State-to-state time-dependent wavepacket approach to reactive scattering: State-resolved cross-sections for $D + H_2(v = 1, j = 1, m) \rightarrow H + DH(\tilde{v}, \tilde{j})$

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In a recent letter (Science, 1992, 257, 522) the time-dependent wavepacket approach to reactive scattering was utilized to extract state-to-state scattering cross-sections for $D + H_2(e, j) \rightarrow H + DH, j$ at high energies. Results from 1.3 to 2.25 eV total energy, with a fine enough grid to enable appropriate averages simulating the experimental conditions, are reported. We briefly review the formalism used for the simulations and explain how coordinate grid-reduction techniques concentrate the numerical information for the continuum range of energies contained in the initial wavepacket. These fundamental advantages, complemented by the development of highly accurate and efficient time-dependent propagators and sparse grid and/or efficient basis representations, have quickly led to very large-scale simulations of photodissociation and inelastic reactions. Among the new methods, the time-dependent wavepacket (TDW) approach to reactive scattering has been very successful, recently being used to compute four-body initial-state selected reactive probabilities.

The basic TDW paradigm is very simple: a grid for the wavepacket is laid out, an initial wavepacket $|\Psi(0)\rangle$ is placed in the reagents asymptote, and the time-evolved wavepacket $\exp(-i\mathcal{H}t)|\Psi(0)\rangle$ is calculated by repeated applications of $\mathcal{H}$, the local Hamiltonian operator (also appropriately constructed on the grid). Here, we use units where $\hbar = 1$. The final-time wavepacket is then analysed to extract the rearrangement scattering amplitude. Alternatively, the definite-energy time-independent Lippmann–Schwinger (causal) scattering wavefunction at energy $E$, in the region on the ‘potential-side’ of the $t = 0$ wavepacket, can be extracted by a ‘half-Fourier transform’ of the wavepacket. Knowing the general form of this LS wavefunction outside the potential, it is easy to extract the scattering amplitudes for any final state. The attractiveness of this simple approach stems from the ease and speed in applying a sparse Hamiltonian on a grid wavepacket, and the fact that a single propagation may, in principle, be used to extract scattering information for the continuum range of energies contained in the initial wavepacket. These fundamental advantages, complemented by the development of highly accurate and efficient time-dependent propagators and sparse grid and/or efficient basis representations, have quickly led to very large-scale simulations of photodissociation and inelastic reactions. For rearrangement scattering, however, the TD approach was initially not optimally efficient, because the numerical grid had to extend far into the asymptotic reagents and product’s arrangements (where the initial wavepacket was placed and the final wavepacket was analysed). During the last few years we have developed a consistent paradigm in which the numerical grid is restricted to a small, physically important, part of the configuration space where all atoms are strongly interacting. The approach was initially developed and applied to extract energy-averaged reaction probabilities for $D + H_2(e, j) \rightarrow H_2(\tilde{e}, \tilde{j}) + H$, and for energy and vibrationally resolved, rotationally summed reaction probabilities for the same system. For rearrangement scattering, however, the TD approach was initially not optimally efficient, because the numerical grid had to extend far into the asymptotic reagents and product’s arrangements (where the initial wavepacket was placed and the final wavepacket was analysed). During the last few years we have developed a consistent paradigm in which the numerical grid is restricted to a small, physically important, part of the configuration space where all atoms are strongly interacting. The approach was initially developed and applied to extract energy-averaged reaction probabilities for $D + H_2(e, j) \rightarrow H_2(\tilde{e}, \tilde{j}) + H$, and for energy and vibrationally resolved, rotationally summed reaction probabilities for the same system. For rearrangement scattering, however, the TD approach was initially not optimally efficient, because the numerical grid had to extend far into the asymptotic reagents and product’s arrangements (where the initial wavepacket was placed and the final wavepacket was analysed). During the last few years we have developed a consistent paradigm in which the numerical grid is restricted to a small, physically important, part of the configuration space where all atoms are strongly interacting. The approach was initially developed and applied to extract energy-averaged reaction probabilities for $D + H_2(e, j) \rightarrow H_2(\tilde{e}, \tilde{j}) + H$, and for energy and vibrationally resolved, rotationally summed reaction probabilities for the same system.

Throughout this paper, barred quantum numbers indicate a final state. After further development of the formalism to extract state-to-state cross-sections, it was applied to extract final-state resolved cross-sections, as a function of energy, for $D + H_2(e, j, m) \rightarrow DH(\tilde{v}, \tilde{j}) + H$, an enormously demanding computational problem for any method.

In this paper we give a detailed account of the methodology used in these simulations of the DH$_2$ scattering system. Before...
going into the details of the methodology and the results, we give a brief introduction to the importance of the simulations.  

The H + H₂ system and its isotopic analogues are well suited for comparing theory and experiment for rearrangement reactions, due to the availability of relatively accurate fits of ab initio potential surface data points and to the light masses of all three atoms. Early investigations yielded remarkable agreement for D + H₂ (v = 0, j = 1) → DH(ν, j) + H cross-sections at intermediate energies (total collision energy near E = 1.2 eV). However, for the reaction D + H₂(v = 1, j = 1) → DH(ν, j) + H at the higher energy E = 1.8 eV, discrepancies were observed for both the rotationally resolved state-to-state cross-sections and the ratios of cross-sections for different final vibrations when summed over final rotations. One way to explore this disagreement was to carry out higher-energy [1.8–2.25 eV] experiments on the D + H₂(v = 1, j = 1) → DH(ν, j) + H reaction, in which translationally hot D atoms are produced by photolysis of DI, rather than DBr, as was used in the lower-energy experiments. Below, we denote these two sets of experiments as ‘high-energy’ and ‘intermediate-energy’. A priori, the DI experiments were supposed to be less susceptible to errors because of the reduced reactivity of the I photolysis product relative to Br, and the lack of spectral-line overlap with the analysed DH components. Comparison between theory and the higher-energy experiments was therefore highly desirable. Time-independent simulations at these energies (up to 2.25 eV) were very challenging, and the comparatively low ‘scaling’ of the effort in the TD method with the DeBroglie momentum and internal-state basis set size has led us to apply the method for this demanding reaction.  

After performing the TD simulations, remarkably good agreement with the high-energy measurements was found. Rotationally summed branching ratios into different DH vibrational states were in excellent agreement, as were also individual state-to-state rearrangement cross-sections, except for a shift of the maximum of the final-state rotational distribution for final states with v = 0. The overall agreement demonstrated the basic consistency of theory and experiment, and established that the remaining discrepancies are due to features in the potential surface utilized by the simulation. It is certain that these discrepancies are a reflection of the fact that much higher energy collisions are being considered and, therefore, portions of the potential surface come into play which are unimportant at the lower energies considered previously. In particular, this implies the existence of some problem with the short-range higher-energy portion of the potential and, in fact, indicate that the first excited electronic surface may be playing a significant role. The present paper reports the more detailed state-to-state rates calculated without taking account of such excited surface effects. It is expected that, as a result, they will not show total agreement with experiment (were it possible to make such magnetic state-resolved measurements). However, the results should still be useful as benchmarks, since they represent the only converged cross-sections for these processes that are available for such a range of total energies.  

First we give a brief review of the methodology used for these DH₂ simulations. In Section 3 we present the detailed results, at the state-to-state resolved level. Section 4 contains our conclusions.

## 2 Time-dependent quantum reactive scattering  

Our algorithm for calculating reactive state-to-state amplitudes is organized in terms of several components. The atom–diatom wavepacket |ψ(t)⟩ is expressed in terms of the usual reagents’ Jacobi coordinates (R, r, γ), these denoting respectively the distance R from D to the H₂ centre-of-mass, the H₂ bond length, r, and the angle γ between R and r. Following the work of Mowrey and Kouri and Sun et al., we represent the overall wavepacket in terms of a close-coupling expansion,

\[
|ψ(t)⟩ = \sum_{i=t} \binom{2J + 1}{4r} D_{\muσ}(A)v_{μσ}(γ, 0) R \psi_{\nuσ}(R, r, t | J, ν, j, \Omega_D) \left( \frac{R}{R} \right)
\]

where we introduce the Wigner function \( D_{\muσ}(A) \) of the appropriate Euler angles (collectively denoted by A), and the spherical harmonic basis function \( v_{μσ}(γ, 0) \) of the internal angle γ. The total angular momentum quantum number is denoted by J, M and Ω denote respectively its projection on the space-fixed and body-fixed z-axis, and j is the angular momentum quantum number of the H₂ diatom. As usual \( R_o \) is also the z-component of the diatom angular momentum along the body-fixed z-axis. Here and below, to simplify notation, we shall often omit explicit indication of the dependence of \( ψ \) on J and the indices of the initial \( H₂ \) vibrational–rotational state (\( v_o, j_o, \Omega_D \)) (or instead represent them by a single ‘super’-index, \( \bar{\gamma} \)).

The essence of a direct TD propagation is a prescription for calculating the evolution of \( ψ \):

\[
\frac{1}{i\hbar} \frac{∂\psi_{\nuσ}}{∂t} = \sum_{i=t} H_{\nuσ,i} ψ_{iσ} \tag{2.2}
\]

where we use \( h = \hbar \). The form of H in the representation eqn. (2.1) is easily derived as a combination of kinetic and potential terms,

\[
H_{\nuσ,i} = \left[ -\frac{1}{2M} \frac{∂^2}{∂R^2} - \frac{1}{2μ} \frac{∂^2}{∂r^2} + j(j+1) \right] δ_{jσ} δ_{\nuσ} + \frac{T^R_{\nuσ}}{2MR^2} δ_{jσ} + V_{\nuσ} δ_{\nuσ} \tag{2.3}
\]

where the \( T^R_{\nuσ} \) are the well-known body-fixed matrix elements of \( P \), the relative orbital angular momentum operator; the \( V_{\nuσ} \) are similar close-coupling matrix elements of the triatomic Born–Oppenheimer potential \( V(R, r, γ) \) and M and μ are the reduced masses for the \( D→H₂ \) motion and the \( H₂ \) bond (see e.g. ref. 12 for further details).

### Grid reduction  

For rearrangement scattering, direct propagation is expensive since the initial and final wavepackets cover large regions in physical space. To circumvent this difficulty, we invoke a projection operator formalism (introduced originally by Neuhäuser and Baer, and used in wavepacket treatments which could yield energy-resolved total and energy-resolved, state-selected cross-sections) to reduce the size of the \( R = H₂ \) motion and the \( H₂ \) bond (see e.g. ref. 12 for further details).
not appear in eqn. (2.6), because a factor of 1/r has been explicitly removed to yield \( \psi_d(R, r', t) \) and \( \phi_d(r') \); see the kinetic energy terms in eqn. (2.3). In practice, one stores the two sets of \([n_n\psi_d(R, r), \chi_n\psi_d(R, r, t)]\) as one ‘super-vector’ \([u]\) containing all relevant values of \( j, \Omega, R, r \) for \( j \) and \( \Omega, R, n \) for \( \eta \), at time \( t \). The evolution of this super-vector in time follows by rewriting the Schrödinger equation in terms of a ‘super-Hamiltonian’, easily shown to be:\(^{14}\)

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \left( \begin{array}{c} \eta \\ \chi \end{array} \right) = \left( \begin{array}{cc} PHP & P(V - v)Q \\ Q(V - v)P & QHQ \end{array} \right) \left( \begin{array}{c} \eta \\ \chi \end{array} \right)
\]

(2.7)

To understand the fundamental advantages of the projection operator formalism, we utilize the fact that in eqn. (2.7) the evolution of \( \chi \) is determined from a source term which is automatically localized in the strong-interaction region

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \langle \chi | H | \chi \rangle = -Q(V - v)\langle \eta | \eta \rangle
\]

(2.8)

where we suppress the \( j, \Omega \) indices. Recast in this form, the scattering process is similar to photodissociation. In both cases a wavepacket (here \( \chi \)) is ‘created’ in the strong interaction (SI) region. Once the wave exits from the SI region towards each asymptote, it is absorbed with a negative imaginary potential\(^{14,15}\) \(-iV_s\) which is adjacent to the SI region. This is an advantage over the direct approach where the grids necessarily include the reagents’ asymptote where the initial wavepacket is placed.

For our simulations \( V_s \) was chosen as a sum of two linear-ramp potentials\(^{14}\) which block the reagents’ and product’s arrangements:

\[
V_s(R, r) = V_s^1(R) + V_s^2(r)
\]

In addition to the imaginary potential which affects \( \chi \), an additional potential\(^{14,15}\) \(-iV_t(R)\) is added to absorb the \( P\Phi \) portion of the wavepacket when it is reflected into the far-asymptotic region, leading to the final equation

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \left( \begin{array}{c} \eta \\ \chi \end{array} \right) = \left( \begin{array}{cc} PHP & P(V - v)Q \\ Q(V - v)P & QHQ \end{array} \right) \left( \begin{array}{c} \eta \\ \chi \end{array} \right)
\]

(2.9)

When included in this manner, the \( V_t \) term which acts on \( \eta \) does not directly influence the \( |\eta\rangle \) part of the wavepacket. The initial wavepacket can therefore be placed outside the \( V_t \) region and is not influenced by it when it propagates inwards into the strong-interaction region (of course, \( \eta \) is indirectly influenced by \( V_t \) through its being coupled to \( \chi \)). Finally, we note that there is some freedom with respect to the choice of the number of \((n, j, \Omega)\) channels employed in \( P \) [eqn. (2.5)]. In the earliest applications, all open channels at the sampled collision energies were used; this choice has the advantage that \( |\chi\rangle \) is formally composed of closed reagents channels solely and therefore vanishes automatically at large \( R \), without the need to incorporate an additional non-zero region for \( V_s^1(R) \). Here, however, we follow ref. 21, in which it was noted that, at high energies, it is more convenient to reduce the number of channels in \( P\Phi \) to a few (rather than all) open channels, thereby avoiding large potential-matrices coupling different channels; \( |\chi\rangle \), which then does not decay automatically at large \( R \), is absorbed away by the incorporation of \( V_s^2(R) \) along an additional ‘strip’ blocking the reagents channel.

Initial wavefunction

For every value of \( J \), three separate simulations are performed (only one arises for the case \( J = 0 \)), corresponding to the possible values of the initial diatom angular momentum orienta-

tion quantum number, \( m_0 \). Each of these initial wavefunctions is a combination of \( DH(t_0 = 1, j_0 = 1, m_0) \) states, i.e.

\[
\eta_{n, j, \alpha}(R, t = 0 | J) = \delta_{n_1} \delta_{j_1} \eta_{n_0, m_0, J}(R)
\]

where the functions \( \eta_{n_0, m_0, J}(R) \) are the proper free initial wave-packets in a body-fixed axis. We use the methods of ref. 12 to obtain these functions.

Propagation

The generalized Hamiltonian \( \hat{H} \) is used to propagate the wavepacket employing the Chebyshev formula\(^{36,33}\)

\[
|u(t + t_0)\rangle = \exp(-i\hat{H}t) |u(t_0)\rangle
\]

\[
= \exp(-iH_{avg}t) \sum_n (2 - \delta_{n0})(-i)^n J_d \Delta H t
\]

\[
\times T_n \left( \frac{H - H_{avg}}{\Delta H} \right) |u(t_0)\rangle
\]

(2.10)

where \( u \equiv |\eta, \chi\rangle \). The parameters \( \Delta H \) and \( H_{avg} \), necessary for adjusting the range of the argument of the Chebyshev function \( T_n \) to \([-1, 1]\), can actually be taken as any reasonable approximation to the width and centre of the spectrum of \( H \). The \( J_d \) are Bessel functions. The introduction of the absorbing potential implies that the expansion eqn. (2.10) is inherently unstable (for essentially the same reasons that a Taylor expansion of \( \exp(-x) \) is numerically inaccurate for large \( x \)). The difficulty is easily resolved by dividing the total propagation time to a few large time-steps of duration \( \tau \) such that \( \Delta H \tau \) does not exceed ca. 200 and, in addition, by artificially enlarging the range \( \Delta H \) by ca. 20%. This has the effect of decreasing the eigenvalues of the shifted argument of the Chebyshev function \( H - H_{avg}/\Delta H \), thus stabilizing the polynomials \( T_n \) up to a large \( n \).

Analysis

Energy-resolved scattering amplitudes are obtained by a two-stage procedure, developed in ref. 18 and 19 (see also ref. 36 and 37). First, during the propagation we calculate the energy-resolved time-independent causal (Lippmann–Schwinger) scattering solution to the Schrödinger wavepacket, evaluated at a scattering distance \( R \), according to

\[
\langle R | \psi^+(E) \rangle = \frac{1}{a_{\Omega}} \int \exp(iEt) \langle R | \psi(t) \rangle \, dt
\]

(11.1)

where the weight that the component \( \psi^+_i(E) \) carries in the initial wavepacket is calculated by

\[
a_{\Omega} = \langle \Phi_i^+(E) | \psi(0) \rangle
\]

(12.12)

and \( \Phi_i^+ \) is the appropriately flux-normalized ‘positive momentum’ free-particle solution for the same target state. One obtains the causal Lippmann–Schwinger state provided that the \( R \)-value is any value on the ‘potential-side’ of the initial wavepacket (i.e. not a value ‘behind’ the initial wavepacket\(^{49,50}\)).

The causal Lippmann–Schwinger solution would be obtained everywhere if the time-integral extended from \( t = -\infty \) to \( t = +\infty \). The 0 to \( \infty \) range is all that is needed because in the expressions used below, only the component \( \psi \) in the strong-interaction region is utilized. In addition, we note that the energy-filter methodology yields

\[
u_{j0}(E) \equiv [n_{j0}(E), \psi(E)]
\]

from a filter of \( u_j(t); \psi^+_i(E) \) is then a sum of the two components.

The ‘filtered’ function \( \psi^+_i(E) \) is easily shown to be, in the strong-interaction region, the properly normalized solution of the time-independent equation \( (H - E)\psi^+_i(E) = 0 \) with the proper boundary condition, i.e. it is composed of an incoming
wave in channel \(i\), supplemented by outgoing waves for all other channels using the few-step Chebychev propagation, \(\psi_i^-(E)\) is numerically obtained as:

\[
\psi_i^-(E) = \sum_{l=0}^{(l+1)_{\text{max}}} \int_{t_{\text{fin}}} \exp(iE\tau) |\psi_l(t)\rangle d\tau
\]

and from eqn. (2.10) it follows that:

\[
\chi_l(E) = \sum_{l=0}^{(l+1)_{\text{max}}} \exp(iE\tau) C_l(E) \\
\times T_m\left(\frac{H - H_{\text{avg}}}{\Delta H}\right) |\psi_l(t_{\text{fin}})\rangle
\]

where:

\[
C_l(E) = (2 - \delta_{\alpha\beta})(-i)^{\alpha} \\
\times \int_{0}^{t_{\text{fin}}} \exp[i(E - H_{\text{avg}})\tau] J_l(t\Delta H) d\tau
\]

and the integrands in eqn. (2.15) are calculated numerically.

The second stage in the analysis is the use of \(|\psi_i^+(E)\rangle\) to extract the state-to-state transition amplitudes, \(S_{if}\), from the well-known expression:

\[
S_{if} = 2\pi i \phi_{f,i}(E) H - H_0 |\psi_i^+(E)\rangle
\]

where \(f\) stands for the final product’s \((\bar{v}, \bar{J}, \bar{\Omega})\) state, \(H_0\) is a single arrangement Hamiltonian which accurately simulates \(H\) in the specific product arrangement (here \(DH + H\)), and \(\phi_{f,i}\) is the corresponding product-channel inelastic wavefunction. By construction, the integrand in eqn. (2.16) vanishes outside the strong-interaction region (in the desired product’s asymptotic region, \(H - H_0\) vanishes, while in the reagents’ and the other products’ asymptotic regions, \(\phi_{f,i}\) vanishes, assuming there can be no dissociation into three free atoms). Eqn. (2.16) is, therefore, appropriate for our case where the grid used in propagating \(\chi_l(t)\) is designed to be limited to a small strong-interaction region. For this study a very simple (elastic type) \(H_0\) is employed; each \(\phi_{f,i}\) is then a combination of single-channel functions, \(\xi_{l,\bar{v},\bar{J}}(\bar{R})\), obtained by solving:

\[
\left( -\frac{1}{2M_{\text{H-DH}}} \frac{\partial^2}{\partial \bar{R}^2} + \frac{\hbar^2(l + 1)}{2M_{\text{H-DH}}} R^2 + V(\bar{R}) \right) \xi_{l,\bar{v},\bar{J}}(\bar{R}) = (E - \epsilon_{l,\bar{v}}) \xi_{l,\bar{v},\bar{J}}(\bar{R})
\]

where \(\epsilon_{l,\bar{v}}(\bar{R})\) is the rovibrational energy of the DH product diatom. The final expression for \(S_{if}\) in terms of \(|\psi_i^+(E)\rangle\) and the \(\xi\) is straightforward; we defer the reader to ref. 19, 36 and 37 for details. We only note here that the resulting three-dimensional integrals are evaluated using the reagents coordinates \((R, r, \gamma)\); this is an additional advantage of the \(T\)-matrix expression, since the \(|\psi_i^+(E)\rangle\) are automatically given on grids defined in terms of the reagents’ Jacobi coordinates, so that they do not need to be interpolated (accurate interpolation of \(|\psi_i^+(E)\rangle\), though possible, is very expensive due to the sparseness of the grid-representation. It is this same feature of sparseness which makes the grid-representation of the Hamiltonian so efficient for propagation). The only required interpolation is of the final \(\phi_{f,i}\) from product to reagent coordinates. Specifically, for every value of \(R, r\) and \(\gamma\) one finds the associated values of \(\bar{R}, \bar{r}\) and \(\bar{\gamma}\), the Jacobi coordinates in the product’s channel, and constructs the \(\xi_{l,\bar{v},\bar{J}}(\bar{R})\) from a stored list of its values on an equipped grid. This is an inexpensive task since the simple \(\xi_{l,\bar{v},\bar{J}}(\bar{R})\) are computed on dense one-dimensional grids, so that a rapid few-point interpolation procedure is highly accurate.

3 Results

The reactive-scattering time-dependent algorithm described above was applied to study \(D + H_2(v = 1, j = 1, m) \rightarrow H + DH(\bar{v}, \bar{J})\) reactive collisions at high energies \((E = 1.8-2.25 eV)\). Below, we present and discuss the detailed results as a function of collision energy, for a specific initial vibrational state \((j, m)\), magnetic quantum number \(m\) and parity state. The calculations were carried out for a sufficient time and fine enough grid parameters to ensure accuracy of the results.

To begin analysing some results, it is useful to note the significance of the various quantum numbers characterizing the system and to remind ourselves of the effects of certain constraints on quantum numbers. First, we emphasize that although the results are reported in a laboratory-fixed coordinate system (with the quantization axis taken along the linear momentum vector of the D atom relative to the \(H_2\) centre-of-mass), the calculations are done in a body frame in which the vector points along the relative scattering vector to the \(H_2\) from the \(H_2\) or HD centre-of-mass (depending on the arrangement in which one is propagating). Thus, \(h_m\) is the \(z\)-component of the \(H_2\) angular momentum measured along the initial linear momentum of the D atom, relative to the \(H_2\) centre-of-mass. Other quantum numbers of interest are \(v\) and \(\bar{v}\), which are the initial vibrational quantum number of the \(H_2\) and the final vibrational quantum number of the HD product, respectively; \(j\) and \(\bar{J}\), which are the reactant and product molecular rotational quantum numbers; \(h_2\), which is the reactant molecules \(z\)-component of angular momentum, measured along the scattering vector, \(R\), from the \(H_2\) centre-of-mass to the incident D atom; and \(s\) or \(a\), which denotes the parity of the wavefunction.

We note that the initial states with \(m = \pm 1\) consist of the \(H_2\) rotating in a plane that wobbles about the initial relative momentum of the D atom, so that its angular momentum precesses. The initial states with \(m = 0\) consist of the \(H_2\) rotating in a plane containing the initial linear relative momentum of the D atom. The angle made by the precession cone of the \(H_2\) angular momentum relative to the incident linear momentum of the D atom is \(\cos^{-1}[-1/\sqrt{2}]\).

We also note that the \(\Omega = \pm 1\) states correspond to the diatom rotating in a plane that precesses about the scattering vector from the diatom centre-of-mass to the atom, \(R\), with the total angular momentum and the diatom angular momentum each also making the angle \(\cos^{-1}[-1/\sqrt{2}]\). The \(\Omega = 0\) state corresponds to the diatom rotating in a plane containing the vector \(R\).

Obviously, an enormous amount of information and data are generated by solving the collision equations. It is instructive to discuss some constraints relating various quantum numbers. In a space frame (Arthurs–Dalgarno) description,\(^{30}\) there are three angular momenta one must consider, \(J, j\) and \(l\), which are, respectively, the total, diatom and the relative orbital angular momenta. Each has a quantum number determined by the length of an angular momentum vector, \(J, j\) or \(l\), so that \([J] = h_{\sqrt{\{J(J + 1)\}}}, [j] = h_{\sqrt{\{j(j + 1)\}}}, [l] = h_{\sqrt{\{l(l + 1)\}}}\) for the reactant state and similar expressions involving \(j\) and \(l\) for product states (\(J\) is the same because of conservation of total angular momentum). These must satisfy the triangle inequalities \(|J - j| \leq l \leq J + j\) and \(|J - j| \leq l \leq J + \bar{j}\). We note that there is not a great deal of diatom angular momentum initially, since \(j = 1\), so the initial \(l\) values can only range from \(l = |J - 1|\), \(J, j + 1\). This implies that the opacity, calculated as a function of \(J\), is approximately similar to that
calculated as a function of $l$ and grazing collisions dominate as $J$ becomes larger. However, one may also think of the reaction as occurring in two stages (this is rigorously true owing to the existence of surfaces-of-no-return, where absorbing potentials can be placed to absorb the amplitude immediately after the HD has been formed$^{10,12-16}$). However, there is still a substantial region of scattering over which one must propagate if one desires the final product state distribution.

This corresponds to a ‘final state interaction,’ and it can play a fundamental role in governing the distribution among final product states. In the exit arrangement scattering in the HD + H arrangement, given values of $J$ and $J$ determine the range of final or ‘exit impact parameters’ that contribute to reaction. The larger $J$ is, the wider the range of $l$ values, and one has $l = [J - j], [J - j] + 1, \ldots, J + j$. These facts will play an important role in interpreting the results we have obtained.

We now begin a consideration of the computational results. First, in Fig. 1 and 2 we display the (total angular momentum) opacities at a single energy, $E = 2.25$ eV, for initial states $v = j = 1$, $m = 0$, 1(s) and 1(a), for the final product states of HD with $v = 1, j = 8$ and $v = 1, j = 12$. We see that there are significant oscillations in the opacities which may be an important interference phenomenon. (To settle unambiguously whether this is the case, additional calculations would need to be done.) One possible source of such oscillations is the result of the unitarity of the $S$ matrix. Thus, oscillations can arise due to the fact that the sum of the probabilities for all possible processes must add up to 1. However, at higher energies, the elastic scattering probability (as a function of $J$) can be approximated by $\sin^2 \delta_j$, where $\delta_j$ is a phase shift for the non-reactive elastic channel. At high energy, $\delta_j$ can vary greatly with $J$ so that the elastic opacity has a ‘sawtooth’ shape$^{51}$.

This fact, combined with conservation of total probability, can result in oscillations in the inelastic and reactive probabilities, which is reflected in the opacity.) However, it is clear that for the $m = 1(a)$ and $m = 0$, the largest opacities are roughly in a range $13 \leq J \leq 20$, corresponding to incident orbital angular momentum in a range $12 \leq J \leq 21$. These are intermediate values, considering that the minimum $l_i$ is zero, and from Fig. 1 and 2, the maximum initial $l$ value is in excess of 35 (the precise value depending on the final $v, j$ state of the HD product). This would indicate that, at higher energies, the usual idea that reaction is dominated by collinear configurations is not likely to be accurate. This is supported by the fact that the largest opacities are those for $m = 1(a)$, and (as discussed above) this state cannot have any contributions from collinear geometries.

In Fig. 3 and 4, we display the opacities for the same range of initial states, but for final states $v = 2, j = 4$ and $v = 2, j = 12$, respectively. We see that for the $v = 2, j = 4$ product, the dominant initial state is the $v = 1, j = 1, m = 1(a)$. The range of $J$ for the reaction out of this initial state, producing the $v = 2, j = 4$ product is $13 \leq J \leq 20$, and for $v = 2, j = 12$, it is $5 \leq J \leq 26$. Thus, the $v = 2, j = 12$ also gets significant contributions from lower $J$ values, corresponding to low initial impact parameter or more nearly ‘head-on’ collisions. Again, significant oscillations are observed.

Considering the results in Fig. 1–4 as a group, we make the following suggestions. For collisions leading to the vibrationally hot, moderate diatomic angular momenta products ($v = 1, j = 4$; $v = 1, j = 12$; $v = 2, j = 4$, the $j_1$, $l_i$ change from approximately 1, $J$ to the set of values $[j, J - j; J - j + 1, \ldots, J, \ldots, J + j - 1, J + j]$). Thus, for $v = 1$ or 2, $j = 4$, we have $J - 4 \leq l \leq J + 4$. Now in one extreme mass ratio situation (the light–heavy–light (LHL) combination$^{52}$), where the projectile and exiting atoms are both light compared to the third atom, it has been argued that approximate selection rules hold

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**Fig. 1** Reactive scattering opacity function vs. total angular momentum quantum number, $J$, for D + H$_2$($v = j = 1, m = 1$) → H + HD($v = 1, j = 8$), for various $J$ values. The magnetic/symmetry states are given on the figure. The $m = 0$ is also symmetric. The final projection quantum number has been summed over.

**Fig. 2** As Fig. 1, except for HD in the $v = 1, j = 12$ state.

**Fig. 3** As Fig. 1, except for HD in the $v = 2, j = 4$ state.

**Fig. 4** As Fig. 1, except for HD in the $v = 2, j = 12$ state.
Fig. 5 Reactive cross-section plotted as a function of the final HD rotational state, $j$. Results are shown for seven total energies (in eV) and have been summed over final HD projection quantum states. The initial state is $v = j = 1, m = 0$ and the final state is $\tilde{v} = 0, j$.

such that $j = j', j'' = l$. The D atom is certainly not infinitely massive, but it does have twice the mass of the H atoms. (Also, the projectile is the D atom, rather than the light H atom). The centre of mass of HD lies $2/3$ of the HD internuclear distance, $r$, away from the H atom and only $r/3$ away from the D atom. This suggests that one may see enhancement of reactivity for producing final rotational $j$ states with the values $j = j' - 1, J$ and $J + 1$.

However, it is also true that, at very high energies, the collisions can probe the short-range anisotropy of the diatom. Furthermore, once the product molecule is distinguishable (just past the point-of-no-return), the anisotropy of the HD will dominate the final-state portion of the collision. This will be significantly more anisotropic than for D scattering off $H_2$, and the anisotropy will be more and more pronounced as the collision energy increases. This can lead to deviations from the simple $j = l, l = l$ LHL situation, so that much wider ranges of final $j$, $l$ can be populated. We believe this is evident in the results in Fig. 1–4, so that the LHL propensity is not nearly so pronounced as it might otherwise be.
The next results, displayed in Figs. 5–13, contain the final rotational–vibrational cross-sections, as a function of \( m \) (for \( m = 0, \, 1(a), \, 1(s), \, m = 1 \) summed over parity, and the initial degeneracy averaged case). Results for seven total energies are given, from 1.74–2.25 eV (the highest energy studied). First, we consider Fig. 5 for \( m = 0 \) and \( \bar{v} = 0 \), and we see that a bimodal distribution occurs with maxima occurring at about (1) \( j = 7 \) and 13 for \( E_{\text{tot}} = 1.74 \) eV, (2) \( j = 8 \) and 13 for \( E_{\text{tot}} = 1.815 \) eV, (3) \( j = 9 \) and 14 for \( E_{\text{tot}} = 1.935 \) eV, (4) \( j = 9 \) and 15 for \( E_{\text{tot}} = 2.00 \) eV, (5) \( j = 10 \) and 15 for \( E_{\text{tot}} = 2.063 \) eV, (6) \( j = 10 \) and 16 for \( E_{\text{tot}} = 2.125 \) eV and (7) \( j = 11 \) and 17 for \( E_{\text{tot}} = 2.25 \) eV. This type of behaviour is reminiscent of the so-called ‘rotational rainbow’ observed in inelastic atom–diatom scattering. We can take the view that owing to the relatively large anisotropy of the HD molecule (especially when undergoing high-energy collisions), there is rotational rainbow scattering in the final-state interaction portion of the collision dynamics. The presence of the bimodal or double rotational rainbow peaks is the result of the difference in the two ends of the molecule (HD is heteronuclear), so that a strongly different anisotropy is experienced depending on whether the exiting H atom leaves from the H- or the D-portion of the HD molecule. We should note that the major source of the anisotropy of the HD molecule can be viewed as a result of the non-symmetric location of the centre-of-mass. That is, the electronic distribution is very little different in HD than in \( H_2 \); however the analogous classical system is a ‘loaded sphere,’ for which the displacement of the mass-centroid from the geometric centre results in much larger torques being produced in collisions with another particle.

The same qualitative behaviour is observed in Fig. 6–12 to a greater or lesser degree. The major changes are a decrease in the \( j \) values of the maxima as the final vibrational state is increased. This is true for \( m = 0, \, 1(s) \) and 1(a), and we interpret this as a result of the fact that the final available kinetic energy decreases as the final vibrational state increases. Thus, as we consider the \( \bar{v} = 0, \, 1 \) and 2 results, the behaviour becomes characteristic of an effective energy \( E(\bar{v}) \) given by \( E(\bar{v}) = E_0 - E_{j, \bar{v}} \). The approximate pure vibrational energies of HD are lower than those of \( H_2 \) by a factor of \( 1/\sqrt{2} \), so that \( \Delta E_{v, 0} \approx 0.36 \) eV, \( \Delta E_{v, 0} \approx 0.56 \) eV and \( \Delta E_{v, 0} \approx 0.76 \) eV. Therefore, scattering in the \( m(H_2) = 0 \) initial state, producing the HD \( \bar{v} = 0, \, \bar{p} \) product occurs at an ‘effective total energy,’ \( E(\bar{v} = 0) = E_{\text{tot}} - 0.36 \) eV. Similarly, the reaction yielding the HD \( \bar{v} = 1, \, \bar{j} \) product occurs at an effective total energy \( E(\bar{v} = 1) = E_{\text{tot}} - 0.56 \) eV. Then we should compare the \( \bar{v} = 1, \, E_{\text{tot}} = 2.25 \) eV results with those of \( \bar{v} = 0 \) at \( E_{\text{tot}} = 2.05 \) eV. Doing this, we see that both \( \bar{v} \) distributions are bimodal, with the \( \bar{v} = 0 \) maxima occurring at \( j = 10 \) and 15, while those for \( \bar{v} = 1 \) occur at \( j = 9 \) and 14. While certainly not exact, we see they are reasonably close. Furthermore, the sizes of these two cross-sections are quite close, while the \( \bar{v} = 0, \, E_{\text{tot}} = 2.25 \) eV cross-section is much larger than for \( \bar{v} = 1, \, E_{\text{tot}} = 2.05 \) eV. At the other extreme, we can compare the \( \bar{v} = 0, \, E_{\text{tot}} = 1.74 \) eV results with those for \( \bar{v} = 1, \, E_{\text{tot}} = 1.935 \) eV (which is close to the value \( 1.74 + 0.20 = 1.94 \) eV). In this instance, the \( m = 0, \, \bar{v} = 1, \, E_{\text{tot}} = 1.74 \) eV maxima are at \( j = 7 \) and 13 while the \( m = 0, \, \bar{v} = 1, \, E_{\text{tot}} = 1.935 \) eV maxima are at \( j = 6 \) and 12; again quite close. If we consider the \( \bar{v} = 2 \) results, we should be able to compare the \( m = 0, \, \bar{v} = 2, \, E_{\text{tot}} = 2.05 \) eV results with those for \( m = 0, \, \bar{v} = 2, \, E_{\text{tot}} = 2.25 \) eV, then the maxima for \( \bar{v} = 1 \) are at \( j = 7 \) and 13 and for \( \bar{v} = 2 \) are at \( 4 \) and 12. Here, the difference is more pronounced, and this may be due to inadequacies in a non-rotating harmonic oscillator model for the energies of the HD molecule. If we look at the lowest energy for \( m = 0, \, \bar{v} = 1, \, \bar{p} \) a clear bimodal distribution is not seen (though a ‘shoulder’ still appears at \( j = 3–4 \)) and a maximum occurs at \( j = 5 \). Thus, the agreement is qualitative, as in the higher-energy results. The disappearance of the bimodal character can be explained in terms of the disappearance of the rotational rainbow for the less anisotropic part of the HD final state interaction as the effective energy is lowered. Then the energy is insufficient to probe the anisotropy and the rotational rainbow for the less anisotropic part of HD will disappear first. This implies that it should be the lower-j maximum which disappears (which is, indeed, what we observe).

Fig. 6–10 contain analogous results for the \( m = 1(s), \, \bar{v} = 0, \, 1 \) and 2 cases. These are interesting in that the bimodal character is less clear cut than the \( m = 0 \) cases. At present, we are unable to account in detail for this qualitative difference.
However, in general, the results behave analogously to those just discussed. There is a lower effective total energy as \( \bar{e} \) increases, and the bimodal character disappears for the lowest energy \( \bar{e} = 2 \) cases. Finally, in Fig. 11–13, analogous results are shown for the \( m = 1(a), \bar{e} = 0, 1, 2 \) cases. In this case, the bimodal character of the results appears to disappear even more rapidly as \( \bar{e} \) increases. Thus, for \( m = 1(a), \bar{e} = 2 \), none of the cross-sections show double maxima as a function of \( j \). However, we still see a systematic reduction in the value of the \( \bar{e} \) at which the maximum occurs.

The fact that the effective energy available for motion of the exiting H atom relative to the HD centre-of-mass decreases with increasing \( \bar{e} \), can also suggest a reason why our calculations begin to disagree significantly with the experimental results\(^{19} \) only for \( \bar{e} = 0 \), while the results for \( \bar{e} = 1 \) and \( \bar{e} = 2 \) agree with experiment very well indeed. If the source of the disagreement has to do with the upper Born–Oppenheimer (BO) surface becoming important, this would clearly occur first for \( \bar{e} = 0 \) products, since these have the largest effective energy and therefore the highest amount of kinetic energy available (to ‘ride up’ the hard core potential surface and thereby be influenced by the neglect of the higher-energy surface).

Finally, we note that as one sums and/or averages the results, the presence of structure in the product-state distribution can be washed out. To see this, in Fig. 14–16, we display the degeneracy-averaged cross-sections as a function of final HD diatom state of \( \bar{e}, j \). We see that the bimodal structure has been almost completely washed out. However, there still remains the highest rotational rainbow maximum in all the results. In addition, we can still see clearly the results of the decreasing effective total energy as \( \bar{e} \) increases. If we compare the \( \bar{e} = 0 \) results at \( E_{\text{tot}} = 2.05 \) eV, we see that the \( \bar{e} = 0 \) maximum occurs at \( j = 16 \), while the \( \bar{e} = 1 \) maximum occurs at \( j = 13 \). The \( \bar{e} = 2 \), \( E_{\text{tot}} = 1.74 \) eV results have a maximum at \( j = 14 \) and the \( \bar{e} = 1 \), \( E_{\text{tot}} = 1.935 \) eV results have a maximum at \( j = 11 \). We can compare the \( \bar{e} = 0 \), \( E_{\text{tot}} = 1.815 \) eV maximum at \( j = 10 \) to the \( \bar{e} = 2 \), \( E_{\text{tot}} = 2.25 \) eV maximum at \( j = 11 \). Similarly, for \( \bar{e} = 0 \), \( E_{\text{tot}} = 1.74 \) eV, the maximum is at \( j = 14 \), while for \( \bar{e} = 2 \), \( E_{\text{tot}} = 2.125 \) eV, it is at \( j = 9 \). Clearly, the agreement is only qualitative, so that scattering into HD in \( \bar{e} = 2 \) is analogous to scattering into HD in \( \bar{e} = 0 \) at a lower total energy.

There is a great deal left to be done on this system. Even continuing to neglect the upper potential surface, one should calculate differential cross-sections. We have not done this primarily because we did not carry out calculations at every \( J \) value. Since the state-resolved differential cross-sections can depend sensitively on the phase of the \( S \) matrix, we did not attempt to interpolate as a function of \( J \). With the increased efficiency now available for doing wavepacket calculations, it should be possible to carry out such detailed calculations for each contributing \( J \), as a function of energy. In addition, it is important to carry out studies that include the upper potential surface and its coupling to the lower surface. This also should be feasible (although it will be an enormous calculation). Thus, we conclude by remarking that this simplest atom–diatom reactive system still poses important and fascinating challenges for theoretical quantum simulations.

**4 Conclusions**

The results we have obtained are useful for several reasons. First, they confirm the quality of the DH\(_2\) potential surface and the accuracy of a detailed experiment designed to study this reaction at the most detailed level to date. Second, at the time that the simulations were performed they demonstrated, for the first time, the enormous power of the time-dependent reactive scattering approach for extracting state-to-state cross-sections in chemical reactions, for systems that are very challenging for more traditional descriptions (there are more than 2000 channels open at the highest energy of the simulations and a large number of energies were extracted in various studies). Subsequent calculations for three- and four-atom systems using TD methods (strongly influenced by our formulation and methods) have borne out the power and promise of this approach\(^{10,12–29,54,55} \).

In this paper we have given a brief a review of our time-dependent reactive-scattering formalism as applied to the
DH$_2$ reactions. We have then taken a closer look at the results of the simulations, and have specifically investigated both energy and final-state effects. We posit that the rotational distributions are consistent with the presence of rotational rainbows which arise in the final state scattering of HD by H. In addition, we found differences between ‘a’ and ‘s’ parities, and noted that the former do not sample the collinear configuration. This can lead to differences in the details of scattering between the two symmetries. We suggest that theoretical calculations which resolve the magnetic substates, yield state-resolved angular distributions of the reaction products, and incorporate the excited BO potential surface, can lead to further understanding of this ‘simplest’ chemical reaction.

As noted above, in the almost three years which have passed since the simulations reported here were performed, the time-dependent reactive scattering method has achieved great success in surmounting the ‘four-body’-barrier for initial- and final-state-resolved reaction probabilities. Several of us have also independently developed this method further, and we enumerate some of the developments below. (i) New initial- and final-state-resolved reaction probabilities. Several


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