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# Contracted Basis Functions for Variational Solutions of Quantum Mechanical Reactive Scattering Problems

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A new method for constructing efficient basis functions for  $\mathcal{L}^2$  variational calculations of quantum mechanical rearrangements is presented and tested. With this method, using the same contracted basis functions for all channels in a given vibrational manifold, we can obtain reactive transition probabilities for  $F + H_2 \rightarrow H + HF(v')$ , where  $v'$  is the final vibrational state, that are accurate to 0.01 absolute accuracy or 5% relative accuracy with 40% less basis functions than are required for the same accuracy using primitive basis sets and with 60% less basis functions than were used for our previous calculations that were converged to 1%.

## 1. Introduction

The use of the contracted basis functions is a very powerful and widely used technique in the calculation of electronic wave functions for atomic and molecular bound states,<sup>1-6</sup> and contraction techniques have also been proposed and used successfully for scattering basis functions.<sup>7-9</sup> Often, when primitive functions are used in scattering calculations, a large number of primitive basis functions are needed to achieve good convergence. Even when efficient variational principles are used in the calculation to decrease the number of basis functions used and to achieve fast convergence, the number of basis functions required to get good convergence may still be challengingly large.<sup>10,11</sup> The use of a large basis set leads to a large linear algebraic system to be solved for the coefficients, and this takes considerable computer resources, both storage and computing time.

Although great progress has been made in minimizing the number of basis functions and computing the required integrals over basis functions,<sup>9,12,13</sup> one is always interested in reducing the basis set requirements even more, in order to allow even more difficult problems to be solved. In this paper we present a very

general technique for achieving such reductions, and we show by calculations on a state-of-the-art problem that it can indeed provide substantial savings.

The basic idea behind the present work is to divide the calculation into two steps. The first step consists in solving a "small" problem, e.g., a model problem, a partially decoupled problem, or one in which the number of channels is less than required for convergence. The basis set used for this step is called the "primitive" basis. The solution vectors to this problem are then used to construct new basis functions, the "contracted" basis, in which the original "large" problem may be solved more efficiently. The method will be judged a success if the sum of the computational efforts for the two steps is less than what would have been required to solve the original problem directly in the primitive basis set. The distinguishing characteristic of the approach considered here, and in our related previous work,<sup>7-9</sup> is that we are concerned with contraction of the translational component of the amplitude density or wave function, as contrasted to, for example,<sup>13</sup> using bound-state techniques to contract basis sets for the components of a scattering wave function corresponding to bound coordinates. In the original application of this approach to scattering problems, it was shown that significant savings could be achieved this way in electron-atom scattering calculations employing the Kohn and Rubinow variational principles.<sup>7</sup> More recently, contracted basis functions were used successfully with the Schwinger variational principle.<sup>8,9</sup> In the present work we consider chemical reactions and the more efficient generalized Newton variational principle.<sup>9,12</sup> Although the basis idea is the same as before, it is now implemented a little differently, primarily to achieve greater computational efficiency without too large an increase in computer storage.

## 2. Theory

A contracted basis function is a linear combination of primitive basis functions. In the present paper, we consider atom-diatom collisions using the generalized Newton variational principle (GNVP).<sup>9,12,14</sup> In this method a basis set expansion is applied to the reactive amplitude densities  $f_\alpha$  in each arrangement  $\alpha$ . Since

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$\zeta_\alpha$  is a square integrable ( $\mathcal{L}^2$ ) function, we use  $\mathcal{L}^2$  basis sets. The trial function for the reactive amplitude density can be written as

$$\zeta_\alpha^{N_0} = \sum_{\beta=\beta_\alpha'}^{\beta_\alpha''} A_{\beta n_0} \Phi_\beta \quad (1)$$

where  $\beta_1' = 1$ ,  $\beta_{\alpha+1}' = \beta_\alpha'' + 1$ ,  $A_{\beta n_0}$  is an expansion coefficient,  $n_0$  is the initial channel, and  $\Phi_\beta$  is a primitive basis function. The total number of basis functions is  $M$ , which equals  $\beta_3''$  for the case of three arrangements. Writing each basis function as a product of an internal-orbital channel function  $\phi_n$  and a sum of radial translational basis functions  $\lambda_{\alpha n \gamma}$ , where  $\alpha_n$  denotes the arrangement of channel  $n$ , this becomes

$$\zeta_\alpha^{N_0} = \sum_{n=n_\alpha'}^{n_\alpha''} \phi_n \sum_{\gamma=1}^{m_n} A_{n \gamma n_0} \lambda_{\alpha n \gamma} \quad (2)$$

where  $n_1' = 1$ ,  $n_{\alpha+1}' = n_\alpha'' + 1$ ,  $m_n$  is the number of primitive basis functions in channel  $n$ , and  $A_{n \gamma n_0}$  is the expansion coefficient, determined by the GNVP. The total number of channels is  $N$ , which equals  $n_3''$  for the case of three arrangements.

In this paper we use distributed Gaussian functions (DGFs)<sup>15-17</sup> for the radial basis functions, i.e.,  $N_{\alpha n \gamma} \exp[-A_{\alpha n \gamma}(R_{\alpha n} - R_{\alpha n \gamma})^2]$  where  $N_{\alpha n \gamma}$  is a normalization factor,  $A_{\alpha n \gamma}$  is a range factor,  $R_{\alpha n \gamma}$  is a Gaussian midpoint for Gaussian  $\gamma$  in the arrangement  $\alpha_n$  associated with channel  $n$ , and  $R_{\alpha n}$  is the mass-scaled translational coordinate<sup>16</sup> in this arrangement. The spacing between Gaussians is fixed for a given arrangement at the value  $\Delta_\alpha = R_{\alpha n, \gamma+1} - R_{\alpha n \gamma}$ , and the range factors are determined by setting the overlap parameter  $c^{15,17}$  equal to 1.4. (To be sure of convergence, one must show that the results are not changed more than the acceptance tolerance by varying  $c$ ; for the calculations in this paper that was done in work not reported here in detail.) We note that this choice of primitive translational basis is not essential to the method.

It is useful to recall at this point that we perform GNVP calculations in two steps. In the first step we find regular solutions and half-integrated Green's functions (HIGFs) for a zero-order distortion Hamiltonian. The reactive amplitude density accounts for the rest of the coupling. In the present paper the distortion Hamiltonian includes all the rotational coupling in each vibrational manifold (specified by the arrangement  $\alpha$  and the vibrational quantum number  $v$ ); each vibrational manifold is therefore called a distortion block, and these blocks are labeled  $\delta = 1, 2, \dots, \delta_{\max}$ . The reactive amplitude density accounts for the vibrational and reactive coupling of the distortion blocks. For later use we define  $\delta_n$  as denoting the distortion block to which a given channel  $n$  belongs, i.e.,  $\delta_n \equiv \alpha_n v_n$ , where  $\alpha_n$  and  $v_n$  are respectively the arrangement and vibrational quantum number associated with channel  $n$ .

The contracted basis functions to be used in channel  $n$  are defined as

$$\tilde{\lambda}_\gamma^{(n)} = \sum_{\gamma=1}^{m_n} d_{\gamma \gamma}^{(n)} \lambda_{\alpha n \gamma} \quad (3)$$

and the amplitude density may be expanded in the contracted basis set as

$$\zeta_\alpha^{N_0} = \sum_{n=n_\alpha'}^{n_\alpha''} \phi_n \sum_{\gamma=1}^{m_n} \tilde{A}_{n \gamma n_0} \tilde{\lambda}_\gamma^{(n)} \quad (4)$$

where  $\tilde{A}_{n \gamma n_0}$  is the expansion coefficient in the contracted basis and is determined variationally, exactly analogously to the determination of  $A_{n \gamma n_0}$  in eq 2. The goal is for the number of contracted basis functions in eq 4, i.e.

$$\tilde{M} \equiv \sum_{n=1}^N \tilde{m}_n \quad (5)$$

to be significantly smaller than the number of primitive basis function in eq 2, i.e.

$$M \equiv \sum_{n=1}^N m_n \quad (6)$$

but without loss of accuracy. The most important problem to be attacked is how to find good contraction coefficients  $d_{\gamma \gamma}^{(n)}$ . For computational efficiency<sup>14</sup> we will set two constraints on this search in the present paper. First, we consider  $m_n$  and  $\tilde{m}_n$  to be functions only of the arrangement  $\alpha$ , so they become  $m_\alpha$  and  $\tilde{m}_\alpha$ .

To motivate the second constraint we consider an example. Suppose we have 500 channels ( $N = 500$ ) with 20 primitive basis functions per channel ( $m_n = 20$ ). Now suppose we wish to use 10 contracted functions in each channel. In principle, we could use different contraction coefficients in every channel and for each possible initial state. There would then be  $500 \times 500 \times 10 = 2.5 \times 10^6$  contracted functions, each requiring 20 parameters for its specification, for a total of 50 million parameters to specify the contracted basis. To avoid specifying and handling such a large number of coefficients, in the present paper we use the same contracted basis in each distortion block, independent of initial state. Then the contraction coefficients  $d_{\gamma \gamma}^{(n)}$  depend only on the arrangement and vibrational quantum numbers,  $\alpha_n$  and  $v_n$ , respectively, associated with channel  $n$ . Thus, we relabel the coefficients  $d_{\gamma \gamma}^{(\delta)}$  when we want to denote them for distortion block  $\delta_n$  and  $d_{\gamma \gamma}^{(\delta)}$  when we want to denote them for an arbitrary distortion block  $\delta$ .

### 3. Contraction Coefficients

Since the goal of the contraction method is to reduce the computational resources required to solve a given problem, the task of obtaining the coefficients  $d_{\gamma \gamma}^{(\delta)}$  should be much less demanding than the rest of the calculation or even computationally insignificant. At the same time, the coefficients should be chosen such that the new basis functions are physically reasonable, and the calculations in the new basis should converge more rapidly than those in the primitive basis. In addition, there is a programming advantage if the calculations with the new basis employ the same methodology as used for calculations with primitive functions.

The basic idea employed here is to obtain the contraction coefficients from a smaller calculation or a series of small calculations. To explain this, we label the channels by three quantum numbers:  $\alpha$ ,  $v$ , and  $\eta$ , where  $\eta = 1, 2, \dots, \eta_{\max, \delta}$  uniquely labels the channels in a given vibrational manifold denoted by  $\alpha$  and  $v$  or equivalently by  $\delta$ . Since the notation rapidly gets complicated, it is helpful to use the more compact distortion block notation. Thus, each channel is labeled by  $\delta$  and  $\eta$  and  $\eta = 1, 2, \dots, \eta_{\max, \delta}$ . Then, by expressing  $n$  as  $\delta \eta$  and  $n_0$  as  $\delta_0 \eta_0$  in the coefficients of eq 2, the solutions to the smaller problem can be written  $\tilde{A}_{\delta \eta \gamma \delta_0 \eta_0}$ , where the tilde denotes that the coefficient is obtained from a smaller calculation. Then the fundamental equation of the scheme used in the present paper is

$$d_{\gamma \gamma}^{(\delta)} = \tilde{A}_{\delta \eta (\delta \gamma) \gamma \delta_0 (\delta \gamma) \eta_0 (\delta \gamma)} \quad (7)$$

This means that the values of  $\eta$ ,  $\delta_0$ , and  $\eta_0$  used for the contraction coefficients for the basis function labeled by  $\delta$  and  $\gamma$  depend on  $\delta$  and  $\gamma$ . We will consider two examples. In both cases we take  $\tilde{m}_n$  independent of  $\eta$ , and so we may write it as  $\tilde{m}_\delta$ ; this means that the same number of contracted basis functions is used for each channel in a given distortion block. Although the notational layering in eq 7 is somewhat formidable, its meaning will be made more clear by considering specific schemes, and we do this next.

**Scheme 1.** In this scheme we decouple the arrangements and perform three calculations, one for each arrangement ( $\alpha = 1, 2, 3$ ). We then take

$$d_{\gamma \gamma}^{(\delta)} = \tilde{A}_{\delta \gamma \gamma G(\delta)} \quad (8)$$

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where  $\bar{\gamma}$  labels the contracted basis functions in vibrational manifold  $\delta$ ,  $\gamma$  labels the primitive basis functions, and  $G(\delta)$  denotes the ground vibrational manifold of whatever arrangement  $\delta$  happens to belong to. Note that in this case  $\bar{\gamma}$  is equal to the  $\eta$  index on  $\bar{A}_{\delta\eta\gamma\delta_0\eta_0}$ . Thus, the last two subscripts on  $\bar{A}_{\delta\eta\gamma\delta_0\eta_0}$  in eq 8 mean that *all* contraction coefficients in the first scheme are taken from solutions to the single-arrangement problem in which the first channel of the ground vibrational manifold of that arrangement is the initial state. This means that the solutions to the nonreactive problems with the first channel as the initial state are the contraction coefficients. There are  $\eta_{\max,\delta}$  such solutions for each vibrational manifold so this yields basis functions with  $\bar{\gamma} = 1, 2, \dots, \eta_{\max,\delta}$  for each  $\alpha v$ . Therefore, this scheme can only be used if  $m_\delta \leq \eta_{\max,\delta}$  in eq 3. Fortunately, we were able to get convergence with respect to increasing  $m_\delta$  before we encountered this limitation.

We can make eq 8 more clear by an example. Let  $\alpha = 2$ ,  $v = 2$ , and  $\bar{\gamma} = 6$ ; that is, consider the sixth contracted basis function for the third vibrational manifold of the second arrangement. Perform a calculation with all channels of the  $\alpha = 2$  arrangement and look at the solution for the initial state with  $v_0 = 0$  and  $\eta_0 = 1$ . In particular, look at the component of the solution with  $v = 2$  because the first subscript on the right side of eq 8 is the same as the superscript on the left. The solution vector of the sixth channel ( $\eta = 6$ ) in this vibrational manifold will be the sixth contracted basis function ( $\bar{\gamma} = \eta = 6$ ) for this vibrational manifold.

**Scheme 2.** In this scheme we perform only one smaller calculation and keep all arrangements in it, but we use small values of the maximum vibrational quantum number  $v_{\max}(\alpha)$  and maximum rotational quantum numbers  $j_{\max}(\alpha v)$  [ $\equiv j_{\max}(\delta)$ ]. We then take

$$d_{\bar{\gamma}\gamma}^{(\delta)} = \bar{A}_{\delta(\delta)\eta\gamma 1\eta_0} \quad (9)$$

where

$$\bar{\delta}(\delta) = \alpha \bar{v}(\alpha v) = \begin{cases} \alpha v & v \leq v_{\max}(\alpha) \\ \alpha v_{\max}(\alpha) & v > v_{\max}(\alpha) \end{cases} \quad (10)$$

and the pair of channel indexes with tildes are assigned in the following order, which depends on  $\bar{\delta}(\delta)$  and  $\bar{\gamma}$  (which is equal to  $\eta$ ):

$$\begin{aligned} (\tilde{\eta}, \tilde{\eta}_0) &= (1,1), (2,1), \dots, (\eta_{\max,\delta}, 1), \\ &(1,2), (2,2), \dots, (2\eta_{\max,\delta}, 2), \\ &(1,3), \dots \end{aligned} \quad (11)$$

We will give an example to illustrate this in section 4.2.

It is interesting to point out that, in scheme 2, if one did not reduce the maximum vibrational and rotational quantum number for the smaller calculation (so it was not actually smaller), one would obtain a basis set such that calculations employing the contracted basis set with all  $m_\delta \geq \eta_{\max,\delta}$  would be exact for all state-to-state transitions with  $\alpha_0 = 1$ ,  $v_0 = 0$ . We hope, however, to get by with smaller values of  $m_\delta$  and to get good results for more than one initial state; thus, computational tests are required and we present these next.

#### 4. Calculations

All test calculations are for total angular momentum zero. They were performed by using a modified version of the program described previously.<sup>14</sup> We took full advantage of identical particle symmetry to simplify the calculations. We calculated the reactive probabilities for the reaction  $H + H_2(v_0j_0) \rightarrow H_2 + H$  and the reaction  $F + H_2(v_0j_0) \rightarrow H + HF(v')$  using both contracted basis functions and primitive DGFs. Comparisons of these results test the contraction schemes.

The reactive probability for initial state  $v_0j_0$  and final vibrational level  $v'$  is defined by

$$P_{v_0j_0v'} = \sum_{\alpha=2}^3 \sum_{j'} |S_{\alpha'v'j'1v_0j_0}|^2 \quad (12)$$

and the total reaction probability is

$$P_{v_0j_0} = \sum_{v'} P_{v_0j_0v'} \quad (13)$$

**4.1.  $H + H_2$ .** First we consider the reaction  $H + H_2(v_0j_0) \rightarrow H_2(v'j') + H$ . We do test runs using the DMBE potential energy surface<sup>18</sup> with total angular momentum  $J = 0$  and total energy  $E = 1.24$  eV. For convergence tests one single set of parameters is used for all three arrangements. For this test, the total number of channels included in the calculation is 183, and the number of open channels is 60. There are five vibrational states with maximum rotational quantum numbers  $j_{\max} = 14, 12, 11, 10, 9$ . The DGF basis consists of evenly spaced Gaussians with  $R_{a1} = 2.2 a_0$  and  $\Delta_a = 1.4 a_0$ .

We employed both schemes 1 and 2. Since the results with the two schemes are similar, we present detailed results only for scheme 2. To calculate the contraction coefficients, we used reactive calculations with  $j_{\max} = 10$  and 9 in two vibrational states, with five translational basis functions included in each channel. The effort in this step is ignorable compared with the full calculation.

**4.2.  $F + H_2$ .** We also tested contracted basis functions for the reaction  $F + H_2$ . In this case we employed only scheme 2. With primitive basis functions, this reaction needs a larger number of DGFs than does the  $H + H_2$  reaction to get good convergence. We do the test runs for the 5A potential energy surface<sup>19</sup> with total angular momentum  $J = 0$  and total energy  $E = 0.34$  eV.

For the test, a single parameter set was used for each of the unique arrangements:  $F + H_2$  and  $H + HF$ . For the  $F + H_2$  arrangement we included five vibrational states,  $v = 0-4$ , with maximum rotational quantum numbers  $j = 12, 10, 8, 6$ , and 4, respectively; for the  $H + HF$  arrangement, we included seven vibrational states,  $v = 0-6$ , with maximum rotational quantum numbers  $j = 22, 18, 15, 11, 7, 4$ , and 3, respectively. The total number of channels included in the calculation is 219, and the number of open channels is 127.

To show that the results are not overly sensitive to the details of the contraction coefficients and also to show that a reasonable physical choice for the contraction coefficients leads to good convergence, we employed two different sets of coefficients, obtained from two different sets of parameters for the smaller calculations used to obtain  $\bar{A}_{\delta\eta\gamma\delta_0\eta_0}$ . In the first set of the calculations, we used maximum rotational quantum numbers  $j_{\max} = 9$  for vibrational levels  $v = 0$  and 1 of the arrangement  $F + H_2$  with 11 basis functions per channel and the same  $j_{\max}$  for vibrational states  $v = 0-3$  of the arrangement  $H + HF$ , with 17 basis functions per channel. This yields 100 channels and 1580 basis functions. For the second set of contraction coefficients, we used maximum rotational quantum numbers of  $j_{\max} = 4$  with 12 basis functions per channel for the first two vibrational states of the arrangement  $F + H_2$ , we used  $j_{\max} = 4$  with 18 basis functions per channel for  $v = 0, 1$ , and 3 of the arrangement  $H + HF$ , and we used  $j_{\max} = 11$  with 18 basis functions per channel for  $v = 2$  in the arrangement  $H + HF$ . This yields 64 channels and 1092 basis functions.

In this paper all calculations with uncontracted basis sets (denoted p in tables) used Gaussian parameters taken from our previous work; in particular,  $R_{FHH,1} = 2.0 a_0$ ,  $\Delta_{FHH} = 0.3 a_0$ ,  $R_{HHF,1} = 2.1 a_0$ ,  $\Delta_{HHF} = 0.2 a_0$ ,  $m_{FHH} \leq 16$ ,  $m_{HHF} \leq 28$ . For the contracted calculations (denoted c in tables), the parameters of the primitive basis set ( $m_{FHH} = 11$  or 12,  $m_{HHF} = 17$  or 18) are  $R_{FHH,1} = R_{HHF,1} = 2.5 a_0$ ,  $\Delta_{FHH} = 0.35 a_0$ , and  $\Delta_{HHF} = 0.26 a_0$ .

We conclude this section with an example to illustrate eqs 9-11. The third subscript of  $\bar{A}_{\delta\eta\gamma\delta_0\eta_0}$  tells which primitive Gaussian is under consideration, and setting  $\delta_0 = 1$  means that all contraction coefficients are obtained from solutions to the smaller problems with one of the  $F + H_2(v=0)$  channels as the initial state. The

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TABLE I: Selected Reaction Probabilities for the Reaction  $H + H_2(v_{0j_0}) \rightarrow H_2(\text{All Final States}) + H$ 

$m^a$	$v_0 = 0, j_0 = 1$		$v_0 = 0, j_0 = 9$		$v_0 = 0, j_0 = 10$		$v_0 = 0, j_0 = 10$		$v_0 = 1, j_0 = 7$	
	$c^b$	$p^c$	$c$	$p$	$c$	$p$	$c$	$p$	$c$	$p$
1	0.731	0.688	0.0302	0.0928	0.00096	0.00448	0.0000023	0.0000011	0.00010	0.00016
2	0.885	0.907	0.0634	0.0251	0.00128	0.00094	0.0000095	0.0000020	0.00063	0.00020
3	0.894	0.904	0.0441	0.0273	0.00203	0.00206	0.0000040	0.0000024	0.00015	0.00048
4	0.861	0.828	0.0547	0.0603	0.00230	0.00212	0.0000059	0.0000117	0.00017	0.00025
5	0.858	0.858	0.0550	0.0550	0.00225	0.00225	0.0000059	0.0000059	0.00017	0.00017
6		0.859		0.0551		0.00222		0.0000059		0.00016
7		0.859		0.0552		0.00224		0.0000057		0.00016
8		0.859		0.0552		0.00224		0.0000059		0.00016
9		0.859		0.0554		0.00222		0.0000061		0.00016
10		0.859		0.0552		0.00224		0.0000060		0.00016

<sup>a</sup>  $m$  means number of basis functions per channel. <sup>b</sup> Contracted basis functions. <sup>c</sup> Primitive basis functions.

TABLE II: Percentage Error for the Reaction  $H + H_2(v_{0j_0}) \rightarrow H_2(\text{All Final States}) + H$ 

$m^a$	$v_0 = 0, j_0 = 1$		$v_0 = 0, j_0 = 9$		$v_0 = 0, j_0 = 10$	
	$c^b$	$p^c$	$c$	$p$	$c$	$p$
1	14.9	19.9	45.3	68.1	57.1	100.0
2	3.0	5.6	14.9	54.5	42.9	58.0
3	4.1	5.2	20.1	50.5	9.4	8.0
4	0.2	3.6	0.9	9.2	2.7	5.4
5	0.1	0.1	0.4	0.4	0.5	0.5
6		0.0		0.2		0.9
7		0.0		0.0		0.0
8		0.0		0.0		0.0
9		0.0		0.4		0.9
10		0.0		0.0		0.0

<sup>a</sup> Number of basis functions per channel. <sup>b</sup> Contracted basis functions. <sup>c</sup> Primitive basis functions.

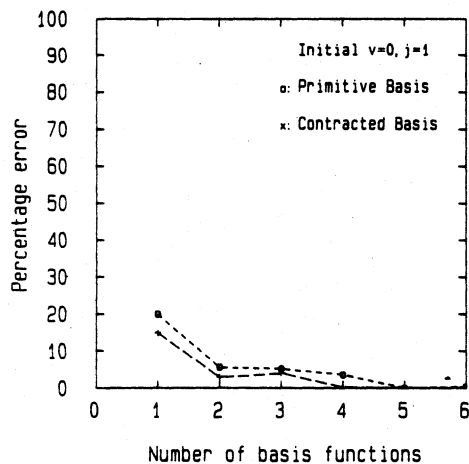


Figure 1. Percentage error of the reaction probability for  $v = 0, j = 1$  in the  $H + H_2$  reaction, as a function of the number of basis functions. The accurate value of the reaction probability is 0.858.

fifth subscript in eq 9 tells us which channel is actually used, as explained below. The first subscript tells us what distortion block  $\delta$  of the solution vector of the small calculation to use for the contraction coefficients of distortion block  $\delta$ . In particular, eq 10 says that if this distortion block occurs in the smaller calculation, we make the natural choice  $\delta = \delta$ . It also tells us that if  $\delta$  does not occur in the smaller problem, we should use the distortion block of the same arrangement with the closest value of the vibrational quantum number that does occur. What still remains to be specified are the values of  $\bar{\eta}$  and  $\bar{\eta}_0$  in the solution matrix to use in assigning contraction coefficients, and we must simultaneously consider the second and fifth subscripts to explain how the chosen scheme works. In particular, we first use the various channels with  $\eta_0 = 1$  [initial state is first channel of  $F + H_2(v=0)$  distortion block], and we continue until all the channels are used; then we start taking contraction coefficients from the solution vector corresponding to the second channel as initial state,

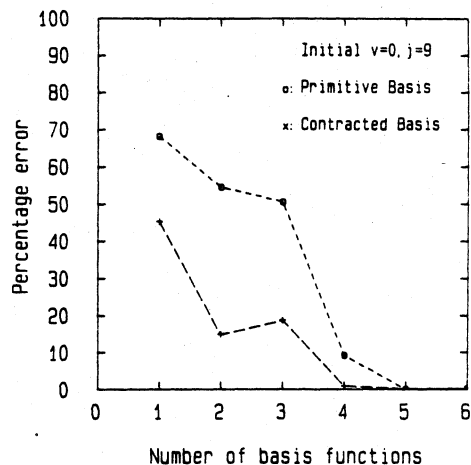


Figure 2. Same as Figure 1 except for the  $v = 0, j = 9$  state, for which the accurate reaction probability is 0.0550.

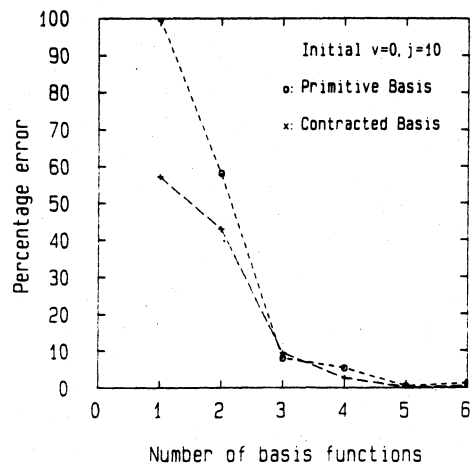


Figure 3. Same as Figure 1 except for the  $v = 0, j = 10$  state, for which the accurate reaction probability is 0.00225.

and so forth, as indicated by (11).

## 5. Results

Selected reaction probabilities for the  $H + H_2$  reaction are given in Table I for the comparison of the performance of contracted and primitive basis functions for the initial states  $v_0 = 0, j_0 = 1, 9, 10, 11; v_0 = 1, j_0 = 7$ . Selected percentage errors are given in Table II. Tables I and II show that four contracted basis functions yield results converged to about the same accuracy as five primitive functions. The results from the contracted basis are indeed converged faster than for the primitive one, but both types of calculation converge so well that there is not much room for improvement by contraction. Plots of the percentage error are given in Figures 1–4. Because the  $H + H_2$  reaction is a simple one and the GNVP is already very efficient (five basis functions

**TABLE III: Quantities Involved in Scaling Analysis of the Computational Effort for F + H<sub>2</sub> Calculations with Contraction Coefficients Based on 100-Channel Calculations**

	$M_1$	$M_e$	$M_o$	$M_e^2 + M_o^2$	$M_e^3 + M_o^3$
a. original converged calculation	5592	2836	2756	1.56 (+7)	4.37 (+10)
b. $M_1 = 11, M_2 = 17$	3453	1754	1699	5.96 (+6)	1.03 (+10)
c. contracted calculation					
i. obtain basis functions	1580	790	790	1.25 (+6)	9.86 (+8)
ii. $M_1 = 7, M_2 = 10$	2055	1045	1010	2.11 (+6)	2.17 (+9)
sum (i + ii)				3.35 (+6)	3.16 (+9)
(sum + a) × 100, %				21	7
(sum + b) × 100, %				56	30

per channel is enough for good convergence), the contraction scheme only provides a small improvement, but it does show successful faster convergence than the primitive one.

In Tables III–X,  $M_1$  denotes either  $m_{\text{FHH}}$  or  $\bar{m}_{\text{FHH}}$ , depending on the context, and  $M_2$  denotes either  $m_{\text{HHF}}$  or  $\bar{m}_{\text{HHF}}$ . Further-

more,  $M_e$  is the number of basis functions in the even  $j$  block,  $M_o$  is the number of basis functions in the odd  $j$  block, and  $M_1$  is the total number of basis functions involved in the calculations. Clearly

$$M_1 = M_1 n_1'' + M_2 (n_3'' - n_1'') = M_e + M_o \quad (14)$$

Table III compares the computational effort for contracted and primitive calculations on F + H<sub>2</sub> with the first set of contraction coefficients ( $j_{\text{max}} = 9$ ;  $M_1 = 1580$ ), and Table VII gives the comparison of computational efforts for the second set of contraction coefficients ( $j_{\text{max}} = 4, 4$  for F + H<sub>2</sub>;  $j_{\text{max}} = 4, 4, 11, 4$  for H + HF;  $M_1 = 1092$ ). The original converged calculations with primitive basis sets involved 5592 functions. The effort to obtain the contraction coefficients for the precalculations for either of the above sets is not significant compared to the effort required to perform such a large calculation with a primitive basis. This is seen by comparing the last two entries in row c.i of Table III

**TABLE IV: Reaction Probabilities for F + H<sub>2</sub>( $v=j=0$ ) → H + HF( $v'$ , Summed over  $j'$ ) + H with Contraction Coefficients Based on 100-Channel Calculations**

$(M_1, M_2)$	$M_1$	$M_e$	$M_o$	$v' = 2$		$v' = 3$		all	
				c	p	c	p	c	p
(6,9)	1836	933	903	0.104	0.202	0.439	0.207	0.555	0.593
(6,10)	2010	1020	990	0.094	0.199	0.448	0.384	0.544	0.596
(7,9)	1881	958	958	0.101	0.116	0.445	0.262	0.553	0.404
(7,10)	2055	1045	1010	0.090	0.212	0.449	0.389	0.540	0.617
(8,10)	2100	1070	1030	0.092	0.181	0.445	0.404	0.538	0.589
(8,11)	2274	1157	1117	0.092	0.104	0.440	0.386	0.536	0.492
(8,12)	2448	1244	1204	0.093	0.114	0.441	0.462	0.535	0.578
(9,12)	2493	1269	1224	0.093	0.077	0.441	0.382	0.535	0.460
(9,13)	2667	1356	1311	0.092	0.089	0.442	0.377	0.536	0.467
(10,12)	2538	1294	1244	0.093	0.089	0.441	0.441	0.535	0.531
(10,13)	2712	1381	1331	0.091	0.092	0.442	0.423	0.535	0.517
(10,14)	2886	1468	1418	0.089	0.082	0.442	0.412	0.532	0.495
(10,15)	3060	1555	1505	0.089	0.082	0.442	0.411	0.532	0.494
(10,16)	3234	1642	1592	0.089	0.081	0.442	0.411	0.531	0.493
(11,17)	3453	1754	1699	0.088	0.089	0.442	0.442	0.531	0.531
(12,18)	3672	1866	1806		0.090		0.447		0.538
(13,19)	3891	1978	1913		0.090		0.446		0.536
(14,20)	4110	2090	2020		0.090		0.445		0.536
(15,21)	4329	2202	2127		0.090		0.445		0.536
(16,22)	4548	2314	2234		0.088		0.447		0.535
(16,28)	5592	2836	2756		0.089		0.442		0.532

**TABLE V: Reaction Probabilities for F + H<sub>2</sub>( $v=0, j=1$ ) → H + HF( $v'$ , Summed over  $j'$ ) + H with Contraction Coefficients Based on 100-Channel Calculations**

$(M_1, M_2)$	$M_1$	$M_e$	$M_o$	$v' = 2$		$v' = 3$		all	
				c	p	c	p	c	p
(6,9)	1836	933	903	0.131	0.270	0.517	0.279	0.665	0.733
(6,10)	2010	1020	990	0.188	0.235	0.522	0.452	0.888	0.703
(7,9)	1881	958	923	0.121	0.295	0.524	0.471	0.651	0.786
(7,10)	2055	1045	1010	0.107	0.475	0.525	0.278	0.634	0.853
(8,10)	2100	1070	1030	0.104	0.224	0.525	0.478	0.630	0.707
(8,11)	2274	1157	1117	0.108	0.129	0.522	0.460	0.633	0.590
(8,12)	2448	1244	1204	0.109	0.094	0.528	0.390	0.637	0.485
(9,12)	2493	1269	1224	0.111	0.095	0.527	0.450	0.639	0.545
(9,13)	2667	1356	1311	0.110	0.107	0.527	0.450	0.639	0.558
(10,12)	2538	1294	1244	0.111	0.102	0.527	0.511	0.639	0.618
(10,13)	2712	1381	1331	0.110	0.111	0.527	0.503	0.638	0.615
(10,14)	2886	1468	1418	0.109	0.100	0.527	0.492	0.637	0.592
(10,15)	3036	1555	1505	0.109	0.099	0.527	0.471	0.637	0.591
(10,16)	3234	1642	1592	0.108	0.099	0.527	0.490	0.636	0.593
(11,17)	3453	1754	1699	0.108	0.108	0.527	0.527	0.637	0.636
(12,18)	3672	1866	1806		0.110		0.534		0.645
(13,19)	3891	1978	1913		0.109		0.533		0.644
(14,20)	4110	2090	2020		0.109		0.533		0.643
(15,21)	4329	2202	2127		0.109		0.533		0.643
(16,22)	4548	2314	2234		0.107		0.534		0.643
(16,28)	5592	2836	2756		0.109		0.529		0.639

**TABLE VI: Reaction Probabilities for  $F + H_2(v=0, j=2) \rightarrow H + HF(m', \text{Summed over } j') + H$  with Contraction Coefficients Based on 100-Channel Calculations**

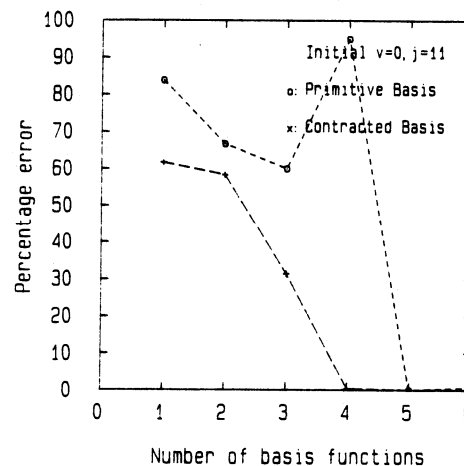
$(M_1, M_2)$	$M_1$	$M_e$	$M_o$	$v' = 2$		$v' = 3$		all	
				c	p	c	p	c	p
(6,9)	1836	933	903	0.022	0.040	0.084	0.039	0.108	0.115
(6,10)	2120	1020	990	0.020	0.039	0.086	0.072	0.106	0.117
(7,9)	1881	958	923	0.021	0.024	0.086	0.050	0.108	0.079
(7,10)	2055	1045	1010	0.019	0.042	0.086	0.073	0.105	0.118
(8,10)	2100	1070	1030	0.019	0.036	0.086	0.076	0.105	0.113
(8,11)	2274	1157	1117	0.019	0.021	0.085	0.074	0.105	0.095
(8,12)	2448	1244	1204	0.019	0.019	0.085	0.074	0.104	0.093
(9,12)	2493	1269	1224	0.019	0.016	0.085	0.072	0.104	0.088
(9,13)	2667	1356	1311	0.019	0.078	0.085	0.071	0.104	0.089
(10,12)	2538	1294	1244	0.019	0.018	0.085	0.084	0.104	0.102
(10,13)	2712	1381	1331	0.019	0.019	0.085	0.080	0.104	0.099
(10,14)	2886	1468	1418	0.019	0.017	0.085	0.078	0.104	0.095
(10,15)	3060	1555	1505	0.019	0.017	0.085	0.078	0.104	0.095
(10,16)	3234	1642	1592	0.019	0.017	0.085	0.078	0.104	0.095
(11,17)	3453	1754	1699	0.019	0.019	0.085	0.085	0.104	0.104
(12,18)	3672	1866	1806		0.019		0.087		0.107
(13,19)	3891	1978	1913		0.019		0.088		0.107
(14,20)	4110	2090	2020		0.019		0.088		0.107
(15,21)	4329	2202	2127		0.019		0.088		0.107
(16,22)	4548	2314	2234		0.019		0.088		0.107
(16,28)	5592	2836	2756		0.019		0.088		0.107

**TABLE VII: Quantities Involved in Scaling Analysis of the Computational Effort for  $F + H_2$  Calculations with Contraction Coefficients Based on 64-Channel Calculations**

	$M_1$	$M_e$	$M_o$	$M_e^2 + M_o^2$	$M_e^3 + M_o^3$
a. original converged calculation	5592	2836	2756	1.56 (+7)	4.37 (+10)
b. $M_1 = 12, M_2 = 18$	3672	1866	1806	6.74 (+6)	1.24 (+10)
c. contracted calculation					
i. obtain basis functions	1092	558	534	5.97 (+5)	3.26 (+8)
ii. $M_1 = 8, M_2 = 10$	2100	1070	1030	2.21 (+6)	2.32 (+9)
sum (i + ii)				2.81 (+6)	2.65 (+9)
(sum + a) $\times 100, \%$				18	6
(sum + b) $\times 100, \%$				42	21

or VII with the last two entries of the first row.

Tables IV-VI give the reaction probabilities associated with the run of Table III. These tables illustrate the number of contracted functions required to obtain a given level of convergence. For the first set (Tables III-VI), the total effort of the contracted calculations is about 30% of the effort of the primitive one to get

**Figure 4.** Same as Figure 1 except for the  $v = 0, j = 11$  state for which the accurate reaction probability is 0.00587.**TABLE VIII: Reaction Probabilities for  $F + H_2(v=j=0) \rightarrow H + HF(v', \text{Summed over } j') + H$  with Contraction Coefficients Based on 64-Channel Calculations**

$(M_1, M_2)$	$M_1$	$M_e$	$M_o$	$v' = 2$		$v' = 3$		all	
				c	p	c	p	c	p
(6,9)	1836	933	903	0.096	0.202	0.453	0.207	0.565	0.593
(6,10)	2010	1020	990	0.106	0.199	0.429	0.384	0.572	0.596
(7,9)	1881	958	923	0.096	0.116	0.460	0.262	0.567	0.404
(7,10)	2055	1045	1010	0.094	0.212	0.460	0.389	0.559	0.617
(8,10)	2100	1070	1030	0.092	0.181	0.447	0.404	0.541	0.589
(8,11)	2274	1157	1117	0.092	0.104	0.447	0.386	0.540	0.492
(8,12)	2448	1244	1204	0.092	0.114	0.449	0.462	0.541	0.578
(9,12)	2493	1269	1224	0.092	0.077	0.448	0.382	0.541	0.460
(9,13)	2667	1356	1311	0.091	0.089	0.449	0.377	0.541	0.467
(10,12)	2538	1294	1244	0.092	0.089	0.448	0.441	0.541	0.531
(10,13)	2712	1381	1331	0.090	0.092	0.448	0.423	0.540	0.517
(10,14)	2886	1468	1418	0.091	0.082	0.447	0.412	0.540	0.495
(10,15)	3060	1555	1505	0.091	0.082	0.448	0.411	0.540	0.494
(10,16)	3234	1642	1592	0.091	0.081	0.447	0.411	0.539	0.493
(11,17)	3453	1754	1699	0.090	0.089	0.447	0.442	0.539	0.531
(12,18)	3672	1866	1806	0.089	0.090	0.447	0.447	0.537	0.538
(13,19)	3891	1978	1913		0.090		0.446		0.536
(14,20)	4110	2090	2020		0.090		0.445		0.536
(15,21)	4329	2202	2127		0.090		0.445		0.536
(16,22)	4548	2314	2234		0.088		0.447		0.535
(16,28)	5592	2836	2756		0.089		0.442		0.532

**TABLE IX: Reaction Probabilities for  $F + H_2(v=0, j=1) \rightarrow H + HF(v', \text{Summed over } j') + H$  with Contraction Coefficients Based on 64-Channel Calculations**

$(M_1, M_2)$	$M_i$	$M_e$	$M_o$	$v' = 2$		$v' = 3$		all	
				c	p	c	p	c	p
(6,9)	1836	933	903	0.157	0.270	0.435	0.279	0.695	0.733
(6,10)	2010	1020	990	0.076	0.235	0.455	0.452	0.561	0.703
(7,9)	1881	958	923	0.130	0.295	0.535	0.471	0.680	0.786
(7,10)	2055	1045	1010	0.121	0.475	0.535	0.278	0.666	0.853
(8,10)	2100	1070	1030	0.115	0.224	0.531	0.478	0.649	0.707
(8,11)	2274	1157	1117	0.115	0.129	0.525	0.460	0.650	0.590
(8,12)	2448	1244	1204	0.116	0.094	0.532	0.390	0.650	0.485
(9,12)	2493	1269	1224	0.115	0.095	0.534	0.450	0.650	0.545
(9,13)	2667	1356	1311	0.114	0.107	0.532	0.450	0.652	0.558
(10,12)	2538	1294	1244	0.114	0.102	0.533	0.511	0.650	0.618
(10,13)	2712	1381	1331	0.114	0.111	0.533	0.503	0.649	0.615
(10,14)	2886	1468	1418	0.112	0.100	0.534	0.492	0.647	0.592
(10,15)	3060	1555	1505	0.112	0.099	0.531	0.471	0.649	0.591
(10,16)	3234	1642	1592	0.112	0.099	0.534	0.490	0.647	0.593
(11,17)	3453	1754	1699	0.110	0.108	0.535	0.527	0.646	0.636
(12,18)	3672	1866	1806	0.109	0.110	0.534	0.534	0.645	0.645
(13,19)	3891	1978	1913		0.109		0.533		0.644
(14,20)	4110	2090	2020		0.109		0.533		0.643
(15,21)	4329	2202	2127		0.109		0.533		0.643
(16,22)	4548	2314	2234		0.107		0.534		0.643
(16,28)	5592	2836	2756		0.109		0.529		0.639

**TABLE X: Reaction Probabilities for  $F + H_2(v=0, j=2) \rightarrow H + HF(v', \text{Summed over } j') + H$  with Contraction Coefficients Based on 64-Channel Calculations**

$(M_1, M_2)$	$M_i$	$M_e$	$M_o$	$v' = 2$		$v' = 3$		all	
				c	p	c	p	c	p
(6,9)	1836	933	903	0.021	0.040	0.088	0.039	0.113	0.115
(6,10)	2010	1020	990	0.023	0.039	0.084	0.072	0.115	0.117
(7,9)	1881	958	923	0.020	0.024	0.090	0.050	0.112	0.079
(7,10)	2055	1045	1010	0.020	0.042	0.090	0.073	0.111	0.118
(8,10)	2100	1070	1030	0.019	0.036	0.087	0.076	0.107	0.113
(8,11)	2274	1157	1117	0.019	0.021	0.087	0.074	0.107	0.095
(8,12)	2448	1244	1204	0.019	0.019	0.088	0.074	0.107	0.093
(9,12)	2493	1269	1224	0.019	0.016	0.088	0.072	0.107	0.088
(9,13)	2667	1356	1311	0.019	0.018	0.088	0.071	0.107	0.089
(10,12)	2538	1294	1244	0.019	0.018	0.087	0.084	0.107	0.102
(10,13)	2712	1381	1331	0.019	0.019	0.088	0.080	0.107	0.099
(10,14)	2886	1468	1418	0.019	0.017	0.087	0.078	0.107	0.095
(10,15)	3060	1555	1505	0.019	0.017	0.088	0.078	0.107	0.095
(10,16)	3234	1642	1592	0.019	0.017	0.087	0.078	0.107	0.095
(11,17)	3435	1754	1699	0.019	0.019	0.087	0.085	0.107	0.104
(12,18)	3672	1866	1806	0.019	0.019	0.087	0.087	0.107	0.107
(13,19)	3891	1978	1913		0.019		0.088		0.107
(14,20)	4110	2090	2020		0.019		0.088		0.107
(15,21)	4329	2202	2127		0.019		0.088		0.107
(16,22)	4548	2314	2234		0.019		0.088		0.107
(16,28)	5592	2836	2756		0.019		0.088		0.107

similar convergence. Tables VIII–X give the comparisons of the reaction probabilities associated with the run of Table VII. In this case it takes about 21% of the effort required for the primitive basis set to yield similar convergence.

## 6. Discussion

Although it has now been shown that variational approaches for reactive scattering lead to great progress in minimizing the number of basis functions, some of the reaction systems studied still require large numbers of basis functions in the expansion to achieve a good accuracy. This leads to a large linear equation system and takes considerable computational resources. The use of contracted basis functions decreases the number of basis functions required in the expansion. This leads to a big savings in computational storage and CPU time. The enhancements available with contracted basis function are very general. The results from the present contracted basis function calculations show that it is a very promising technique for scattering calculations, and it provides an efficient approach to obtaining converged results in quantum mechanical calculations.

From the equations and tests presented above, it is clear that the contracted basis function technique is general and can be used to greatly improve the convergence of linear algebraic expansions

of the amplitude density for molecular scattering. Similar savings are anticipated for methods that expand the wave function, and indeed the GNVP itself can be interpreted as an expansion of the wave function in a dynamically adapted basis.<sup>20</sup> The present paper is concerned entirely with contractions involving the basis set for the translational coordinate. In addition, we are using asymptotic contraction in the vibrational coordinate; i.e., the vibrational basis functions are linear combinations of harmonic oscillator functions with coefficients determined by diagonalizing the asymptotic Hamiltonian.<sup>16</sup> We expect that these techniques could also be combined profitably with other types of contraction in the bound modes or with multidimensional contraction schemes. For example, the vibrational basis could be contracted basis on the shape of the surface at small  $R_{a\gamma}$ , or a different set of contracted bound functions could be used in conjunction with each  $\lambda_{a\gamma}$  and their coefficients could be found either by dynamical contraction as used here or by adiabatic contraction based on  $R_{a\gamma} = R_{a\gamma}$ , as used previously in other contexts.<sup>13</sup> Or the dynamical methods proposed here could be used to associate different contracted functions for

(20) Sun, Y.; Kouri, D. J.; Truhlar, D. G.; Schwenke, D. W. *Phys. Rev. A*, in press. Sun, Y.; Kouri, D. J.; Truhlar, D. G. *Nucl. Phys.* **1990**, *A508*, 41c.



the bound degrees of freedom with various  $\bar{\lambda}_i^{(n)}$  or to obtain completely arbitrary (cross-channel) contraction coefficients.

Even for contraction of only the translational basis the techniques employed so far can be improved in many ways. Further studies will be performed to test whether it might be advantageous to use a different contracted basis set for every channel. This might allow for smaller basis set sizes, but the number of matrix elements and the amount of storage will increase. The success achieved here in contracting only the translational basis and in constraining the contraction coefficients to be the same for all channels in a given vibrational manifold bodes well for more general schemes.

The accuracy of the contracted basis function method, as for other basis set methods, can be systematically improved by increasing the basis sizes. Therefore, one can achieve a required accuracy without losing the advantage of the contraction. This was shown in the examples throughout the paper. In these examples the case of total angular momentum,  $J = 0$ , was considered, and one would expect more savings for cases with  $J > 0$ .

The general approach presented here is not restricted to molecular scattering; it has been used already for electron-atom scattering processes.<sup>7</sup> Similar procedures should be able to be used in conjunction with other variational approaches to molecular scattering as well. The method is attractive because of its simplicity. Because it uses the same procedures to obtain the contraction coefficients as to do the final calculations, the complexity for the programming is kept to a minimum.

Contracted basis functions should be a powerful tool for exploring more complicated collision problems in a variety of contexts.<sup>21</sup>

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(21) While this paper was being reviewed, another preprint concerning contraction of the translational basis for algebraic variational calculations of reactive scattering appeared: Manolopoulos, D. E.; D'Mello, M.; Wyatt, R. E. *J. Chem. Phys.*, in press.