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Chapter 17

Problem Decomposition Techniques in Quantum Mechanical Reactive Scattering*

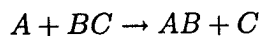
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Abstract

In this chapter we discuss strategies for efficiently solving quantum mechanical reactive and inelastic scattering problems using algebraic variational methods. First we review the outgoing wave variational principle. Then we review three aspects of its implementation where problem decomposition techniques are used to make the calculations efficient. The first of these involves partitioning the Hamiltonian into a distortion part that is solved numerically and a coupling part that is treated by expanding the difference of the full outgoing wave and the distortion-potential-induced part of the outgoing wave in a basis. The second involves problem decomposition in channel space or physical space in order to obtain efficient basis functions for the fully coupled problem. In this section we also propose a new pre-diagonalization technique that may be used as the basis of a divide-and-conquer approach. Finally, we consider schemes for partitioning basis functions into Hilbert subspaces as direct analogs of domain decomposition in physical subspaces.

1 Introduction

In this chapter we consider the problem of predicting the rate of a chemical reaction



where A , B , and C are atoms. The motion and interactions of these particles are assumed to be governed by the laws of quantum mechanics. We restrict

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ourselves to the gas phase where the density is low enough so that only bimolecular collisions are important and wall interactions are negligible. In this case, we can separate out the motion of the center of mass of ABC and hence reduce the number of coordinates by three. We further assume in the present work that the Born-Oppenheimer [1,2] approximation has been invoked to decouple the motion of the electrons from the nuclei. This makes the quantum mechanical description of the reaction equivalent to that for the motion of two point masses on a potential energy hypersurface (PES). The PES can be determined using methods described in other chapters in this book [3,4].

In comparing the structure of the multi-particle Schrödinger problem to partial differential equation problems that arise in other chapters of this volume, it is useful to consider some general characteristics of the problem. We consider only the time-independent formulation, which leads to a six-dimensional, linear, elliptic partial differential equation. The relationship of the solution to the physical observables is contained in the total energy, which is a parameter in the equations, and in the complex traveling-wave boundary conditions where one particle is far from the other two; at the energies considered here there is not enough energy to simultaneously break all the bonds, so only the atom-diatom limit need be considered.

The solution of the quantum mechanical equation of motion (the Schrödinger equation) for this problem yields a scalar function of the six internal degrees of freedom. This function is called the wave function, and all observable attributes of the collision can be determined from it. When A and BC are widely separated, the wave function can be written in the form

$$(1) \quad \Psi_{n_0}^{JM(+)} = \frac{1}{R_1} \sum_{vj\ell} \phi_{1vj}(r_1) \mathcal{Y}_{j\ell}^{JM}(\theta_1, \phi_1, \Theta_1, \Phi_1) f_{1vj\ell, n_0}^{J(+)}(R_1),$$

where the coordinates are (r_1, θ_1, ϕ_1) , the spherical polar coordinates of the vector from B to C , and (R_1, Θ_1, Φ_1) , the spherical polar coordinates of the vector from the center of mass of BC to A . The subscript 1 indicates the arrangement $A + BC$ rather than $B+AC$ (arrangement index $\alpha = 2$) or $C+AB$ (arrangement index $\alpha = 3$). The function $\phi_{\alpha vj}$ is an easily determined real square integrable (\mathcal{L}^2) function that describes the vibration of BC , and is labeled by its number of nodes (v , the vibrational quantum number) and by the equation it solves (which in turn is labeled by j and α , and here $\alpha = 1$). For given $j\alpha$, the $\phi_{\alpha vj}$ form a complete orthonormal set. The function $\mathcal{Y}_{j\ell}^{JM}$ is a linear combination of the product of two spherical harmonics and describes the rotations of the system. The quantum number j specifies the rotational angular momentum of BC , ℓ the orbital angular momentum of A with respect to BC , J the angular momentum of the system as a whole, and M the orientation of total angular momentum vector. Since

space is isotropic, the equations of motion contain no explicit M dependence, and thus the only part of the wave function depending on M is $\mathcal{Y}_{j\ell}^{JM}$. There is no coupling between wave functions with different values of J and M . The final function in (1), $f_{1\nu j\ell, n_0}^{J(+)}$, describes the radial relative motion of A and BC , and it is not an \mathcal{L}^2 function. It is labeled by the previously introduced quantum numbers as well as the boundary condition index n_0 . The radial function is regular (*i.e.*, zero) at the origin and satisfies the large- R_1 boundary condition

$$(2) \quad \lim_{R_1 \rightarrow \infty} f_{n, n_0}^{J(+)} = \delta_{nn_0} k_n^{-\frac{1}{2}} \exp[-i(k_n R_1 - \ell_n \pi / 2)] - S_{nn_0}^J k_n^{-\frac{1}{2}} \exp[i(k_n R_1 - \ell_n \pi / 2)],$$

where n denotes a particular set of $\alpha\nu j\ell$ (each such set is called a channel), δ_{nn_0} is the Kronecker delta function (which is one if $n = n_0$ and zero otherwise), k_n is the wave vector defined by

$$(3) \quad k_n^2 = 2\mu(E - \epsilon_n) / \hbar^2,$$

where μ is the reduced mass of the system (we mass scale all coordinates to a single reduced mass [5]), E is the total energy of the system, ϵ_n is the internal energy for the choice of $\alpha\nu j$ specified by n , \hbar is Planck's constant divided by 2π , and $S_{nn_0}^J$ is a complex coefficient. The matrix with elements $S_{nn_0}^J$ is called the scattering matrix and is a dense, complex, symmetric, unitary matrix. The scattering matrix depends parametrically on the total energy E and from it we can compute all measurable quantities of the collision using simple formulas [6,7,8]. Thus the focus of the remainder of this work is on the calculation of the scattering matrix.

The inclusion of $\mathcal{Y}_{j\ell}^{JM}$ in (1) deserves special emphasis. Use of this kind of basis function, which is intrinsically delocalized, allows us to take account of conservation of J and M , which is absolutely essential for efficiency as it greatly cuts down on the number of basis functions that must be considered at one time for convergence. The necessity to use basis functions corresponding to definite J and M is a principal reason for emphasizing delocalized basis functions in quantum mechanics.

For nonreactive problems, the most straightforward approach to determining the scattering matrix is to expand the wave function as in (1), substitute this into the Schrödinger equation, and project in turn on each of the known products $\phi_{1\nu' j'} \mathcal{Y}_{j'\ell'}^{JM*}$. This yields a set of coupled second order ordinary differential equations (ODEs) for the unknown radial functions $f_{nn_0}^{J(+)}$. A linearly independent set of solutions is then numerically integrated outwards from the small- R_1 region, where the $f_{nn_0}^{J(+)}$ are negligible, to the large- R_1 asymptotic region, where the numerical solutions can be matched to (2) to give the scattering matrix. For reactive problems, this straightforward approach cannot be used because basis functions defined in terms

of a single set of coordinates cannot efficiently describe all three possible reactants or products. Thus we turn to an alternate approach of using basis functions to describe all degrees of freedom defining some of the basis functions in terms of $r_\alpha, \theta_\alpha, \phi_\alpha, R_\alpha, \Theta_\alpha, \Phi_\alpha$ with $\alpha = 1$ and others in terms of such coordinates with $\alpha = 2$ and 3, and using a variational principle equivalent to the Schrödinger equation to determine the scattering matrix. This reduces the problem to performing quadratures and linear algebra. Both steps can be performed efficiently on modern computers, and this approach provides considerable scope for introducing the ideas of problem decomposition. Another approach to the coordinate problem of reactive scattering is to use hyperspherical coordinates and wave function matching [9,10,11,12,13]. This allows one to return to the coupled ODE description, but with new complications. The hyperspherical approach will not be discussed further in this article.

Although the main motivation for the algebraic approach is the difficulty of treating reactive scattering with the coupled-ODE approach, it turns out that all of the details of our formalism that are important for the present discussion also arise in nonreactive scattering. Thus to simplify the following discussion of our formalism, we will only consider nonreactive scattering, and hence we drop the label α . We also drop the quantum numbers J and M , which do not play an important role in the following discussion. Extension to reactive scattering essentially only involves adding back the extra quantum number (the arrangement index α) and carrying out a new class of integrals. The explicit form of the integrals is given elsewhere [14].

In Section 2 we summarize the algebraic variational principle that we use, and in Sections 3-5 we discuss three ways in which problem decomposition is invoked to make the calculations efficient. Since our emphasis is on problem decomposition techniques, we shall not discuss specific applications in detail, but the reader is referred to a review [15] and a typical application [16] for such background.

2 Variational Principle

We first sketch out the derivation of the variational principle we use. We start with the Schrödinger equation which takes the form

$$(4) \quad (H - E)\Psi^{(+)\alpha_0} = 0,$$

where H is the Hamiltonian operator, which is the sum of the six-dimensional Laplacian times $\frac{-\hbar^2}{2\mu}$ (the kinetic energy) and a scalar function (the PES). We partition the Hamiltonian as

$$(5) \quad H = H^D + VC,$$

where V^C is defined by

$$(6) \quad V^C = H - H^D,$$

and H^D takes the form

$$(7) \quad H^D = T + V^{vib} + V^D,$$

where T is the kinetic energy operator, V^{vib} is the potential energy of the isolated diatomic, and V^D is a distortion potential, the choice of which is discussed in the next section. All potentials are assumed to be represented as analytic functions of the internal coordinates possibly combined with nonlocal projection operators (which will be called projectors). We assume that we have numerically obtained the Green's function

$$(8) \quad G^{D(\pm)} = \lim_{\epsilon \rightarrow 0^+} -\frac{\hbar^2}{2\mu} (E - H^D \pm i\epsilon)^{-1},$$

and the distorted waves $\psi^{(\pm)n}$ which solve

$$(9) \quad (H^D - E)\psi^{(\pm)n} = 0.$$

The function $\psi^{(+n)}$ is expanded as in (1) and its radial part is regular at the origin and is subject to the boundary conditions of (2); $\psi^{(-n)}$ is its time reversed counterpart. In practice the $G^{D(\pm)}$ and $\psi^{(\pm)n}$ functions are obtained by the coupled-ODE approach that is discussed in the introduction. In fact, in most cases we do not actually construct $G^{D(\pm)}$ but rather we directly solve the coupled ODEs for required integrals over the $G^{D(\pm)}$ [17]; that detail of implementation need not concern us here, but the efficiency of this technique is critical to the issues discussed in Section 4. Then a formal solution to the full problem is given by [18,19]

$$(10) \quad \Psi^{(\pm)n} = \psi^{(\pm)n} - G^{D(\pm)}\mathcal{U}\Psi^{(\pm)n},$$

where

$$(11) \quad \mathcal{U} = -\frac{2\mu}{\hbar^2}V^C.$$

Referring to (2) and constructing wave packets from wave functions with such boundary conditions, $\Psi^{(+n)}$ is used to construct wave packets with an unscattered wave and outgoing scattered waves, whereas $\Psi^{(-n)}$ is used to construct wave packets with an unscattered wave and incoming scattered

waves, which is the time-reversed description [20]. It is convenient to define the quantity

$$(12) \quad \Psi_{OW}^{(\pm)n} = -G^{D(\pm)}\mathcal{U}\Psi^{(\pm)n},$$

which may be called the outgoing wave. (Note that actually $\Psi_{OW}^{(\pm)n}$ is the difference between the full outgoing wave and the part induced by the distortion potential, but we always call it just the outgoing wave.) Thus

$$(13) \quad \Psi^{(\pm)n} = \psi^{(\pm)} + \Psi_{OW}^{(\pm)n},$$

and it can be shown by taking the large- R limit of (10) that the scattering matrix is given by

$$(14) \quad S_{nn_0} = {}^0S_{nn_0} + \mathcal{S}_{nn_0},$$

where ${}^0S_{nn_0}$ is the scattering matrix due to the distortion potentials, and

$$(15) \quad \mathcal{S}_{nn_0} = \langle \psi^{(-)n} | \mathcal{U} | \Psi^{(+n_0)} \rangle.$$

In (15) and the equations that follow, $\langle a|b|c \rangle$ means the integral

$$(16) \quad \langle a|b|c \rangle = \int_0^\infty R^2 dR \int_{-1}^1 d \cos \Theta \int_0^{2\pi} d\Phi \int_0^\infty r^2 dr \int_{-1}^1 d \cos \theta \int_0^{2\pi} d\phi \\ \times a^*(R, \Theta, \Phi, r, \theta, \phi) b(R, \Theta, \Phi, r, \theta, \phi) c(R, \Theta, \Phi, r, \theta, \phi),$$

where $*$ denotes the complex conjugation. In practice three of the six integrations in (16) can be carried out analytically. The remaining three-dimensional integration is carried out by direct products of Gaussian quadratures [14].

Equation (15) could be used with some trial $\Psi^{(+n_0)}$ to compute an approximation to the scattering matrix, but the results would be very sensitive to the choice of the trial function since if the trial function differs from the exact one by the amount $\delta\Psi^{(+n_0)}$, the computed scattering matrix elements differ from the exact ones by $\langle \psi^{(-)n} | \mathcal{U} | \delta\Psi^{(+n_0)} \rangle$. We seek instead a stationary expression for the scattering matrix which gives rise to errors which involve integrals containing the product $\delta\Psi^{(-)n*} \delta\Psi^{(+n_0)}$, which should be much smaller. This can be done in several ways. In the method we use, we write

$$(17) \quad \mathcal{S}_{nn_0} = \mathcal{S}_{nn_0} + \mathcal{S}_{nn_0} - \mathcal{S}_{nn_0},$$

where we use three different expressions for \mathcal{S}_{nn_0} on the right hand side. The first is obtained by substituting (13) into (15):

$$(18) \quad \mathcal{S}_{nn_0} = \langle \psi^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle + \langle \psi^{(-)n} | \mathcal{U} | \Psi_{OW}^{(+n_0)} \rangle.$$

In the second we substitute $\psi^{(-)n}$ obtained from inverting (10) into (15) to obtain

$$(19) \quad \mathcal{S}_{nn_0} = \langle \Psi^{(-)n} | \mathcal{U} | \Psi^{(+n_0)} \rangle + \langle \Psi^{(-)n} | \mathcal{U} G^D(+)\mathcal{U} | \Psi^{(+n_0)} \rangle.$$

In the third, we start with (19), substitute (13) into the second terms and simplify using (12) to get

$$(20) \quad \mathcal{S}_{nn_0} = \langle \Psi^{(-)n} | \mathcal{U} | \Psi^{(+n_0)} \rangle - \langle \Psi_{OW}^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle - \langle \Psi_{OW}^{(-)n} | \mathcal{U} | \Psi_{OW}^{(+n_0)} \rangle.$$

Putting (18)-(20) into (17) and using (8) to simplify to result, we have

$$(21) \quad \begin{aligned} \mathcal{S}_{nn_0} = & \langle \psi^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle + \langle \psi^{(-)n} | \mathcal{U} | \Psi_{OW}^{(+n_0)} \rangle + \langle \Psi_{OW}^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle \\ & - \frac{2\mu}{\hbar^2} \langle \Psi_{OW}^{(-)n} | H - E | \Psi_{OW}^{(+n_0)} \rangle. \end{aligned}$$

The error in the scattering matrix obtained using this expression with a trial function is $-\frac{2\mu}{\hbar^2} \langle \delta \Psi^{(-)n} | H - E | \delta \Psi^{(+n_0)} \rangle$. An additional feature of this expression is that it gives a symmetric scattering matrix for all choices of $\Psi^{(+n_0)}$ and $\Psi^{(-)n}$.

Equation (21) gives us a prescription to compute the scattering matrix given a trial function, but it does not indicate how to choose parameters contained in the trial function. We reinforce the stationary nature of (21) by using the following procedure. Represent the trial function as a linear combination of known basis functions:

$$(22) \quad \Psi_{OW}^{(+n)} = \sum_{\beta} \tilde{A}_{\beta n} \tilde{\Gamma}_{\beta}.$$

The basis functions are regular at the origin and must either be \mathcal{L}^2 or have the limit

$$(23) \quad \lim_{R \rightarrow \infty} \tilde{\Gamma}_{\beta} = \frac{1}{R} \sum_{vj\ell} \phi_{vj}(r) \mathcal{Y}_{j\ell}^{JM}(\theta, \phi, \Theta, \Phi) p_{\beta vj\ell} \exp[i(k_{vj}R - \ell\pi/2)],$$

where $p_{\beta vj\ell}$ is some coefficient. Other choices either cause the matrix element integrals to diverge or introduce incorrect boundary conditions. Then (21) can be written as

$$(24) \quad \underline{\underline{\mathcal{S}}} = \underline{\underline{\mathcal{S}}}^B + \underline{\underline{\tilde{A}}}^T \underline{\underline{\tilde{B}}} + \underline{\underline{\tilde{B}}}^T \underline{\underline{\tilde{A}}} - \underline{\underline{\tilde{A}}}^T \underline{\underline{\tilde{C}}} \underline{\underline{\tilde{A}}},$$

where double underline denotes a matrix,

$$(25) \quad (\underline{\underline{\mathcal{S}}}^B)_{nn_0} = \langle \psi^{(-)n} | \mathcal{U} | \psi^{(+n_0)} \rangle,$$

$$(26) \quad (\underline{\tilde{B}})_{\beta n} = \langle A_T \tilde{\Gamma}_\beta | \mathcal{U} | \psi^{(+n)} \rangle,$$

$$(27) \quad (\underline{\tilde{C}})_{\beta\beta'} = \frac{2\mu}{\hbar^2} \langle A_T \tilde{\Gamma}_\beta | H - E | \tilde{\Gamma}_{\beta'} \rangle,$$

where the superscript T means transpose and A_T denotes the time reversal [8] operator. Note that $\underline{\tilde{C}}$ is square and very large, $\underline{\mathcal{S}}^B$ is square and its row and column dimensions are about an order of magnitude smaller, and $\underline{\tilde{A}}$ and $\underline{\tilde{B}}$ are rectangular. We then require that

$$(28) \quad \frac{\partial \Re \mathcal{S}_{nn_0}}{\partial \Re \tilde{A}_{\beta n}} = \frac{\partial \Re \mathcal{S}_{nn_0}}{\partial \Im \tilde{A}_{\beta n}} = \frac{\partial \Im \mathcal{S}_{nn_0}}{\partial \Re \tilde{A}_{\beta n}} = \frac{\partial \Im \mathcal{S}_{nn_0}}{\partial \Im \tilde{A}_{\beta n}} = 0,$$

for all n , n_0 and β , where \Re means real part, and \Im means imaginary part. This results in the linear equations

$$(29) \quad \underline{\tilde{C}} \underline{\tilde{A}} = \underline{\tilde{B}},$$

and thus

$$(30) \quad \underline{\mathcal{S}} = \underline{\mathcal{S}}^B + \underline{\tilde{B}}^T \underline{\tilde{C}}^{-1} \underline{\tilde{B}}.$$

This is our final result. We call this the outgoing wave variational principle (OWVP), and we attribute the original derivation of a variational principle with this flexibility to Schlessinger [21]. In Schlessinger's work and our original derivation [22], we used boundary conditions based on the T matrix instead of the S matrix, where the T matrix is defined by

$$(31) \quad \underline{\mathcal{T}} = \underline{\mathcal{S}} - \underline{1}.$$

This version of the variational principle is called the scattered wave variational principle (SWVP); since (31) is linear in the two matrices, the OWVP and SWVP yield identical results. For other kinds of variational principles, see, for example, Refs. [23,24].

The appearance of a time reversal operator in (26) and (27) may at first be surprising, but it becomes clear by elaborating on the discussion below (11). The natural formulation of a transition amplitude in quantum mechanics is $\langle \Psi_f | \mathcal{H}' | \Psi_i \rangle$, where Ψ_i is the initial state, \mathcal{H}' is the operator causing the transition, and Ψ_f is the final state. For scattering the final state is the time reversal of the initial state because the initial state evolves from a pure state in the infinite past into a mixture of states in the infinite future [25], whereas the final state evolves from a mixture of states in the infinite past to a pure state at the detector [20]. Thus the natural description

of scattering phenomena involves the time reversal operator in the bra [26]. In practical work when spin-orbit coupling may be neglected, one typically chooses a phase convention such that application of A_T reduces to complex conjugation on the radial components of the wave function or trial function but no conjugation on angular parts [8]. In our work $\phi_{vj}(r)$ is real, and the trial function consists of sums of terms, each of which is a function of R times a function independent of R . Thus A_T reduces to complex conjugation of the functions of R .

If desired, one can solve for a single column of $\underline{\tilde{A}}$, which yields a single column of $\underline{\mathcal{S}}$, which is sufficient to calculate all observables for collisions involving a particular initial state. This is useful when one employs iterative methods [27,28].

In practice, we have found it efficient to expand $\Psi_{OW}^{(+n)}$ using a mixture of \mathcal{L}^2 functions and functions with the boundary conditions of (23). Since our choice of \mathcal{L}^2 functions leads to matrix elements of $\underline{\tilde{C}}$ which are real when two \mathcal{L}^2 functions are involved, it is valuable to solve the linear equations in (30) by blocks, with the real block eliminated before considering the complex blocks [see (42-45) below]. The largest calculations we have carried out to date involved on the order 10^4 basis functions, about half of which were real. The dimension of the scattering matrix was about a factor of ten smaller. The cost of the calculation was about evenly split between the construction of the matrices $\underline{\mathcal{S}}^B$, $\underline{\tilde{B}}$, and $\underline{\tilde{C}}$ and the determination of $\underline{\mathcal{S}}$ by (30).

Although we have focussed on a trial function with complex boundary conditions, this is not essential. Similar ideas can be used to solve for wave functions with real, standing-wave boundary conditions, from which the S or T matrix can be constructed by a transformation, and we have solved some large-scale problems this way [29]. However we have found that the direct variational solution for wave functions with the complex, traveling-wave boundary conditions leads to more stable results [29], and it will be the focus of the rest of this chapter.

3 Distortion Potentials

In this section we discuss the simplest aspect of problem decomposition in the OWVP, namely the choice of the distortion potential V^D in (7). In order to conveniently discuss the distortion potentials, we introduce the scalar product $(n|a|n')$ defined by

$$(32) \quad \begin{aligned} (n|a|n') = & \int_{-1}^1 d \cos \Theta \int_0^{2\pi} d\Phi \int_0^\infty r^2 dr \int_{-1}^1 d \cos \theta \int_0^{2\pi} d\phi \phi_{v_n j_n}(r) \mathcal{Y}_{j_n \ell_n}^{JM*}(\theta, \phi, \Theta, \Phi) \\ & \times a(R, \Theta, \Phi, r, \theta, \phi) \phi_{v_{n'} j_{n'}}(r) \mathcal{Y}_{j_{n'} \ell_{n'}}^{JM}(\theta, \phi, \Theta, \Phi), \end{aligned}$$

where a is some operator. In practice it is possible to transform the scalar

products so that three of the five integrations can be carried out analytically. The remaining two-dimensional integration is not expensive. Then admissible distortion potentials are dependent on the form of the matrix elements $(n|H|n')$ in the limit $R \rightarrow \infty$. In particular, it is necessary that

$$(33) \quad \lim_{R \rightarrow \infty} (n|H|n') = \lim_{R \rightarrow \infty} (n|H^D|n')$$

and

$$(34) \quad \lim_{R \rightarrow \infty} R^2[(n|H|n') - H_{nn'}^\infty] = \lim_{R \rightarrow \infty} R^2[(n|H^D|n') - H_{nn'}^\infty],$$

where $H_{nn'}^\infty$ is the result of the limits in (33). If these two relations are not satisfied, then the correct boundary conditions cannot be obtained.

It is advantageous to consider distortion potentials which exploit some or all of the decoupling permissible by (33) and (34). The basis functions specified by $n = vj\ell$ are eigenfunctions of the operator $T + V^{vib}$, and $\lim_{R \rightarrow \infty} R^2V = 0$, so any distortion potential that also satisfies $\lim_{R \rightarrow \infty} R^2V^D = 0$ is possible. In general, we will want to use basis functions which are linear combinations of terms corresponding to different $vj\ell$. In this case, off-diagonal coupling can come from $T + V^{vib}$. This can restrict the choices of the coupling in the distortion Hamiltonian.

The simplest possible choice is thus $V^D = 0$. In this case the radial part of the distorted waves are Bessel functions, which are easily calculated. However this choice is not practical except for very large ℓ because of the nature of the potential energy V . Atoms have hard cores so that in the limit $R \rightarrow 0$, the potential energy is very repulsive and since we are concerned with relatively low energies, there will be a finite distance R_0 below which all radial functions will be negligible. Unless ℓ is large, the regular Bessel functions will not be negligible for R smaller than R_0 , and so $\underline{\underline{S}}^B$ in (24) would have elements orders of magnitude larger than $\underline{\underline{S}}$. Although in principle the remaining terms of (24) would cancel out the spurious larger contributions if the basis were large enough, in practice this would be almost impossible for real problems. [Note that the two terms on the right side of (30) are not separately unitary, although the left side becomes unitary as the solution converges.] One possible fix is to multiply the Bessel functions by some arbitrary cutoff function. This would implicitly define a new V^D , but it is an unnatural way to proceed. Next we discuss distortion potentials which do not suffer from these drawbacks.

In our work we use distortion potentials which take the general form

$$(35) \quad V^D = \sum_{nn'} \Delta_{nn'} |n)(n|V|n')(n'|,$$

where $\Delta_{nn'}$ is a coefficient which specifies a particular distortion potential scheme, V is the potential energy of the interaction of the diatomic with the atom, and $|n\rangle\langle n|$ and $|n'\rangle\langle n'|$ are projectors. The projectors are defined so that

$$(36) \quad \langle n''|V^D|n'''\rangle = \Delta_{n''n'''}\langle n''|V|n'''\rangle,$$

which is a function of R . The coefficient $\Delta_{nn'}$ is defined by partitioning the set of n into disjoint sets. These sets are called distortion potential blocks. Then if n and n' belong to the same distortion potential block, $\Delta_{nn'} = 1$. Otherwise it is zero.

The use of distortion potentials effects a problem decomposition. Part of the coupling is in the distortion problem, for which we solve (8) and (9), and the rest, defined by (6) and (11), is treated by the algebraic variational principle. The optimal distortion Hamiltonian coupling is the compromise between making either of the two sides of the problem decomposition too large. As the distortion blocks become larger, less coupling needs to be taken care of by the variational principle, so fewer basis functions are required to expand $\Psi_{OW}^{(+n)}$, and less work is required in evaluating the right hand side of (30). On the other hand, as the distortion blocks become larger, the amount of work to determine the distorted waves of (9) and distorted-wave Green's functions of (8) increases, the amount of memory or disk needed to store these functions increases, and the work in evaluating the matrix elements for the right hand side of (30) increases.

In our work, we include the basis functions most strongly coupling to the initial ones of interest in a single distortion block while decoupling as much as possible other less important functions. Further discussion of the tradeoffs is provided elsewhere [30].

4 Basis Function Contraction

In this section we are concerned with the choice of basis functions used to expand the outgoing wave, *i.e.*, the functions $\tilde{\Gamma}_\beta$ in (22), and how the ideas of problem decomposition can be used to improve efficiency.

In our work we have used two types of basis functions to expand $\Psi_{OW}^{(+n)}$. The first are \mathcal{L}^2 functions which take the form

$$(37) \quad \tilde{\Gamma}_{\beta,\mathcal{L}^2} = \frac{1}{R}\phi_{vj}(r)\mathcal{Y}_{j\ell}^{JM}(\theta,\phi,\Theta,\Phi)t_m(R),$$

where $t_m(R)$ is a Gaussian centered at R_m and having width parameter w_m . Here β indicates a particular choice of v , j , ℓ , and m . These functions are not orthogonal because different Gaussians will overlap, however orthogonality is not required in our formalism. In fact, when treating reactive processes,

we expand $\Psi_{OW}^{(+n)}$ in terms of three such sets of basis functions, with each set using the coordinates most natural for the particular partitioning of the three atoms into atom and diatom. Thus each set uses a different set of coordinates, and hence each basis function of one set has nonzero overlap with all basis functions of the other sets. It also has nonzero overlap with functions in the same set that have the same v , j , and ℓ .

The second type of basis functions that we use are the continuum functions, and these are generated by applying a Green's function to a \mathcal{L}^2 basis function of the form of (37):

$$(38) \quad \tilde{\Gamma}_{\beta,c} = G^{D(+)} \tilde{\Gamma}_{\beta,\mathcal{L}^2}.$$

These functions can be computed using similar techniques as used to determine the distorted waves [14,17]. In particular, these functions have the explicit form

$$(39) \quad \tilde{\Gamma}_{\beta,c} = \frac{1}{R} \sum_{vj\ell} \Delta_{vj\ell, v\beta j\beta\ell\beta} \phi_{vj}(\tau) \mathcal{Y}_{j\ell}^{JM}(\theta, \phi, \Theta, \Phi) \dot{g}_{vj\ell,\beta}^{(+)}(R),$$

where the functions $\dot{g}_{vj\ell,\beta}^{(+)}(R)$ solve an inhomogeneous second order differential equation subject to the boundary conditions that they be regular at $R = 0$ and (23) is satisfied. We call these radial functions half-integrated Green's functions (HIGFs). As we have presented them, these HIGFs are obtained using the Green's function for the distortion Hamiltonian used to generate the distorted wave. However it is clear from (21) and (22) that this is not necessary. It is not clear what advantage there would be to use a different distortion Hamiltonian to generate the HIGFs. The motivation for (38) arises when one considers the variational principle [17,23] for the amplitude density, which is equal to $\mathcal{U}\Psi^{(+n)}$. The result is equivalent to (21) with the restriction that only basis functions of the type given by (38) are used. The present formulation is much more general. It is generally desirable to use the \mathcal{L}^2 functions of (37) rather than those of (38), because they are cheaper to deal with, but some HIGFs are required to ensure that $\Psi_{OW}^{(+n)}$ has the correct boundary conditions at large R . However we typically find we need fewer HIGFs than \mathcal{L}^2 functions to obtain a given level of convergence, so it can be advantageous to use more than the minimum number of HIGFs.

Although we have had good success using Gaussian basis functions for the R coordinate, we note that the function being expanded is far from Gaussian. Our formalism is not limited to Gaussians, and thus it should be possible to improve the efficiency of the calculations by introducing a different set of basis functions carefully tailored to the problem. One strategy

is to form these as linear combinations of the Gaussian basis functions, and in such a case they are termed contracted basis functions. This contraction can be done in several ways. For the \mathcal{L}^2 functions, it is possible to energy adapt [17,31] the basis functions by diagonalizing a small matrix, and then using the eigenvectors whose local wavelength is approximately correct as contracted basis functions. (This may be considered to be a problem decomposition in that one transforms to energy to take advantage of the natural decoupling of states of widely differing average energy.) Another option is to solve a one-dimensional scattering problem [24,32].

For the HIGFs, we have considered in previous work [33] the contraction of the R part of the \mathcal{L}^2 functions on the right hand side of (38). In this case the contraction coefficients were based on full scattering calculations with restricted $avj\ell$ basis sets. The results were quite encouraging. These calculations were carried out using the variational principle for the amplitude density, and with the more general framework presented here, it is clear that possibilities also exist for contracting after applying the Green's function.

The techniques used in some of the previous work to obtain contracted basis functions correspond to problem decomposition in channel space. In particular the scattering problem is fully solved for one channel [32] or a subset of channels [33], and the resulting solutions are used as basis functions for treating the fully coupled set of all the channels.

So far we have just considered contracting functions for the coordinate R . Since the Gaussian functions are highly localized, we can consider contracting the $\phi_{vj}\mathcal{Y}_{j\ell}^{JM}$ of (37) by diagonalizing the full Hamiltonian averaged over R weighted by a single Gaussian. This would yield functions approximately adiabatic with respect to the coordinate R . The use of adiabatic functions has proven its value many times in calculations not using a variational principle [34]. Zhang and Miller [35] have shown that this technique is also valuable in algebraic variational calculations.

Another valuable option, although not really basis function contraction, is to use more general vibrational functions in (37) [14]. Both this option and the others discussed in the previous paragraph are problem decomposition techniques in that one first treats the coupling in coordinates other than R , for a fixed R or averaged over a narrow range of R , and one then uses the results as basis functions for the full problem spanning all R .

It is also possible to form contracted functions coupling all degrees of freedom. For example, would could diagonalize the purely \mathcal{L}^2 part of \tilde{C} required in (30), but use only a subset of the eigenvectors (selected on the basis of their energy eigenvalues or the character of the eigenvector) to form the inverse in (30). This could be advantageous since for this part of \tilde{C} , the basis functions are independent of E , so the diagonalization would have to be performed only once. This idea could be implemented in a divide-

and-conquer way by partitioning the basis functions into several groups, each diagonalized separately. The partitioning might be based on channel indices, or — for localized basis functions — on physical space.

A characteristic of the techniques discussed in this section is that a part of the problem is decoupled from the other parts to get good basis functions for treating the fully coupled problem. Then the basis functions are combined *variationally* for the full problem. The variational character of the final step makes up to some extent for the deficiencies of the basis due to the fact that it was obtained in decoupled steps.

5 Optical Potentials and Related Approaches

In previous sections we considered methods for improving the efficiency of our calculations that did not lead obviously to simplifying approximations. In this section we manipulate our equations to reveal the possibilities of introducing a phenomenological function, called an optical potential, which hopefully allows results of useful accuracy to be obtained at reduced cost.

We start by partitioning the basis functions $\tilde{\Gamma}_\beta$ into two groups called P and Q so that we can write

$$(40) \quad \underline{\underline{\tilde{B}}} = \begin{pmatrix} \underline{\underline{\tilde{B}^Q}} \\ \underline{\underline{\tilde{B}^P}} \end{pmatrix},$$

and

$$(41) \quad \underline{\underline{\tilde{C}}} = \begin{pmatrix} \underline{\underline{\tilde{C}^{QQ}}} & \underline{\underline{\tilde{C}^{QP}}} \\ \underline{\underline{\tilde{C}^{PQ}}} & \underline{\underline{\tilde{C}^{PP}}} \end{pmatrix}.$$

Next we solve (30) by blocks, obtaining

$$(42) \quad \underline{\underline{\mathcal{S}}} = \underline{\underline{\mathcal{S}^{Bf}}} + \underline{\underline{\tilde{B}^f}}^T \underline{\underline{\tilde{C}^f}}^{-1} \underline{\underline{\tilde{B}^f}},$$

where

$$(43) \quad \underline{\underline{\mathcal{S}^{Bf}}} = \underline{\underline{\mathcal{S}^B}} + \underline{\underline{\tilde{B}^Q}}^T \underline{\underline{\tilde{C}^{QQ}}}^{-1} \underline{\underline{\tilde{B}^Q}},$$

$$(44) \quad \underline{\underline{\tilde{B}^f}} = \underline{\underline{\tilde{B}^P}} - \underline{\underline{\tilde{C}^{PQ}}}^T \underline{\underline{\tilde{C}^{QQ}}}^{-1} \underline{\underline{\tilde{B}^Q}},$$

and

$$(45) \quad \underline{\underline{\tilde{C}^f}} = \underline{\underline{\tilde{C}^{PP}}} - \underline{\underline{\tilde{C}^{PQ}}}^T \underline{\underline{\tilde{C}^{QQ}}}^{-1} \underline{\underline{\tilde{C}^{QP}}}.$$

If the Q functions are all real, then (42-45) form an attractive solution to (30) since $\underline{\underline{\tilde{C}^{QQ}}}$ will be real. However, in this section we want to consider

the more general case. First though, we make a connection to work in other fields. If our basis functions were localized, P and Q could be associated with different domains of the physical space. Then (43)-(45) would provide a generalization of traditional domain decomposition techniques [36,37]. We may, for example, consider (45) to represent the Schur complement of function space P connected to function space Q .

Consider (43) in more detail. It can be rewritten as

$$(46) \quad \begin{aligned} S_{nn_0}^{Bf} = & \langle \psi^{(-)n} | \mathcal{U} | \psi^{(+)n_0} \rangle \\ & + \sum_{\beta, \beta'} \langle \psi^{(-)n} | \mathcal{U} | \tilde{\Gamma}_\beta \rangle (\underline{\tilde{C}}^{QQ}{}^{-1})_{\beta\beta'} \langle \tilde{\Gamma}_{\beta'} | \mathcal{U} | \psi^{(+)n_0} \rangle. \end{aligned}$$

Now provided

$$(47) \quad \langle \psi^{(-)n} | \mathcal{U} | \tilde{\Gamma}_\beta \rangle = \frac{2\mu}{\hbar^2} \langle \psi^{(-)n} | E - H | \tilde{\Gamma}_\beta \rangle,$$

which will be true if the internal part of $\tilde{\Gamma}_\beta$ is orthogonal to the internal part of $\psi^{(+)n_0}$ or if $\lim_{R \rightarrow \infty} \tilde{\Gamma}_\beta = 0$, where R is the continuum coordinate for $\psi^{(+)n_0}$, we can write

$$(48) \quad S_{nn_0}^{Bf} = \langle \psi^{(-)n} | \mathcal{U} + \mathcal{U}^{opt} | \psi^{(+)n_0} \rangle,$$

$$(49) \quad \tilde{B}_{\beta n}^f = \langle A_T \tilde{\Gamma}_\beta | \mathcal{U} + \mathcal{U}^{opt} | \psi^{(+)n} \rangle,$$

$$(50) \quad \tilde{C}_{\beta\beta'}^f = \langle A_T \tilde{\Gamma}_\beta | \frac{2\mu}{\hbar^2} (H - E) - \mathcal{U}^{opt} | \tilde{\Gamma}_{\beta'} \rangle,$$

where

$$(51) \quad \langle a | \mathcal{U}^{opt} | b \rangle = \sum_{\beta\beta'} \langle a | \frac{2\mu}{\hbar^2} (H - E) | \tilde{\Gamma}_\beta \rangle (\underline{\tilde{C}}^{QQ}{}^{-1})_{\beta\beta'} \langle \tilde{\Gamma}_{\beta'} | \frac{2\mu}{\hbar^2} (H - E) | b \rangle.$$

We define

$$(52) \quad V^{opt} = -\frac{\hbar^2}{2\mu} \mathcal{U}^{opt},$$

and we call this the optical potential. This kind of partitioning was first introduced into quantum mechanical scattering theory by Feshbach [38] and was introduced into algebraic variational calculations by Nesbet [39].

The usefulness of the optical potential is that if we can evaluate it simply, it is possible to carry out a small calculation including only the P functions

and adding the optical potential to the interaction potential and obtain the same result as the larger calculation including both the P and Q functions. The problem is that the exact optical potential of (51) is no easier to determine than solving the problem explicitly including both the P and Q functions. However, it may be possible to obtain an approximate optical potential which gives results of useful accuracy.

Let us consider some of the properties of the optical potential. It is energy dependent, both explicitly as indicated by (51) and implicitly through $\underline{\tilde{C}}^{QQ}$, which contains the energy [see (27) and (41)]. It is nonlocal so that more work may be required to evaluate its matrix elements as compared to \mathcal{U} . If all of the Q functions are \mathcal{L}^2 and hence real, the optical potential will be real. Otherwise the optical potential will have nonzero real and imaginary parts.

Perhaps the most troublesome property of the optical potential is its non locality. There is extensive literature on using local phenomenological optical potentials in electron scattering [40], and these are mostly based on physical arguments relating to the role of electronically excited states. Local approximations to the optical potential are also widely used in nuclear physics, in which case they are typically justified by energy averaging but determined in practice by empirical considerations [38]. Neither the electron scattering or nuclear reaction literature is particularly helpful in the present context. Local approximations more suitable for scattering processes involving molecular vibrational and rotational motions have also been advanced [41], but they are less well developed.

It is possible to obtain local potentials that are fully equivalent to the nonlocal optical potential, but these show strong energy-dependent structure as a function of scattering energy; useful approximations can be obtained by smoothing these potentials [42]. Other approaches include treating the optical potential by perturbation theory [43] or attempting to collapse its effects into a smaller number of "effective" channels [44].

Considerable progress should also be possible employing nonlocal optical potentials, though, by choosing the Q space to make the calculations convenient. For the present application to reactive scattering, one could consider several choices for the Q functions. One choice, considered by Baer and coworkers [45] and Seideman and Miller [46], is to have Q include all continuum functions. In that work the phenomenological optical potentials were taken to be purely imaginary, with negative imaginary parts, nonzero only at the boundaries where the interaction potential is small. The assumed form of the phenomenological optical potentials was quite simple — nevertheless quite encouraging results were obtained.

Another partitioning would be to assign functions with $\epsilon_{\nu\beta j\beta\alpha\beta} > E$ to Q and other functions to P . In this case all Q functions are \mathcal{L}^2 (the HIGFs

are \mathcal{L}^2 in this case since $k_{v\beta j\beta\alpha\beta}^2 < 0$), and the optical potential would be real.

Perhaps the most promising avenue of approach is based on returning to the domain decomposition analog. For example, suppose we choose our basis functions such that

$$(53) \quad \underline{\underline{\tilde{C}}} = \begin{pmatrix} \underline{\underline{\tilde{C}}}^{PP} & 0 & \underline{\underline{\tilde{C}}}^{PR} \\ 0 & \underline{\underline{\tilde{C}}}^{QQ} & \underline{\underline{\tilde{C}}}^{QR} \\ \underline{\underline{\tilde{C}}}^{PR^T} & \underline{\underline{\tilde{C}}}^{QR^T} & \underline{\underline{\tilde{C}}}^{RR} \end{pmatrix}.$$

Let the sizes of the partitions be M^P , M^Q , and M^R such that the order of $\underline{\underline{\tilde{C}}}$ is

$$(54) \quad M = M^P + M^Q + M^R.$$

Then, instead of solving the $M \times M$ complex equations for $\underline{\underline{\tilde{A}}}$, we may solve the following much simpler set [36]:

$$(55) \quad \underline{\underline{\tilde{C}}}^{PP} (\underline{\underline{\tilde{W}}}^P \underline{\underline{\tilde{X}}}^P) = (\underline{\underline{\tilde{B}}}^P \underline{\underline{\tilde{C}}}^{PR}),$$

$$(56) \quad \underline{\underline{\tilde{C}}}^{QQ} (\underline{\underline{\tilde{W}}}^Q \underline{\underline{\tilde{X}}}^Q) = (\underline{\underline{\tilde{B}}}^Q \underline{\underline{\tilde{C}}}^{QR}),$$

$$(57) \quad (\underline{\underline{\tilde{C}}}^{RR} - \underline{\underline{\tilde{C}}}^{PR^T} \underline{\underline{\tilde{X}}}^P - \underline{\underline{\tilde{C}}}^{QR^T} \underline{\underline{\tilde{X}}}^Q) \underline{\underline{\tilde{A}}}^R = \underline{\underline{\tilde{B}}}^R - \underline{\underline{\tilde{C}}}^{PR^T} \underline{\underline{\tilde{W}}}^P - \underline{\underline{\tilde{C}}}^{QR^T} \underline{\underline{\tilde{W}}}^Q,$$

$$(58) \quad \underline{\underline{\tilde{A}}}^P = \underline{\underline{\tilde{W}}}^P - \underline{\underline{\tilde{X}}}^P \underline{\underline{\tilde{A}}}^R,$$

$$(59) \quad \underline{\underline{\tilde{A}}}^Q = \underline{\underline{\tilde{W}}}^Q - \underline{\underline{\tilde{X}}}^Q \underline{\underline{\tilde{A}}}^R.$$

Extension of this three-partition approach to four or more partitions is clearly possible. Any number of basis set partitioning schemes may be imagined to make the smaller problems real, independent of energy, and/or particularly convenient for solution by iterative or parallel methods.

The new ideas presented in this section are topics of current research.

6 Concluding Remarks

We have seen that techniques for solving quantum mechanical scattering problems with linear variational principles and delocalized basis functions allow for a number of divide-and-conquer strategies. Some of these are

analogous in spectral space of techniques used in other fields in physical space, whereas other problem decomposition avenues are specialized approaches based on the specific nature of the scattering problem.

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