_2 - R_1 = R_1 - R_0 = R_0 - R_{-1} = R_{-1} - R_{-2} \dots \quad (5.48)$$

Note that in our published work so far,  $N^{\sigma}$  has been taken as 1, but the use of  $N^{\sigma} > 1$  is expected to allow for more efficient calculations in the future.

### 5.7. Calculation of the Finite Difference Coefficients

The finite difference coefficients,  $c_{\nu}^i$ , at grid point  $i$  are determined by the requirement that

$$\frac{d^2 F(R)}{dR^2} \Big|_{R_i} = \sum_{\nu=-\nu_{L,i}}^{\nu_{U,i}} c_{\nu}^i F(R_{i+\nu}) \quad (5.49)$$

for all polynomials  $F$  of order less than or equal to  $\nu_{U,i} + \nu_{L,i}$ . Such polynomials may be evaluated exactly at nearby grid points by the finite Taylor series

$$F(R_k) = \sum_{\nu=1}^{\nu_{U,i} + \nu_{L,i} + 1} \frac{d^{\nu-1} F(R)}{dR^{\nu-1}} \Big|_{R_i} \frac{(R_k - R_i)^{\nu-1}}{(\nu-1)!}. \quad (5.50)$$

This can be written in the form

$$\mathbf{A} \mathbf{d} = \mathbf{F}, \quad (5.51)$$

where

$$[\mathbf{A}]_{\nu\nu'} = \frac{(R_{i-\nu_{L,i}+\nu'} - R_i)^{\nu-1}}{(\nu-1)!}, \quad (5.52)$$

$$d_{\nu} = \frac{d^{\nu-1} F(R)}{dR^{\nu-1}} \Big|_{R_i}, \quad (5.53)$$

and

$$F_{\nu} = F(R_{i-\nu_{L,i}+\nu-1}). \quad (5.54)$$

Multiplying Eq. (5.51) by  $\mathbf{A}^{-1}$  and selecting  $d_3$  gives

$$d_3 = \frac{d^2 F(R)}{dR^2} \Big|_{R_i} = \sum_{\nu} [\mathbf{A}^{-1}]_{3\nu} F(R_{i-\nu_{L,i}+\nu-1}), \quad (5.55)$$

and we may now identify the  $[\mathbf{A}^{-1}]_{3\nu}$  as the desired coefficients. The  $c_{\nu}^i$ , thus solve the linear system

$$\mathbf{A} \mathbf{c} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \quad (5.56)$$

The system of Eqs. (5.56) is often ill conditioned, so we instead solve [22]

$$\bar{\mathbf{A}}\bar{\mathbf{c}} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad (5.57)$$

where

$$[\bar{\mathbf{A}}]_{vv'} = \left( \frac{R_{i-v_{Lj}} + v'-1 - R_i}{h} \right)^{v'-1}, \quad (5.58)$$

$$h = \max_{i-v_{Lj} \leq k \leq i+v_{Uj}} |R_i - R_k|, \quad (5.59)$$

and

$$c_v^i = \frac{1}{2} h^2 c_v^i. \quad (5.60)$$

$\bar{\mathbf{A}}$  is a Vandermonde matrix [58], and we use a specialized algorithm [58] to solve (5.57).

## 5.8. Selection of the Finite Difference Parameters

The two principal sources of difficulty in the finite difference method arise from the use of unevenly spaced grid points and the need to use lower-order formulas at the large- $R$  edge of the grid. This first consideration can be partially ameliorated by using low-order Gaussian quadratures in the generation of the grid, as these have the most evenly spaced nodes. Care must be taken, however, that this does not significantly increase the cost of the quadratures since the quadratures are typically the more expensive step. When we use  $N^\alpha = 1$ , we typically use values of  $N_\alpha^{QGL}$  in the range of 7–12.

To increase accuracy of the final results without increasing the number of quadrature points, we can add additional grid points for the finite difference calculation and/or increase the number of points used in the approximation of the second derivative operator. In the past we have used values of  $N_\alpha^{FD}$  in the range of 7–15. For the lower values, stable results usually require a significant number of additional grid points, whereas it is often possible to use only the quadrature points at the higher values. The optimal choice will depend on the particular system studied, but we have found the higher orders preferable in recent work.

The treatment of the large- $R_\alpha$  edge of the grid is a matter of special concern. The spacing between the last few points must be considerably smaller than that used in the main part of the grid due to the lower values of  $N_\alpha^{FD}$  required, as discussed in Section 5.5. Sudden decreases in the stepsize cause unstable results so we have adopted a gradual geometric decrease by a factor  $f_\alpha^{SD}$  over  $N_\alpha^{SD}$  points. For low values of  $N_\alpha^{FD}$  we can use  $f_\alpha^{SD}$  in the range of 0.7, but the higher values require a much more gradual change, typically in the range of 0.9–0.95. High requirements on the value of  $f_\alpha^{SD}$  require a concomitant increase in  $N_\alpha^{SD}$  to reach the required stepsize reduction, and for some problems that require relatively few quadrature points this can account for an appreciable fraction of the grid points.

The region over which the finite difference calculation needs to be solved is often significantly larger than the region required for the matrix element quadratures. Additionally, the most intensive quadratures—those for the reactive matrix elements—typically have nonnegligible contributions only from a small region of the grid. Thus, the quadratures on the large- $R_\alpha$  portion of the grid may often be evaluated with less effort than those for the small- $R_\alpha$  region or even completely neglected. We can take advantage of this by treating some segments of the grid with a lower density of quadrature points.

## 5.9. Obtaining ${}^0\mathbf{K}$ and the Regular Radial Functions

In the space frame the numerical solutions,  $\mathbf{f}(R_i)$ , obtained from (5.24) are, in the large- $R_\alpha$  limit, of the form

$$\mathbf{f}(R_i) = \mathbf{J}(R_i)\mathbf{P} + \mathbf{N}(R_i)\mathbf{Q}, \quad (5.61)$$

where the matrices  $\mathbf{P}$  and  $\mathbf{Q}$  are independent of  $R$ ,

$$J_{nn'}(R_i) = \begin{cases} \delta_{nn'} k_n^{1/2} R_i j_n(k_n R_i) & k_n^2 > 0 \\ \delta_{nn'} (2|k_n|)^{-1/2} \exp[|k_n|(R_i - R_j)] & k_n^2 < 0 \end{cases} \quad (5.62)$$

and

$$N_{nn'}(R_i) = \begin{cases} -\delta_{nn'} k_n^{1/2} R_i n_{l_n}(k_n R_i) & k_n^2 > 0 \\ \delta_{nn'} (2|k_n|)^{-1/2} \exp[-|k_n|(R_i - R_j)] & k_n^2 < 0. \end{cases} \quad (5.63)$$

The regular radial functions can therefore be obtained by

$${}^0\mathbf{f}(R_i) = \mathbf{f}(R_i)\mathbf{P}^{-1}. \quad (5.64)$$

and we also observe that

$${}^0\mathbf{K} = \mathbf{Q}\mathbf{P}^{-1}. \quad (5.65)$$

We could solve for  $\mathbf{P}$  and  $\mathbf{Q}$  by using (5.61) at two different values of  $R_i$ , but for increased stability we employ a least squares fit involving a larger number of points. This results in the system

$$\begin{aligned} \sum_i \mathbf{J}(R_i)\mathbf{f}(R_i) &= \sum_i [\mathbf{J}(R_i)]^2\mathbf{P} + \sum_i \mathbf{J}(R_i)\mathbf{N}(R_i)\mathbf{Q}, \\ \sum_i \mathbf{N}(R_i)\mathbf{f}(R_i) &= \sum_i \mathbf{N}(R_i)\mathbf{J}(R_i)\mathbf{P} + \sum_i [\mathbf{N}(R_i)]^2\mathbf{Q}, \end{aligned} \quad (5.66)$$

where we include values for the last  $N^{\text{asym}}$  points. We typically use a value for  $N^{\text{asym}}$  of about 12. For calculations in the body frame we first form the  $\mathbf{J}(R_i)$  and  $\mathbf{N}(R_i)$  matrices in the space frame using (5.62) and (5.63), we then transform them to the body frame using (5.17) and solve (5.66).

### 5.10. Quadratures

In this section we give details of the various numerical quadratures required in the calculation.

#### Nonreactive Potential Matrix Elements

For the case where  $\alpha = \alpha'$  we calculate matrix elements of the interaction potential using

$$U_{\beta\beta'}(R_\alpha) = -\frac{2\mu}{\hbar^2} \sum_{i=1}^{N_\alpha^{QV}} \omega_{\beta\beta'}^i \sum_{\lambda=0}^{\lambda_{\max_\alpha}} \nu_\lambda^{\text{int},\alpha}(R_\alpha, r_i) f_{\beta\beta'}^{\lambda\alpha}, \quad (5.67)$$

where the  $\omega_{\beta\beta'}^i$ , and  $r_i$  are, respectively, the weights and nodes of an  $N_\alpha^{QV}$ -point optimized [59] vibrational quadrature, and the  $f_{\beta\beta'}^{\lambda\alpha}$  are the Percival–Seaton coefficients [44] in the space frame and generalizations of these coefficients in the body frame. The  $\nu_\lambda$  are potential expansion coefficients.

The expansion coefficients are obtained by numerical integration of

$$\nu_\lambda^{\text{int},\alpha} = \frac{2\lambda + 1}{2} \int d(\cos \gamma_\alpha) P_\lambda(\cos \gamma_\alpha) V^{\text{int},\alpha}(R_\alpha, r_\alpha, \gamma_\alpha), \quad (5.68)$$

where  $P_\lambda(\cos \gamma_\alpha)$  is a Legendre polynomial of order  $\lambda$ . The integral (5.68) is calculated by an  $N_{\alpha\alpha}^{QA}$ -point Gauss–Legendre formula. We input the

quadrature size and compute the upper limit of the potential expansion,  $\lambda_{\max_\alpha}$ , which is given by

$$\lambda_{\max_\alpha} = \min[2j_{\max_\alpha} + 1, N_{\alpha\alpha}^{QA}], \quad (5.69)$$

where  $j_{\max_\alpha}$  is the largest rotational quantum number used in arrangement  $\alpha$ .

In the space frame we have [44]

$$f_{\beta\beta'}^{\lambda\alpha} = \int d\hat{\mathbf{R}}_\alpha d\hat{\mathbf{r}}_\alpha \tilde{\mathcal{Y}}_{j_\beta}^{JM_\beta}(\hat{\mathbf{r}}_\alpha, \hat{\mathbf{R}}_\alpha) P_\lambda(\cos \gamma_\alpha) \tilde{\mathcal{Y}}_{j_{\beta'}}^{JM_{\beta'}}(\hat{\mathbf{r}}_\alpha, \hat{\mathbf{R}}_\alpha). \quad (5.70)$$

This can be evaluated in terms of 3- $j$  and 6- $j$  symbols as [44]

$$\begin{aligned} f_{\beta\beta'}^{\lambda\alpha} &= (-1)^{j_\beta + j_{\beta'}} + J [(2j_\beta + 1)(2j_{\beta'} + 1)(2\ell_\beta + 1)(2\ell_{\beta'} + 1)]^{1/2} \times \\ &\quad \begin{pmatrix} j_\beta & \lambda & j_{\beta'} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_\beta & \lambda & \ell_{\beta'} \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \ell_\beta & j_\beta & J \\ j_{\beta'} & \ell_{\beta'} & \lambda \end{Bmatrix}. \end{aligned} \quad (5.71)$$

In the body frame we have [47,50]

$$f_{\beta\beta'}^{\lambda\alpha} = \int d\hat{\mathbf{R}}_\alpha d\hat{\mathbf{r}}_\alpha \tilde{\mathcal{Z}}_{j_\beta}^{JM_\beta}(\hat{\mathbf{r}}_\alpha, \hat{\mathbf{R}}_\alpha) P_\lambda(\cos \gamma_\alpha) \tilde{\mathcal{Z}}_{j_{\beta'}}^{JM_{\beta'}}(\hat{\mathbf{r}}_\alpha, \hat{\mathbf{R}}_\alpha), \quad (5.72)$$

which can be evaluated as [47,50]

$$f_{\beta\beta'}^{\lambda\alpha} = (-1)^{\Omega_\beta} \delta_{\Omega_\beta \Omega_{\beta'}} [(2j_\beta + 1)(2j_{\beta'} + 1)]^{1/2} \begin{pmatrix} j_\beta & \lambda & j_{\beta'} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_\beta & \lambda & j_{\beta'} \\ \Omega_\beta & 0 & -\Omega_{\beta'} \end{pmatrix}. \quad (5.73)$$

A large fraction of the Percival–Seaton coefficients are zero. For instance the coefficient in Eq. (5.70) is nonzero only if  $(j_\beta + \lambda + j_{\beta'}) = 0 \pmod{2}$ ,  $(\ell_\beta + \lambda + \ell_{\beta'}) = 0 \pmod{2}$ , and the triangle rule holds for both triplets  $(j_\beta, \lambda, j_{\beta'})$  and  $(\ell_\beta, \lambda, \ell_{\beta'})$ . We calculate and store only the nonzero coefficients. Equation (5.67) is then implemented using a matrix-vector multiply to treat the sum over the index  $i$  followed by a sparse SAXPY for each value of  $\lambda$ .

#### Vibrational Quadratures

The optimized vibrational quadrature scheme that is used to obtain the weights and nodes required for the quadrature over  $r_\alpha$  is detailed elsewhere [59], so this section will consider only two recent modifications. In the past we have used nodes obtained only from the asymptotic  $v = 0$  wavefunction, but we now permit any  $v$  level to be used. In parameter set specifications this new parameter is called  $v_\alpha^{QV}$ , and it should be assumed to be 0 when not specified. (For all choices of  $v_\alpha^{QV}$  the nodes are obtained from the wavefunction with the lowest allowed value

of the rotational quantum number  $j$  in the JP or JPS block being considered.) The inclusion of this new option is motivated by the observation that the matrix elements involving the higher  $\nu j$  states are the hardest to converge. By selecting the quadrature nodes to be optimal for the hardest cases, we obtain more rapid convergence.

In general the new nonasymptotic vibrational functions will span a larger region of space than the type  $e$  functions, so we have modified the vibrational quadratures to handle this complication. For example, when we use distributed Gaussians to span the vibrational coordinate, we generate the  $N_{\alpha}^{QV}$  optimized nodes as before and also calculate  $N_{\alpha}^{QV}$  candidate nodes for *each* nonasymptotic vibrational function according to Gauss–Hermite rules. The list of candidate nodes is then ordered and all those less than the largest optimized node are discarded. Next we calculate the spacing,  $D$ , between the largest two optimized nodes. We then accept the first candidate node farther than  $D$  from the largest current node and discard all smaller candidate nodes. This procedure is repeated until all candidate nodes are exhausted. For each basis function pair, nonzero weights are assigned only to the  $N_{\alpha}^{QV}$  nodes that fall closest to the maximum in the overlap between the two functions.

### Exchange Angular Quadratures

The exchange angular quadratures are always performed in the body frame. For basis functions of the form in Eq. (5.10), which includes those of Eq. (5.9) as a special case, the  $C_{\beta\beta'}^{\alpha\alpha'}$  matrix elements are given by

$$C_{\beta\beta'}^{\alpha\alpha'} = \pi(\mathcal{M}^{\alpha\alpha'})^3 R_{\alpha} R_{\alpha'} \int d(\cos\Delta_{\alpha\alpha'}) \frac{1}{r_{\alpha}} \chi_{\beta}(r_{\alpha}) Y_{j_{\beta}\Omega_{\beta}}(\gamma_{\alpha}, 0) \times \left( \frac{2\mu}{\hbar^2} \right) V^{\text{int},\alpha} (R_{\alpha}, \mathbf{x}_{\alpha}) \frac{1}{r_{\alpha'}} \chi_{\beta'}(r_{\alpha'}) Y_{j_{\beta'}\Omega_{\beta'}}(\gamma_{\alpha'}, 0) d_{\Omega_{\beta'}\Omega_{\beta}}^{j_{\beta'}j_{\beta}}(\Delta_{\alpha\alpha'}), \quad (5.74)$$

where  $r_{\alpha}$ ,  $\cos\gamma_{\alpha}$ ,  $r_{\alpha'}$ ,  $\cos\gamma_{\alpha'}$ , and  $\mathcal{M}^{\alpha\alpha'}$  are given by Eqs. (4.37)–(4.41), respectively. The modified rotation matrix elements are given by

$$d_{\Omega_{\beta'}\Omega_{\beta}}^{j_{\beta'}j_{\beta}} = [(1 + \delta_{\Omega_{\beta'}0})(1 + \delta_{\Omega_{\beta}0})]^{-1/2} \times [d_{\Omega_{\beta'}\Omega_{\beta}}^{j_{\beta'}j_{\beta}} + (-1)^{\Omega_{\beta'}+\Omega_{\beta}} d_{-\Omega_{\beta'}-\Omega_{\beta}}^{j_{\beta'}j_{\beta}} + P(-1)^{j_{\beta'}+\Omega_{\beta'}} d_{-\Omega_{\beta'}\Omega_{\beta}}^{j_{\beta'}j_{\beta}} + P(-1)^{j_{\beta}+\Omega_{\beta}} d_{\Omega_{\beta'}-\Omega_{\beta}}^{j_{\beta'}j_{\beta}}], \quad (5.75)$$

and Eq. (5.74) is evaluated using  $N_{\alpha\alpha'}^{O\alpha}$ -point Gauss–Legendre quadrature. We proceed by forming the intermediate quantities

$$b_{\beta i} = \frac{1}{r_{\alpha}(i)} \chi_{\beta}(r_{\alpha}(i)) Y_{j_{\beta}\Omega_{\beta}}[\gamma_{\alpha}(i), 0], \quad (5.76)$$

$$V_i = -\frac{2\mu}{\hbar^2} V^{\text{int},\alpha} [R_{\alpha}, \mathbf{x}_{\alpha}(i)] R_{\alpha} R_{\alpha'} \pi(\mathcal{M}^{\alpha\alpha'})^3 w_i d_{\Omega_{\beta'}\Omega_{\beta}}^{j_{\beta'}j_{\beta}} [\Delta_{\alpha\alpha'}(i)], \quad (5.77)$$

and

$$\tilde{b}_{i\beta} = b_{\beta i} V_i, \quad (5.78)$$

where  $w_i$  and  $\mathbf{x}(i)$  are, respectively, the quadrature weights and nodes. The final result is then obtained by a matrix multiplication:

$$C_{\beta\beta'}^{\alpha\alpha'} = \sum_i b_{\beta i} \tilde{b}_{i\beta'}. \quad (5.79)$$

The matrix elements of  $B_{\beta\beta'}^{\alpha\alpha'}$  are obtained in a similar manner except that the  $-2\mu V^{\text{int},\alpha}/\hbar^2$  factor is dropped from Eqs. (5.74) and (5.77).

If space-frame matrix elements are required, we then transform via

$$(C_{\beta\beta'}^{\alpha\alpha'})_{\text{space}} = \sum_{\Omega_{\beta'}} \sum_{\Omega_{\beta''}} T_{\Omega_{\beta'}\Omega_{\beta''}}^{j_{\beta}j_{\beta'}} T_{\Omega_{\beta''}\Omega_{\beta}}^{j_{\beta'}j_{\beta}} (C_{\beta\beta'}^{\alpha\alpha'})_{\text{body}} \quad (5.80)$$

using the transformation of Eq. (5.17).

### Screening Parameters

The three-dimensional numerical quadrature required for the exchange matrix elements has nonnegligible contributions over a considerably smaller region of space than that covered by the quadrature grids. By including only those points that are required, huge reductions in cost may be achieved. We have introduced five separate screening parameters to control the selection of grid points to be included in the calculation [22,35]. The first of these,  $\epsilon_{\chi}$  (where the subscript  $\chi$  refers to the vibrational functions, *not* electronic functions), acts by rejecting all points for which the diatomic vibrational functions  $\chi_{\alpha\nu j}(r_{\alpha})$  and/or  $\chi_{\alpha'\nu' j'}(r_{\alpha'})$  are small. In particular, for each arrangement, upper and lower bounds on  $r_{\alpha}$  are calculated such that  $|\chi_{\alpha\nu j}| < \epsilon_{\chi}$  for all  $\nu$  and  $j$ . Then during the innermost quadrature (over  $\cos\Delta_{\alpha\alpha'}$ ), we neglect all points for which  $r_{\alpha}$  and/or  $r_{\alpha'}$ , which can be determined from  $R_{\alpha}$ ,  $R_{\alpha'}$  and  $\cos\Delta_{\alpha\alpha'}$  using (4.37) and (4.39), fall outside the allowed region. This reduces the work required to construct the  $B$  and  $C$  matrices at a given pair of  $R_{\alpha}$  and  $R_{\alpha'}$  values. If all angular quadrature points are neglected, additional savings are attained during the calculation of the  $\mathcal{T}$ ,  $\tilde{\mathcal{T}}$ ,  $\mathcal{F}$ , and  $\mathcal{G}$  matrices. Savings are also realized in the final quadrature to obtain the  $\mathcal{H}^B$ ,  $B$ , and  $C$  matrix elements if all angular quadrature points are rejected for every  $R_{\alpha}$  at a given value of  $R_{\alpha'}$ . Since the inner radial quadrature involves the bulk of the work, the second effect is by far the most important.

The second and third screening parameters,  $\epsilon_B$  and  $\epsilon_W$ , are used in the inner radial quadrature. We determine the element of maximum magnitude of the  $W^{\alpha\alpha}$ ,  $C^{\alpha\alpha(\text{eff})}$ , and  $B^{\alpha\alpha}$  matrices and, if these are less than  $\epsilon_W$ ,  $\epsilon_B$ , and  $\epsilon_B$ , respectively, the contribution of these matrices at this  $R_\alpha, R_\alpha$  pair is neglected.

The radial screening parameter,  $\epsilon_{\text{rad}}$ , determines the starting points for the radial quadratures. We find the largest value of  $R_\alpha$  such that every regular radial function and radial HIGF in arrangement  $\alpha$  is less than the fraction  $\epsilon_{\text{rad}}$  of its maximum magnitude, and we exclude all radial quadrature points less than this value.

The final screening parameter,  $\epsilon_r$ , is used to set the value of the non-HIGF basis functions and the  $t_{m_p, p}(R_\alpha)$  associated with the HIGFs to zero when their radial part is less than the fraction  $\epsilon_r$  of its maximum.

### Radial Quadratures

The radial quadratures are performed separately for each pair of arrangements subject to the constraint that  $\alpha \leq \alpha_0$ . The  $B$  matrix elements for the case  $\alpha > \alpha_0$  are obtained using the alternate forms of (4.54)–(4.56). These formulas express the remaining  $B$  matrix elements only in terms of auxiliary matrices  $\mathcal{F}$ ,  $\mathcal{F}^{\text{eff}}$ , and  $\mathcal{T}$  with  $\alpha \leq \alpha_0$ . This provides a significant savings because the calculation of the auxiliary matrices is the most computationally expensive portion of the numerical quadratures. For a given  $\alpha, \alpha_0$  pair, the contributions to the various  $\mathcal{Z}^B, B$ , and  $C$  matrix elements are accumulated simultaneously at each pair of radial quadrature points, and this permits most of the computational work to be written as matrix multiplications and to be performed using efficient library routines.

### 5.11. Contraction

The contraction scheme outlined here is similar to that used in other contexts for locally adiabatic basis functions [3–6,32]. We need to obtain the  $B$  and  $C$  matrices in terms of contracted basis functions, but we calculate them first in the primitive basis set as described above. The primitive basis functions,  $\Gamma_\beta$ , span three arrangements and can be part of the  $c$  subspace or the  $\mathcal{L}$  subspace (as defined in Section 3.2). The  $\mathcal{L}$  subspace is decomposed into parts called  $d$  and  $F$ , where  $d$  contains the  $\mathcal{L}^2$  HIGFs, and  $F$  contains the type  $e$  and type  $a$  functions. We define the subspace  $G$  as the union of subspaces  $d$  and  $c$ , that is,  $G$  contains all the HIGFs. The contraction is performed within the  $F$  subspace, and the  $G$  subspace is not contracted.

The reason that we contract the basis is that it is expected that fewer contracted functions will be needed to obtain converged calculations. The contraction is performed in terms of a matrix which we designate as  $\mathbf{Z}$ . The  $\mathbf{Z}$  matrix in the primitive basis is square and orthogonal; its columns are the eigenvectors of a partially decoupled Hamiltonian matrix, and it has the same row and column dimensions as the square  $C^{FF}$  matrix. To form  $\mathbf{Z}$  in the contracted basis we discard those columns that correspond to linear combinations of primitive basis functions that are to be excluded. This results in a rectangular  $\mathbf{Z}'$  matrix which is used to obtain the  $B$  and  $C$  matrices in the contracted basis. These matrices are given by

$$\mathbf{B}' = (\mathbf{Z}')^T \mathbf{B} \quad (5.81)$$

and

$$\mathbf{C}' = (\mathbf{Z}')^T \mathbf{C} \mathbf{Z}', \quad (5.82)$$

where  $\mathbf{B}'$  and  $\mathbf{C}'$  are in the contracted basis and  $\mathbf{B}$  and  $\mathbf{C}$  are in the primitive basis.

### General Form of the $B, C$ , and $Z$ Matrices

When we distinguish between the  $G$  and  $F$  subspaces, the  $B$  and  $C$  matrices have the general form

$$\mathbf{B} = \begin{pmatrix} \mathbf{B}^G \\ \mathbf{B}^F \end{pmatrix} \quad (5.83)$$

and

$$\mathbf{C} = \begin{pmatrix} \mathbf{C}^{GG} & \mathbf{C}^{GF} \\ \mathbf{C}^{FG} & \mathbf{C}^{FF} \end{pmatrix}. \quad (5.84)$$

The various matrix elements of (5.83) and (5.84) are given by (4.31) and (4.32).

Consider the case where the translational parts of each of the primitive type  $e$  and type  $a$  functions are Gaussians with centers specified by  $R_{\alpha m_p}^G$ , where  $1 \leq m \leq N^T$ , and  $N^T$  is the total number of distinct Gaussian translational basis functions in the  $F$  subspace. In particular  $1 \leq m \leq N_1^T$  for arrangement 1,  $N_1^T + 1 \leq m \leq N_1^T + N_2^T$  for arrangement 2, and  $N^T = N_1^T + N_2^T + N_3^T$ . We arrange the  $F$  subspace basis functions such that all of those with  $m = 1$  come first, those with  $m = 2$  come next, and so on. Then the  $B$  matrix can be written as

$$\mathbf{B} = \begin{pmatrix} \mathbf{B}^G \\ \mathbf{B}^F(m=1) \\ \mathbf{B}^F(m=2) \\ \vdots \\ \mathbf{B}^F(m=N^T) \end{pmatrix}, \quad (5.85)$$

and the  $\mathbf{C}$  matrix can be written as

$$\mathbf{C} = \begin{pmatrix} \mathbf{C}^{GG} & \mathbf{C}^{GG}(m'=1) & \dots & \mathbf{C}^{GF}(m'=N^T) \\ \mathbf{C}^{FG}(m=1) & \mathbf{C}^{FF}(m=m'=1) & \dots & \mathbf{C}^{FF}(m=1, m'=N^T) \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{C}^{FG}(m=N^T) & \mathbf{C}^{FF}(m=N^T, m'=1) & \dots & \mathbf{C}^{FF}(m=m'=N^T) \end{pmatrix}, \quad (5.86)$$

The  $\mathbf{Z}'$  matrix is a block diagonal rectangular matrix with the form

$$\mathbf{Z}' = \begin{pmatrix} \mathbf{I} & 0 & \dots & 0 \\ 0 & \mathbf{Z}_m^{FF'} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \mathbf{Z}_N^{FF'} \end{pmatrix}, \quad (5.87)$$

where the various diagonal blocks,  $\mathbf{Z}_m^{FF'}$ , of  $\mathbf{Z}'$  contain a subset of the eigenvectors of the decoupled Hamiltonian matrix,  $\mathbf{H}_m^{FF}$ , defined by

$$\mathbf{H}_m^{FF} = \frac{\hbar^2}{2\mu} \mathbf{C}^{FF}(m=m') + E\mathbf{O}^{FF}(m=m'), \quad (5.88)$$

where the matrix elements of the  $\mathbf{O}^{FF}$  are overlaps of basis function pairs in the  $F$  subspace.

### Calculation of the $\mathbf{Z}$ Matrix and Performing the Contraction

The contraction is performed by blocks in the following fashion. First we diagonalize  $\mathbf{H}_m^{FF}$ , and we collect the resulting eigenvectors by columns into the square matrix,  $\mathbf{Z}_m^{FF'}$ . Eigenvectors are retained in  $\mathbf{Z}_m^{FF'}$  if they satisfy some criterion, for example,

$$E_i \leq E + \delta_E, \quad (5.89)$$

where  $E_i$  is the eigenenergy associated with the eigenvector,  $E$  is the total scattering energy, and  $\delta_E$  is an arbitrary parameter. This eliminates some basis functions and produces the rectangular  $\mathbf{Z}_m^{FF'}$  where a prime is added to the right superscript to denote the contraction. The appropriate sub-blocks of  $\mathbf{B}$  and  $\mathbf{C}$  are contracted using

$$\mathbf{C}^{F'F'}(m, m') = [\mathbf{Z}_m^{FF'}]^T \mathbf{C}^{FF}(m, m') \mathbf{Z}_m^{FF'}, \quad (5.90)$$

$$\mathbf{C}^{GF'}(m, m') = \mathbf{C}^{GF}(m, m') \mathbf{Z}_m^{FF'}, \quad (5.91)$$

$$\mathbf{C}^{F'G}(m) = [\mathbf{Z}_m^{FF'}]^T \mathbf{C}^{FG}(m, m'), \quad (5.92)$$

and

$$\mathbf{B}^{F'}(m) = [\mathbf{Z}_m^{FF'}]^T \mathbf{B}^F(m). \quad (5.93)$$

### 5.12. Symmetry

Simplifications exist for systems having identical atoms [35,37]. In these cases some arrangements are indistinguishable and the basis functions are the same to within a phase factor. As a result, the basis functions, distorted waves, and HIGFs need be obtained only for the unique arrangements. Also the number of unique *arrangement pairs* is less than the total number of arrangements pairs, and the  $\mathcal{H}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  matrix elements need be calculated only for the unique cases.

If identical atoms are present, at least one arrangement will contain a homonuclear diatomic molecule. When this is the case, the interaction potential is an even function of  $\gamma_\alpha$  (the angle between  $\mathbf{r}_\alpha$  and  $\mathbf{R}_\alpha$ ) for that arrangement, and as a result, the coefficients in the interaction potential are only nonzero for even values of  $\lambda$  in the Legendre expansion of Eqs. (5.67) and (5.68). Furthermore, the amount of effort to perform the quadrature, Eq. (5.68), for the potential expansion coefficients is cut in half because the domain of the integral in Eq. (5.68) can be reduced to  $0 < \gamma_\alpha < \pi/2$  as opposed to  $0 < \gamma_\alpha < \pi$ .

Since the potential expansion includes only even values of  $\lambda$  for homonuclear arrangements, the distortion potential couples even rotational states or odd rotational states, but it does not couple even  $j$  with odd  $j$ . This decreases the size of the distortion blocks, resulting in less computational effort to obtain the radial functions of the distorted waves and HIGFs for the homonuclear arrangement.

Another use of symmetry [35,37] concerns the correction to the reactance matrix due to the coupling potential, which is given by

$$\mathcal{S} = \mathcal{S}^B + \bar{\mathbf{B}}^T \bar{\mathbf{C}}^{-1} \bar{\mathbf{B}}. \quad (5.94)$$



Specifically, we exploit the symmetry of  $\mathcal{S}^B$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  by introducing the unitary transformation [35,37]

$$\mathbf{U}_k^\dagger \mathcal{S} \mathbf{U}_k = \mathbf{U}_k^\dagger \mathcal{S}^B \mathbf{U}_k + \mathbf{U}_k^\dagger \tilde{\mathbf{B}}^\dagger \mathbf{U}_c (\mathbf{U}_c^\dagger \tilde{\mathbf{C}} \mathbf{U}_c)^{-1} \mathbf{U}_c^\dagger \tilde{\mathbf{B}} \mathbf{U}_k, \quad (5.95)$$

where  $\mathbf{U}_k$  and  $\mathbf{U}_c$  are chosen such that  $\mathcal{S}^B$ ,  $\tilde{\mathbf{B}}$ , and  $\tilde{\mathbf{C}}$  are block diagonalized or symmetrized. After these matrices are block diagonalized,  $\mathcal{S}$  is formed separately for each block, resulting in significant savings in computation time and memory use. For the  $A + B_2$  case the savings in computation time over the ABC case is approximately a factor of 4, and for the  $A_3$  case the savings is approximately a factor of 21.6. For further details see Ref. [35].

For cases involving identical atoms, the contraction procedure described in section 5.11 can also be carried out more efficiently by using Eq. (5.95).

### 5.13. Linear Algebra

After the matrix elements are calculated and the basis set contractions are performed, we must solve the linear system of (2.71). Since  $\mathbf{C}$  is symmetric, we may form the  $UDU^T$  decomposition [57] or an LU decomposition. The latter requires about twice the memory and twice the operation count of the  $UDU^T$  algorithm, but it is often faster on vector-pipeline supercomputers. In certain cases we perform a row and column scaling of the  $C$  matrix using the inverse of the square roots of the absolute values of the diagonal elements as scaling factors. The calculation proceeds in two steps. First we decompose  $\mathbf{C}^{\mathcal{Z}\mathcal{Z}}$  and solve (3.44)–(3.46), which involves a large real linear equation solution to form  $[\mathbf{C}^{\mathcal{Z}\mathcal{Z}}]^{-1} \mathbf{B}^{\mathcal{Z}}$ , and  $[\mathbf{C}^{\mathcal{Z}\mathcal{Z}}]^{-1} \mathbf{C}^{\mathcal{Z}c}$ . We then transform to complex boundary conditions using (3.49)–(3.51), decompose  $\tilde{\mathbf{C}}$ , and construct  $\mathbf{S}$  by (3.52), which involves a small complex linear equation solution to form  $[\mathbf{C}^c]^{-1} \mathbf{B}$ .

## 6. MEMORY CONSIDERATIONS

In this section we outline the memory requirements of the major stages of the algorithm. An extensive discussion of memory management is available elsewhere [22], so here we only summarize the results and indicate recent modifications. The following notation will be required:

$\alpha_{\max}$ :	number of arrangements (typically three)
$\alpha_{\text{unique}}$ :	number of unique arrangements (1 for $A_3$ , 2 for $A + B_2$ , or 3 for $A + BC$ )
$M$ :	total number of basis functions
$M_x^:$ :	total number of basis functions of type $x$ ( $x = e, a, \text{ or } g$ )
$M_\alpha^x$ :	number of basis functions of type $x$ ( $x = e, a, \text{ or } g$ ) in arrangement $\alpha$
$M_\alpha^{x\delta}$ :	number of basis functions of type $x$ ( $x = e \text{ or } g$ ) in distortion block $\delta$ for arrangement $\alpha$
$M_\alpha^\delta$ :	$M_\alpha^{e\delta} + M_\alpha^{g\delta}$
$M(S)$ :	number of basis functions in symmetry block $S$
$m_{\max}$ :	the maximum number of translational functions per vibrational–rotational–orbital function
$N$ :	number of channels
$N_\alpha$ :	number of channels in arrangement $\alpha$
$N_\alpha^\delta$ :	number of channels in distortion block $\delta$ of arrangement $\alpha$
$N(S)$ :	number of channels in symmetry block $S$
$N_\alpha^{QRS}$ :	number of radial quadrature points in arrangement $\alpha$
$N_\alpha^{QV}$ :	number of optimized [59] vibrational quadratures nodes for arrangement $\alpha$
$N_\alpha(F)$ :	number of finite difference grid points in arrangement $\alpha$
$N_\alpha^\lambda$ :	number of potential expansion coefficients in arrangement $\alpha$
$O_\alpha$ :	number of distinct $\phi_\beta(\mathbf{x}_\alpha)$ and $\phi_{n\beta}(\mathbf{x}_\alpha)$ rotational–vibrational–orbital basis functions in arrangement $\alpha$
$\chi_\alpha$ :	The number of distinct vibrational functions $\chi_\beta(r_\alpha)$ in arrangement $\alpha$ .

The code begins by calculating a number of energy-independent quantities. This requires storage (in words) equal to

$$M^{\text{Eind}} = \sum_{\alpha=1}^{\alpha_{\text{unique}}} N_\alpha^{QV} \frac{\chi_\alpha^2}{2} + (5\alpha_{\max} + 3\alpha_{\text{unique}}) m_{\max} \max_{\alpha} O_\alpha. \quad (6.1)$$

The first part of  $M^{\text{Eind}}$  accounts for the optimized vibrational quadrature weights, and the remainder contains various pointers. The next major use of storage is in the calculation of the radial functions. We require

$$M_{\alpha}^{\text{rad}} = N_{\alpha}^{\text{QRS}} \sum_{\delta \in \alpha} N_{\alpha}^{\delta} (N_{\alpha}^{\delta} + M_{\alpha}^{\delta}) + 3 \sum_{\delta \in \alpha} N_{\alpha}^{\delta} M_{\alpha}^{\delta} \quad (6.2)$$

words of storage to hold the radial functions and boundary condition matrices for arrangement  $\alpha$ . The sums in (6.2) include all distortion blocks that have open channels and/or HIGFs. We have not specified the effect of using localized type  $g$  functions in (6.2); if this option is used we need store only the nonzero portion of the HIGFs, and this significantly reduces the first term. During the calculation of the radial functions we also require storage for the  $\Lambda$  matrix of (5.35) and the potential expansion coefficients. This requires

$$M_{\alpha}^{\text{rad,loc}(\delta)} = N_{\alpha}(F)[(N_{\alpha}^{\delta})^2 (3N_{\alpha}^{\text{FD}} + 1)/2] + N_{\alpha}^{\text{QV}} N_{\alpha}^{\lambda} \quad (6.3)$$

words of storage. Thus the maximum storage used during the calculation of the radial functions in arrangement  $\alpha$  is about  $M^{\text{Eind}} + \sum_{\alpha=1}^{\alpha} M_{\alpha}^{\text{rad}} + \max_{\delta \in \alpha} M_{\alpha}^{\text{rad,loc}(\delta)}$ . Some of the  $U_{nr}^{\alpha}$  matrix elements that are calculated during the distorted-wave problems are also required during the calculation of the  $\mathcal{H}^B$ ,  $B$ , and  $C$  matrix elements. The amount of storage required to save them, however, is quite large, so we instead recalculate them when needed. Much of the work involved in the calculation of the  $U_{nr}^{\alpha}$  matrix elements is in the calculation of the potential expansion coefficients,  $v_{\lambda}^{\text{int},\alpha}$ , given by (5.68), and these can be retained since the storage required is slight. Our code has several options in which the  $v_{\lambda}^{\text{int},\alpha}$  are also recalculated [22,35] but for most applications the additional savings in storage is too small to compensate for the added computational expense of these options.

The space required to store the  $\mathcal{H}^B$ ,  $B$ , and  $C$  matrix elements obtained for arrangements  $\alpha' \leq \alpha$  is

$$M^{\text{KBC}}(\alpha) = \sum_{\alpha'=1}^{\alpha} s_{\alpha'} (M_{\alpha'} + N_{\alpha'})^2 + \sum_{\alpha'=1}^{\alpha} s_{\alpha',\alpha'+1} (M_{\alpha'} + N_{\alpha'}) (M_{\alpha'+1} + N_{\alpha'+1}), \quad (6.4)$$

where  $\alpha' + 1$  is defined modulo  $\alpha_{\text{unique}}$ ,  $s_{\alpha'}$  is a symmetry factor approximately equal to  $1/2$  when  $\alpha'$  is homonuclear and 1 otherwise,  $s_{\alpha',\alpha'+1}$  is equal to  $1/2$  when arrangements  $\alpha'$  and  $\alpha' + 1$  are equivalent by symmetry and 1 otherwise. We also require temporary local storage equal to

$$M_{\alpha}^{\text{loc}} = O_{\alpha}(2O_{\alpha+1} + N_{\alpha+1}) + (M_{\alpha} + N_{\alpha}) \{ (O_{\alpha+1} + 2N_{\alpha+1}) + \max_{\delta \in \alpha+1} (N_{\alpha+1}^{\delta} + M_{\alpha+1}^{\delta}) \} \quad (6.5)$$

to hold the  $W$ ,  $B$ ,  $C^{\text{eff}}$ ,  $\mathcal{F}$ ,  $\mathcal{F}^{\text{eff}}$ ,  $G$ ,  $G^{\text{eff}}$ ,  $\mathcal{T}$ , and  $\tilde{\mathcal{T}}$  matrices as well as the work space needed for the matrix multiplications. Notice the strong dependence on  $O_{\alpha}$ . Since we do not require elements of  $\mathcal{H}^B$  and  $B$  associated with closed channels we need not calculate them; thus if we take advantage of this we can replace  $N_{\alpha}$  in (6.4) and (6.5) and the equations to follow with the number of open channels in the  $\alpha$ th arrangement. After all the quadratures are finished we discard the radial functions and reorder the matrix elements. This reordering requires

$$M^{\text{Eind}} + M^{\text{KBC}}(\alpha_{\text{unique}}) + \sum_{S=1}^{S_{\text{max}}} M^{\text{K},B,C}(S)$$

words, where

$$M^{\text{K},B,C}(S) = \frac{1}{2} [N(S) + M(S)]^2. \quad (6.6)$$

We then discard the disordered matrix elements and solve (2.72) for each symmetry block. Assuming we use the UDU<sup>T</sup> algorithm [57] and complex boundary conditions without contraction and without presolving a subblock in real arithmetic, the maximum storage required during the linear algebra is

$$M^{\text{alg}} = \max_S \left( \sum_{S'=1}^S M^{\text{K},B,C}(S') + 2(M^{\text{K},B,C}(S) + N(S)M(S)) + \sum_{S'=S+1}^{S_{\text{max}}} N(S')^2 \right). \quad (6.7)$$

If instead we use (3.44)–(3.46) and  $M^a + M^e \gg M^b$ , the middle term is reduced by a factor of 2. Also, if we contract the primitive  $B$  and  $C$  matrix elements as in Section 5.11, a slight increase in the storage requirements may be incurred during this procedure beyond that required just after reordering. However, the magnitude of  $M^{\text{alg}}$  as well as the memory integral, that is, the time weighted memory requirements, for the entire calculation will be significantly decreased by contraction.

The maximum storage required by the program is given by

$$M^{\text{Eind}} + \max \left\{ \begin{array}{l} \max_{\alpha} \left( \sum_{\alpha'=1}^{\alpha} M_{\alpha'}^{\text{rad}} + \max_{\delta \in \alpha} M_{\alpha}^{\text{rad,loc}(\delta)} \right), \max_{\alpha} (M^{\text{KBC}}(\alpha) + M_{\alpha}^{\text{loc}}), \\ \left( M^{\text{KBC}}(\alpha_{\text{unique}}) + \sum_{S=1}^S M^{\text{K},B,C}(S) \right), M^{\text{alg}} \end{array} \right\}.$$

We have also implemented a number of options to store part of the required data on disk and these are detailed elsewhere [22].

## 7. SUMMARY

We have presented a very general linear algebraic variational method for reactive scattering, and we discussed our numerical implementation in detail. The equations presented here should allow for the extension of converged quantum mechanical dynamics calculations to a more difficult class of problems.

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