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Four-center reactions: A quantal model for H_4

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We develop a quantal model for studying four-center reactions, $A_2+B_2\rightarrow 2AB$, and collision induced dissociation $A_2+B_2\rightarrow A+B_2+A$. The method involves using hyperspherical coordinates to describe vibrations of the A_2 and B_2 bonds and a global vibration and rotation of the exchange products. Application to the H_4 system is presented, using a realistic potential energy surface. The reaction goes through a four-center linear transition state located just above the dissociation threshold. In the energy range studied (5–5.5 eV), collision induced dissociation competes with the four-center reaction and is the dominant process. It is found that vibrational energy, originally deposited in one of the diatomic partners, is much more efficient than translational energy in promoting reaction. Vibrational and rotational final distributions show that the products are internally hot. This simple quantal model, yet very demanding computationally, illustrates in detail many features of the H_4 dynamics above the dissociation threshold, and could serve to study other four center reactions with trapezoidal or linear transition states. © 1996 American Institute of Physics. [S0021-9606(96)02821-8]

I. INTRODUCTION

Quantum scattering theory provides the most rigorous description of the nuclear dynamics in chemical reactions. Since the first converged calculation of cross sections for the H_3 system,¹ in the last 20 years there has been a remarkable progress in applying the quantum theory to reactions in triatomic systems.² Recently, great interest has been addressed to reactions involving four atoms. Starting with studies on the $H_2+CN\rightarrow H+HCN$ reaction in collinear geometry,³ many articles have subsequently appeared where the $AB+CD\rightleftharpoons ABC+D$ reaction is studied with many different quantal methods.⁴ Nowadays it is becoming possible to perform exact quantum calculations for the simplest exchange reactions of this type.^{5–7} Many of these studies have shown the importance of quantum effects on rate constants and cross sections. A special kind of four-atom reaction, namely, the four-center (4C) reactions,

often appear in a variety of gas-phase processes and have been widely studied in the past both experimentally and theoretically.⁸ One of the main characteristics of 4C reactions is that they usually present very high barriers⁹ (comparable to or higher than a covalent bond energy). Raz and Levine have predicted (within a simple kinematic model) a strong kinematic constraint on the formation of products so that the effective energy threshold (dynamic threshold) for reaction becomes higher than the static barrier on the potential energy surface (energy threshold).¹⁰ Energy requirements and energy disposal in this kind of reaction are interesting

subjects which have been considered by the same authors in a series of recent classical trajectories studies on 4C reactions induced by cluster impact.¹¹

To the best of our knowledge, the dynamics of 4C reactions has not been studied within a quantum framework previously. Most of the dynamical studies have been based on classical or quasiclassical trajectories.^{8,10,11,25} The lack of quantal studies is probably due to a double difficulty appearing in 4C reactions. First, quantum calculations usually become too demanding for reactions with very high barriers because of the large number of states that are populated. The second difficulty arises on the distinct reaction mechanism involved in 4C reactions. Whereas in three-center reactions ($A+BC\rightleftharpoons AB+C$, or $AB+CD\rightleftharpoons ABC+D$) only one bond is broken and formed during the course of the reaction, 4C reactions entail the simultaneous breakage and formation of *two* bonds. Extending quantum scattering theory from the simplest models to the most sophisticated theories for 4C reactions remains a considerable challenge.

In this paper we present a simple quantal model to study 4C reactions. The four atoms are constrained to a plane and form an isosceles trapezium. The method allows the study of reactions of the type $A_2(v_1)+B_2(v_2)\rightarrow 2AB(v,m)$, where v_1 , v_2 , and v are vibrational quantum numbers and m is a rotational quantum number. Because of the restricted geometry, the reaction products necessarily have “concerted” vibrations and rotations. Besides, the collision induced dissociation (CID) process, $A_2(v_1)+B_2(v_2)\rightarrow A+B_2(v'_2)+A$, is investigated within this model. This process is frequently very important at the high energies where 4C reactions take place. Hyperspherical coordinates are used to compute the exchange (4C) and CID reaction probabilities. In the hyperspherical method the double-continuum associated with the CID process is naturally discretized. Since the early developments on hyperspherical methodologies,¹² their ability to describe all the inelastic, exchange and dissociation channels on an equal footing has been acknowledged. Several works

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has been devoted to study the competition between exchange and dissociation processes in collinear triatomic systems, employing hyperspherical coordinates,^{13–15} as well as time-dependent wave packet methods.^{16,17} In this work we investigate such competition but with a different exchange reaction in its nature, the 4C reaction.

The method is applied to the H_4 system. This is an important system in quantum chemistry since it is the simplest test case of four-body interactions. The H_2-H_2 dynamics is also of astrophysical interest, particularly in the study of reactions involving highly excited H_2 molecules, which take place in star forming regions.¹⁸ (Theoretical studies of these reactions are important since the very low densities in the clouds are not reproducible in the laboratory.) Besides, rate constants for reactions involving four H atoms are needed to model hydrogen combustion processes which in turn are relevant in the design of hydrogen containing systems.¹⁹

The mechanism of the 4C (or exchange, indistinctly) reaction in the H_4 system has been a subject of controversy in the past several decades.²⁰ Most of the experiments used the single pulse shock tube technique in order to investigate the kinetics of the $H_2 + D_2 \rightleftharpoons 2HD$ isotopic reaction. From experimental results obtained in the 1960s, a molecular path was proposed with a 4C transition state located well below the dissociation threshold of either reactant.²¹ It was also argued that vibrational excitation of the reactants is much more effective for reactivity than equivalent amounts of translational energy.²² Experiments were not, however, completely conclusive since it was found that low levels of impurities played a rather important role. Hydrogen atoms generated by the impurities would initiate the chain reactions $H + D_2 \rightarrow HD + D$, $D + H_2 \rightarrow HD + H$; hence the percentage of HD arising from the 4C reaction was difficult to ascertain. More recently, Lifshitz and co-workers²³ carried out experiments with an ultraclean shock tube, where the concentration of H atoms could be obtained from Lyman- α absorption. They found that, when no H atoms are detected, no (or $\leq 1\%$) HD products are found. They concluded that the formation of a 4C transition state is highly doubtful, at least below the dissociation threshold of H_2 .

On the theoretical side, there have been several studies of reaction paths on the H_4 potential energy surface (PES).²⁴ Silver and Stevens²⁴ investigated the largest variety of nuclear geometries and found a path on the H_4 PES for the exchange reaction leading from trapezoidal to linear structures for energies just above the dissociation energy of the H_2 molecule. No reaction path requiring less energy than a single H_2 dissociation was found, which is in accordance with the later experiment of Lifshitz *et al.*²³ Brown and Silver carried out quasiclassical trajectory calculations on different London-type and valence-bond surfaces finding that the branching ratios for the inelastic, exchange reaction and dissociative processes are extremely sensitive to the details of the PES.²⁵ Schwenke¹⁹ carried out quasiclassical trajectories calculations on the three-body recombination rates of H_2 in the presence of H_2 , allowing the possibility of the exchange process. Calculated rate constants differ for a factor of 2 with the experimental ones,²⁶ and this difference was

attributed to the neglect of both nonequilibrium and quantum effects and, to a less extent, inaccuracies in the *ab initio* PES. Recently, Boothroyd *et al.*²⁷ calculated 6046 *ab initio* points for the H_4 PES to “chemical accuracy,” obtaining the most accurate PES for a tetraatomic system to date. Later, Aguado *et al.*²⁸ published a global fit to this surface, which satisfies the criteria needed in scattering calculations.

In this work the analytical fit of Aguado *et al.* is used. The general features of this fit are in accordance with the Silver and Stevens’²⁴ reaction path. Note that our dynamical model makes use of that proposed mechanism. (A similar reaction path has been presented very recently from accurate calculations on the H_2I_2 PES.²⁹ The model could also be applied to this reaction.) In view of the accuracy of the H_4 PES (the estimated rms error is of 1–2 kcal/mol), the main restriction for the results reported here to be comparable with experiments is, therefore, that inherent to the approximations used in the dynamical model. We expect, however, that this work will show the main features of the H_4 dynamics at energies above the dissociation threshold.

The paper is organized as follows. Section II describes the coordinate system, the model Hamiltonian and the method used to solve the reactive problem. In Sec. III, details regarding the application to the H_4 system are given. Results on reaction probabilities are reported and discussion is provided in Sec. IV. Finally, Sec. V is devoted to some concluding remarks.

II. THEORY

A. Quantal model

We use Jacobi coordinates for the interaction of two diatomic molecules A_2 and B_2 , which are defined as $\mathbf{r}_1, \mathbf{r}_2$, the vectors joining the atoms of subsystems A_2 and B_2 , respectively, and $\mathbf{R}$, the vector joining the centers of mass of the two diatoms. After separation of the center of mass motion, writing the vectors $\mathbf{r}_1, \mathbf{r}_2$, and $\mathbf{R}$ in spherical coordinates and the wave function as $\Psi' = \Psi/(Rr_1r_2)$, the Schrödinger equation can be written as

$$\left[-\frac{\hbar^2}{2\mu_{A_2}} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_{B_2}} \frac{\partial^2}{\partial r_2^2} - \frac{\hbar^2}{2\mu_{A_2-B_2}} \frac{\partial^2}{\partial R^2} + \frac{j_1^2}{2\mu_{A_2}r_1^2} + \frac{j_2^2}{2\mu_{B_2}r_2^2} + \frac{L^2}{2\mu_{A_2-B_2}R^2} + V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) \right] \Psi = E\Psi, \quad (2)$$

where μ_{A_2} , μ_{B_2} , and $\mu_{A_2-B_2}$, are the reduced masses of A_2 , B_2 , and A_2-B_2 , respectively; V is the interaction potential; E is the collision energy, and $\mathbf{j}_1, \mathbf{j}_2$, and $\mathbf{L}$ are angular momentum operators associated with $\mathbf{r}_1, \mathbf{r}_2$, and $\mathbf{R}$, respectively.

Our model to describe the exchange reaction $A_2 + B_2 \rightarrow 2AB$ (as well as the CID process $A_2 + B_2 \rightarrow A + B_2 + A$) assumes that the tetra-atomic system is constrained to be on a plane and the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ are restricted to be parallel and both perpendicular to $\mathbf{R}$. This geometry is shown in Fig. 1. As suggested by the studies of Silver and Stevens,²⁴ this should be the best three-degrees-of-freedom model for studying the exchange reaction in the

FIG. 1. Geometry and coordinates in the reduced dimension model for the four-center reaction $A_2 + B_2 \rightarrow 2 AB$.

H_4 system. This assumption makes the three angular operators in Eq. (2) to be zero and the interaction potential only dependent on r_1 , r_2 , and R (taking into account that the potential is always evaluated for the restricted geometry shown in Fig. 1). Thus the model Hamiltonian only depends on three Cartesian-type coordinates which are further scaled and transformed to hyperspherical coordinates (ρ, θ, ϕ) ,

$$\begin{aligned} r_1 &= \left[\frac{\mu}{\mu_{A_2}} \right]^{1/2} \rho \sin \theta \cos \phi, \\ r_2 &= \left[\frac{\mu}{\mu_{B_2}} \right]^{1/2} \rho \sin \theta \sin \phi, \\ R &= \left[\frac{\mu}{\mu_{A_2+B_2}} \right]^{1/2} \rho \cos \theta, \end{aligned} \quad (3)$$

where

$$\mu = (\mu_{A_2} \mu_{B_2} \mu_{A_2+B_2})^{1/3} = \left[\frac{m_A^2 m_B^2}{2(m_A + m_B)} \right]^{1/3}, \quad (4)$$

is the total reduced mass of the system. The coordinate ρ is the “hyper-radius” and represents the size of the system. The interaction region corresponds to small values of ρ . When ρ is very large, reactant, exchange product and CID product channels are found localized in well defined regions in the (θ, ϕ) -coordinate space. The Schrödinger equation is now written in these coordinates

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\rho^2} \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) + V(\theta, \phi, \rho) \right] \Phi = E \Phi, \quad (5)$$

with

$$\Phi = \rho \Psi. \quad (6)$$

B. Reactive scattering formulation

To solve the scattering problem given by Eq. (5) we have used the R -matrix propagation method of Stechel, Walker, and Light.³⁰ In this method, the configuration space

is divided in N_{sect} sectors in the coordinate ρ and, within each sector i , the total wave function for initial state n is expanded as

$$\Phi_n(\rho, \theta, \phi; \rho_i) = \sum_{n'=1}^N g_{n,n'}(\rho; \rho_i) \psi_{n'}(\theta, \phi; \rho_i), \quad (7)$$

where N is the total number of channels included in the expansion and $\psi_{n'}$ are eigenfunctions of the so-called surface Hamiltonian,

$$\begin{aligned} H_s(\theta, \phi; \rho_i) &= -\frac{\hbar^2}{2\mu} \left(\frac{1}{\rho_i^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right. \\ &\quad \left. + \frac{1}{\rho_i^2} \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) + V(\theta, \phi; \rho_i). \end{aligned} \quad (8)$$

Beginning in the classically forbidden region, the wave functions $g_{n,n'}(\rho; \rho_i)$ are propagated from one sector to the next, by means of the R -matrix propagation method.³⁰ Once the asymptotic region has been reached, boundary conditions can be imposed in order to obtain the scattering matrix S . We apply approximate boundary conditions as proposed by Römelt,³¹

$$g_{n,n'}(\rho; \rho_i) \rightarrow \delta_{n,n'} \frac{\exp[-i\lambda_{n',i}\rho]}{\sqrt{\lambda_{n',i}}} - S_{n,n',i} \frac{\exp[i\lambda_{n',i}\rho]}{\sqrt{\lambda_{n',i}}}, \quad (9)$$

where

$$\lambda_{n,i}^2 = \frac{2\mu}{\hbar^2} [E - \epsilon_n(\rho_i)], \quad (10)$$

and $\epsilon_n(\rho_i)$ are the eigenvalues of the surface Hamiltonian. These boundary conditions are successively applied for the last N_{last} sectors in the propagation. State-to-state probabilities are defined by the average

$$P(n \rightarrow n') = \frac{1}{N_{\text{last}}} \sum_{i=N_{\text{sect}}-N_{\text{last}}}^{N_{\text{sect}}} |S_{n,n',i}|^2. \quad (11)$$

The need of averaging stems from the well known phenomenon of damped oscillations of the probabilities as functions of the hyper-radius. Provided that the averaging region is large enough, it has been shown³¹ that the calculated reaction probabilities converge to those accurately obtained by transforming to the exact arrangements in Jacobi coordinates.

In this point, it is necessary to assign the asymptotic channels $\{n\}$ to quantum numbers for reactants or products. The procedure followed here is described in the next section, for the specific application to the $H_2 + H_2$ reaction. Particularly for the assignment of 4C product states, a more detailed discussion is given in the Appendix.

C. Solutions of the surface Hamiltonian

Solving the surface Hamiltonian is the crucial part in reactive scattering calculations of this type. At every value of ρ_i , the potential changes very much its shape and powerful methods to diagonalize the Hamiltonian in a flexible and

efficient way are essential. In this work we use the potential optimized discrete variable representation (PO-DVR) of Echave and Clary,³² which is combined with the ray-eigenvector (rev-DVR) procedure of Light and co-workers.³³ The surface Hamiltonian [Eq. (8)] resembles in many aspects that of Bačić *et al.* in their study on the F+H₂ reaction,³⁴ so our implementation of the rev-DVR scheme is close to that of Ref. 34.

The primitive basis set (which is common to all the sectors) is given as a direct product of two DVR basis functions depending on the coordinates ϕ and θ . For the coordinate ϕ , the fixed-node DVR of Muckerman³⁵ is used

$$\chi_k(\phi) = 2 \left[\frac{2}{\pi(M+1)} \right]^{1/2} \sum_{m=1}^M \sin \left(\frac{\pi m k}{M+1} \right) \sin 2m\phi, \quad (12)$$

$$k = 1, \dots, M.$$

On the other hand, DVR functions for the θ coordinate, $[\varphi_j(\cos \theta), j=1, \dots, L+1]$, are obtained from diagonalization of $\cos \theta$ in a basis set of $L+1$ Legendre polynomials.

In the rev-DVR scheme, the surface Hamiltonian at sector i is written as

$$H_s(\theta, \phi; \rho_i) = h_\theta(\theta; \rho_i) + h_\phi(\phi, \theta; \rho_i), \quad (13a)$$

$$h_\theta(\theta; \rho_i) = -\frac{\hbar^2}{2\mu\rho_i^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta}, \quad (13b)$$

$$h_\phi(\phi, \theta; \rho_i) = -\frac{\hbar^2}{2\mu\rho_i^2} \frac{\partial^2}{\sin^2 \theta \partial \phi^2} + V(\theta, \phi; \rho_i). \quad (13c)$$

The procedure is outlined as follows:

- (1) *Calculation of a PO-DVR basis set for the coordinate θ .* First, a one-dimensional reference Hamiltonian is defined

$$h^{\text{ref}}(\theta) = h_\theta(\theta; \rho_i) + V^{\text{ref}}(\theta; \phi_m; \rho_i), \quad (14)$$

where V^{ref} is obtained by finding the value of ϕ , ϕ_m , which gives a minimum in the interaction potential at each value of θ . This reference Hamiltonian is diagonalized in the DVR functions $\{\varphi_j(\cos \theta)\}$, mentioned above. The basis set of eigenstates of the reference Hamiltonian is truncated by the elimination of all those eigenstates whose energies are larger than a conveniently chosen energy cutoff, E_1^{cut} . The new basis size is J_{PO} , with $J_{\text{PO}} < L+1$. The PO-DVR basis set, $\{\varphi_{j_{\text{PO}}}(\cos \theta)\}$, is then obtained by diagonalizing $\cos \theta$ in this new truncated basis.

- (2) *Diagonalization of h_ϕ at every point $\theta_{j_{\text{PO}}}$.* The so-called ray Hamiltonian of Eq. (13c) is diagonalized in the basis given by Eq. (12) at every point $\theta_{j_{\text{PO}}}$, $j_{\text{PO}}=1, \dots, J_{\text{PO}}$. The eigenstates so obtained obey

$$h_\phi(\phi; \theta_{j_{\text{PO}}}, \rho_i) \psi_\nu^{j_{\text{PO}}}(\phi) = \epsilon_\nu^{j_{\text{PO}}} \psi_\nu^{j_{\text{PO}}}(\phi). \quad (15)$$

The superindex j_{PO} indicates that both eigenvalues and eigenfunctions depend parametrically on j_{PO} (for simplicity, dependence on the sector center, i , is not explicitly stated). The new basis set is again truncated, i.e., only functions such that the corresponding $\epsilon_\nu^{j_{\text{PO}}}$ are

smaller than a certain energy cutoff E_2^{cut} will be included in the next step of this procedure. The new basis size is $M_{j_{\text{PO}}}$, which also depends parametrically on j_{PO} .

- (3) *Obtaining the eigenstates of the surface Hamiltonian.* The surface eigenvalues, $\epsilon_n(\rho_i)$, and eigenvectors, $\psi_n(\theta, \phi; \rho_i)$ are finally obtained by diagonalization of the surface Hamiltonian matrix, given in the smaller (adiabatic) basis set

$$\Omega_{j_{\text{PO}}\nu}(\theta, \phi) = \varphi_{j_{\text{PO}}}(\cos \theta) \psi_\nu^{j_{\text{PO}}}(\phi), \quad \begin{cases} \nu = 1, \dots, M_{j_{\text{PO}}}, \\ j_{\text{PO}} = 1, \dots, J_{\text{PO}}; \end{cases} \quad (16)$$

where the total number of basis functions is $I = M_1 + M_2 + \dots + M_{J_{\text{PO}}}$.

To apply the R -matrix propagation method, information is also needed regarding the overlaps between the surface eigenfunctions corresponding to two adjacent sectors i and $i+1$, $O_{n,n'}(i, i+1) = \langle \psi_n(\theta, \phi; \rho_i) | \psi_{n'}(\theta, \phi; \rho_{i+1}) \rangle$. They are computed by using the expansion of the surface states ψ_n and $\psi_{n'}$ on the primitive DVR functions. Since this basis set is common to all the sectors and is orthogonal, overlap matrices are easily obtained, although this is certainly a step quite demanding computationally.

III. APPLICATION TO THE H₄ SYSTEM

A. Interaction potential and assignment of the asymptotic states

We have used the global PES of Aguado *et al.*²⁸ for the adiabatic ground state of the H₄ system which fits *ab initio* data of Boothroyd *et al.*²⁷ The global fit characterizes accurately the asymptotic H₂ and H₃ regions. Regarding the H₂ fragment, its equilibrium distance and dissociation energy are 1.401 a_0 and 4.74 eV, respectively. The saddle point for this fit (taking into account all the six internal degrees of freedom) has been found³⁶ to be linear, with a distance between the two nearest and furthest atoms of 1.413 a_0 and 7.826 a_0 , respectively, and an energy of 4.82 eV (measured from the bottom of the H₂+H₂ potential well). This geometry is very close to that found by Silver and Stevens in their *ab initio* calculations.²⁴

Insight on the reactive process can be gained by plotting the interaction potential at several values of the hyper-radius as a function of θ and ϕ . This is shown in Figs. 2(a)–2(d). Notice that the range for the angle θ is $[0, \pi]$. In other words, the range for the intermolecular coordinate R is $[-\infty, \infty]$, to allow for the “transmission” scattering mode.³⁷ Since the transition state configuration is linear (which corresponds to $R=0$), one diatom approaching this configuration can cross to regions where $R \leq 0$. (In Fig. 1, this would correspond to the diatom B₂ being below A₂.)

The asymptotic region (ρ very large) is illustrated in Fig. 2(a). There are three potential wells, two of them symmetric (for $\theta \rightarrow 0; \pi$) corresponding to the initial arrangement H₂+H₂. The third one, right at the center of Fig. 2(a) ($\theta \rightarrow \pi/2$, $\phi \rightarrow \pi/4$), is ring-shaped and connects with the exchange products. Besides, the region around $\theta \rightarrow \pi/2$ and $\phi \rightarrow 0$ (or $\pi/2$) corresponds with the dissociation channel

FIG. 2. Contour plots of the interaction potential (Ref. 28) as a function of θ and ϕ . (a) For $\rho=13$ a.u. Contours are at intervals of 1 eV, the lowest one being at 1 eV; shaded areas are for regions where $V \leq 1$ eV. (b) Same as (a), for $\rho=7$ a.u. (c) Same as (a), for $\rho=6$ a.u. (d) For $\rho=3.5$ a.u. Contours are at intervals of 1 eV, the lowest one being at 3 eV; shaded areas are for regions where $V \leq 3$ eV. The zero of energy corresponds to the bottom of the H_2+H_2 valley.

($\text{H}+\text{H}_2+\text{H}$). Assignment of the surface states in the asymptotic region has been performed as follows. First, the surface states having the largest probability density in the regions where $\theta \leq 25^\circ$ or $\geq 155^\circ$ correspond to reactants. We have checked that those states localized in any of these regions have energies corresponding to the energy $E_{v_1} + E_{v_2}$ of the diatoms $\text{H}_2(v_1)+\text{H}_2(v_2)$. Thus, reactant states are easily assigned by comparing the eigenvalues of the surface Hamiltonian with the vibrational levels of two separate H_2 molecules. On the other hand, dissociative states were identified as those having their largest probability density in the regions defined by $25^\circ \leq \theta \leq 155^\circ$ and $\phi \leq 20^\circ$ or $\geq 70^\circ$. No further analysis was done on this channel. Finally, states localized in the region $25^\circ \leq \theta \leq 155^\circ$ and $20^\circ \leq \phi \leq 70^\circ$ concern the exchange products. A detailed analysis of this channel is presented in the Appendix. It is shown there that these products can be labeled by the quantum numbers (v, m) , corresponding to “concerted” vibrational and rotational motions of the two diatomic products (see also Fig. 7). Assignment for these states is incorporated in the computer program by counting nodes of the surface wave function along the ring and radial directions of the potential well, to obtain the quantum numbers m and v , respectively.

Figure 2(b) shows the interaction potential at $\rho=7$ a.u., near the transition state region [to be precise, hyperspherical

coordinates for the saddle point are $(\rho, \theta, \phi) = (7.085 \text{ a.u.}, 90^\circ, 79.77^\circ)$]. In view of Fig. 2(b), the saddle point is located in the region correlating with the $\text{H}+\text{H}_2+\text{H}$ channel. In Fig. 2(c), for $\rho=6$ a.u., it can be seen that the barrier between exchange and dissociation wells (near the linear configuration) has been removed. Still, the reactants and products wells remain well separated at this value of the hyper-radius. The situation is basically the same at $\rho=3.5$ a.u. [Fig. 2(d)] although it is foreseen that at more compact conformations both types of wells will eventually join. In anticipation of the dynamics results, it appears that (at energies near the dissociation threshold of H_2) the reaction path has to go necessarily through a linear complex with a near dissociated molecule which undergoes later (for a smaller ρ) bond exchange to finally yield the desired products. At much higher energies, at which more compact configurations can be reached, reaction might rather proceed in a more direct way. These paths are qualitatively in agreement with those pointed out in Ref. 24.

B. Symmetries

The present model accounts for two symmetry operations which are well illustrated in Figs. 2. First, the system is symmetric under the operation $P_\theta(\theta) = \pi - \theta$ or, analogously,

TABLE I. Parameters used in the reactive scattering calculations.

Number of sectors, N_{sect}	170
Number of channels, N	400
Initial sector center, ρ_0 (a.u.)	2.7
Sector width, $\Delta\rho$ (a.u.)	0.1
Number of sectors to average Probs., N_{last}	67
Size primitive DVR basis (ϕ), M	250
Size primitive DVR basis (θ), $L+1$	570
First energy cutoff, E_1^{cut} (eV)	$1.5 E_2^{\text{cut}}$
Second energy cutoff, E_2^{cut} (eV)	$279e^{-1.04\rho} + 7.25$

$R \rightarrow -R$; that is, dynamics is independent of the position of the A_2 diatom relative to B_2 . Second, it is also seen in Figs. 2 that there is no change in the system when the operation $P_\phi(\phi) = \pi/2 - \phi$ is performed. This operation is equivalent to exchange of the coordinates r_1 and r_2 , and appears when the four atoms are identical, as is the case of the H_4 system. In the calculations, we have exploited these symmetries by constructing symmetry-adapted DVR functions for the ϕ coordinate as well as the PO-DVR functions for the coordinate θ . The surface Hamiltonian is diagonalised in four separate blocks, where the basis sets are correspondingly even–even, even–odd, odd–even, and odd–odd under the operations P_θ and P_ϕ , respectively. The R -matrix propagation is then performed separately for the four symmetry blocks. After obtaining reaction probabilities for each block, the procedure indicated in Ref. 5 allows combining them in order to get nonsymmetrized reaction probabilities.

In this work we only present results for the *even–even* block. The very large computer time that would be required has prevented us from carrying out the calculations for the other symmetry blocks. In the even–even block, asymptotic reactant states are given by an *even* linear combination of the initial states $H_2(v_1) + H_2(v_2)$ and $H_2(v_2) + H_2(v_1)$, for $v_1, v_2 = 0, 1, \dots$. On the other hand, product states are given by an *even* linear combination of states $2H_2(v, m)$ and $2H_2(v, -m)$ where m is an *even* integer ($m = 0, 2, 4, \dots$) and $v = 0, 1, 2, \dots$. Reaction probabilities should then be labeled as $P^{++}(v_1, v_2 \rightarrow v, \bar{m})$, where $\bar{m} = |m|$. Hereafter we drop the superindex “++” for simplicity.

C. Numerical details

Calculations were carried out on a Cray-J90 computer. The surface-state calculation took about 140 central process unit (cpu) hours and roughly 300 Mb of main store. Overlap matrices (taking up 225 Mb) were stored for further use in the solution of the close-coupling equations. In Table I the parameters used in our calculations (defined in previous sections) are presented. The mass of hydrogen was taken as $m_H = 1.007\,825$ a.m.u. giving a total reduced mass $\mu = 0.634\,890$ a.m.u. As has been done in similar calculations,^{5,34} the energy cutoff E_2^{cut} was varied from sector to sector decreasing exponentially as ρ_i increases, and E_1^{cut} was chosen to be 1.5 times E_2^{cut} at any value of ρ_i . In Table II is shown the performance of the PO-DVR basis as well as the ray-DVR method, for several sectors. The primitive DVR basis set size (for the ++ symmetry block) is $(250/2) \times (570/2) = 35\,625$.

TABLE II. Energy cutoffs and sizes of the PO-DVR basis set (J_{PO}) and the final (truncated) surface Hamiltonian matrix, for different sector centers.

Sector	ρ (a.u.)	E_1^{cut} (eV)	E_2^{cut} (eV)	J_{PO}	I
1	2.7	36.25	24.17	106	504
17	4.3	15.69	10.46	124	763
34	6.0	11.70	7.80	150	1047
51	7.7	11.02	7.34	184	1216
68	9.4	10.90	7.27	222	1291
102	12.8	10.88	7.25	300	1454
136	16.2	10.88	7.25	376	1633
170	19.6	10.88	7.25	450	1791

After the procedure described in Sec. II C is performed, the final surface Hamiltonian matrices to be diagonalized have sizes of about 500–1800. Note how the computational effort increases with ρ_i . This is a typical effect due to the smaller regions that potential wells occupy as ρ_i increases [see Fig. 2(a)]. The use of a PO-DVR basis has been crucial in order to achieve converged results in the asymptotic region at an affordable computational cost.

Many convergence tests were done to gain confidence on the reliability of the results presented in this work. The parameters M , L , E_1^{cut} , E_2^{cut} , $\Delta\rho$, N , and ρ_0 were varied to find that reaction probabilities, at a given value of ρ in the asymptotic region, are essentially accurate. A severe numerical challenge has come from the fact that, at the high collision energies involved in the calculations, the reaction probabilities depend strongly on the value of the hyperradius, as they oscillate with very large amplitudes and periods. This feature has been noted by Nyman and Clary,³⁸ who found that, as the collision energy is increased, the period and amplitudes in the oscillation of reaction cross sections increased as well. The coexistence of a CID process together with the 4C reactions made convergence particularly difficult to achieve, as the adiabats corresponding to the dissociative channel have good asymptotic behaviour only at very large values of ρ . An accurate treatment of CID processes requires averaging of probabilities over a very large grid, as has been pointed out by Kuppermann and co-workers.¹³ In this work, we estimate that the total cumulative probabilities (both 4C and CID) are converged to within 15%, whereas the initial state selected cumulative probabilities usually have an uncertainty much larger, ranging from 20 (for the largest probabilities) to 70% (for the smallest ones). The probabilities would need to be averaged over a much larger asymptotic region in order to achieve a more satisfactory convergence. The difficulty in increasing this averaging region relies on the need of using a much larger primitive DVR basis, which is out of our computational capabilities. Nevertheless, we think that results presented here do show the important trends of exchange and CID processes.

IV. RESULTS AND DISCUSSION

A. Hyperspherical adiabats

A plot of the hyperspherical adiabatic energy levels ($\{\epsilon_n(\rho_i)\}$, as functions of the sector center) is presented in

FIG. 3. Hyperspherical adiabatic energy levels as functions of the hyperradius. A total of 285 adiabatic curves are displayed.

Fig. 3. In this figure, energy is measured from the minimum of the interaction potential for the $\text{H}_2 + \text{H}_2$ channel. As ρ_i becomes large, this diagram shows the ordering of the energy levels of reactants and products. In the lower energy range of that figure and for $\rho \rightarrow \infty$, clustering of the adiabats stand out around 0.25 eV, 0.75 eV, 1.25 eV, etc. These curves correlate with product states $2\text{H}_2(v, \bar{m} = \text{low})$, for $v = 0, 1, 2$, etc. Higher rotational states lie in the midst of states with higher v manifolds. (Recall that, within the dynamical model, the products energy spectra is not realistic, as is discussed in the Appendix.) The reactants ground state ($v_1 = 0, v_2 = 0$) is located at about 0.51 eV, with the correct zero point energy. Above 5 eV it can be noticed a rather high density of states. Most of the curves correspond to discretised continuum states correlating with the dissociation products $\text{H} + \text{H}_2 + \text{H}$. This channel becomes open asymptotically at 5.00 eV, which is exactly the dissociation energy of H_2 (4.74 eV) plus the zero point energy of a bounded H_2 (0.26 eV). Below $E = 5$ eV there are 191 states asymptotically open, 39 of them correlating with reactants. There are many exchange product states because of the proliferation of rotational excitations associated with a given vibrational state. Between 5 and 5.51 eV [where the channel $\text{H} + \text{H}_2(v_2 = 1) + \text{H}$ becomes open], there are 94 additional open channels, most of them correlating with $\text{H} + \text{H}_2(v_2 = 0) + \text{H}$.

In Fig. 3, it can also be seen that most of the adiabatic curves have an exponential-type shape indicating that there is not an intermediate stable complex in the reaction. Only at high energies (from 4.3 eV upwards) some wells are developed (centered around $\rho = 6.5$ a.u.). These wells are associ-

FIG. 4. Total cumulative CID and exchange (4C) reaction probabilities vs collision energy.

ated with a linear configuration of the tetraatomic complex.

B. Reaction probabilities

We report exchange (4C) as well as CID reaction probabilities for total collision energies ranging from values just below the energetic dissociation threshold (5 eV) up to 5.5 eV, where the $\text{H} + \text{H}_2(v_2 = 1) + \text{H}$ channel becomes open. The total cumulative 4C reaction probability

$$N^{4C}(E) = \sum_{v_1, v_2, v, \bar{m}} P(v_1 v_2 \rightarrow v, \bar{m}) \quad (17)$$

and the total cumulative CID probability

$$N^{\text{CID}}(E) = \sum_{v_1, v_2, k} P(v_1 v_2 \rightarrow k) \quad (18)$$

are presented in Fig. 4 as functions of collision energy. In Eq. (18), the index k stands for any discretised dissociative state. Several interesting features emerge from simple inspection at that figure. First, 4C reactivity is clearly noticeable. The CID process, however, appears to be more important than the exchange reaction over the whole energy range studied. 4C reaction might become more competitive at higher energies, as the slope of the exchange cumulative probability suggests. Another aspect regards the dynamic thresholds for the 4C and the CID reactions. On the one hand, the dissociation process readily appears when that channel becomes open (5 eV). In other words, energetic and dynamic energy thresholds coincide for the CID reaction. On the other hand, the 4C reaction shows up later, about 0.2 eV above the CID threshold. Taking into account that the saddle point for this reaction is 0.08 eV above the H_2 bond energy (see Sec. III A), the exchange reaction seems to have a dynamic threshold slightly higher than the energetic one. This is in accordance with Raz and Levine's predictions for the effective energy thresholds in 4C reactions.¹⁰ Tunneling might play a role in this very light system but, in any case, it does not seem sufficiently important so as to lower significantly the threshold for the 4C reaction.

FIG. 5. CID cumulative reaction probabilities vs collision energy for some state selected $\text{H}_2(v_1)+\text{H}_2(v_2)$ reactants, labeled by the initial state (v_1, v_2) .

Cumulative CID probabilities selected on the initial state (v_1, v_2)

$$P_{(v_1, v_2)}^{\text{CID}}(E) = \sum_k P(v_1 v_2 \rightarrow k) \quad (19)$$

are presented in Fig. 5, where only those transitions which contribute significantly to the process are displayed (i.e., cumulative probabilities not reaching 20% at their maximum value are not shown here). The first noticeable result is that only a small group of initial states exhibit reactivity and, for these initial state selected processes, dissociation probabilities are rather high. It should be noted that $v_1=14$ corresponds to the highest vibrational state of H_2 for the interaction potential used in this work. All initial states important for dissociation are of the form $\text{H}_2(v_1=\text{large})+\text{H}_2(v_2=0)$. It is sensible that one of the reactant diatoms is in its ground vibrational state; such states must have a large overlap with states correlating with products $\text{H}+\text{H}_2(v_2=0)+\text{H}$. The reactivity dependence with the initial vibrational states exhibits the effect known as “vibrational enhancement;”^{13,17} dissociation probabilities increase with v_1 . Regarding dependence of the cumulative probabilities with the collision energy, all curves increase quite rapidly up to a maximum value, after which probabilities tend to stabilize or even decrease. The positions of the maxima are shifted towards higher energies as v_1 decreases. Figure 5 also shows that dynamic threshold tends to the energetic one as v_1 increases. This feature was

FIG. 6. Exchange (4C) cumulative reaction probabilities vs collision energy for some state selected $\text{H}_2(v_1)+\text{H}_2(v_2)$ reactants, labeled by the initial state (v_1, v_2) .

found similarly by Sakimoto and Onda¹⁵ in their study of dissociation and reaction dynamics on a model $\text{H}+\text{HD}$ system.

Analogously to Fig. 5, cumulative 4C probabilities,

$$P_{(v_1, v_2)}^{4\text{C}}(E) = \sum_{v, \bar{m}} P(v_1, v_2 \rightarrow v \bar{m}) \quad (20)$$

are displayed in Fig. 6, for the most important transitions from a given (v_1, v_2) initial state. Only cumulative probabilities higher than 5% are shown in this figure. Similarly to the CID process, it is noticed here that just a few states are really reactive, precisely those with $v_1=\text{large}$, $v_2=0$. This finding reinforces the picture that reaction occurs through a transition state where one vibrationally cold diatom is inserted into a near dissociated molecule. Notice that this set of initial states coincide with those yielding important CID (compare Figs. 5 and 6), suggesting that both CID and 4C processes compete in a rather intricate manner. As can be seen in Fig. 6, cumulative 4C probabilities increase smoothly with collision energy. Probabilities are larger for initial states more excited vibrationally (vibrational enhancement), although large differences are not seen for the initial states $v_1=12, 13, 14$. It is also noticed that dynamic thresholds are higher as reactants are colder. Hence, internal excitation of the reactants is more efficient than relative translational energy in promoting reaction.

C. 4C product distributions

Results presented in this section on the product distribution of the exchange reaction should be regarded as qualitative trends for the energy disposal of the products. This is because of the nonrealistic energy spectrum of the products and the difficulties in obtaining converged probabilities state selected in the individual product states. For this reason, we do not report detailed results in this section. Vibrational product distributions

$$P_{(v_1, v_2; v)}^{4C}(E) = \sum_m P(v_1 v_2 \rightarrow v \bar{m}) \quad (21)$$

have been analyzed for the transitions from the most reactive initial states (those whose cumulative probabilities have been shown in Fig. 6). It has been found that all the vibrational distributions are quite similar, with a nearly gaussian shape centered at a rather high vibrational quantum number v . Rotational product distributions, $P(v_1 v_2 \rightarrow v \bar{m})$ have been also studied, for the most probable final vibrational quantum numbers. It was found that such distributions are peaked around very high rotational quantum numbers. As products are more excited vibrationally, the peak of the rotational product distribution shifts towards lower rotational quantum numbers. Thus, the main conclusion for this section is that products are yielded internally hot as the result of the 4C reaction. As a crude average, it can be said that, almost independently of the initial state, about 70% to 80% of the total energy goes to products vibrational motion, 10% to 20% to rotational motion, and only 5% to 10% to products translation.

Before ending this section, it is worthwhile to compare our results with the predictions of the kinematical model of Raz and Levine.¹⁰ Within that model, reactants internal energy is redistributed both to internal and translational energy of the products, but reactants translational energy is entirely transferred to products internal excitation. The “kinematic constraint” in this kind of reaction stems from the difficulty in obtaining the translational energy needed to drive the products apart. Indeed, Raz and Levine argue that product translational energy is only efficiently provided if just *one* of the reactants is excited vibrationally, and not by vibrational excitation of both. The main features of the 4C reaction studied in this work—reactivity is achieved only when one of the diatomic partners is vibrationally excited, products are yielded internally excited, existence of high dynamic thresholds—agree well with the description provided by this model.

V. CONCLUSION

We have developed a quantal model to study the four center reactions, $A_2 + B_2 \rightarrow 2AB$, where the atoms are constrained to have a trapezoidal geometry. Hyperspherical coordinates were used in order to compute reaction probabilities. The method has been applied to the study of the reaction $H_2(v_1) + H_2(v_2) \rightarrow 2H_2(v, m)$, as well as the competitive process $H_2(v_1) + H_2(v_2) \rightarrow H + H_2(v_2) + H$. Symmetry has been exploited for this system of four identical atoms, reducing

the size of the matrices involved in the numerical calculations. The reactive scattering calculations have been very expensive computationally since many states are populated at the high collision energies involved and, in addition, propagation out to very large values of the hyper-radius was necessary in order to obtain a moderate convergence in the cumulative probabilities.

It has been found that the four-center reaction is a non-negligible process occurring in the high-energy $H_2 + H_2$ collision dynamics, although the collision-induced-dissociation process is more important over the energy range studied. The four-center reaction dynamics has been found to be very selective in the reactants initial state. The most reactive initial states are those where one of the diatoms is vibrationally very hot and the other one in its ground vibrational state, suggesting that the reaction goes through a four-center linear transition state where the cold diatom is inserted into the near dissociated one. Four-center reaction and dissociation process appear to be closely related, since both processes exhibit several common features (selectivity on the same initial states, vibrational enhancement, etc.). Products resulting from the four-center reaction are found to be vibrationally and rotationally excited. Most of the results reported here are in agreement with predictions based on inspections of both the *ab initio* PES and kinematical models.

More quantum-mechanical calculations (where some of the approximations applied in this work are removed) are required to test the results reported here. It would also be of interest to compare with quasiclassical trajectories. New quantum formulations in the theory of four center reactions are needed as well, as these reactions are likely to be quite general for polyatomic systems, including organic molecules.^{11,39} Although the model presented here is very simple, it does raise interesting questions and is a useful starting point for the theory of four-center reactions.

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APPENDIX

In this work, we have used hyperspherical coordinates based on Jacobi coordinates which are suitable for reactants and within a restricted geometry. For this reason, the products of the exchange reaction have different quantum number labels to the reactants in the present model. In the upper diagram of Fig. 7 it is shown how the products are described

FIG. 7. (a) Products arrangement for the restricted geometry model. (b) Internal coordinates for the product arrangement.

in the (R, r_1, r_2) coordinates where, asymptotically, $r_1, r_2 \rightarrow \infty$ and $R \rightarrow 0$. It can also be seen that, with this restricted geometry, both diatomic products are restricted to have the same bond length (q) and complementary orientations χ , as is shown in the lower panel of Fig. 7. Thus, the product motion consists of “concerted” vibrations and rotations. In this appendix we map a transformation between the surface coordinates (θ, ϕ) and the coordinates (q, χ) . This enables us to correlate nodal patterns of the surface wave functions to the quantum numbers associated with the coordinates q and χ .

Asymptotically ($\rho \rightarrow \infty$), exchange products are localized in the region $\theta \rightarrow \pi/2$, $\phi \rightarrow \pi/4$ of the (θ, ϕ) -coordinate space [see Fig. 2(a)]. We introduce the new variables (s, φ) ,

$$s^2 = (\theta - \pi/2)^2 + (\phi - \pi/4)^2, \quad (\text{A1a})$$

$$\tan \varphi = -\frac{\theta - \pi/2}{\phi - \pi/4}, \quad (\text{A1b})$$

which represent the “radial” and “ring” motions along the potential well. Assuming that (for $\rho \rightarrow \infty$) $\sin \theta \approx 1$, the surface Hamiltonian [Eq. (8)] can be written in the new coordinates

$$H_s(\rho \rightarrow \infty) \approx -\frac{\hbar^2}{2\mu\rho^2} \left(\frac{1}{s} \frac{\partial}{\partial s} s \frac{\partial}{\partial s} + \frac{1}{s^2} \frac{\partial^2}{\partial \varphi^2} \right) + V(s, \varphi; \rho). \quad (\text{A2})$$

In view of Fig. 7, $q = \sqrt{R^2 + (r_2 - r_1)^2/4}$ and $\cos \chi = (r_2 - r_1)/2q$. On the other hand, s and φ can be obtained as functions of (R, r_1, r_2) by using Eq. (A1) and carrying out suitable expansions in Taylor series (up to the first order) of θ and ϕ as functions of (R, r_1, r_2) . The result is that the set of coordinates (s, φ) and (q, χ) are related by

$$s \approx \left(\frac{2\mu_{\text{H}_2}}{\mu} \right)^{1/2} \frac{q}{\rho}, \quad (\text{A3a})$$

$$\varphi \approx \chi. \quad (\text{A3b})$$

After writing surface eigenfunctions as $\psi = s^{-1/2} f$ and transforming to the new coordinates (q, χ) , the Schrödinger equation for the products can be finally written as

$$\left[-\frac{\hbar^2}{2\mu'} \frac{\partial^2}{\partial q^2} - \frac{\hbar^2}{2\mu' q^2} \frac{\partial^2}{\partial \chi^2} + 2V_{\text{H}_2}(q) - \frac{\hbar^2}{8\mu' q^2} \right] f(q, \chi) = E_{\text{prod}} f(q, \chi), \quad (\text{A4})$$

where

$$\mu' = 2\mu_{\text{H}_2} \quad (\text{A5})$$

and it has been taken into account that $V(q, \chi; \rho \rightarrow \infty) \rightarrow 2V_{\text{H}_2}(q)$. Equation (A4) resembles the rovibrational Schrödinger equation of a diatomic molecule whose reduced mass and interaction potential are twice those of the H_2 molecule. [The term $\hbar^2/(8\mu' q^2)$ is unimportant since $2V_{\text{H}_2}(q)$ is dominant for any value of q .] The rotational constant is half of the H_2 one whereas the vibrational frequency is equal to that of H_2 . Thus, the products states can be assigned to vibrational (v') and rotational (m) quantum numbers which represent “coordinated motions” of two diatomic fragments.

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