

On the Effect of Initial Rotation on Reactivity. A Multi-Configuration Time-Dependent Hartree (MCTDH) Wave Packet Propagation Study on the H + D₂ and D + H₂ Reactive Scattering Systems[†]

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Cumulative initial-state-selected reaction cross sections of the H + D₂ and D + H₂ systems are analyzed for collision energies up to 1.3 eV. Initial states of the diatom with rotational quantum numbers $j_0 = 0-4$ and vibrational quantum number $\nu_0 = 0$ are considered. The Liu–Siegbahn–Truhlar–Horowitz (LSTH) potential energy surface is taken as interaction potential. The geometric phase is ignored but no further (nonnumerical) approximations are made. The cross sections are computed by propagating wave packets employing the multiconfiguration time-dependent Hartree scheme. The reactive flux, which determines the integral cross section, is evaluated through the interaction of the wave packet with a complex absorbing potential. The initial-state-selected integral cross sections, $\sigma_{j_0}(E)$, in particular those for $j_0 = 0$, show weak oscillations, which we attribute to transition state resonances associated with excitations of the bending motion. Some of the present results are discussed in comparison with results obtained by using the coupled states approximation.

1. Introduction

The H + H₂ system and its isotopic variants are certainly prototype systems for studying quantum molecular reaction dynamics. As quantum reactive scattering is a difficult problem as such, the smallest system plays a distinguished role. Over more than 30 years, this system has been extensively studied quantum mechanically, and many new methods have been developed for or tested on it. Already in 1969 McCullough and Wyatt investigated the quantal flux in the vicinity of the saddle point region for collinear H + H₂ scattering.^{1,2} This study is also a very early example of using the time-dependent picture. Full 3D calculations to determine total or differential cross sections appeared about 10 years later. A large variety of methods have been used for this purpose, e.g., close coupling expansion in hyperspherical coordinates,³⁻⁵ complex Kohn⁶⁻⁹ and log-derivative Kohn^{10,11} variational calculations (the latter being equivalent to an R-matrix approach), the generalized Newton variational principle,¹² the Toeplitz approach,¹³ and wave packet propagation methods.^{14,15} For further references see the review of W. H. Miller.¹⁶

The effect of the initial rotation on the reactivity for the H + H₂ system and its isotopic variants has been investigated both quasiclassically¹⁷⁻²³ and quantum mechanically (QM).^{13,24-26} The quasiclassical trajectory (QCT) calculations for the H + H₂^{17,18} and D + H₂¹⁹⁻²³ systems showed, at low translational energies, a decrease of the reaction cross sections with increasing rotational excitation for small j_0 's. (Initial quantum numbers are always specified by the index 0.) For larger j_0 's the opposite effect is observed. In the QCT calculations a decrease of the cross sections with increasing j_0 's starts in the vicinity of the threshold, which is shifted upward with increasing j_0 . The QM calculations for the D + H₂($\nu_0 = 1$, $j_0 = 0-3$) system²⁴ also indicate the negative influence of initial rotation on reactivity,

but here the same threshold for all j_0 's is obtained. In the QCT calculations for the H + D₂ system^{22,23} an increase of reactivity with increasing rotational excitation has been observed in the post threshold region.

In the present paper we will solve the H + D₂ and D + H₂ reactive scattering problem by wave packet propagation and adopt the multi-configuration time-dependent Hartree (MCTDH) algorithm to perform the propagation. MCTDH²⁷⁻²⁹ is a propagation method that can be very efficient, in particular for large systems.^{30,31} The H + D₂ and D + H₂ systems studied here are too small to fully exploit the high efficiency of MCTDH, but when turning to larger reactive systems we expect the use of MCTDH to be of considerable advantage. A recent calculation on reaction rates of H + CH₄³² further supports this expectation.

The present work was partially motivated by the critique by Aoiz et al.²⁶ of our previous study of the H + D₂ system.³³ There we used the *coupled states* (also known as *centrifugal sudden*) (CS) approximation to simplify the Hamiltonian (see Section 2.1). Using the CS approximation, it was found that for collision energies between 0.4 and 0.95 eV, the initial rotation of the D₂-diatom slightly hinders reaction. Using the exact kinetic energy operator, however, Aoiz et al. showed that internal rotation slightly enhances reaction—at least for the particular energy (0.54 eV) they probed.²⁶ The approximate treatment of the kinetic energy by the CS approximation hence reverses the ordering of the σ_{j_0} cross sections.

In the present paper we investigate the initial-state-selected reaction cross sections of the H + D₂ and D + H₂ systems. The diatom is assumed to be initially in its vibrational ground state, $\nu_0 = 0$, and in a specific rotational state, $j_0 = 0, 1, 2, 3$, or 4. The range of collision energies investigated is 0.3–1.3 eV. The geometric phase was ignored. It has been shown that the geometric phase effect cancels out when summing over total J .³⁴

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We confirm the results of Aoiz et al., but more importantly, we find that a weak resonance structure appears in the $\sigma_{j_0=0}(E)$ cross section. Thus, in contrast to the CS results, the resonant structure is not completely washed out by the summation over the total J 's. Despite its very weak appearance, this is, to our knowledge, the first transition state resonance reported for a calculation on the total cross section of the H + H₂ system or its isotopic variants.

2. Theory

2.1. Hamiltonian. The triatomic scattering system is described by body-fixed (BF) Jacobian coordinates R, r, θ and by three Euler angles relating the BF to the space-fixed system. Here, R denotes the distance between the projectile and the center of mass of the diatom, r is the internuclear distance of the diatom, and θ the angle between \mathbf{R} and \mathbf{r} .

As the total angular momentum operator $\hat{\mathbf{J}}$ commutes with the Hamiltonian, one may consider the individual J -components, Ψ^J , of the total wave function. One finds that Ψ^J depends only on the third Euler angle ϕ , which is the azimuthal angle specifying the orientation of the BF-system around \mathbf{R} . As only the kinetic energy depends on ϕ , it is advantageous to replace ϕ by the momentum variable K , which is the projection of the total angular momentum \mathbf{J} onto \mathbf{R} (i.e., onto the BF z -axis). Hence we expand the wave function

$$\Psi^J(R, r, \theta, \phi) = (2\pi)^{-1/2} \sum_K \Psi^{JK}(R, r, \theta) e^{iK\phi} \quad (1)$$

and write the time-dependent Schrödinger equation as^{35–37}

$$i\dot{\Psi}^{JK} = H_{KK}^J \Psi^{JK} + H_{K, K+1}^J \Psi^{J, K+1} + H_{K, K-1}^J \Psi^{J, K-1} \quad (2)$$

where

$$H_{KK}^J = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \frac{\hat{j}^2}{2\mu_r r^2} + \frac{1}{2\mu_R R^2} [J(J+1) - 2K^2 + \hat{j}^2] + V(R, r, \theta) \quad (3)$$

$$H_{K\pm 1, K}^J = -\frac{1}{2\mu_R R^2} \sqrt{J(J+1) - K(K\pm 1)} \hat{j}_{\pm} \quad (4)$$

$$\hat{j}^2 = -\left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - \frac{K^2}{\sin^2 \theta} \right) \quad (5)$$

and

$$\hat{j}_{\pm} = \mp \frac{\partial}{\partial \theta} - K \cot \theta \quad (6)$$

The symbols μ_R and μ_r denote the usual reduced masses and V is the interaction potential. The interpretation of eq 2 is clear. The motion of the BF-system couples the various K -states through the coupling terms $H_{K, K\pm 1}^J$ (Coriolis coupling). When dropping these terms, one arrives at the well-known *coupled states* or *centrifugal sudden* (CS) approximation.^{38–40} Within the CS approximation the quantum number K is conserved and thus treated as a parameter, reducing the four-dimensional problem to a three-dimensional one.

Note that in the BF-system $J_z = j_z = K$ holds (because $l_z = 0$ by construction). The initial K is thus the initial magnetic rotational quantum number of the diatom.

In the present work we will treat the scattering problem beyond the CS approximation, including the full Hamiltonian (eqs 3, 4), but we will occasionally compare with CS results.

2.2. MCTDH. The scattering process is studied within a time-dependent framework and the wave packet propagation is performed by using the multi-configuration time-dependent Hartree (MCTDH) approach. As the MCTDH method has recently been thoroughly reviewed,²⁷ the technique is discussed here only very briefly.

The ansatz for the MCTDH wave function of f degrees of freedom reads

$$\Psi(Q_1, \dots, Q_f, t) = \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}(t) \prod_{\kappa=1}^f \varphi_{j_{\kappa}}^{(\kappa)}(Q_{\kappa}, t) \quad (7)$$

where the Q_i denote the f nuclear coordinates, the $A_{j_1 \dots j_f}$ are the time-dependent expansion coefficients, and the $\varphi_{j_{\kappa}}^{(\kappa)}(Q_{\kappa}, t)$ are n_{κ} expansion functions for each degree of freedom κ , known as *single-particle functions* (spf's). Giving the ansatz eq 7, equations of motion for the expansion coefficients and spf's are derived from the Dirac–Frenkel variational principle, as discussed in refs 27–29. Here we only note that the MCTDH equations of motion are nonlinear and comparatively complicated. However, there are much fewer equations to be solved as compared to the standard method (i.e., expanding the wave function in a time-independent product basis set). This is because the number of spf's, n_{κ} , is in general considerably smaller than the number, N_{κ} , of primitive basis functions or grid points needed to represent the spf $\varphi^{(\kappa)}$.

The MCTDH algorithm can be very efficient when treating large systems. This is demonstrated by recent calculations of the absorption spectrum of pyrazine^{30,31} where a 24-dimensional wave packet was propagated on two coupled potential energy surfaces.

Returning to the MCTDH ansatz (eq 7) we note that the spf's need not be one-dimensional but may depend on several coordinates.^{27,31,41} In the present investigation, the two degrees of freedom θ and K are combined and are represented by a single set of spf's. For the three-particle scattering problem under discussion the MCTDH wave function thus reads

$$\Psi^{JK}(R, r, \theta) = \sum_{j_1 j_2 j_3} A_{j_1 j_2 j_3}^J(t) \varphi_{j_1}^{(1)}(R, t) \varphi_{j_2}^{(2)}(r, t) \varphi_{j_3}^{(3)}(\theta, K, t) \quad (8)$$

where the variable K takes, of course, only integer values.

For an efficient implementation of the MCTDH algorithm, it is necessary for the system Hamiltonian to be given in product form, i.e., the Hamiltonian must be represented as a linear combination of products of one-dimensional operators^{27,29}

$$H = \sum_{r=1}^s c_r \prod_{\kappa=1}^f h_r^{(\kappa)} \quad (9)$$

This treatment allows us to write the Hamiltonian matrix elements and mean fields, which determine the time evolution according to the MCTDH equations of motion, as sums of products of one-dimensional integrals.

The kinetic energy operator which we use is, as is usually the case, of the required product form. However, the interaction potential, for which we adopted the Liu–Siegbahn–Truhlar–Horowitz (LSTH) potential energy surface of H₃ in its lowest electronic state,^{42–44} does not possess a product form. We thus generated an accurate fit to V_{LSTH} using the algorithm described

in refs 27,45,46. The potential then assumes the form

$$V(R,r,\theta) = \sum_{i=1}^{m_r} \sum_{j=1}^{m_\theta} D_{ij}(R) v_i^{(2)}(r) v_j^{(3)}(\theta) \quad (10)$$

where $D, v^{(2)}$ and $v^{(3)}$ are given numerically, i.e., they are defined only on the grid points.

2.3. Initial State. The initial state is taken as a single Hartree product of a Gaussian wave packet in R , a vibrational eigenfunction in r , and a rotational eigenfunction in θ ; i.e.,

$$A_{j_0 v_0}^J(t=0) = \delta_{j_1 1} \delta_{j_2 2} \delta_{j_3 3} \quad (11)$$

$$\begin{aligned} \varphi_1^{(1)}(R, t=0) &\equiv \chi_0(R) = \\ &(\sqrt{2\pi}d_R)^{-1/2} \exp\left[-\left(\frac{R-R_0}{2d_R}\right)^2\right] e^{-ip_0(R-R_0)} \end{aligned} \quad (12)$$

$$\varphi_1^{(2)}(r, t=0) \equiv \varphi_{j_0 v_0}(r) = \text{vibrational eigenfunction} \quad (13)$$

$$\varphi_1^{(3)}(\theta, K, t=0) = \sqrt{\frac{2j_0+1}{2} \frac{(j_0-m_0)!}{(j_0+m_0)!}} P_{j_0}^{m_0}(\cos \theta) \delta_{K, m_0} \quad (14)$$

where j_0, m_0, v_0 are the initial ro-vibrational quantum numbers of the free diatom. P_j^m denotes the associated Legendre function, and δ is the Kronecker symbol. The parameter R_0 should be chosen such that the initial wave function is placed outside the range of the potential. However, the initial wave function may be put much closer to the scattering center if a correction is made on the wave function and its energy distribution ΔE (see below) such as to account for the influence of the tail of the potential. We have used here the so-called *adiabatic correction* scheme which is discussed in detail in refs 27,47.

The momentum p_0 and the width d_R determine the energy distribution $\Delta(E)$ of the initial wave packet. We have previously determined this energy distribution by evaluating the distorted wave $\tilde{\chi}_E(R)$, which will be defined below, by the Wentzel–Kramers–Brillouin (WKB) approximation. We now prefer to generate this function numerically using the Numerov method⁴⁸ since this is very easily done.

The energy distribution of the initial state is defined as

$$\Delta(E) = \langle \tilde{\chi}_E | \chi_0 \rangle \quad (15)$$

where $\tilde{\chi}_E(R)$ is the Jost-solution⁴⁹ of the vibrational adiabatic Hamiltonian, i.e.,

$$\left(-\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} + V_{j_0 m_0 v_0}^{J, ad}(R) - E\right) \tilde{\chi}_E(R) = 0 \quad (16)$$

subject to the boundary condition

$$\tilde{\chi}_E(R) \xrightarrow{R \rightarrow \infty} \sqrt{\frac{\mu_R}{2\pi k_{j_0 v_0}}} \exp(-ik_{j_0 v_0} R) \quad (17)$$

with

$$k_{j_0 v_0} = \sqrt{2\mu_R(E - E_{j_0 v_0})} \quad (18)$$

The vibrationally adiabatic potential $V_{j_0 m_0 v_0}^{J, ad}$ is defined by eq 17

of ref 33 (see also refs 27,47). E denotes the total energy and $E_{j_0 v_0}$ the energy of the diatom in its $(j_0 v_0)$ ro-vibrational state.

2.4. Analysis of Reactive Flux; Cross Sections. The initial-state-selected reaction probabilities, $P_{j_0 m_0 v_0}^J(E)$, are determined by analyzing the reactive flux into the arrangement channel of the products. This was achieved by employing a recently developed combined flux operator/complex absorbing potential approach.^{27,50} In reactive scattering complex absorbing potentials (CAP's) have been used for the first time by Neuhauser and Baer,⁵¹ and Seideman and Miller⁵² have related the cumulative reaction probability to a trace over the CAP times a Green's function.

In the present work the CAP, $-iW$, is defined as a sum of two one-dimensional potentials

$$W(R,r) = W_R(R) + W_r(r) \quad (19)$$

with the generic form of the arrangement CAPs given by

$$W_Q(Q) \equiv \eta_Q h(Q - Q_C)(Q - Q_C)^{\beta_Q} \quad (20)$$

where h denotes the Heaviside step function, Q_C is the point at which the CAP starts, η_Q is a strength parameter, and β_Q denotes the order of the monomial CAP.

The initial-state-selected reaction probabilities are then related to the interaction of the time evolved wave packet $\Psi^J(t)$ with the product arrangement channel CAP, W_r . The working equation reads⁵⁰

$$P_{j_0 m_0 v_0}^J(E) = \frac{2}{\pi |\Delta(E)|^2} \text{Re} \int_0^\infty g_{j_0 m_0 v_0}^J(\tau) e^{iE\tau} d\tau \quad (21)$$

where Re denotes the “real part of”, and where

$$g_{j_0 m_0 v_0}^J(\tau) = \int_0^\infty \langle \Psi^J(t) | W_r | \Psi^J(t + \tau) \rangle dt \quad (22)$$

The energy distribution $\Delta(E)$ (see eq 15) of the initial wave packet determines the energy range, for which all cumulative reaction probabilities can be computed by a single propagation.

Having computed the reaction probabilities $P_{j_0 m_0 v_0}^J(E)$, the reaction cross sections can readily be determined

$$\sigma_{j_0 m_0 v_0}(E) = \frac{\pi}{k_{j_0 v_0}^2} \frac{2J+1}{2j_0+1} P_{j_0 m_0 v_0}^J(E) \quad (23)$$

$$\sigma_{j_0 m_0 v_0}(E) = \sum_{J=m_0}^{J_{\max}} \sigma_{j_0 m_0 v_0}^J(E) \quad (24)$$

$$\sigma_{j_0 v_0}(E) = \sum_{m_0=-j_0}^{j_0} \sigma_{j_0 m_0 v_0}(E) \quad (25)$$

where $k_{j_0 v_0}$ is given by eq 18.

The rotationally temperature-averaged reaction cross sections shown in Section 3 are computed similarly as discussed in refs 33,53.

2.5. Numerical Details. The numerical parameters for the reactive scattering calculation discussed here are chosen in a fashion similar to that of our previous calculation on the H + D₂ system,³³ where the CS approximation had been adopted. Here, only some additional parameters are to be mentioned. The number of spf's for the combined rotational degrees of freedom (θ, K) , n_3 , depends on the total J quantum number. To achieve convergence we varied the number of spf's between 12 ($J=0$)

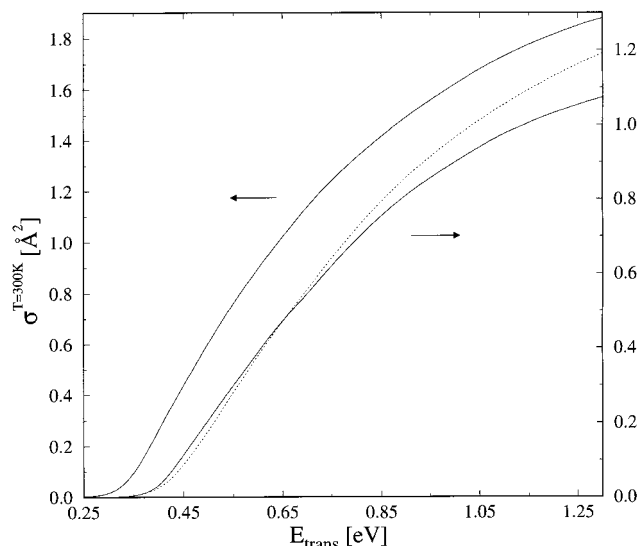


Figure 1. Thermally averaged reaction cross sections. The solid lines represent present MCTDH exact calculations, where the lower curve (scale on the right) is for $\text{H} + \text{D}_2(v_0 = 0)$ and the upper (scale on the left) for the $\text{D} + \text{H}_2(v_0 = 0)$ reaction. The dashed line represents the MCTDH CS calculation for the $\text{H} + \text{D}_2(v_0 = 0)$ reaction taken from ref 33. All cross sections are rotationally averaged over the $T = 300$ K Boltzmann distribution.

and 32 ($J = 12-14$). For $J > 14$ it was decreased with increasing J , arriving at 21 spf's for $J = 30$. The length of the K grid depends on J as well. The whole allowed K range, i.e., $[-J, J]$ is necessary for small J 's (up to $J = 10$). For the values $J > 10$ a reduced range $[-10, 10]$ was sufficient. The number of grid points for the angular θ degree of freedom is reduced from 31³³ to 23. The values of η_Q is 0.001 and $\eta_Q = 3$ for $Q = R$ or r . The number of spf's for the R and r degrees of freedom, n_R and n_r , are 18 and 16, respectively.

The initial momentum p_0 , and width d_R of the Gaussian wave packet χ_0 (eq 12) were chosen in accordance with the desired initial energy distribution $\Delta(E)$ (eq 15). For energies up to 1.3 eV the values $p_0 = -7.0(-7.9)$ and $d_R = 0.24(0.21)$ for the $\text{H} + \text{D}_2$ ($\text{D} + \text{H}_2$) have been chosen. The number of natural potentials was $m_r = 12$ and $m_\theta = 9$ for the product representation of the LSTH potential energy surface (see eq 10).

Each single propagation is specified by a set of initial quantum numbers (j_0, m_0, J) . Total angular momentum values up to $J_{\text{max}} = 30$ were necessary to obtain converged results in the energy range under investigation (up to 1.3 eV). Hence 445 independent wave packet propagations were performed for each system. The computational cost for a single calculation varies between 30 min ($J = 0$) and 3 h ($J = 12-14$) CPU-time on a Dec-alpha 21264 AXP-500 MHz processor.

We believe that the cross sections computed are correct to 1% or at most 2% for collision energies below 1.2 eV. At higher energies the accuracy gradually deteriorates because the initial energy distribution $\Delta(E)$ becomes small.

3. Results and Discussion

3.1. $\text{H} + \text{D}_2(v_0 = 0) \rightarrow \text{HD} + \text{D}$ Reaction. In Figure 1 the rotationally averaged ($T = 300$ K) reaction cross sections are depicted as a function of the collision energy. The two lower curves, corresponding to the scale of the right of the figure, show the results for the $\text{H} + \text{D}_2(v_0 = 0)$ reaction obtained by the present (solid line) and the former CS³³ (dotted line) MCTDH calculations. For low translational energies (up to 0.7 eV) the CS results are in a quite good agreement with the exact

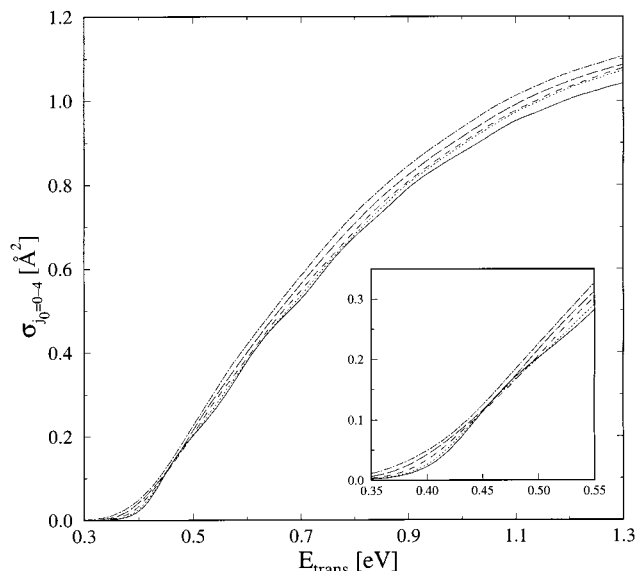


Figure 2. Initial-state-selected cross sections, $\sigma_{j_0 v_0}$, for the $\text{H} + \text{D}_2(v_0 = 0)$ reaction as a function of translational energy ($j_0 = 0$: solid line, $j_0 = 1$: dotted line, $j_0 = 2$: dashed line, $j_0 = 3$: long-dashed line, $j_0 = 4$: dot-dashed line). The insert displays the $\sigma_{j_0 v_0}$ near the first transition state resonance.

ones. Considerable differences occur at higher energies. The CS cross section is larger than the exact one, and the difference increases with increasing collision energy. A detailed analysis of the partial cross sections, $\sigma_{j_0 m_0 v_0, J}(E)$, given by eq 23, shows that the difference in the cross sections for the CS vs exact calculations is due to the partial cross sections corresponding to high values of the J quantum number. The higher the J value is, the more significant the role of the K -coupling appears to be, and therefore the more pronounced are the differences between the two calculations.

Figure 2 shows the initial-state-selected integral cross sections, $\sigma_{j_0 v_0}(E)$, for the $\text{H} + \text{D}_2(v_0, j_0) \rightarrow \text{D} + \text{HD}$ reaction for $v_0 = 0$ and $j_0 = 0, \dots, 4$ as a function of translational energy. One may infer from the figure that the rotational excitations slightly increase the reaction cross section. This result is in agreement with QCT and QM calculations.^{22,23,26} The opposite effect has been found in our previous CS calculations³³ for the energy range from post-threshold up to ca. 0.95 eV. This indicates that the CS approximation becomes less reliable the more detailed the information is.

Let us consider this problem in detail. Using the CS approximation the magnetic quantum number K remains unchanged during the reaction. Using the exact kinetic energy, K changes and may be characterized by its average value $K_0(t)$ and width $\Delta K(t)$ as a function of the propagation time. For the calculations with an initial $K_0 \equiv m_0 > 0$ value the functions $K_0(t)$ show a general tendency to decrease during the reaction time, where the rate of decrease increases with increasing total J quantum number. As the transition state is linear for the $\text{H} + \text{D}_2$ system, the reactivity for $K = 0$ is larger than for $K \neq 0$. One thus may conclude that the CS approximation will overestimate the reactivity of the $m_0 = 0$ channels, but underestimate the reactivity of the $m_0 > 0$ channels. Because the role of the $m_0 > 0$ channels for the given j_0 increases with growing j_0 , the overestimation of the CS approximation in the total $\sigma_{j_0 v_0}$ cross section for small j_0 's gradually turns into an underestimation for large j_0 's. In the case of the present reaction it leads to the observed re-ordering of the $\sigma_{j_0 v_0}$ cross sections with j_0 . The fact that the CS approximation cannot account for

TABLE 1: Comparison of MCTDH and QM Exact Integral Cross Sections for the H + D₂($\nu_0 = 0$) → HD + D Reaction Using the LSTH Potential Energy Surface

E_{tr} (eV)	j_0	MCTDH ^a	other
0.52515	2	0.256	0.260 ^d
0.53100	0	0.250	0.254 ^b
0.54000	0	0.264	0.261 ^c
0.54000	1	0.273	0.271 ^c , 0.274 ^d
0.54000	2	0.285	0.282 ^c
0.54736	0	0.277	0.277 ^d
0.55000	0	0.282	0.284 ^d , 0.280 ^e
1.30000	0	1.041	1.060 ^e

^a Present work. ^b Ref 54. ^c Ref 26. ^d Ref 55. ^e Ref 10.

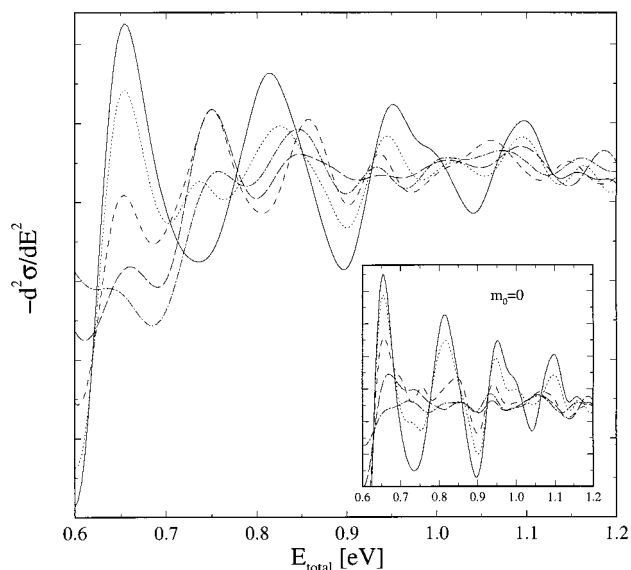


Figure 3. Second derivatives of the initial-state-selected cross sections, $-d^2\sigma_{j_0\nu_0}/dE^2$, for the H + D₂($\nu_0 = 0$) reaction as a function of total energy ($j_0 = 0$: solid line, $j_0 = 1$: dotted line, $j_0 = 2$: dashed line, $j_0 = 3$: long-dashed line, $j_0 = 4$: dot-dashed line). The insert displays second derivatives of $\sigma_{j_0m_0\nu_0}$, with $m_0 = 0$. The total energy is measured with respect to the bottom of the D₂-potential energy curve. The internal energies $E_{j_0\nu_0}$ are, e.g., $E_{00} = 0.1915$ eV and $E_{40} = 0.2651$ eV.

the initial rotational effect on the reactivity indicates once more the important role of the K -coupling.

Table 1 compares the present MCTDH results with exact QM calculations of initial-state-selected integral cross sections for the H + D₂($\nu_0 = 0$) → HD + D reaction taken from the literature.^{10,26,54,55} The comparison gives an excellent agreement of the MCTDH results with the literature values.

Besides the initial rotational effect, the presence of weak transition state resonances can be observed in Figure 2. The resonance structure is most pronounced for the $j_0 = 0$ case and disappears with increasing j_0 . The insert in Figure 2 shows the cross sections near the first transition state resonance. The $j_0 = 0$ cross section is here larger than the $j_0 = 1, 2, 3$ ones.

The resonances appear more clearly in Figure 3, where the second derivatives of the cross sections for $j_0 = 0, \dots, 4$ are displayed as a function of the total energy. As we already mentioned, the resonances are clearly visible for $j_0 = 0$ but almost disappear for $j_0 = 4$. A detailed analysis of the cross sections $\sigma_{j_0m_0\nu_0}$ yields the resonances at approximately the same values of the total energy for the same values of the m_0 quantum number. For example, the cross sections $\sigma_{j_0m_0\nu_0}$ for $m_0 = 0$ and $j_0 = 1, \dots, 4$ are shown in the insert in Figure 3. Similarly we can find that the second resonance in cross sections $\sigma_{j_0m_0\nu_0}$ for $j_0 \geq 1$ in Figure 3 at $E_{tot} \approx 0.75$ eV is associated with the $m_0 = 1$ cross sections. We should mention that no such resonances

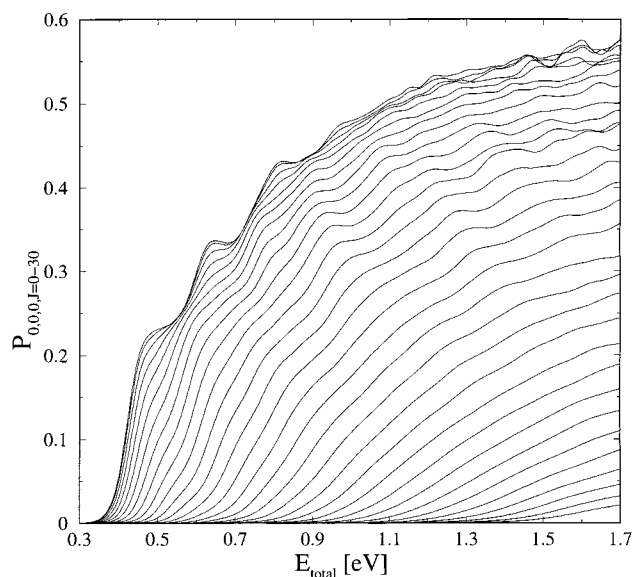


Figure 4. H + D₂ reaction probabilities, $P_{j_0m_0\nu_0}^J$, for the $j_0 = 0$, $m_0 = 0$, $\nu_0 = 0$, and $J = 0, \dots, 30$ as a function of total energy. The uppermost curve corresponds to $J = 0$, and the lower curves to $J = 1, 2, \dots, 30$, respectively.

have been detected when applying the CS approximation, neither for the total cross sections $\sigma_{j_0\nu_0}$ nor for the cross sections $\sigma_{j_0m_0\nu_0}$. Resonances do occur for particular ($j_0m_0\nu_0J$) channels, but they are shifted with increasing J quantum number and are washed out by the summation over J . The quenching of all resonance structures in the total reaction cross section is discussed in detail in ref 56. However, as shown in Figures 2 and 3, a small signature of the resonance remains visible in the H + D₂ total reaction cross section. The behavior of the exact partial cross sections, $\sigma_{j_0m_0\nu_0J}$, shows that only the resonances corresponding to small J contribute to the resonance structure of the cross sections $\sigma_{j_0m_0\nu_0}$. With further increasing J the resonances become less visible, are shifted, and are washed out by the summation. The two first points can be observed from Figure 4, where the reaction probabilities $P_{j_0m_0\nu_0}^J(E)$ for (j_0, m_0, ν_0) = (0,0,0) and $J = 0, \dots, 30$ are depicted.

To understand the nature of the transition state resonances appearing in our cross sections we analyzed the resonances of the single partial cross section corresponding to the channel defined by (j_0, m_0, J) = (0,0,0) quantum numbers. This cross section is depicted in Figure 5 (solid line). In the same figure filled circles represent the resonance positions and the “error bars” give the corresponding widths of the ground state and the first and second excited states of the bending vibrational motion of the HD₂ triatom ($J = 0$). The triangles correspond to the first and second excited states of the symmetric stretch motion of the triatom. The resonances have been calculated using the *filter diagonalization* scheme,^{57–59} in conjunction with the MCTDH method for the propagation of the initial wave function of the relevant states. Similar calculations of resonances of the H + H₂ system have been discussed in refs 60,61. One may infer from Figure 5 that the resonances in the cross section curve presumably correspond to the bending motion rather than to the other modes. For a fixed total J quantum number the resonances appear (to a very good approximation) at the same values of the total energy when considering cross sections for different j_0 but identical m_0 . However, the resonance positions are shifted with respect to each other for different m_0 . The resonance structures are weakened for $j_0 > 0$. This can be

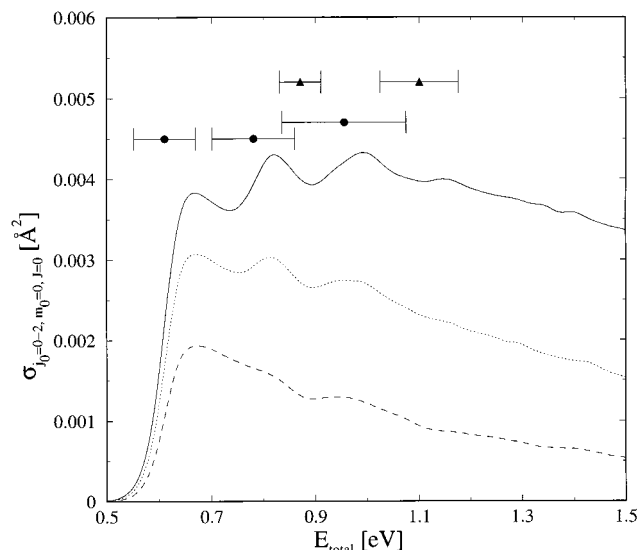


Figure 5. Partial cross section $\sigma_{j_0 m_0 v_0 J}$ for $m_0 = 0$, $v_0 = 0$, $J = 0$, and $j_0 = 0$ (solid line), $j_0 = 1$ (dotted line), and $j_0 = 2$ (dashed line) as a function of total energy. Also shown are the transition state resonance energies for bending vibrational motion (circles) and symmetric stretch motion (triangles) for $J = 0$. The corresponding resonance widths are indicated by "error bars".

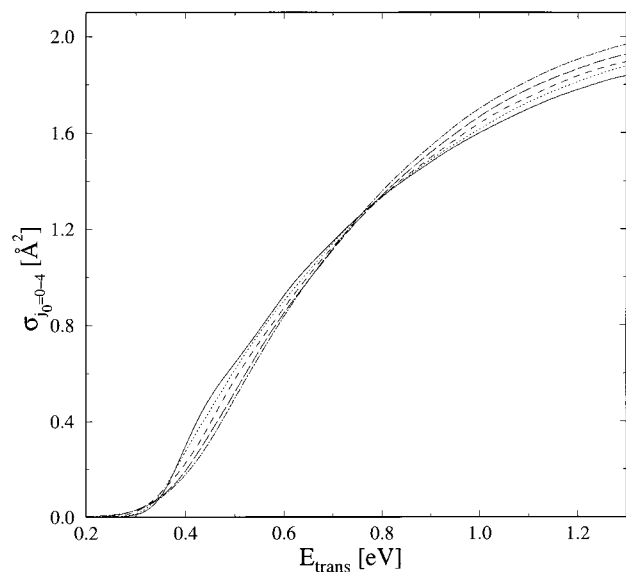


Figure 6. Initial-state-selected integral cross sections, $\sigma_{j_0 v_0}$, for the $D + H_2(v_0 = 0)$ reaction as a function of translational energy ($j_0 = 0$: solid line, $j_0 = 1$: dotted line, $j_0 = 2$: dashed line, $j_0 = 3$: long-dashed line, $j_0 = 4$: dot-dashed line).

observed from Figure 5, where the partial cross sections for the channels defined by $m_0 = 0$, $J = 0$ and $j_0 = 0, 1, 2$ are shown.

3.2. $D + H_2(v_0 = 0) \rightarrow DH + H$ Reaction. The upper curve (scale on the left) of Figure 1 displays the rotationally averaged ($T = 300$ K) reaction cross sections for the $D + H_2(v_0 = 0) \rightarrow DH + H$ reaction as a function of translational energy. Due to the higher zero-point energy of the H_2 vibration, the threshold is lowered as compared to the $H + D_2$ system.

Figure 6 shows the initial-state-selected integral cross sections for $v_0 = 0$ and $j_0 = 0, \dots, 4$ from the threshold up to $E_{trans} = 1.3$ eV. One may infer from Figure 6 a mixed effect of the rotational excitations on the reactivity. For translational energies between 0.35 and 0.77 eV an initial H_2 rotation decreases the reactivity but for other energies it increases the reactivity. This result was also found by QCT calculations reported by Aoiz et al.,²⁰ where

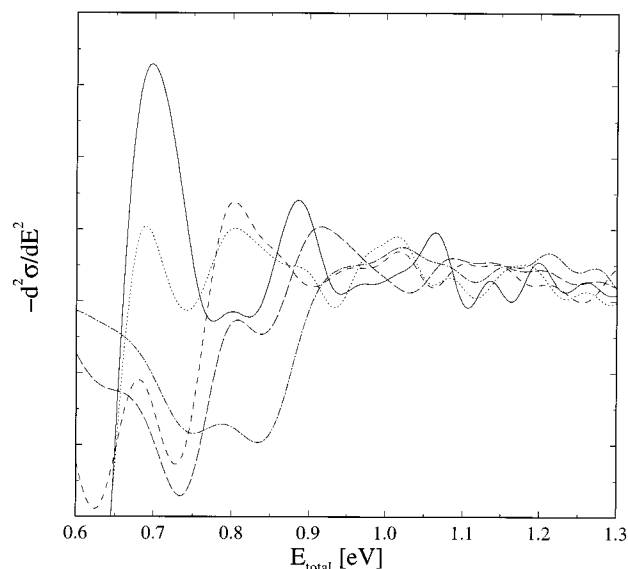


Figure 7. Second derivatives of the initial-state-selected cross sections, $-d^2 \sigma_{j_0 v_0} / dE^2$ for the $D + H_2(v_0 = 0)$ reaction as a function of total energy ($j_0 = 0$: solid line, $j_0 = 1$: dotted line, $j_0 = 2$: dashed line, $j_0 = 3$: long-dashed line, $j_0 = 4$: dot-dashed line). The total energy is measured with respect to the bottom of the H_2 potential energy curve. The internal energies $E_{j_0 v_0}$ are, e.g., $E_{00} = 0.27$ eV and $E_{40} = 0.415$ eV.

the quasiclassical cross sections for $j = 0, 3, 5, 7$ were presented (see also refs 21, 23). The crossing of the $j = 0$ and $j = 3$ cross section curves at approximately 0.8 eV collision energy, which was found by Aoiz et al., is also in a good agreement with our results. However the QCT calculations did not show the behavior of the effect of the rotation on the reactivity at the energies near the threshold.

The traces of transition state resonances which we found in the $H + D_2$ reaction are seen here again, but even less clearly pronounced. Only the first resonance of the $\sigma_{j_0=0, v_0=0}$ cross section can be clearly recognized. The second derivatives of the rotational cross sections as a function of the total energy are shown in Figure 7. Comparing Figure 7 with Figure 3 one again notes that the resonance structure of the $D + H_2$ system is much weaker than for the $H + D_2$ system.

4. Summary

The influence of the initial rotation on reactivity for the $H + D_2$ and $D + H_2$ systems has been investigated. The QM cumulative initial-state-selected cross sections for the initial quantum numbers $v_0 = 0$ and $j_0 = 0, \dots, 4$ have been calculated employing the MCTDH wave packet propagation scheme. The calculations for the $H + D_2$ system showed that the initial rotation enhances the reactivity of the system, which is in agreement with previous QCT^{22,23} and QM²⁶ calculations. The comparison of the present results with previous CS results, where the opposite effect has been detected, leads to the conclusion that the K -coupling, which is neglected in CS approximation, is responsible for the effect. In the case of the $D + H_2$ system, a negative effect of the initial rotation on the reactivity has been found for translational energies between 0.35 and 0.77 eV. This is also in agreement with the previous QCT¹⁹⁻²³ calculations. Furthermore, an excellent agreement of MCTDH and QM exact calculations is demonstrated.

The signature of transition state resonances has been found in the initial-state-selected total reaction cross sections. The resonances of the $H + D_2$ system are pronounced in the $j_0 = 0$

cross section but are quenched for larger j_0 and disappear for $j_0 = 4$. For the D + H₂ system the presence of these resonances is even less clearly pronounced.

In contrast to the CS results, the resonance structure is not completely washed out by the summation over the total J . Only the partial cross sections corresponding to the small J 's contribute to the final resonance structure. We find that the cross sections for the same initial magnetic quantum number m_0 , $\sigma_{j_0 m_0 \nu_0}$, but different j_0 , show transition state resonance maxima at identical total energies. The location of the maxima differ for different m_0 , in particular for odd and even m_0 . We show that these resonances correspond to the bending motion of the transition state, rather than to the other modes. Despite its very weak appearance, this is, to our knowledge, the first transition state resonance reported for a calculation on the total cross section of the H + H₂ system or its isotopic variants.

The reaction cross sections thermally averaged over rotational states at $T = 300$ K have been computed for both reactive systems under study. For the H + D₂ reactive system at high translational energies, a significant difference has been found between the thermally averaged cross sections calculated using the CS approximation and the present calculation using the exact kinetic energy.

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Appendix

Extended Legendre DVR. In the MCTDH program the operation of Hamiltonian terms on the spf's is accomplished by standard DVR's. For the two-dimensional spf's $\varphi^{(3)}(\theta, K)$, however, a special two-dimensional DVR is needed as there are no (separable) product DVR's that correctly represent the kinetic energy operator \hat{j}^2 (see eq 5). This is because of the singular term $K^2/\sin^2 \theta$. In the following we shall derive the two-dimensional extended Legendre DVR, called "K-Leg-DVR" for brevity. Here we largely follow the work of Corey, Tromp, and Lemoine.^{62,63}

We start by defining the L^2 -normalized associated Legendre functions

$$\tilde{P}_j^K(\theta) = (-1)^K \sqrt{\frac{(2j+1)(j-K)!}{2(j+K)!}} P_j^K(\cos \theta) \quad (26)$$

which will serve as a family of basis sets underlying the K-Leg-DVR.

The effect of the operations \hat{j}^2 and \hat{j}_\pm on these basis functions is well-known:

$$\hat{j}^2 \tilde{P}_j^K = j(j+1) \tilde{P}_j^K \quad (27)$$

$$\hat{j}_\pm \tilde{P}_j^K = \sqrt{j(j+1) - K(K \pm 1)} \tilde{P}_j^{K \pm 1} \quad (28)$$

Corey, Tromp and Lemoine realized that using the grid points θ_α and the weights w_α of the standard Gauss-Legendre quadrature may yield exact results even for quadratures over *associated*

Legendre functions; i.e.,

$$\langle \tilde{P}_j^K | \cos^k \theta | \tilde{P}_{j'}^K \rangle = \sum_{\alpha=1}^N w_\alpha \tilde{P}_j^K(\theta_\alpha) \cos^k \theta_\alpha \tilde{P}_{j'}^K(\theta_\alpha) \quad (29)$$

if $j + j' + k \leq 2N - 1$. Since $j \geq |K|$ there are fewer exact quadratures as for Legendre polynomials (i.e., $K = 0$), but as long as $K < N/2$, say, the above relation is very useful. Note that the grid points θ_α and the weights w_α are most conveniently generated by diagonalizing $\cos \theta$ in the basis set $\{\tilde{P}_j^0\}_{j=0}^{j_{\max}}$, where $j_{\max} = N - 1$.^{27,64}

Next, a set of transformation matrixes relating basis functions and grid points is introduced:

$$U_{j\alpha}^K = w_\alpha^{1/2} \tilde{P}_j^K(\cos \theta_\alpha) \quad (30)$$

The rows of $U_{j\alpha}^K$ are orthonormal as long as $j \leq j_{\max}$. This follows immediately from eq 29. However, if one restricts j to $j \leq j_{\max}$, there are only $j_{\max} + 1 - |K|$ rows but $N = j_{\max} + 1$ columns. To make U^K square and unitary we let j run from $|K|$ to $j_{\max} + |K|$ and successively Schmidt-orthonormalize the rows $j_{\max} + 1, \dots, j_{\max} + |K|$ to the lower ones. This ad hoc procedure is justified as long as the basis set is large enough such that the functions for \tilde{P}_j^K have negligible contributions to the wave function for $j > j_{\max}$.

After having established the family of DVR transformations U^K one now can define the DVR representation of the operators \hat{j}^2 and \hat{j}_\pm :

$$j^2(\alpha, \beta, K) = \sum_{j=|K|}^{|K|+j_{\max}} U_{j\alpha}^K(j+1) U_{j\beta}^K \quad (31)$$

$$j_+(\alpha, \beta, K) = \sum_{j=\max(|K|, |K+1|)}^{\min(|K|, |K+1|)+j_{\max}} U_{j\alpha}^{K+1} \sqrt{j(j+1) - K(K+1)} U_{j\beta}^K \quad (32)$$

$$j_-(\alpha, \beta, K) = j_+(\beta, \alpha, K-1) \quad (33)$$

The effect of the operators \hat{j}^2 and \hat{j}_\pm on $\varphi^{(3)}$ is finally given by

$$(\hat{j}^2 \varphi^{(3)})(\theta_\alpha, K) = \sum_{\beta=1}^N j^2(\alpha, \beta, K) \varphi^{(3)}(\theta_\beta, K) \quad (34)$$

$$(\hat{j}_\pm \varphi^{(3)})(\theta_\alpha, K \pm 1) = \sum_{\beta=1}^N j_\pm(\alpha, \beta, K) \varphi^{(3)}(\theta_\beta, K) \quad (35)$$

The matrix operations above have to be performed for each K out of the K -grid. For diatomic target molecules one may use symmetry to reduce the number of θ -grid points by a factor of 2. This can be accomplished by using only odd or even j 's when expanding $\varphi^{(3)}$ in the set $\{\tilde{P}_j^K\}$.²⁷

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