

Exact Quantum Dynamics and Tests of the Distorted-wave Approximation for the $O(^3P) + HD$ Reaction

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We present accurate quantum-dynamical calculations of isotopic branching probabilities in the $O + HD \rightarrow OH + D$ or $OD + H$ reaction on a realistic potential-energy surface. The results are used to test several versions of distorted-wave theory in the threshold region. We find that at low energies and low initial rotational quantum numbers, calculations based on distorted waves that are fully coupled within each arrangement are in excellent agreement with accurate quantal reaction probabilities, but deviations occur for higher energies and higher initial rotational quantum numbers. Uncoupled distorted waves or distorted waves with rotational but not vibrational coupling do not lead to accurate reaction probabilities under any conditions, but the relative product vibrational-rotational distributions are quite accurate not only for the fully coupled distorted-wave approximation but also for the rotationally coupled distorted-wave approximation.

1. Introduction

This special issue of the *Faraday Transactions* on New Theoretical Methods for Inelastic and Reactive Scattering is indeed timely since there are many research groups working on one or more new such methods at this time. Since this issue features a keynote paper by Connor, we will refer the reader to that paper and our own other recent papers for references to this work, and we will proceed directly to the two methods which form the subject of the present study, the generalized Newton variational principle (GNVP) for reactive scattering calculations with square-integrable (\mathcal{L}^2) expansions of the reactive amplitude density, and the distorted wave Born approximation (DWBA) for reactive scattering with a hierarchy of choices for the distortion potential.

Newton's book¹ gives an overview of the most popular variational approaches, including the Hulthén-Kohn approach based on differential equations^{2,3} and the Schwinger approach based on integral equations.⁴ In the latter category he also presented a new stationary expression for the T operator which we call the Newton variational principle. Alternative treatments and extensions to multichannel scattering and rearrangements were published by Sloan and Brady,^{5,6} one of the authors and Levin,^{7,8} Rabitz and Conn,^{9,10} and Sloan and Adhikari.^{11,12} The convergence efficiency of the Newton variational principle was studied in detail by Staszewska and one of the present authors.^{13,14} We and our co-workers have applied a generalization of this method, the GNVP,^{15,16} for several converged calculations of three-dimensional reactive scattering dynamics.¹⁵⁻²⁸ Considerable progress on reactive scattering has also been achieved with a method of moments²⁹⁻³⁶ for the amplitude density (MMAD) that results^{8,16} from inserting a finite-basis approximation to the identity to separate the Green's function and the potential in the basic matrix elements of the GNVP. In both the MMAD and the GNVP we have explored various choices for arrangement channel coupling of the reactive amplitude densities, for distortion potentials that define the intra-arrangement coupling, for \mathcal{L}^2 basis sets, and

for the boundary conditions on the distorted wave Green's functions. We have found the Fock scheme³⁷⁻⁴¹ to be more efficient than the Baer-Kouri-Levin-Tobocman scheme,⁴²⁻⁴⁴ which was employed in earlier⁴⁵ MMAD calculations; we found that rotationally coupled distortion potentials^{15,16} lead to faster convergence of the \mathcal{L}^2 expansions of the reactive amplitude density than do single-channel distortion potentials;^{17,18} we found a basis set^{29,30} of products of distributed Gaussians^{46,47} for the radial relative translational coordinate, Percival-Seaton-Arthurs-Dalgarno functions^{48,49} for coupled orbital-rotational motions and asymptotic vibrational eigenstates³⁰ is very efficient; and both real^{16-19,29,30} and complex^{19,23} Green's functions have provided useful accuracy and stability for various problems.

The distorted-wave approximation^{50,51} (DWA) also has an extensive literature. It was originally developed in nuclear physics (where it is often called the distorted-wave Born approximation or DWBA), but subsequently it has also been carefully studied in atomic and chemical physics. There have been many formulations and applications to chemical reactions^{38,52-110} (including collinear, coplanar, 3D, adiabatic, non-adiabatic *etc.*). The theory is usually considered to be most useful in the threshold region. A critical element in distorted-wave calculations is the choice of distortion potential. Most previous calculations have used uncoupled distorted waves, but, for chemical rearrangements, allowing full coupling within a given arrangement⁹²⁻⁹⁵ in determining the distorted waves (a procedure introduced earlier in electron-atom scattering¹¹¹ and nuclear physics¹¹²⁻¹¹⁵) leads to significantly more accurate results. In the present article we test both uncoupled and fully coupled (within an arrangement) distorted waves as well as an intermediate choice, allowing for rotational but not vibrational coupling.

Earlier critical tests of the DWA were presented by Schatz, who tested the theory for the $H + H_2$,¹⁰⁶ $D + H_2$,¹⁰⁶ and $Cl + HCl$ ¹¹⁶ reactions. Schatz also carried out DWA calculations for $O + H_2$, $O + D_2$ and $O + HD$,¹⁰⁰ and we will compare our results to his for $O + HD$ as part of the present study.

2. Theory

The GNVP may be applied with either real or complex Green's functions.^{15,16,19,23} We briefly review here the central equations for the former choice. The Hamiltonian in each arrangement α is written as:

$$H = H_{\alpha}^D + V_{\alpha}^C \quad (1)$$

where H_{α}^D is a distortion Hamiltonian corresponding to non-reactive scattering, and V_{α}^C is the remaining part of H which goes to zero in each arrangement α for a large separation of the atomic and diatomic fragments. We define G_{α}^D as the principal value Green's function for H_{α}^D , given by

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

where μ is a reduced mass and E is the total energy. We also define a matrix G^D , diagonal in α , containing these Green's functions for various channels, and we define another matrix U which couples the arrangements and provides the residual coupling, if any, within arrangements:

$$U_{\alpha\alpha'} = (-2\mu/\hbar^2)[H - E + \delta_{\alpha\alpha'}(E - H_{\alpha}^D)]. \quad (3)$$

The reactance matrix for the rearrangement problem defined by the full H may be written¹⁶

$$K = {}^0K + \mathcal{K} \quad (4)$$

where 0K is the reactance matrix corresponding to the distortion problem defined by H_{α}^D and is diagonal in α , and \mathcal{K} is the correction due to $U_{\alpha\alpha'}$. The GNVP yields

$$\mathcal{K} = \mathcal{K}^B + B^T C^{-1} B \quad (5)$$

where B and C are, respectively, the matrix representations of the operators UG^D and $(1 - G^D U)G^D$, and \mathcal{K}^B is the Born term with elements

$$\mathcal{K}_{nn'}^B = \langle \psi^{an} | U_{\alpha\alpha'} | \psi^{a'n'} \rangle \quad (6)$$

where ψ^{an} is the regular distorted wave satisfying the equation

$$(H_{\alpha}^D - E)\psi^{an} = 0 \quad (7)$$

with real standing-wave boundary conditions. The scattering matrix, from which all state-to-state reaction probabilities can be calculated, is obtained by:

$$S = (1 - iK)^{-1}(1 + iK). \quad (8)$$

The distorted wave approximation to the reactance matrix is given by

$$K^{DWA} = {}^0K + \mathcal{K}^B \quad (9)$$

and the DWA to the scattering matrix is given by

$$S^{DWA} = (1 - iK^{DWA})^{-1}(1 + iK^{DWA}). \quad (10)$$

Since this is obtained with real boundary conditions (RBC) on the solution to eqn (7), it is called DWA-RBC.

The DWA can be formulated in terms of either the real functions ψ^{an} , as in eqn (6), or in terms of the complex incoming and outgoing solutions $(\pm)\psi^{an}$ of eqn (7). Whereas the boundary conditions used for the solution of eqn (7) are strictly a matter of convenience in the GNVP, and a converged reactance matrix K may be obtained with either choice, the DWA does depend on this choice. With the complex boundary conditions (CBC), the DWA to the scattering matrix is given by

$$S^{DWA} = {}^0S + \mathcal{S}^B \quad (11)$$

where 0S is the scattering matrix, diagonal in α , corresponding to H_{α}^D , and \mathcal{S}^B is the Born term:

$$\mathcal{S}_{nn'}^B = \langle (-)\psi^{an} | U_{\alpha\alpha'} | (+)\psi^{a'n'} \rangle \quad (12)$$

where $(-)\psi^{an}$ and $(+)\psi^{a'n'}$ are, respectively, the incoming and outgoing distorted waves satisfying:

$$(H_{\alpha}^D - E)(\pm)\psi^{an} = 0. \quad (13)$$

The results obtained with eqn (11) are labelled DWA-CBC.

For either the DWA-RBC or DWA-CBC, H_{α}^D may be chosen in various ways. For example, it may include all the coupling within a given arrangement; we call this the fully coupled (FC) distorted-wave approximation (FCDWA). If H_{α}^D couples only the channels in arrangement α that have the same vibrational quantum number v , *i.e.* if it includes only the rotational coupling within individual vibrational manifolds, we call the theory the rotationally coupled distorted-wave approximation (RCDWA). Finally, if H_{α}^D corresponds to completely uncoupled channels, we refer to the results as the uncoupled distorted wave approximation (UDWA). The mathematical forms of H_{α}^D for these choices are given elsewhere.¹⁶ We note for completeness that other choices are also possible, *e.g.* adiabatic distorted waves or distorted waves based on model potentials, but they will not be considered here. (However, the present accurate quantal benchmark results could be used to test such theories, and we encourage workers developing such methods to use our accurate results to carry out such tests.)

We note that a wide variety of formulations and abbreviations has been employed by other researchers, but we are concerned only with the approximations mentioned above. Thus, *e.g.* adiabatic uncoupled theories may be more accurate than the UDWA defined above in terms of diabatic channels, but they are not tested here.

3. Calculations and Results

Converged quantum-dynamical calculations for the reaction $O + HD$ have been presented in two previous papers, and details of the application of the GNVP to this problem are given in those references.^{23,25} In particular, we have used real Green's functions, *i.e.* GNVP-RGF, for the present converged calculations although in previous work we showed²³ that the same converged results can be obtained with complex Green's functions for both $O + H_2$ and $O + HD$. All results presented here are for total angular momentum J equal to zero because in a few trial runs we found that the results are not very sensitive to raising J , at least for $J = 1-3$. Thus we expended our efforts on a thorough set of calculations for a single J rather than on studying the relatively minor dependence on J . The calculation of converged quantal cross-sections including all J would require considerably more effort, and the comparisons would be harder to analyse because they involve cancellation of errors for different J .

Calculations were performed for the Johnson-Winter-Schatz^{100,117} potential-energy surface, which consists of a LEPS function plus a three-centre HOH barrier term, in the range of total energies, E , from 9.2 to 17 kcal mol⁻¹. This energy range includes the threshold regions for both possible chemical products, OH and OD, for this potential-energy surface. We will compare the above to the coupled states distorted-wave results (denoted CSDWA-CBC) of Schatz and to several sets of our own distorted-wave calculations. In particular, we consider the fully coupled distorted-wave Born approximations with both real and complex boundary conditions (FCDWA-RBC and FCDWA-CBC), the rotationally coupled distorted-wave approximations with both real and

complex boundary conditions (RCDWA-RBC and RCDWA-CBC), and the uncoupled distorted-wave approximation with real boundary conditions (UDWA-RBC).

We concentrate on reaction probabilities from the initial arrangement O + HD to either of the final products summed over the final vibrational and rotational states of that product. We consider only the ground vibrational level ($v=0$) of HD, but we consider several initial rotational states, with rotational quantum number j . In a few cases we also show cumulative reaction probabilities.

The GNVP calculations are well converged. Since convergence was demonstrated previously,²⁵ we will not detail it here. The DWA calculations also were well converged. Surprisingly we found this to be rather difficult; in particular, it is harder to converge the FCDWA results with respect to the number of channels than it is to converge the GNVP results. After extensive tests, we developed the parameter sets given in tables 1-3. Set 1 and set 2 in table 1 have all parameters different with set 2 better converged than set 1; for example,

the number of channels is increased from 146 in set 1 to 175 in set 2. These two sets of parameters are used to perform the RCDWA-RBC, RCDWA-CBC, and UDWA-RBC calculations. With these parameter sets we achieved very good convergence (*ca.* three significant figures for most of the probabilities) of the reaction probabilities to produce OH or OD with respect to all the parameters at all the energies considered here; the convergence checks are given in table 4. We also used parameter sets 1 and 2 to perform calculations with the FCDWA-RBC and FCDWA-CBC methods. Tables 4 and 5 show that at the lower energies, parameter sets 1 and 2 yield very good (better than 1%) convergence for the FCDWA reaction probabilities. However, at energies higher than 14 kcal mol⁻¹, more channels are needed to get converged results. To converge the energies higher than 14 kcal mol⁻¹, we chose parameter sets 3 and 4 for FCDWA-RBC calculations and sets 5 and 6 for FCDWA-CBC calculations. Convergence checks for sets 3-6 are also given in tables 4 and 5. Table 6 shows the convergence of the reaction probabilities

Table 1. Parameter sets 1 and 2 for the tests of the distorted-wave approximation

	set 1			set 2		
	O + HD	H + OD	D + OH	O + HD	H + OD	D + OH
$j_{\max}(v=0)^a$	9	16	11	10	17	12
$j_{\max}(v=1)^a$	8	14	10	9	15	11
$j_{\max}(v=2)^a$	7	12	9	8	13	10
$j_{\max}(v=3)^a$	6	10	8	7	11	9
$j_{\max}(v=4)^a$		8		4	9	4
$j_{\max}(v=5)^a$		4			6	
$j_{\max}(v=6)^a$					3	
N_z^b	34	70	42	43	81	51
$N(\text{HO})^c$	50	50	50	55	55	55
$R_{1,F}(a_0)^d$	1.8	0.9	1.4	1.6	0.8	1.3
$R_{N(F),F}(a_0)^d$	15.0	12.0	13.0	15.5	12.5	13.5
$N_{\alpha\alpha}(\text{QA})^e$	70	70	70	75	75	75
$N_{\alpha\alpha}(\text{QA})^f$	30	30	30	35	35	35
$N(\text{QV})^g$	12	12	12	13	13	13
$N(\text{QGL})^h$	12	12	12	14	14	14
$N(\text{QR})^i$	14	14	14	13	13	13

^a Maximum rotational quantum number included in the basis for a given vibrational level. ^b Number of channels included in the basis for a given arrangement. ^c Number of harmonic oscillator functions used to expand the asymptotic vibrational eigenstate. ^d First and last point in finite difference grid for distorted waves. ^e Number of points in angular quadrature for integrals coupling different arrangements. ^f Number of points in angular quadrature for intra-arrangement integrals. ^g Number of quadrature points for intra-arrangement vibrational integrals. ^h Number of points in radial Gauss-Legendre quadratures in exchange integrals. ⁱ Number of repetitions of Gauss-Legendre quadratures for radial parts of exchange integrals.

Table 2. Parameters sets 3 and 4 for the tests of the distorted-wave approximation

	set 3			set 4		
	O + HD	H + OD	D + OH	O + HD	H + OD	D + OH
$j_{\max}(v=0)^a$	15	20	18	16	21	19
$j_{\max}(v=1)$	12	16	16	13	17	17
$j_{\max}(v=2)$	10	13	14	11	14	15
$j_{\max}(v=3)$	9	11	12	10	12	13
$j_{\max}(v=4)$	6	9	10	7	10	11
$j_{\max}(v=5)$	3	6	4	4	7	5
$j_{\max}(v=6)$		3		2	4	2
$j_{\max}(v=7)$					1	
N_z	61	85	80	70	94	89
$N(\text{HO})$	50	50	50	55	55	55
$R_{1,F}(a_0)$	1.8	0.9	1.4	1.6	0.8	1.3
$R_{N(F),F}(a_0)$	15.0	12.0	13.0	15.5	12.5	13.5
$N_{\alpha\alpha}(\text{QA})$	70	70	70	75	75	75
$N_{\alpha\alpha}(\text{QA})$	30	30	30	35	35	35
$N(\text{QV})$	12	12	12	13	13	13
$N(\text{QGL})$	12	12	12	14	14	14
$N(\text{QR})$	14	14	14	13	13	13

^a See Table 1 for explanations of row labels.

Table 3. Parameter sets 5 and 6 for the tests of the distorted-wave approximation

	set 5			set 6		
	O + HD	H + OD	D + OH	O + HD	H + OD	D + OH
$j_{\max}(v = 0)^a$	14	19	17	15	20	18
$j_{\max}(v = 1)$	11	15	14	12	16	15
$j_{\max}(v = 2)$	10	12	13	11	13	14
$j_{\max}(v = 3)$	9	10	12	10	11	13
$j_{\max}(v = 4)$	8	9	11	9	10	12
$j_{\max}(v = 5)$	7	8	10	8	9	11
$j_{\max}(v = 6)$		2		1	3	
$j_{\max}(v = 7)$				1		
N_α	65	82	83	73	91	89
$N(\text{HO})$	50	50	50	55	55	55
$R_{1, \text{F}(a_0)}$	1.8	0.9	1.4	1.6	0.8	1.3
$R_{N(\text{F}), \text{F}(a_0)}$	15.0	12.0	13.0	15.5	12.5	13.5
$N_{\alpha\alpha}(\text{QA})$	70	70	70	75	75	75
$N_{\alpha\alpha}'(\text{QA})$	30	30	30	35	35	35
$N(\text{QV})$	12	12	12	13	13	13
$N(\text{QGL})$	12	12	12	14	14	14
$N(\text{QR})$	14	14	14	13	13	13

^a See table 1 for explanations of row labels.

with respect to channel basis. In particular, the first three columns of table 6 give the maximum rotational quantum number $j_{\max}(v)$ included in the basis set for each vibrational manifold v . Notice especially the high sensitivity of the FCDWA-RBC transition probabilities for O + HD($v = j = 0$) → OH + D to the channel basis of the initial arrangement O + HD. The RCDWA and UDWA results are much more stable with respect to increasing the channel basis set (as well as with respect to quadratures), which is reasonable since these methods do not include the full-channel coupling.

Table 7 gives convergence checks for cumulative reaction probabilities (defined as the sum of the state-to-state reaction probabilities over all open initial and final states at a given total energy); table 8 summarizes the number of open channels as a function of energy; tables 9 and 10 list the best converged DWA reaction probabilities for each case and compare them to the GNVP results.

The reaction probabilities in tables 4–7, 9 and 10 are summed over final vibrational quantum number v' and final rotational quantum number j' (those in table 7 are summed over initial v and j as well). Tables 11–13 show relative final-state distributions defined by

$$\rho_{v'j'}(v, j; \alpha') = \frac{P_{\alpha=1, v, j \rightarrow \alpha', v', j'}}{\sum_{v'} \sum_{j'} P_{\alpha=1, v, j \rightarrow \alpha', v', j'}} \quad (14)$$

where $\alpha = 1$ denotes O + HD, $\alpha' = 2$ denotes OH + D, $\alpha' = 3$ denotes OD + H and $P_{\alpha, v, j \rightarrow \alpha', v', j'}$ is a state-to-state reaction probability for $J = 0$.

Table 14 gives average values of the absolute value for the relative errors in these relative probabilities; the precise definition of these average relative errors is more easily stated in an equation:

$$\% \text{error} = \left\langle \frac{|\rho_{v'j'}(\text{DWA}) - \rho_{v'j'}(\text{GNVP})|}{\rho_{v'j'}(\text{GNVP})} \right\rangle \times 100\%. \quad (15)$$

4. Discussion

The comparison between our results and the results obtained with the coupled states distorted-wave approximation¹⁰⁰ (CSDWA) is presented in table 7. [The cumulative reaction probabilities in table 7 are from personal communications from G. C. Schatz. They are a factor of two smaller than the private communication results in ref. (25) because Schatz has

now informed us that there was a factor of two error in his computer printout. This error did not affect the results published in ref. (105) and (116).] For $J = 0$, the coupled-states approximation is exact;⁹⁴ thus because complex boundary conditions are used in ref. (100), the CSDW results should be identical to the FCDWA-CBC ones in table 7. Instead, however, the table shows that although the FCDWA-CBC calculations are very close ($\approx 1\%$) to the accurate quantal GNVP results, there are significant differences (20–36%) between the CSDWA calculations and the FCDWA results of the present study for the D + OH product. To try to understand this, we used a smaller channel basis set comparable to that of ref. (100). This is called parameter set S ; it has $j_{\max}(v)$ values identical to those in ref. (100) and all other parameters as in set 4. In particular, the $\{j_{\max}(v)\}$ values are $\{7, 5, 5, 3\}$ for O + HD and $\{9, 7, 7, 3\}$ for the product arrangements. Results for parameter set S are shown in tables 4 and 5 as well as table 7. Table 7 shows that the results of Schatz do not differ from ours solely due to incompleteness of the channel basis set. This is one reason for carefully documenting the convergence of our own calculations with respect to all numerical parameters, and we again refer the reader to tables 4–6 for examples of these convergence checks. We particularly note the good stability in table 4 of the 13.8 kcal mol⁻¹ FCDWA-CBC transition probabilities with respect to variations in the channel basis set and all other numerical parameters for six different parameter sets. We conclude that the results presented here are well converged, and the discrepancy between the CSDWA calculations and the present ones is presumed to be due to numerical uncertainties in the calculations of ref. (100).

We next concentrate on table 9, which compares the present DWA calculations by the various schemes to the accurate quantal ones for $j = 0-2$. Consider first the FCDWA-CBC method. Table 9 shows very good agreement ($\approx 1\%$ for O + HD → OD + H and $\approx 4\%$ for O + HD → OH + D) of these results with the accurate quantal ones from the lowest energy up to 14 kcal mol⁻¹. For higher energies, the accuracy progressively deteriorates, becoming 6–9% at 15 kcal mol⁻¹, 21–27% at 16 kcal mol⁻¹ and $>400\%$ at 17 kcal mol⁻¹ for O + HD → OD + H and 20–22%, 8–11% and *ca.* 300%, respectively, for O + HD → OH + D. Because the adiabatic ground-state total energy at the saddle point of the potential surface is 16.2 kcal mol⁻¹ for O + HD → OH + D and 16.3 kcal mol⁻¹ for

Table 4. Convergence of reaction probabilities for O + HD($v = 0, j$) as a function of total energy E (in kcal mol⁻¹)

products	E	set	$j = 0$	$j = 1$	$j = 2$	products	E	set	$j = 0$	$j = 1$	$j = 2$
UDWA-RBC						FCDWA-RBC—continued					
H + OD	11	1	3.24 (-10)	9.96 (-11)	2.25 (-10)	17	3	1.6 (-1)	3.5 (-1)	3.0 (-1)	
		2	3.23 (-10)	9.97 (-11)	2.25 (-10)		4	1.6 (-1)	3.6 (-1)	3.1 (-1)	
15	1	1	1.77 (-7)	1.19 (-6)	8.08 (-7)	D + OH	9.2	1	2.60 (-11)	1.18 (-10)	2.17 (-10)
		2	1.77 (-7)	1.19 (-6)	8.08 (-7)			2	2.61 (-11)	1.18 (-10)	2.17 (-10)
D + OH	11	1	6.29 (-6)	1.11 (-6)	6.17 (-6)	13.8	1	9.26 (-4)	3.19 (-3)	6.77 (-3)	
		2	6.29 (-6)	1.11 (-6)	6.17 (-6)		2	9.40 (-4)	3.23 (-3)	6.87 (-3)	
15	1	1	4.96 (-4)	2.27 (-4)	8.29 (-4)	3	9.53 (-4)	3.28 (-3)	6.97 (-3)		
		2	4.96 (-4)	2.27 (-4)	8.29 (-4)	4	9.53 (-4)	3.28 (-3)	6.97 (-3)		
RCDWA-RBC						FCDWA-CBC					
H + OD	9.2	1	5.66 (-11)	5.65 (-11)	1.42 (-11)	H + OD	9.2	1	6.82 (-10)	6.81 (-10)	1.71 (-10)
		2	5.66 (-11)	5.65 (-11)	1.42 (-11)			2	6.82 (-10)	6.81 (-10)	1.71 (-10)
13.8	1	1	9.09 (-5)	1.89 (-4)	1.26 (-4)	S	6.62 (-10)	6.62 (-10)	6.57 (-10)	1.64 (-10)	
		2	9.09 (-5)	1.89 (-4)	1.26 (-4)			1	2.64 (-3)	5.52 (-3)	3.71 (-3)
17	1	1	8.24 (-3)	1.72 (-2)	1.71 (-2)	13.8	2	2.65 (-3)	5.55 (-3)	3.73 (-3)	
		2	8.24 (-3)	1.72 (-2)	1.71 (-2)		3	2.66 (-3)	5.57 (-3)	3.75 (-3)	
D + OH	9.2	1	5.11 (-12)	2.32 (-11)	4.30 (-11)	4	2.66 (-3)	5.57 (-3)	3.74 (-3)		
		2	5.10 (-12)	2.32 (-11)	4.30 (-11)		5	2.66 (-3)	5.57 (-3)	3.75 (-3)	
13.8	1	1	9.24 (-5)	3.34 (-4)	6.91 (-4)	S	2.45 (-3)	5.09 (-3)	3.36 (-3)		
		2	9.24 (-5)	3.34 (-4)	6.91 (-4)		15	1	2.6 (-2)	5.9 (-2)	4.4 (-2)
17	1	1	1.61 (-3)	6.46 (-3)	1.01 (-2)	2	2.6 (-2)	5.9 (-2)	4.5 (-2)		
		2	1.60 (-3)	6.42 (-3)	1.00 (-2)		3	2.7 (-2)	5.9 (-2)	4.5 (-2)	
RCDWA-CBC						FCDWA-CBC					
H + OD	9.2	1	5.66 (-11)	5.65 (-11)	1.42 (-11)	H + OD	9.2	1	6.82 (-10)	6.81 (-10)	1.71 (-10)
		2	5.66 (-11)	5.65 (-11)	1.42 (-11)			2	6.82 (-10)	6.81 (-10)	1.71 (-10)
13.8	1	1	9.09 (-5)	1.89 (-4)	1.26 (-4)	S	6.62 (-10)	6.62 (-10)	6.57 (-10)	1.64 (-10)	
		2	9.10 (-5)	1.89 (-4)	1.26 (-4)			1	2.64 (-3)	5.52 (-3)	3.71 (-3)
17	1	1	7.93 (-3)	1.88 (-2)	1.62 (-2)	13.8	2	2.65 (-3)	5.55 (-3)	3.73 (-3)	
		2	7.93 (-3)	1.88 (-2)	1.62 (-2)		3	2.66 (-3)	5.57 (-3)	3.75 (-3)	
D + OH	9.2	1	5.11 (-12)	2.32 (-11)	4.30 (-11)	4	2.66 (-3)	5.57 (-3)	3.74 (-3)		
		2	5.10 (-12)	2.32 (-11)	4.30 (-11)		5	2.66 (-3)	5.57 (-3)	3.75 (-3)	
13.8	1	1	9.26 (-5)	3.35 (-4)	6.93 (-4)	S	2.45 (-3)	5.09 (-3)	3.36 (-3)		
		2	9.26 (-5)	3.35 (-4)	6.93 (-4)		15	1	2.6 (-2)	5.9 (-2)	4.4 (-2)
17	1	1	7.25 (-3)	2.47 (-2)	4.82 (-2)	2	2.6 (-2)	5.9 (-2)	4.5 (-2)		
		2	7.25 (-3)	2.47 (-2)	4.82 (-2)		3	2.7 (-2)	5.9 (-2)	4.5 (-2)	
FCDWA-RBC						FCDWA-CBC					
H + OD	9.2	1	6.82 (-10)	6.81 (-10)	1.71 (-10)	H + OD	9.2	1	6.82 (-10)	6.81 (-10)	1.71 (-10)
		2	6.82 (-10)	6.81 (-10)	1.71 (-10)			2	6.82 (-10)	6.81 (-10)	1.71 (-10)
13.8	1	1	2.57 (-3)	5.56 (-3)	3.52 (-3)	S	6.62 (-10)	6.62 (-10)	6.57 (-10)	1.64 (-10)	
		2	2.58 (-3)	5.59 (-3)	3.54 (-3)			1	2.64 (-3)	5.52 (-3)	3.71 (-3)
15	1	1	2.59 (-3)	5.61 (-3)	3.55 (-3)	13.8	2	2.65 (-3)	5.55 (-3)	3.73 (-3)	
		2	2.59 (-3)	5.61 (-3)	3.55 (-3)		3	2.66 (-3)	5.57 (-3)	3.75 (-3)	
15	1	1	2.6 (-2)	4.9 (-2)	3.9 (-2)	4	2.66 (-3)	5.57 (-3)	3.74 (-3)		
		2	2.7 (-2)	4.6 (-2)	4.4 (-2)		5	2.66 (-3)	5.57 (-3)	3.75 (-3)	
3	2.7 (-2)	4.6 (-2)	4.7 (-2)	6.6 (-2)	S	8.94 (-4)	3.23 (-3)	6.61 (-3)			
		4.6 (-2)	4.7 (-2)	6.6 (-2)		15	1	8.9 (-3)	3.1 (-2)	6.3 (-2)	
4	2.7 (-2)	4.6 (-2)	4.7 (-2)	6.6 (-2)	2	9.1 (-3)	3.2 (-2)	6.5 (-2)			
		4.6 (-2)	4.7 (-2)	6.6 (-2)		3	9.2 (-3)	3.2 (-2)	6.6 (-2)		
17	5	9.4 (-2)	3.2 (-1)	6.3 (-1)	6	9.2 (-3)	3.2 (-2)	6.6 (-2)			
		9.4 (-2)	3.2 (-1)	6.3 (-1)		17	5	9.4 (-2)	3.2 (-1)	6.3 (-1)	
6	9.4 (-2)	3.2 (-1)	6.3 (-1)	6.3 (-1)	6	9.4 (-2)	3.2 (-1)	6.3 (-1)			

O + HD → OD + H, and most of the reaction probabilities are of the order of magnitude of 0.1 at 16 and 17 kcal mol⁻¹, the breakdown of the first-order calculations is not too surprising in a general way, although of course it is useful to document quantitatively its extent.

Next we discuss the DWA-RBC results. The DWA-RBC method has been used previously for inelastic molecular collisions, where the motivation has been that approximations to K , as long as they are symmetric, automatically make S unitary.^{118,119} In principle, this may enable DWA methods to remain valid longer as the coupling strength is increased,¹¹⁹ and the Heitler relation (8) also includes back-coupling, competition and successive first-order processes within a single collision.¹²⁰⁻¹²⁴ To the best of our knowledge the present paper is the first example of applying this approach to reactive scattering, perhaps because of the extra work involved. The extra work is a consequence, first of all, of the fact that to apply the DWA-CBC methods, one needs calculate only the

S matrix elements of interest, but to apply DWA-RBC methods one must calculate the whole reactance matrix to calculate the inverse in eqn (8). We found, in addition, that it is numerically harder to converge the DWA-RBC calculations than the DWA-CBC ones, which may be closely related to the first fact, *i.e.* one must, in principle, converge all coupled elements of K to obtain a converged value for a single element of S .

Table 9 shows that the extra work involved in the RBC calculations does not improve the accuracy at 15–16 kcal mol⁻¹ where the CBC method first becomes significantly inaccurate. Only at 17 kcal mol⁻¹, where the CBC transition probabilities greatly exceed unity, does the RBC method offer any improvement.

The last three columns of table 9 show results obtained by the UDWA and RCDWA approximations. Table 9 shows that neither method is quantitatively accurate at any energy. It is perhaps interesting to notice that the rotationally

Table 5. Convergence of reaction probabilities for O + HD($v=0$, $j=5$ or 7) as a function of total energy E (in kcal mol⁻¹)

E	set	H + OD		D + OH	
		$j=5$	$j=7$	$j=5$	$j=7$
FCDWA-RBC					
11	1	1.56 (-11)	closed	5.56 (-8)	closed
	2	1.56 (-11)	closed	5.56 (-8)	closed
11.5	1	3.04 (-10)	closed	9.69 (-7)	closed
	2	3.04 (-10)	closed	9.69 (-7)	closed
13	1	4.08 (-7)	1.0 (-13)	4.10 (-4)	1.7 (-9)
	2	4.09 (-7)	1.2 (-13)	4.13 (-4)	1.8 (-9)
	3	4.10 (-7)	1.2 (-13)	4.17 (-4)	1.7 (-9)
13.8	1	7.6 (-6)	2.1 (-10)	4.0 (-3)	1.1 (-6)
	2	7.7 (-6)	2.2 (-10)	4.0 (-3)	1.1 (-6)
14	1	2.7 (-5)	2.5 (-8)	5.3 (-3)	2.6 (-6)
	2	2.9 (-5)	2.9 (-8)	5.3 (-3)	2.9 (-6)
	3	2.9 (-5)	2.8 (-8)	5.3 (-3)	2.9 (-6)
15	2	1.7 (-3)	5.4 (-6)	1.5 (-2)	7.1 (-5)
	3	2.7 (-3)	3.3 (-9)	4.5 (-2)	3.5 (-4)
	4	2.8 (-3)	3.4 (-9)	4.6 (-2)	3.5 (-4)
16	2	2.0 (-2)	7.4 (-4)	4.2 (-3)	2.1 (-3)
	3	8.3 (-4)	2.4 (-5)	9.6 (-3)	5.5 (-3)
	4	8.3 (-4)	2.4 (-5)	9.6 (-3)	5.5 (-3)
17	1	5.4 (-3)	5.7 (-4)	2.0 (-1)	3.3 (-2)
	3	5.3 (-3)	3.0 (-4)	9.4 (-2)	1.3 (-2)
	4	5.3 (-3)	2.9 (-4)	9.4 (-2)	1.3 (-2)
FCDWA-CBC					
11	1	1.56 (-11)	closed	5.56 (-8)	closed
	2	1.56 (-11)	closed	5.56 (-8)	closed
11.5	1	3.03 (-10)	closed	9.69 (-7)	closed
	2	3.05 (-10)	closed	9.70 (-7)	closed
	S	2.68 (-10)	closed	9.41 (-7)	closed
13	1	2.71 (-7)	4.8 (-15)	4.23 (-4)	1.7 (-9)
	2	2.71 (-7)	4.9 (-15)	4.23 (-4)	1.7 (-9)
13.8	1	4.37 (-6)	3.2 (-13)	4.11 (-3)	1.3 (-6)
	2	4.38 (-6)	3.4 (-13)	4.11 (-3)	1.3 (-6)
	S	3.34 (-6)	4.4 (-12)	3.63 (-3)	8.1 (-7)
14	1	8.2 (-6)	2.1 (-11)	6.7 (-3)	3.6 (-6)
	2	8.3 (-6)	2.3 (-11)	6.9 (-3)	3.7 (-6)
15	1	1.3 (-4)	3.5 (-9)	5.4 (-2)	3.0 (-4)
	2	1.3 (-4)	3.6 (-9)	5.6 (-2)	3.1 (-4)
	3	1.3 (-4)	3.7 (-9)	5.6 (-2)	3.1 (-4)
16	2	9.0 (-4)	1.3 (-7)	1.8 (-1)	4.2 (-3)
	5	1.1 (-3)	1.6 (-7)	2.1 (-1)	4.6 (-3)
	6	1.1 (-3)	1.5 (-7)	2.1 (-1)	4.6 (-3)
17	1	1.8 (-3)	1.4 (-6)	1.9 (-1)	1.3 (-2)
	5	3.6 (-3)	2.0 (-6)	1.8 (-1)	3.2 (-2)
	6	3.6 (-3)	2.0 (-6)	1.7 (-1)	3.2 (-2)

coupled DWA method is typically in error by 'only' 1 or 1.5 orders of magnitude even when the uncoupled version is in error by 3–5 orders of magnitude. We also note that the UDWA results are not monotonically increasing functions of energy. We conclude that intra-arrangement vibrational couplings are too large to be treated by first-order perturbation theory, even when back-coupling and successive first-order transitions within a single collision are included.

The uncoupled and rotationally coupled DWA transition probabilities are not particularly more accurate for higher initial rotational quantum numbers, and so we present only the fully coupled DWA results for these initial states. The FCDWA results for $j=5$ and 7 are compared to accurate quantal reaction probabilities in table 10. Here the accuracy is not so good as for $j=0-2$, especially for the RBC method. It is disappointing that the errors are so large (30–50%) even when the accurate transition probabilities are as small as 10^{-3} .

The simultaneous consideration of tables 11 and 14 along with tables 9 and 10 proves very interesting. Even though the

RCDWA reaction probabilities at 9.2 kcal mol⁻¹ are too small by factors of 5–12, the relative product distributions are accurate to better than 10%. The relative product distributions for the uncoupled distorted-wave approximation are, however, not very accurate. Tables 12–14 show that the RCDWA relative product distributions remain much more accurate than the reaction probabilities even as the energy is increased. At 16 kcal mol⁻¹, where even the FCDWA reaction probabilities are becoming inaccurate, the relative product distributions remain accurate to 10% or better. Since FCDWA calculations are much less demanding than converged quantum dynamics, and RCDWA calculations are much less demanding than FCDWA ones, these comparisons are very encouraging about the use of DWA methods for practical calculations of relative product-state distributions in cases where fully converged quantum dynamics calculations are not available.

Thermal averaging and higher total-angular-momentum contributions are required to compare quantum-mechanical results to experiment or to semiclassical rate constants and are beyond the scope of the present paper. The interested reader is referred to previous papers^{25,105,125–130} for theoretical/experimental and quantal/semiclassical comparisons for the present system.

5. Conclusions

We have presented accurate quantum-mechanical reaction probabilities for the reaction of O with HD for a range of energies and initial rotational states, and we have used these results to carry out systematic tests of several versions of the distorted-wave approximations (DWA). The tests of the DWA theories are more reliable than were previously possible because the present quantum results are numerically converged to high precision. We have considered three different kinds of distortion potentials and two kinds of boundary conditions for the distorted waves. We find that at low energies and low initial rotational quantum numbers, calculations based on distorted waves that are fully coupled within each arrangement are in excellent agreement with accurate quantal reaction probabilities, but deviations occur for higher energies and higher initial rotational quantum numbers. Uncoupled distorted waves or distorted waves with rotational but not vibrational coupling do not lead to accurate reaction probabilities under any conditions.

The product vibrational–rotational distributions are quite accurate not only for the fully coupled distorted-wave approximation but also for the rotationally coupled distorted-wave approximation.

Our convergence checks show that distorted-wave calculations in which the distortion potential is fully coupled within each arrangement are very sensitive to the channel basis. Previous fully coupled distorted-wave cumulative reaction probabilities for this system agree with the present ones to within 36%.

The accurate probabilities from GNVP calculations can be used, in future work, to test other approximate methods such as semiclassical tunnelling models or distorted-wave approximations with adiabatic distortion potentials.

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Table 6. Convergence of reaction probabilities with respect to the channel basis set for $O + HD(v = 0, j) \rightarrow H + OD$ or $D + OH$ at $E = 15$ kcal mol⁻¹^a

channel basis sets			<i>j</i>	reaction probabilities	
HD	OD	OH		H + OD	D + OH
FCDWA-RBC					
9 8 7 6	16 14 12 10 8 4	11 10 9 8	0	2.58 (-2)	1.93 (-4)
			1	4.87 (-2)	6.57 (-3)
			2	3.94 (-2)	1.32 (-3)
10 9 8 7	16 14 12 10 8 4	11 10 9 8	0	2.59 (-2)	2.15 (-4)
			1	4.85 (-2)	7.21 (-3)
			2	3.97 (-2)	1.73 (-3)
10 9 8 7	17 15 13 11 9 6	11 10 9 8	0	2.59 (-2)	1.97 (-4)
			1	4.88 (-2)	6.59 (-3)
			2	3.95 (-2)	1.31 (-3)
10 9 8 7	17 15 13 11 9 6	12 11 10 9	0	2.58 (-2)	1.93 (-4)
			1	4.87 (-2)	6.58 (-3)
			2	3.94 (-2)	1.33 (-3)
9 8 7 6 5	17 15 13 11 9 6	12 11 10 9	0	2.70 (-2)	1.32 (-3)
			1	4.57 (-2)	1.80 (-2)
			2	4.48 (-2)	1.31 (-2)
9 8 7 6 5	16 14 12 10 8 6 4	12 11 10 9	0	2.59 (-2)	1.98 (-4)
			1	4.89 (-2)	6.61 (-3)
			2	3.95 (-2)	1.31 (-3)
9 8 7 6 5	16 14 12 10 8 6 4	11 10 9 8 7	0	2.58 (-2)	1.88 (-4)
			1	4.89 (-2)	6.36 (-3)
			2	3.93 (-2)	1.29 (-3)
10 9 8 7 6	16 14 12 10 8 4	11 10 9 8	0	2.72 (-2)	1.70 (-3)
			1	4.53 (-2)	2.04 (-2)
			2	4.57 (-2)	1.64 (-2)
10 9 8 7 6 4	16 14 12 10 8 4	11 10 9 8	0	2.77 (-2)	3.16 (-3)
			1	4.55 (-2)	2.75 (-2)
			2	4.84 (-2)	2.82 (-2)
10 9 8 7 6 5 4	16 14 12 10 8 4	11 10 9 8	0	2.84 (-2)	4.58 (-3)
			1	4.75 (-2)	3.22 (-2)
			2	5.08 (-2)	3.84 (-2)
FCDWA-CBC					
9 8 7 6	16 14 12 10 8 4	11 10 9 8	0	2.62 (-2)	8.85 (-3)
			1	5.87 (-2)	3.11 (-2)
			2	4.42 (-2)	6.29 (-2)
10 9 8 7	16 14 12 10 8 4	11 10 9 8	0	2.62 (-2)	8.88 (-3)
			1	5.87 (-2)	3.12 (-2)
			2	4.43 (-2)	6.32 (-2)
9 8 7 6 5	16 14 12 10 8 4	11 10 9 8	0	2.65 (-2)	8.87 (-3)
			1	5.93 (-2)	3.12 (-2)
			2	4.47 (-2)	6.31 (-2)
9 8 7 6	16 14 12 10 8 6 4	11 10 9 8	0	2.63 (-2)	8.85 (-3)
			1	5.90 (-2)	3.11 (-2)
			2	4.45 (-2)	6.29 (-2)
RCDWA-RBC					
9 8 7 6	16 14 12 10 8 4	11 10 9 8	0	6.73 (-4)	6.81 (-4)
			1	1.51 (-3)	2.37 (-4)
			2	1.11 (-3)	4.84 (-3)
9 8 7 6 5	16 14 12 10 8 4	11 10 9 8	0	6.73 (-4)	6.81 (-4)
			1	1.51 (-3)	2.37 (-4)
			2	1.11 (-3)	4.84 (-3)
9 8 7 6	16 14 12 10 8 6 4	11 10 9 8	0	6.73 (-4)	6.81 (-4)
			1	1.51 (-3)	2.37 (-4)
			2	1.11 (-3)	4.84 (-3)
9 8 7 6	16 14 12 10 8 4	11 10 9 8 7	0	6.73 (-4)	6.81 (-4)
			1	1.51 (-3)	2.37 (-4)
			2	1.11 (-3)	4.84 (-3)
10 9 8 7	16 14 12 10 8 4	11 10 9 8	0	6.73 (-4)	6.81 (-4)
			1	1.51 (-3)	2.37 (-4)
			2	1.11 (-3)	4.84 (-3)
9 8 7 6	17 15 13 11 9 5	11 10 9 8	0	6.73 (-4)	6.81 (-4)
			1	1.51 (-3)	2.37 (-4)
			2	1.11 (-3)	4.84 (-3)
9 8 7 6	16 14 12 10 8 4	12 11 10 9	0	6.73 (-4)	6.81 (-4)
			1	1.51 (-3)	2.37 (-4)
			2	1.11 (-3)	4.84 (-3)

Continued

Table 6—continued

channel basis sets			<i>j</i>	reaction probabilities	
HD	OD	OH		H + OD	D + OH
RCDWA-CBC					
9 8 7 6	16 14 12 10 8 4	11 10 9 8	0	6.77 (-4)	7.08 (-4)
			1	1.51 (-3)	2.49 (-3)
			2	1.13 (-3)	5.05 (-3)
9 8 7 6 5	16 14 12 10 8 4	11 10 9 8	0	6.77 (-4)	7.08 (-4)
			1	1.51 (-3)	2.49 (-3)
			2	1.13 (-3)	5.05 (-3)
9 8 7 6	16 14 12 10 8 6 4	11 10 9 8	0	6.77 (-4)	7.08 (-4)
			1	1.51 (-3)	2.49 (-3)
			2	1.13 (-3)	5.05 (-3)
9 8 7 6	16 14 12 10 8 4	11 10 9 8 7	0	6.77 (-4)	7.08 (-4)
			1	1.51 (-3)	2.49 (-3)
			2	1.13 (-3)	5.05 (-3)
10 9 8 7	16 14 12 10 8 4	11 10 9 8	0	6.77 (-4)	7.08 (-4)
			1	1.51 (-3)	2.49 (-3)
			2	1.13 (-3)	5.05 (-3)
9 8 7 6	17 15 13 11 9 5	11 10 9 8	0	6.77 (-4)	7.08 (-4)
			1	1.51 (-3)	2.49 (-3)
			2	1.13 (-3)	5.05 (-3)
9 8 7 6	16 14 12 10 8 4	12 11 10 9	0	6.77 (-4)	7.08 (-4)
			1	1.51 (-3)	2.49 (-3)
			2	1.13 (-3)	5.05 (-3)

^a For all calculations in this table, all parameters except the channel basis set are the same as parameter set 1.

Table 7. Cumulative reaction probabilities ($J = 0$) for O + HD as functions of total energy E (in kcal mol⁻¹)

products	E	CSDWA-CBC	FCDWA-CBC			GNVP-RGF
			S	set 1	set 2	
H + OD	9.2	1.66 (-9)	1.49 (-9)	1.54 (-9)	1.54 (-9)	1.54 (-9)
	11.5	2.69 (-5)	2.44 (-5)	2.44 (-5)	2.44 (-5)	2.44 (-5)
	13.8	1.35 (-2)	1.20 (-2)	1.31 (-2)	1.31 (-2)	1.31 (-2)
D + OH	9.2	6.7 (-10)	4.78 (-10)	4.92 (-10)	4.93 (-10)	4.88 (-10)
	11.5	4.15 (-5)	5.25 (-5)	5.16 (-6)	5.16 (-5)	5.15 (-5)
	13.8	2.61 (-2)	3.25 (-2)	3.49 (-2)	3.54 (-2)	3.53 (-2)

Table 8. Number of open channels^a for parameter set 1 at various total energies E (in kcal mol⁻¹)

E	O + HD		H + DO		D + HO		total
	$v' = 0$	$v' = 1$	$v' = 0$	$v' = 1$	$v' = 0$	$v' = 1$	
9.2	6	0	10	0	5	0	21
11	7	0	12	0	7	0	26
11.5	7	0	13	0	8	0	28
13	8	0	15	0	10	0	33
13.8	8	0	16	0	10	0	34
14	8	0	16	0	11	0	35
15	9	0	17	6	12	0	44
16	9	2	17	8	12	0	48
17	10	3	17	10	12	0	52

^a The total number of channels included in parameter set 1 is 146, with 34 for O + HD, 42 for H + DO and 70 for D + HO.

Table 9. Reaction probabilities for O + HD($v = 0, j$) at various total energies E (in kcal mol⁻¹)

products	E	j	GNVP	FCDWA-RBC	FCDWA-CBC	RCDWA-RBC	RCDWA-CBC	UDWA-RBC
H + OD	9.2	0	6.80 (-10)	6.82 (-10)	6.82 (-10)	5.66 (-11)	5.66 (-11)	2.12 (-12)
		1	6.80 (-10)	6.81 (-10)	6.81 (-10)	5.65 (-11)	5.65 (-11)	1.60 (-12)
		2	1.71 (-10)	1.71 (-10)	1.71 (-10)	1.42 (-11)	1.42 (-11)	6.76 (-13)
	11	0	1.32 (-6)	1.32 (-6)	1.32 (-6)	8.42 (-8)	8.42 (-8)	3.24 (-10)
		1	2.01 (-6)	2.01 (-6)	2.01 (-6)	1.28 (-7)	1.28 (-7)	9.96 (-11)
		2	8.68 (-7)	8.69 (-7)	8.69 (-7)	5.51 (-8)	5.51 (-8)	2.25 (-10)
	11.5	0	6.79 (-6)	6.80 (-6)	6.80 (-6)	3.97 (-7)	3.97 (-7)	3.79 (-10)
		1	1.12 (-5)	1.12 (-5)	1.13 (-5)	6.54 (-7)	6.54 (-7)	7.34 (-9)
		2	5.39 (-6)	5.39 (-6)	5.39 (-6)	3.12 (-7)	3.12 (-7)	2.74 (-10)
	13	0	4.27 (-4)	4.18 (-4)	4.27 (-4)	1.80 (-5)	1.80 (-5)	7.07 (-9)
		1	8.41 (-4)	8.28 (-4)	8.39 (-4)	3.51 (-5)	3.52 (-5)	5.33 (-8)
		2	5.13 (-4)	4.97 (-4)	5.12 (-4)	2.13 (-5)	2.12 (-5)	1.78 (-8)
	13.8	0	2.64 (-3)	2.59 (-3)	2.66 (-3)	9.09 (-5)	9.09 (-5)	4.10 (-8)
		1	5.53 (-3)	5.61 (-3)	5.57 (-3)	1.89 (-4)	1.89 (-4)	2.50 (-7)
		2	3.55 (-3)	3.75 (-3)	3.50 (-3)	1.26 (-4)	3.71 (-3)	3.57 (-8)
	14	0	4.00 (-3)	3.95 (-3)	4.05 (-3)	1.31 (-4)	1.31 (-4)	1.20 (-7)
		1	8.50 (-3)	8.73 (-3)	8.60 (-3)	2.77 (-4)	2.77 (-4)	1.19 (-7)
		2	5.83 (-3)	6.79 (-3)	5.90 (-3)	1.91 (-4)	1.89 (-4)	2.36 (-10)
	15	0	2.45 (-2)	2.7 (-2)	2.6 (-2)	6.73 (-4)	6.77 (-4)	1.77 (-7)
		1	5.49 (-2)	4.6 (-2)	5.9 (-2)	1.51 (-3)	1.51 (-3)	1.19 (-6)
		2	4.14 (-2)	4.7 (-2)	4.5 (-2)	1.12 (-3)	1.13 (-3)	8.08 (-7)
	16	0	7.88 (-2)	3.5 (-2)	1.0 (-1)	2.39 (-3)	2.61 (-3)	5.70 (-7)
		1	1.83 (-1)	7.5 (-2)	2.3 (-1)	6.09 (-3)	6.03 (-3)	4.50 (-6)
		2	1.49 (-1)	6.1 (-2)	1.8 (-1)	4.40 (-3)	4.87 (-3)	1.24 (-7)
17	0	1.26 (-1)	1.6 (-1)	6.8 (-1)	8.24 (-3)	7.93 (-3)	2.88 (-6)	
	1	2.95 (-1)	3.6 (-1)	1.6	1.72 (-2)	1.88 (-2)	1.31 (-6)	
	2	2.55 (-1)	3.1 (-1)	1.4	1.71 (-2)	1.62 (-2)	8.36 (-6)	
D + OH	9.2	0	2.58 (-11)	2.60 (-11)	2.60 (-11)	5.11 (-12)	5.11 (-12)	9.75 (-9)
		1	1.17 (-10)	1.18 (-10)	1.18 (-10)	2.32 (-11)	2.32 (-11)	4.36 (-8)
		2	2.15 (-10)	2.17 (-10)	2.17 (-10)	4.30 (-11)	4.30 (-11)	1.68 (-8)
	11	0	2.71 (-7)	2.72 (-7)	2.72 (-7)	4.39 (-8)	4.39 (-8)	6.29 (-6)
		1	1.09 (-6)	1.09 (-6)	1.09 (-6)	1.77 (-7)	1.77 (-7)	1.11 (-6)
		2	2.33 (-6)	2.33 (-6)	2.33 (-6)	3.78 (-7)	3.78 (-7)	6.17 (-6)
	11.5	0	1.71 (-6)	1.71 (-6)	1.71 (-6)	2.57 (-7)	2.57 (-7)	2.32 (-6)
		1	6.68 (-6)	6.69 (-6)	6.70 (-6)	1.01 (-6)	1.01 (-6)	1.15 (-5)
		2	1.43 (-5)	1.43 (-5)	1.43 (-5)	2.16 (-6)	2.16 (-6)	7.64 (-6)
	13	0	1.46 (-4)	1.38 (-4)	1.44 (-4)	1.66 (-5)	1.68 (-5)	8.87 (-5)
		1	5.38 (-4)	5.37 (-4)	5.32 (-4)	6.19 (-5)	6.23 (-5)	5.41 (-5)
		2	1.13 (-3)	1.08 (-3)	1.12 (-3)	1.29 (-4)	1.31 (-4)	1.74 (-4)
	13.8	0	9.41 (-4)	9.53 (-4)	9.60 (-4)	9.24 (-5)	9.26 (-5)	3.11 (-5)
		1	3.40 (-3)	3.28 (-3)	3.47 (-3)	3.34 (-4)	3.35 (-4)	5.41 (-5)
		2	7.03 (-3)	6.97 (-3)	7.17 (-3)	6.91 (-4)	6.93 (-4)	7.25 (-5)
	14	0	1.42 (-3)	1.10 (-3)	1.47 (-3)	1.33 (-4)	1.35 (-4)	1.31 (-4)
		1	5.12 (-3)	3.87 (-3)	5.28 (-3)	4.79 (-4)	4.86 (-4)	8.06 (-5)
		2	1.05 (-2)	8.04 (-3)	1.09 (-2)	9.88 (-4)	1.00 (-3)	2.05 (-6)
	15	0	7.57 (-3)	3.8 (-3)	9.2 (-3)	6.81 (-4)	7.08 (-4)	4.96 (-4)
		1	2.66 (-2)	2.5 (-2)	3.2 (-2)	2.37 (-3)	2.49 (-3)	2.27 (-4)
		2	5.39 (-2)	2.5 (-2)	6.6 (-2)	4.84 (-3)	5.05 (-3)	8.29 (-4)
	16	0	1.75 (-2)	1.4 (-2)	1.6 (-2)	2.18 (-3)	2.62 (-3)	5.69 (-4)
		1	6.05 (-2)	9.4 (-3)	5.5 (-2)	7.60 (-3)	9.04 (-3)	4.54 (-4)
		2	1.20 (-1)	6.0 (-2)	1.1 (-1)	1.55 (-2)	1.80 (-2)	2.88 (-4)
17	0	2.32 (-2)	1.6 (-2)	9.4 (-2)	1.61 (-3)	7.25 (-3)	9.52 (-4)	
	1	7.85 (-2)	9.5 (-2)	3.2 (-1)	6.46 (-3)	2.47 (-2)	9.02 (-5)	
	2	1.51 (-1)	1.2 (-1)	6.3 (-1)	1.01 (-2)	4.82 (-2)	1.14 (-3)	

Table 10. Reaction probabilities for $O + HD(v = 0, j)$ as functions of total energy E (in kcal mol⁻¹)

products	E	j	GNVP	FCDWA-RBC	FCDWA-CBC	
H + OD	11	5	1.55 (-11)	1.56 (-11)	1.56 (-11)	
	11.5	5	3.02 (-10)	3.04 (-10)	3.05 (-10)	
	13	5	2.71 (-7)	4.1 (-7)	2.71 (-7)	
	13.8	5	4.37 (-6)	7.7 (-6)	4.38 (-6)	
	14	5	8.17 (-6)	2.9 (-5)	8.3 (-6)	
	15	5	1.23 (-4)	2.8 (-3)	1.3 (-4)	
	16	5	8.33 (-4)	8.3 (-4)	1.1 (-3)	
		7	1.20 (-7)	2.4 (-5)	1.5 (-7)	
	17	5	2.86 (-3)	5.3 (-3)	3.6 (-3)	
		7	1.78 (-6)	2.9 (-4)	2.0 (-6)	
	D + OH	11	5	5.50 (-8)	5.56 (-8)	5.56 (-8)
		11.5	5	9.64 (-7)	9.69 (-7)	9.70 (-7)
		13	5	4.26 (-4)	4.1 (-4)	4.23 (-4)
13.8		5	4.14 (-3)	4.0 (-3)	4.11 (-3)	
14		5	6.74 (-3)	5.3 (-3)	6.9 (-3)	
15		5	4.63 (-2)	4.6 (-2)	5.6 (-2)	
16		5	1.22 (-1)	9.6 (-3)	2.1 (-1)	
		7	2.99 (-3)	5.5 (-3)	4.6 (-3)	
17		5	1.71 (-1)	9.4 (-2)	1.7 (-1)	
		7	1.46 (-2)	1.3 (-2)	3.2 (-2)	

Table 11. Comparison of accurate quantum mechanics to the distorted-wave approximation for state-to-state reaction probabilities greater than 1.0×10^{-6} of $O + HD(v = 0, j)$ at an energy of 9.2 kcal mol⁻¹

products	j	v'	j'	GNVP	FCDWA-CBC	RCDWA-CBC	UDWA-RBC
H + OD	0	0	0	5.80 (-2)	5.80 (-2)	5.81 (-2)	6.81 (-2)
			1	1.60 (-1)	1.60 (-1)	1.60 (-1)	1.75 (-1)
			2	2.22 (-1)	2.22 (-1)	2.22 (-1)	2.39 (-1)
			3	2.28 (-1)	2.28 (-1)	2.28 (-1)	1.22 (-1)
			4	1.81 (-1)	1.80 (-1)	1.80 (-1)	3.17 (-1)
			5	1.05 (-1)	1.05 (-1)	1.05 (-1)	1.42 (-2)
			6	3.97 (-2)	3.97 (-2)	3.99 (-2)	6.19 (-2)
			7	6.85 (-3)	6.86 (-3)	6.91 (-3)	3.46 (-3)
D + OH	0	0	8	1.50 (-4)	1.51 (-4)	1.53 (-4)	4.43 (-5)
			0	4.69 (-2)	4.65 (-2)	4.58 (-2)	2.61 (-3)
			1	2.06 (-1)	2.05 (-1)	2.04 (-1)	6.32 (-1)
			2	4.42 (-1)	4.42 (-1)	4.41 (-1)	2.83 (-1)
H + OD	2	0	3	3.05 (-1)	3.05 (-1)	3.09 (-1)	8.29 (-2)
			4	6.12 (-4)	6.07 (-4)	6.01 (-4)	2.97 (-4)
			0	5.47 (-2)	5.49 (-2)	5.42 (-2)	5.58 (-2)
			1	1.52 (-1)	1.53 (-1)	1.54 (-1)	1.45 (-1)
			2	2.15 (-1)	2.15 (-1)	2.13 (-1)	2.09 (-1)
			3	2.26 (-1)	2.26 (-1)	2.25 (-1)	1.19 (-1)
			4	1.85 (-1)	1.85 (-1)	1.85 (-1)	3.71 (-1)
			5	1.13 (-1)	1.13 (-1)	1.13 (-1)	1.76 (-2)
D + OH	2	0	6	4.49 (-2)	4.50 (-2)	4.57 (-2)	7.77 (-2)
			7	8.25 (-3)	8.30 (-3)	8.52 (-3)	4.97 (-3)
			8	1.95 (-4)	1.95 (-4)	2.03 (-4)	5.04 (-5)
			0	5.63 (-2)	5.60 (-2)	5.56 (-2)	2.77 (-3)
			1	2.24 (-1)	2.24 (-1)	2.23 (-1)	6.67 (-1)
			2	4.38 (-1)	4.38 (-1)	4.37 (-1)	2.53 (-1)
			3	2.28 (-1)	2.83 (-1)	2.84 (-1)	7.86 (-2)
			4	5.53 (-4)	5.51 (-4)	5.37 (-4)	3.19 (-4)
H + OD	5	0	0	5.42 (-2)	5.33 (-2)	5.27 (-2)	5.73 (-2)
			1	1.51 (-1)	1.49 (-1)	1.47 (-1)	1.47 (-1)
			2	2.13 (-1)	2.11 (-1)	2.10 (-1)	2.09 (-1)
			3	2.25 (-1)	2.25 (-1)	2.25 (-1)	1.18 (-1)
			4	1.86 (-1)	1.87 (-1)	1.89 (-1)	3.69 (-1)
			5	1.15 (-1)	1.17 (-1)	1.19 (-1)	1.74 (-2)
			6	4.68 (-2)	4.80 (-2)	4.95 (-2)	7.66 (-2)
			7	8.94 (-3)	9.21 (-3)	9.65 (-3)	5.06 (-3)
D + OH	5	0	8	2.21 (-4)	2.27 (-4)	2.43 (-4)	5.11 (-5)
			0	5.92 (-2)	5.92 (-2)	4.58 (-2)	2.61 (-3)
			1	2.25 (-1)	2.15 (-1)	2.04 (-1)	6.32 (-1)
			2	4.22 (-1)	4.24 (-1)	4.42 (-1)	2.83 (-1)
			3	2.93 (-1)	3.05 (-1)	3.09 (-1)	8.29 (-2)
			4	6.31 (-4)	6.31 (-4)	6.01 (-4)	2.97 (-4)

Table 12. Comparison of accurate quantum mechanics to the distorted-wave approximation for state-to-state reaction probabilities greater than 1.0×10^{-6} of $O + HD(v = 0, j)$ at an energy of $13.8 \text{ kcal mol}^{-1}$

products	j	v'	j'	GNVP	FCDWA-CBC	RCDWA-CBC	UDWA-RBC			
H + OD	0	0	0	3.11 (-2)	3.09 (-2)	3.20 (-2)	1.01 (-2)			
			1	8.90 (-2)	8.83 (-2)	9.12 (-2)	1.32 (-1)			
			2	1.34 (-1)	1.33 (-1)	1.38 (-1)	4.27 (-2)			
			3	1.60 (-1)	1.59 (-1)	1.63 (-1)	2.31 (-1)			
			4	1.64 (-1)	1.63 (-1)	1.65 (-1)	4.20 (-2)			
			5	1.48 (-1)	1.47 (-1)	1.47 (-1)	2.88 (-1)			
			6	1.16 (-1)	1.15 (-1)	1.14 (-1)	2.44 (-2)			
			7	7.94 (-2)	7.86 (-2)	7.69 (-2)	1.74 (-1)			
			8	4.58 (-2)	4.55 (-2)	4.35 (-2)	2.44 (-3)			
			9	2.15 (-2)	2.13 (-2)	1.99 (-2)	4.87 (-2)			
			10	7.73 (-3)	7.67 (-3)	6.97 (-3)	6.56 (-4)			
			11	1.91 (-3)	1.90 (-3)	1.67 (-3)	4.05 (-3)			
			12	2.61 (-4)	2.60 (-4)	2.19 (-4)	5.66 (-5)			
D + OH	0	0	13	1.12 (-5)	1.12 (-5)	8.92 (-6)	2.59 (-5)			
			0	1.63 (-2)	1.62 (-2)	1.51 (-2)	2.01 (-1)			
			1	5.28 (-2)	5.26 (-2)	4.99 (-2)	2.91 (-2)			
			2	9.97 (-2)	9.94 (-2)	9.51 (-2)	3.23 (-2)			
			3	1.55 (-1)	1.55 (-1)	1.50 (-1)	8.23 (-2)			
			4	2.03 (-1)	2.03 (-1)	2.02 (-1)	1.43 (-1)			
			5	2.11 (-1)	2.11 (-1)	2.14 (-1)	6.56 (-2)			
			6	1.64 (-1)	1.64 (-1)	1.69 (-1)	2.62 (-1)			
			7	8.06 (-2)	8.10 (-2)	8.58 (-2)	1.70 (-1)			
			8	1.69 (-2)	1.73 (-2)	1.87 (-2)	6.42 (-3)			
			9	2.25 (-4)	2.27 (-4)	2.49 (-4)	8.71 (-3)			
			H + OD	2	0	0	2.76 (-2)	2.75 (-2)	2.67 (-2)	8.15 (-3)
						1	7.96 (-2)	7.92 (-2)	7.71 (-2)	1.01 (-1)
2	1.22 (-1)	1.22 (-1)				1.19 (-1)	3.53 (-2)			
3	1.50 (-1)	1.49 (-1)				1.47 (-1)	2.11 (-1)			
4	1.60 (-1)	1.59 (-1)				1.57 (-1)	4.15 (-2)			
5	1.50 (-1)	1.50 (-1)				1.49 (-1)	3.05 (-1)			
6	1.25 (-1)	1.25 (-1)				1.26 (-1)	2.76 (-2)			
7	9.08 (-2)	9.03 (-2)				9.29 (-2)	2.10 (-1)			
8	5.63 (-2)	5.60 (-2)				5.84 (-2)	3.00 (-3)			
9	2.88 (-2)	2.86 (-2)				3.03 (-2)	5.32 (-2)			
10	1.13 (-2)	1.12 (-2)				1.21 (-2)	5.69 (-4)			
11	3.07 (-3)	3.08 (-3)				3.42 (-3)	2.83 (-3)			
12	4.74 (-4)	4.75 (-4)				5.40 (-4)	6.19 (-5)			
D + OH	2	0	13	2.31 (-5)	2.31 (-5)	2.72 (-5)	4.31 (-5)			
			0	1.69 (-2)	1.68 (-2)	1.63 (-2)	2.99 (-1)			
			1	5.48 (-2)	5.45 (-2)	5.30 (-2)	5.68 (-2)			
			2	1.02 (-1)	1.02 (-1)	9.99 (-2)	8.62 (-2)			
			3	1.58 (-1)	1.57 (-1)	1.55 (-1)	7.88 (-2)			
			4	2.03 (-1)	2.03 (-1)	2.03 (-1)	1.37 (-1)			
			5	2.09 (-1)	2.10 (-1)	2.11 (-1)	6.34 (-2)			
			6	1.61 (-1)	1.61 (-1)	1.64 (-1)	2.10 (-1)			
			7	7.89 (-2)	7.93 (-2)	8.16 (-2)	6.59 (-2)			
			8	1.69 (-2)	1.72 (-2)	1.79 (-2)	1.72 (-3)			
			9	2.36 (-4)	2.36 (-4)	2.46 (-4)	2.17 (-3)			
			H + OD	5	0	0	2.03 (-2)	2.02 (-2)	1.64 (-2)	9.38 (-3)
						1	5.95 (-2)	5.94 (-2)	4.88 (-2)	1.23 (-1)
2	9.42 (-2)	9.45 (-2)				7.96 (-2)	4.18 (-2)			
3	1.24 (-1)	1.23 (-1)				1.08 (-1)	2.38 (-1)			
4	1.42 (-1)	1.41 (-1)				1.30 (-1)	4.38 (-2)			
5	1.46 (-1)	1.45 (-1)				1.42 (-1)	3.03 (-1)			
6	1.36 (-1)	1.35 (-1)				1.41 (-1)	2.58 (-2)			
7	1.13 (-1)	1.13 (-1)				1.26 (-1)	1.81 (-1)			
8	8.15 (-2)	8.15 (-2)				9.80 (-2)	2.26 (-3)			
9	4.92 (-2)	4.91 (-2)				6.39 (-2)	3.05 (-2)			
10	2.33 (-2)	2.35 (-2)				3.31 (-2)	3.88 (-4)			
11	7.96 (-3)	7.95 (-3)				1.22 (-2)	2.14 (-3)			
12	1.55 (-3)	1.55 (-3)				2.63 (-3)	4.69 (-6)			
D + OH	5	0	13	9.68 (-3)	9.68 (-3)	1.82 (-4)	4.16 (-5)			
			0	1.59 (-2)	1.60 (-2)	1.64 (-2)	1.11 (-1)			
			1	5.10 (-2)	5.13 (-2)	5.23 (-2)	1.49 (-2)			
			2	9.42 (-2)	9.44 (-2)	9.61 (-2)	1.21 (-2)			
			3	1.44 (-1)	1.45 (-1)	1.46 (-1)	1.65 (-2)			
			4	1.89 (-1)	1.89 (-1)	1.88 (-1)	8.26 (-2)			
			5	2.05 (-1)	2.05 (-1)	2.02 (-1)	5.14 (-2)			
			6	1.73 (-1)	1.73 (-1)	1.71 (-1)	3.19 (-1)			
			7	9.98 (-2)	9.93 (-2)	9.93 (-2)	3.52 (-1)			
			8	2.80 (-2)	2.82 (-2)	2.89 (-2)	1.85 (-2)			
9	5.43 (-4)	5.38 (-4)	5.80 (-4)	2.18 (-2)						

Table 13. Comparison of accurate quantum mechanics to the distorted-wave approximation for state-to-state reaction probabilities greater than 1.0×10^{-6} of $O + HD(v = 0, j)$ at an energy of 16 kcal mol^{-1}

products	j	v'	j'	GNVP	FCDWA-CBC	RCDWA-CBC	UDWA-RBC
H + OD	0	0	0	2.67 (-2)	2.62 (-2)	2.96 (-2)	2.01 (-2)
			1	7.68 (-2)	7.52 (-2)	8.45 (-2)	1.03 (-1)
			2	1.17 (-1)	1.15 (-1)	1.28 (-1)	1.36 (-5)
			3	1.43 (-1)	1.41 (-1)	1.53 (-1)	3.35 (-1)
			4	1.51 (-1)	1.50 (-1)	1.58 (-1)	7.07 (-3)
			5	1.43 (-1)	1.43 (-1)	1.45 (-1)	2.56 (-1)
			6	1.22 (-1)	1.23 (-1)	1.18 (-1)	1.48 (-2)
			7	9.26 (-2)	9.43 (-2)	8.47 (-2)	7.41 (-2)
			8	6.24 (-2)	6.42 (-2)	5.31 (-2)	2.04 (-2)
			9	3.66 (-2)	3.81 (-2)	2.87 (-2)	3.09 (-2)
			10	1.82 (-2)	1.91 (-2)	1.28 (-2)	1.08 (-2)
			11	7.38 (-3)	7.83 (-3)	4.56 (-3)	1.20 (-3)
			12	2.28 (-3)	2.44 (-3)	1.21 (-3)	2.56 (-3)
			13	4.86 (-4)	5.28 (-4)	2.10 (-4)	5.65 (-4)
			14	5.65 (-5)	6.19 (-5)	1.92 (-5)	6.53 (-5)
D + OH	0	0	15	2.09 (-6)	2.33 (-6)	5.21 (-7)	5.70 (-6)
			0	3.35 (-5)	3.38 (-5)	3.60 (-5)	2.93 (-3)
			1	8.85 (-5)	8.96 (-5)	1.80 (-4)	4.42 (-2)
			2	1.12 (-4)	1.14 (-4)	1.61 (-4)	1.48 (-2)
			3	9.95 (-5)	1.03 (-4)	6.36 (-5)	4.96 (-2)
			4	6.20 (-5)	6.52 (-5)	1.15 (-4)	1.16 (-3)
			5	2.39 (-5)	2.57 (-5)	1.23 (-5)	9.28 (-3)
			6	3.88 (-6)	4.29 (-6)	3.22 (-6)	1.35 (-3)
			0	1.89 (-2)	1.83 (-2)	1.54 (-2)	4.69 (-2)
			1	5.91 (-2)	5.72 (-2)	4.86 (-2)	1.46 (-3)
			2	1.04 (-1)	1.01 (-1)	8.76 (-2)	6.84 (-2)
			3	1.51 (-1)	1.47 (-1)	1.32 (-1)	1.00 (-1)
			4	1.86 (-1)	1.82 (-1)	1.72 (-1)	6.82 (-2)
			5	1.91 (-1)	1.89 (-1)	1.90 (-1)	2.19 (-1)
			6	1.55 (-1)	1.58 (-1)	1.71 (-1)	2.60 (-1)
7	9.20 (-2)	9.77 (-2)	1.16 (-1)	1.70 (-1)			
8	3.61 (-2)	4.03 (-2)	5.39 (-2)	4.80 (-2)			
9	6.70 (-3)	8.98 (-3)	1.44 (-2)	1.53 (-2)			
10	2.70 (-4)	3.36 (-4)	1.04 (-4)	2.11 (-3)			
H + OD	2	0	0	2.36 (-2)	2.39 (-2)	2.21 (-2)	9.76 (-3)
			1	6.83 (-2)	6.91 (-2)	6.44 (-2)	4.50 (-2)
			2	1.06 (-1)	1.07 (-1)	1.01 (-1)	7.31 (-6)
			3	1.33 (-1)	1.34 (-1)	1.27 (-1)	2.18 (-1)
			4	1.45 (-1)	1.46 (-1)	1.43 (-1)	5.16 (-3)
			5	1.43 (-1)	1.43 (-1)	1.42 (-1)	2.40 (-1)
			6	1.27 (-1)	1.27 (-1)	1.28 (-1)	1.86 (-2)
			7	1.01 (-1)	1.01 (-1)	1.05 (-1)	1.24 (-1)
			8	7.15 (-2)	7.09 (-2)	7.67 (-2)	3.87 (-2)
			9	4.42 (-2)	4.38 (-2)	4.89 (-2)	6.52 (-2)
			10	2.32 (-2)	2.29 (-2)	2.64 (-2)	3.98 (-2)
			11	9.95 (-3)	9.78 (-3)	1.17 (-2)	1.15 (-2)
			12	3.26 (-3)	3.20 (-3)	3.96 (-3)	9.96 (-3)
			13	7.37 (-4)	7.24 (-4)	9.22 (-4)	1.37 (-3)
			14	9.07 (-5)	8.98 (-5)	1.18 (-4)	6.62 (-4)
15	3.52 (-6)	3.55 (-6)	4.76 (-6)	1.56 (-5)			
D + OH	2	0	0	2.94 (-5)	2.98 (-5)	3.38 (-5)	2.88 (-3)
			1	8.02 (-5)	8.11 (-5)	2.03 (-4)	4.97 (-2)
			2	1.08 (-4)	1.09 (-4)	1.64 (-4)	1.94 (-2)
			3	1.04 (-4)	1.05 (-4)	7.63 (-5)	8.04 (-2)
			4	7.16 (-5)	7.24 (-5)	1.42 (-4)	2.10 (-3)
			5	3.09 (-5)	3.12 (-5)	4.37 (-6)	1.76 (-2)
			6	5.68 (-6)	5.71 (-6)	6.26 (-6)	2.77 (-3)
			0	1.85 (-2)	1.79 (-2)	1.58 (-2)	1.43 (-1)
			1	5.77 (-2)	5.58 (-2)	4.97 (-2)	1.29 (-2)
			2	1.02 (-1)	9.86 (-2)	8.91 (-2)	1.27 (-1)
			3	1.47 (-1)	1.44 (-1)	1.36 (-1)	1.34 (-1)
			4	1.82 (-1)	1.79 (-1)	1.71 (-1)	7.81 (-2)
			5	1.88 (-1)	1.87 (-1)	1.87 (-1)	1.85 (-1)
			6	1.57 (-1)	1.59 (-1)	1.67 (-1)	1.71 (-1)
			7	9.75 (-2)	1.02 (-1)	1.14 (-1)	1.09 (-1)
8	4.05 (-2)	4.51 (-2)	5.44 (-2)	3.24 (-2)			
9	9.00 (-3)	1.12 (-2)	1.50 (-2)	4.79 (-3)			
10	5.02 (-4)	7.79 (-4)	1.18 (-3)	2.51 (-3)			
H + OD	5	0	0	2.01 (-2)	2.09 (-2)	1.74 (-2)	9.70 (-3)
			1	5.83 (-2)	6.05 (-2)	5.07 (-2)	4.03 (-2)
			2	9.09 (-2)	9.36 (-2)	7.95 (-2)	6.29 (-6)
			3	1.15 (-1)	1.18 (-1)	1.01 (-1)	1.94 (-1)
			4	1.29 (-1)	1.30 (-1)	1.15 (-1)	4.58 (-3)

Continued

Table 13—continued

products	j	v'	j'	GNVP	FCDWA-CBC	RCDWA-CBC	UDWA-RBC
			5	1.30 (-1)	1.30 (-1)	1.21 (-1)	1.98 (-1)
			6	1.22 (-1)	1.20 (-1)	1.18 (-1)	1.38 (-2)
			7	1.06 (-1)	1.02 (-1)	1.09 (-1)	1.10 (-1)
			8	8.57 (-2)	7.76 (-2)	9.53 (-2)	4.71 (-2)
			9	6.30 (-2)	6.47 (-2)	7.70 (-2)	8.63 (-2)
			10	4.16 (-2)	4.53 (-2)	5.60 (-2)	4.90 (-2)
			11	2.42 (-2)	2.50 (-2)	3.47 (-2)	1.89 (-2)
			12	1.03 (-2)	9.25 (-3)	1.70 (-2)	3.32 (-2)
			13	3.24 (-3)	3.54 (-3)	5.90 (-3)	4.36 (-3)
			14	5.76 (-4)	5.41 (-4)	1.15 (-3)	2.01 (-3)
			15	3.14 (-5)	2.98 (-5)	7.19 (-5)	1.46 (-5)
		1	0	1.43 (-5)	1.52 (-5)	2.73 (-5)	2.63 (-3)
			1	4.32 (-5)	4.53 (-5)	1.09 (-4)	5.12 (-2)
			2	7.07 (-5)	7.14 (-5)	8.92 (-5)	2.09 (-2)
			3	8.70 (-5)	8.42 (-5)	5.19 (-5)	9.09 (-2)
			4	7.91 (-5)	7.35 (-5)	1.49 (-4)	2.45 (-3)
			5	4.63 (-5)	4.13 (-5)	1.48 (-5)	2.02 (-2)
			6	1.17 (-5)	1.01 (-5)	1.89 (-5)	2.73 (-3)
D + OH	5	0	0	1.25 (-2)	1.27 (-2)	1.37 (-2)	5.24 (-2)
			1	3.94 (-2)	4.00 (-2)	4.27 (-2)	2.60 (-3)
			2	7.14 (-2)	7.25 (-2)	7.59 (-2)	3.53 (-2)
			3	1.09 (-1)	1.10 (-1)	1.13 (-1)	8.28 (-2)
			4	1.49 (-1)	1.48 (-1)	1.48 (-1)	6.14 (-2)
			5	1.80 (-1)	1.80 (-1)	1.70 (-1)	2.01 (-1)
			6	1.85 (-1)	1.82 (-1)	1.70 (-1)	2.74 (-1)
			7	1.14 (-1)	1.24 (-1)	1.40 (-1)	2.05 (-1)
			8	9.73 (-2)	9.65 (-2)	8.73 (-2)	6.17 (-2)
			9	3.74 (-2)	3.41 (-2)	3.37 (-2)	2.51 (-2)
			10	4.58 (-3)	4.49 (-3)	4.39 (-3)	2.83 (-3)
			11	1.29 (-5)	1.30 (-5)	1.34 (-5)	2.90 (-5)

Table 14. The average percentage absolute relative error of the distorted-wave approximation for relative reaction probabilities greater than 1.0×10^{-6} as compared to the accurate quantum-mechanical results for the reaction $O + HD(v = 0, j)$ at total energy E (in kcal mol $^{-1}$)

E	products	j	FCDWA-CBC	RCDWA-CBC	UDWA-RBC
9.2	H + OD	0	0.15	0.46	46
		2	0.21	1.4	48
		5	1.6	4.0	47
D + OH	0	0.43	1.3	92	
	2	0.25	1.1	90	
	5	1.8	9.4	87	
13.8	H + OD	0	0.66	6.3	88
		2	0.38	5.4	75
		5	0.36	29	81
D + OH	0	0.50	5.3	540	
	2	0.45	2.7	280	
	5	0.43	2.3	526	
16	H + OD	0	4.2	32	8 590
		2	0.96	27	12 000
		5	5.3	47	14 800
D + OH	0	8.5	30	126	
	2	10	29	121	
	5	2.4	8.0	77	

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