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TIME-DEPENDENT WAVE PACKET DYNAMICS OF
 $\text{H}_2 + \text{D}_2$ REACTION

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Abstract

In this work, the initial state selected time-dependent wave packet method has been used to study the $\text{H}_2(v_1 = \text{high}) + \text{D}_2(v_2 = \text{low})$ reaction on two realistic global potential energy surfaces (PESs) - BMKP and ASP within the reduced-dimensional (3D) and full-dimensional (6D) models. The role of both vibrationally excited and rotationally excited reagents was examined by varying the initial vibrational and rotational states. The isotope substitution effects and the accuracy of the centrifugal sudden (CS) approximation were also explored.

Firstly, the 3D calculations within six different restricted geometries (H, X, X', T_I, T_{II} and L) indicated that the orientation of the cold diatom did not greatly affect the reaction processes, while the orientation of the hot diatom had a significant effect. The BMKP surface generally gave lower energy thresholds than the ASP surface, except for the collision induced dissociation (CID) within the T_{II} geometry where the hot diatom comes in head-on perpendicular to the cold diatom. The $\text{H}_2 + \text{D}_2$ reaction was more effective for CID and showed more structured probability curves for single exchange (SE) reaction and three-body complex formation (3BC) than the $\text{H}_2 + \text{H}_2$ reaction.

Secondly, the 6D total reaction probabilities were computed for the three competitive processes (CID, four center (4C) reaction and SE) in $\text{H}_2 + \text{D}_2$ reaction with the total angular momentum $J = 0$. It was shown that the vibrational excitation of the hot diatom gave an enhancement effect on the CID process, while the vibrational excitation of the cold diatom gave an inhibition effect.

The rotational excitation of both reagents had a significant effect on the reaction process. The 4C and SE probabilities were at least one order of magnitude smaller than the CID probabilities over the energy range considered. Isotope substitution effects were studied by substituting the collider D_2 by H_2 and HD . The CID process is most efficient for the $H_2 + D_2$ combination and least efficient for the $H_2 + H_2$ combination, and is different for the 4C and SE processes.

Finally, the 6D integral cross sections for the $H_2 + D_2$ reaction were calculated with and without the CS approximation by including all important K (the projection of the total angular momentum on the body-fixed axis) blocks. The first fully converged coupled-channel (CC) cross sections for different competitive processes from the ground rotational state were presented. We concluded that the CID and SE processes occur in a wide range of J values while the 4C process can only take place in a narrow window of J values. For this reason, the CC cross section for the 4C channel is merely comparable to the SE channel. A comparison of the integral cross sections from CC and CS calculations revealed that the CS approximation works well for the CID process but not for the 4C and SE processes, and the discrepancy between the CC and CS cross sections grows larger as the translational energy and/or the vibrational energy increase(s).

General Introduction

Molecular reaction dynamics has proved to be a central and fruitful field in physical chemistry and chemical physics since its very beginning in the 1950s. It has given crucial support to atmospheric chemistry, interstellar chemistry as well as combustion chemistry, mainly facilitated by the synergy which exists between theory and experiment [1]. The rapid development of reaction dynamics has greatly enhanced our understanding of the nature of elementary bimolecular and unimolecular chemical reactions, and intermolecular and intramolecular energy transfer processes [2, 3].

Many new experimental techniques have been proposed in the last several decades on studying molecular reaction dynamics, which make it possible to compare very detailed experimental observables with exact theoretical calculations on fully ab initio potential energy surfaces (PESs). These new techniques comprise the velocity map imaging setup for photochemistry and chemical reactions, the high resolution highly sensitive H-atom Rydberg tagging time-of-flight apparatus, the Doppler selected “core” mapping setup, the crossed molecular beams technique, the coincident imaging method, and so on. The most powerful one is undoubtedly the crossed molecular beam technique, which allows for the best specification of initial conditions and operates on a very simple principle: two molecular beams containing the reactants are crossed at a chosen angle, reaction takes place at the point of intersections, and products scattered at a particular angle can be detected by a mass spectrometer equipped with an electron-impact ion source. This classical setup can be used to measure the product velocity and the velocity-angle distributions.

In modern improved crossed beam experiments, the mass spectrometer is often replaced with a laser-based detection apparatus. The apparatus could provide product quantum state selectivity and improved sensitivity together with product angular momentum polarization effect [4, 5].

Theoretical dynamics studies, accompanying the development of experimental techniques, have also made tremendous progress during the past several decades, driven by the dramatic increase of computing power and the development of new algorithms. A widely used approach to study molecular reaction dynamics is the quasi-classical trajectory (QCT) method [6], which is computational faster and less demanding than quantum methods. The QCT method integrates the classical equation of motion in some way and the initial conditions are chosen such that the initial internal energy corresponds to a quantum rovibrational state. Although the QCT method has been proved that it could generally provide very accurate results especially in the energy region after the reaction threshold, it has several shortcomings which may be problematic in some case. The absence of quantum tunneling effects, which is expected to be important at energy region near the threshold, and zero-point energy (ZPE) leakage, which may be dominant for a large molecule at thermal energies, can introduce significant errors. There also exist kinds of strategies to deal with them. For the ZPE problem, remedies have traditionally fallen into two categories: “passive” and “active”. Passive methods do not alter the classical trajectories themselves but, instead, re-interpret the results of such trajectories to account for ZPE leakage. Active methods make some modification to the equations of motion in order to assure preservation of ZPE [7, 8, 9].

Quantum effects are considered to be prominent in the region near the energy threshold for light reactive systems in which only a few quantum states are accessible. For these reactive systems, the most accurate and acceptable method of simulating the reaction dynamics is undoubtedly to solve the motion equation from the first principle directly. In this respect, quantum molecular collision theory can be easily applied to the bimolecular chemical reactions in which scattering boundary conditions are suitable for reactants and/or products. Time-independent (TI) and time-dependent (TD) quantum scattering methods have been developed to study elementary chemical reactions [10, 11]. The traditional TI method consists of two different implementations. One uses variational methods that involve an expansion of the wavefunction in

a basis set consisting of rovibrational states of both reagents and products [12]. The other one uses the hyperspherical method in which Jacobi coordinates are transferred to an appropriate set of polar coordinates [13]. Another alternative is to solve TD Schrödinger equation, in which an initial wave packet is prepared in the reagent asymptotic region and then is propagated by applying the time-evolution operator to it. A plot of the wave packet as function of the elapsed time yields an intuitive movie of the reaction dynamics [14, 15, 16, 17, 18].

There are respective advantages and disadvantages for the TD and TI methods. One key advantage of the TD method is that the “movie” obtained by tracing the initial wave packet gives a clear and direct physical picture of the reaction dynamics, while it is difficult to acquire by the TI method. Next, the TD method, being a vector-matrix multiplication scheme, scales better than N^2 , where N is the number of basis functions. However, the TI approach scales as N^3 . Although it is possible to employ iterative method in the TI approach that could lower the scaling to N^2 provided that one can obtain converged results with a relative small number of iteration steps, the convergence property of iteration method actually depends on the specific problem on hand. Furthermore, many of the complex problems are not easily susceptible to standard TI treatments, such as those involve complicated boundary conditions and/or time-dependent Hamiltonians. However, if there exist long-lived resonances in the reaction dynamics, the TD calculation may require the wave packet to be propagated for an unfeasible number of time steps, which makes the TD method prohibitive. The information obtained by one-time calculation is also different for the two methods. The TI method yields the whole S-matrix, and calculations have to be repeated for different collision energies, whereas the TD method yields a single column of the S-matrix over a continuous range of energies [11, 19].

The scaling advantages of the TD method make it possible to perform full-dimensional (6D) TD quantum scattering calculations on four-atom reactions. Since the first benchmark wave packet calculations of the total reaction probabilities for the reaction $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ with the total angular momentum $J = 0$ [20, 21, 22, 23], remarkable progress has been made in the area of accurate quantum-dynamics simulation of four-atom reactions. Nowadays it is capable of providing fully-converged total and/or state-to-state reaction probabilities, integral and

differential cross sections and thermal rate constants for elementary atom-triatom and diatom-diatom reactions by the TD approach [24, 25]. Full-dimensional quantum scattering calculations for polyatomic reactions involving as many as six atoms were also reported in the literature very recently [26, 27, 28, 29, 30, 31, 32].

The collision between two hydrogen molecules is of great interest in astrophysics [33], combustion [34, 35] and spacecraft modeling [36]. Because collisional events between hydrogen molecules are popular in the interstellar clouds where hydrogen molecule is one of the most abundant molecular species and the shock waves can induce internal rovibrational excitation and collisional dissociation [37]. The H_4 system is also an ideal tetra-atomic system in quantum chemistry due to the light masses involved. Extensive high level *ab initio* calculations for the H_4 complex have been performed and thus global PESs with spectral accuracy have been reported [38, 39].

In contrast to the widely studied abstraction process in atom-triatom and diatom-diatom reactions, progress has been slow in the study of $H_2 + H_2$ reaction, in which three different processes will occur in a moderate energy region: collision induced dissociation (CID), four-center (4C) reaction, and single exchange (SE) reaction. It has still been a great challenge to study the $H_2 + H_2$ reaction in a full-dimensional quantum mechanical (QM) frame since one must treat all bonds as reactive ones. The collision energies involved in the reaction process are of order of a covalent bond energy. Therefore, a quite large number of grid points or basis functions must be used to gain well-converged results. In this regard, most theoretical studies have been performed using reduced-dimensional QM and classical or quasi-classical trajectory (QCT) techniques in the past [40, 41, 42, 43, 44, 45, 46, 33, 47, 48, 49, 50, 51, 52, 53]. The important step forward in the accurate simulation of $H_2 + H_2$ reaction was represented by the work of Lu *et al.* [54], who reported firstly fully converged full-dimensional initial state-selected probabilities with the total angular momentum $J = 0$ using the time-dependent wave packet (TDWP) method.

The 4C reactions, being one of the three competitive processes in $H_2 + H_2$ reaction, have many novel dynamical features and thus have been a hot topic in the past several decades [55, 56, 57, 58, 59]. On the one hand, there are simultaneous cleavage and formation of two bonds in 4C reactions, which are quite different from the three-center reactions in which only one old

bond is broken and one new bond is formed. On the other hand, 4C reactions usually have higher reaction barriers than other types of reactions. Raz and Levine [56, 57, 58, 59] have predicted a strong kinematic constraint on the occurring of 4C reactions within a simple kinematic model and have found that the effective energy threshold (dynamic threshold) for reaction is higher than the static barrier on the potential energy surface (energy threshold). The energy requirements and energy disposal in 4C reactions are of key relevance which have also been studied by them using classical trajectory methods. In their simulations, 4C reactions are induced and then are stabilized by cluster impact.

The $\text{H}_2 + \text{H}_2$ reaction and its isotopic variants are at the forefront of 4C collision dynamics. The mechanism of 4C reaction in the H_4 system has also been a subject of controversy for chemists. Thus, in this project, we employed the TDWP method to study the $\text{H}_2(v_1 = \text{high}) + \text{D}_2(v_2 = \text{low})$ reaction and its isotopic variants on two realistic PESs - ASP [38] and BMKP [39] within the reduced-dimensional (3D) and full-dimensional (6D) models. We mainly focus on the following topics: 1) the role of both vibrationally excited and rotationally excited reagents; 2) the isotope substitution effects; 3) the accuracy of the centrifugal sudden (CS) approximation.

The thesis is organized as follows. Chapter 2 briefly reviews the theory and methodology: the Born-Oppenheimer PES, the time-dependent quantum dynamics and its numerical implementations. In Chapter 3, we describe the 3D TDWP calculations and the results are discussed. Chapter 4 presents the 6D quantum dynamics study of $\text{H}_2 + \text{D}_2$ reaction and its isotopic variants with the total angular momentum $J = 0$. The integral cross sections and the accuracy of the CS approximation in $\text{H}_2 + \text{D}_2$ reaction are presented and discussed in Chapter 5. Finally, a brief summary highlights the central results and a prospect introduces the future plan in Chapter 6.

Time-Dependent Quantum Dynamics

Time-dependent wave packets (TDWPs) have been used for quantum scattering calculations since the late 1960s [60]; however, they did not become popular until the late 1980s due to computing limitations [61]. Nowadays the TDWP method has evolved to be a very powerful theoretical tool in simulating molecular reaction dynamics and has been widely used to study reaction mechanism of elementary chemical reactions. In this Chapter, we present a brief review of the basic theory in molecular reaction dynamics: the Born-Oppenheimer potential energy surface (PES) and the TDWP method. Some important numerical techniques, finite basis representation (FBR) and discrete variable representation (DVR), split operator method, Chebyshev method and Lanczos method, and absorbing potential, are also included.

2.1 The Born-Oppenheimer Potential Energy Surface

2.1.1 The Born-Oppenheimer Approximation

The non-relativistic Hamiltonian operator describing the motion of a coupled system consisting of nuclei and electrons can be written as

$$\begin{aligned}\hat{H} &= \sum_i \frac{\hat{P}_i^2}{2M_i} + \sum_j \frac{\hat{p}_j^2}{2m_e} + \sum_{k>i} \frac{Z_k Z_i e^2}{|R_k - R_i|} + \sum_{k>j} \frac{e^2}{|r_k - r_j|} - \sum_{ij} \frac{Z_i e^2}{|R_i - r_j|} \\ &= \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{eN},\end{aligned}\tag{2.1}$$

where $\{r, \hat{p}\}$ represents the electron coordinates and momenta and $\{R, \hat{P}\}$ represents the nuclear coordinates and momenta. Z_i is the charge of i th nucleus. The five terms in Eq. (2.1), which

are symbolized shortly in Eq. (2.2), correspond to nuclear kinetic energy, electron kinetic energy, nuclear-nuclear potential energy, and electron-electron potential energy, and electron-nuclear potential energy, respectively. The time-independent (TI) Schrödinger equation in the full space of electron and nuclear coordinates is expressed as

$$\hat{H}(r, R)\Psi(r, R) = E\Psi(r, R), \quad (2.3)$$

where E and $\Psi(r, R)$ denote the eigenvalue and eigenfunction of the molecular system in the full coordinate space. In order to solve Eq. (2.3), two approximations are generally applied: the adiabatic approximation and the diabatic approximation.

In the adiabatic representation, one fixes all the nuclei in space (R fixed), and then gets the following equation, which describes the motion of electrons,

$$\hat{H}_e\phi_n(r, R) = \epsilon_n(R)\phi_n(r, R), \quad (2.4)$$

where $\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{NN} + \hat{V}_{eN}$. $\phi_n(r, R)$ and $\epsilon_n(R)$ are called adiabatic eigenfunctions and eigenvalues of the electrons at the fixed nuclear coordinates R . Since the adiabatic eigenfunctions $\{\phi_n(r, R)\}$ construct a complete orthonormal basis set, the full wave function $\Psi(r, R)$ in Eq. (2.3) can be expanded in the adiabatic basis as

$$\Psi(r, R) = \sum_n \chi_n(R)\phi_n(r, R), \quad (2.5)$$

where $\chi_n(R)$ is the corresponding nuclear wave function in the adiabatic representation. Substituting Eq. (2.5) into Eq. (2.3) and integrating over the electron coordinates, one can obtain the coupled equations

$$[\hat{T}(R) + \epsilon_m(R)]\chi_m(R) + \sum_n \hat{\Lambda}_{mn}(R)\chi_n(R) = E\chi_m(R). \quad (2.6)$$

Here, $\hat{\Lambda}_{mn}(R)$ is the nonadiabatic coupling matrix operator which accounts for the action of the nuclear kinetic energy operator $\hat{T}(R)$ on the electron wave function $\phi_n(r, R)$ and is given by

$$\hat{\Lambda}_{mn}(R) = -\hbar^2 \sum_i \frac{1}{M_i} \left(A_{mn}^i \frac{\partial}{\partial R_i} + \frac{1}{2} B_{mn}^i \right), \quad (2.7)$$

where the matrices A and B are defined as

$$A_{mn}^i = \left\langle \phi_m \left| \frac{\partial}{\partial R_i} \right| \phi_n \right\rangle = \int \phi_m^* \frac{\partial}{\partial R_i} \phi_n dr, \quad (2.8)$$

$$B_{mn}^i = \left\langle \phi_m \left| \frac{\partial^2}{\partial R_i^2} \right| \phi_n \right\rangle = \int \phi_m^* \frac{\partial^2}{\partial R_i^2} \phi_n dr. \quad (2.9)$$

Solving Eqs. (2.6), one can obtain accurate nuclear wave functions in the adiabatic representation. The nonadiabatic coupling between different adiabatic states given by Eq. (2.7) arises from nonadiabatic transitions. Ideally, one can solve the coupled equations directly. However, it is usually a very difficult task to calculate the nonadiabatic coupling matrix in quantum chemistry. As we know, the nuclear mass is much larger than the electron mass and therefore the nuclei move much slower than the electrons, which makes the nonadiabatic coupling matrices A and B resulting from nuclear motions generally very small. Thus, one can discard the nonadiabatic coupling $\hat{\Lambda}_{mn}(R)$ ($m \neq n$) defined in Eq. (2.7), which is called the “adiabatic approximation”. This is the reason why the adiabatic representation is so powerful.

If one retains just a single term and omits all the nonadiabatic coupling, Eq. (2.5) can be reduced as

$$\Psi(r, R) = \chi_n(R)\phi_n(r, R). \quad (2.10)$$

Substituting Eq. (2.10) into Eq. (2.3) and integrating over the electron coordinates, one can obtain

$$\hat{H}_n^{ad}\chi_n(R) = E\chi_n(R), \quad (2.11)$$

in which the adiabatic Hamiltonian is defined as

$$\hat{H}_n^{ad} = \hat{T}_N + \epsilon_n(R) + \hat{\Lambda}_{nn}(R). \quad (2.12)$$

Since the electronic eigenfunction $\phi_n(r, R)$ has a free phase factor, $e^{if(R)}$, one can specify it so that the electronic eigenfunction is real. In this case, the matrix A in Eq. (2.8) becomes zero and accordingly the diagonal operator $\hat{\Lambda}_{nn}(R)$ does not include differential operators. Generally, the dependence of $B_{nn}(R)$ on nuclear coordinates R is weaker than that of the adiabatic potential $\epsilon_n(R)$. Thus, the term $\hat{\Lambda}_{nn}(R)$ is often omitted in the adiabatic approximation, *viz.*, the “Born-Oppenheimer approximation”, which leads to

$$[\hat{T}_N + \epsilon_n(R)]\chi_n(R) = E\chi_n(R). \quad (2.13)$$

It is clear that in Eq. (2.13) one completely separates the motion of electrons from the motion of nuclei in the adiabatic or Born-Oppenheimer approximation. Thus, as discussed above, one

can firstly solve Eq. (2.4) at a set of fixed geometries to get adiabatic eigenvalues of electrons and then solve Eq. (2.13) with $\epsilon_n(R)$ as a PES of nuclei. The physical meaning of the Born-Oppenheimer approximation is “the slow nuclear motion only leads to the deformation of the electronic states but not to transitions between different electronic states and the electronic wave function deforms instantaneously to adjust to the slow motion of nuclei” [62]. Thus, the Born-Oppenheimer approximation generally works well for the systems in which the slow nuclear motion does not cause transitions between electronic states but only distorts electronic states.

The diabatic representation is not involved in this work and thus interested authors are referred to Ref. [62].

2.1.2 Potential Energy Surface

The Born-Oppenheimer approximation introduces the important concept of the electronic state and of the PES which defines the variation in electronic energy of a particular electronic state with nuclear coordinates.

In order to generate a PES, Eq. (2.4) must be solved at a set of fixed values of nuclear coordinates R . Generally, $3N$ coordinates are needed to completely specify the positions of the N nuclei, in which three coordinates are needed to specify the position of the center of mass of the system and the other $3N - 3$ coordinates account for the internal degrees of freedom, *i.e.* overall orientation and internuclear coordinates. The internuclear coordinates are defined as coordinates that are invariant to overall translation and rotation and can be chosen as, for example, internuclear distances and bond angles. Thus, for a molecule (or complex) with N atomic nuclei, the number of internuclear coordinates required equals $3N - 7$ for a linear molecule or $3N - 6$ for a nonlinear molecule.

There are generally two approaches (direct and nondirect) to study a chemical reaction. The most straightforward one is to carry out “one the fly” (“direct dynamics”) calculations, in which an energy, gradient, and/or Hessian at each sampled configuration must be computed every time from molecular mechanics methods or *ab initio* calculations. For the cases when high-level *ab initio* energies are required and/or polyatomic systems are treated, it is prohibitive due to the high computational cost. The other alternative is to construct a global PES that can provide

potential energy for any given geometry of the system. In this regard, three basic approaches have been implemented: interpolation, fitting and analytical. The classification is arbitrary and here we follow J. Espinosa-Garcia *et al.*'s suggestions [63].

The interpolation methods have been widely used in the construction of PESs and different strategies have been developed [64, 65, 66, 67, 68, 69]. M. A. Collins *et al.* [67, 69] proposed a modified Shepard interpolation method and generated some PESs. The potential energy at any configuration (Z) is given by a weighted average of Taylor series $T_i(R)$ as

$$V = \sum_{i=1}^{N_{data}} w_i(Z) T_i(R), \quad (2.14)$$

where N_{data} is the number of sampled configurations, $w_i(Z)$ is the normalized weighing factor, R is a set of internal coordinates. The Taylor series are expanded at the configuration (Z_i) to a second order as

$$T_i(R) = V(R) + \sum_{k=1}^{3n-6} \frac{\partial V}{\partial R_k} [R_k - R_k(i)] + \frac{1}{2!} \sum_{k=1}^{3n-6} \sum_{j=1}^{3n-6} [R_k - R_k(i)] \frac{\partial^2 V}{\partial R_k \partial R_j} [R_j - R_j(i)]. \quad (2.15)$$

In this method, the new electronic energies can be easily incorporated into the data base to enhance the PES. And the PES is invariant with the permutation of indistinguishable nuclei. However, the requirement of the first and second derivatives at each configuration (Z) in the constructing process makes the computation very expensive. In addition, the interpolation methods often yield artificial oscillations in equipotential contours and vibrational frequencies, which would cause errors when one studies quantum tunneling effects.

The second alternative, fitting method, was also very powerful [70, 71, 72]. A famous one is based on the many-body expansion (MBE) method [73], which is further developed by A. J. C. Varandas [24] as the so-called double many-body expansion (DMBE) method. The MBE potential is given by a sum of one-body energy, two-body energy, three-body energy, $\dots$, and N -body energy for a system consisting of N atoms. For the DMBE potential, each many-body terms is split into two parts: one accounts for the long range interaction and the other for the short range interaction. The recent progress in representing PESs is made by J. M. Bowman *et al.* [74, 75], which is based on global fitting of *ab initio* electronic energies using a fitting basis that is manifestly invariant with respect to all permutation of like atoms. The permutational

symmetry invariant polynomial has the form

$$V = p(x) + \sum_{i < j} q_{i,j} \cdot y_{i,j}, \quad (2.16)$$

where x is an n -dimensional vector, depending on n internuclear distances, with $x_{i,j} = \exp(-r_{i,j})$, $r_{i,j}$ being the distance between nuclei i and j . $p(x)$ and $q(x)$ are polynomials constructed to satisfy the permutation symmetry of like nuclei. $y_{i,j}$ is given by

$$y_{i,j} = \frac{e^{-r_{i,j}}}{r_{i,j}}. \quad (2.17)$$

For the third alternative, *ab initio* energies are fitted to a valence bond(VB) functional form, augmented with molecular mechanics (MM) terms which give great flexibility to the PES [76, 77]. The approach has been further developed by J. Espinosa-Garcia *et al.* [65, 76, 77] and was firstly applied to construct the PES of the $\text{H} + \text{CH}_4$ hydrogen abstraction reaction [78, 79]. The potential energy V consists of three terms, stretching potential, harmonic bending potential, and anharmonic out-of-plan potential,

$$V = V_{stretch} + V_{harm} + V_{op}. \quad (2.18)$$

Once the functional form is available, the fitting procedure is started. The advantage for the VB/MM method is the transferability of the functional form and the fitted parameters, the capability of reproducing the energetic interactions of the chemical systems in region not included in the fit and the smoothness of VB/MM PESs.

2.2 The Basic Theory of Time-Dependent Quantum Dynamics

2.2.1 Time-Dependent Schrödinger Equation

The time-dependent (TD) Schrödinger equation for the nuclei is

$$i\hbar \frac{\partial}{\partial t} \Psi(R, t) = \hat{H} \Psi(R, t), \quad (2.19)$$

where R is the ensemble of coordinates defining the positions of the nuclei, $\hat{H}$ is the Hamiltonian operator, $\Psi(R, t)$ is the TD wave function. The form solution of this equation is

$$\Psi(R, t + \Delta) = \exp\left(\frac{-i\hat{H}\Delta}{\hbar}\right) \Psi(R, t), \quad (2.20)$$

which enables us to relate the wavefunction at time “ $t+\Delta$ ” to that at time “ t ” and is valid only if the Hamiltonian is not an explicit function of time.

The most straightforward way to see what is indicated by Eq. (2.20) is to expand the exponential on the right hand side of Eq. (2.20) as

$$\exp\left(\frac{-i\hat{H}\Delta}{\hbar}\right)\Psi(R, t) = \left\{1 - \left(\frac{i\hat{H}\Delta}{\hbar}\right) + \frac{1}{2!}\left(\frac{i\hat{H}\Delta}{\hbar}\right)^2 - \frac{1}{3!}\left(\frac{i\hat{H}\Delta}{\hbar}\right)^3 + \dots\right\}\Psi(R, t). \quad (2.21)$$

This equation shows that one must be able to operate with the Hamiltonian operator on the wavefunction. There are generally three steps to solve the TD Schrödinger Equation within the TDWP approach. One first prepares an initial wavefunction, then propagates it, and finally collects the scattering information in a proper flux plane.

The initial wave packet is usually chosen to be a Gaussian function [16, 80, 81] and has the form

$$\Psi(R, 0) = \left(\frac{1}{\pi\delta^2}\right)^{1/4} e^{-(R-R_0)^2/2\delta^2} e^{-ik_0 R}. \quad (2.22)$$

The time evolution of the initial wavefunction (the product of a localized translational wave packet and a specific rovibrational eigenfunction) is determined by a number of methods, such as split operator method, Chebyshev method and Lanczos method, which will be discussed further below (*vide infra*).

After the wavefunction $\Psi(R, t)$ is propagated for sufficiently long time, one can calculate the TI scattering wavefunction by performing a Fourier transform

$$\begin{aligned} |\psi_i^+(E)\rangle &= \frac{1}{a_i(E)} \delta(E - H) |\Psi(0)\rangle \\ &= \frac{1}{2\pi a_i(E)} \int_{-\infty}^{\infty} e^{iEt} |\Psi(t)\rangle dt, \end{aligned} \quad (2.23)$$

where the energy-dependent coefficient is given by

$$a_i(E) = [\langle \Psi(0) | \delta(E - H) | \Psi(0) \rangle]^{-1/2} \quad (2.24)$$

which normalizes the stationary solution to the δ -function in energy [20], *viz.*,

$$\langle \psi_i^+(E) | \psi_i^+(E') \rangle = \delta(E - E'). \quad (2.25)$$

The coefficient $a_i(E)$ can be calculated as

$$a_i(E) = \langle \psi_i^+(E) | \Psi(0) \rangle$$

$$\begin{aligned}
&= \lim_{t \rightarrow -\infty} \langle \phi_i(E) | e^{(i/\hbar)\hat{H}_0 t} e^{(-i/\hbar)\hat{H}t} | \varphi_i(0) \rangle \\
&= \langle \phi_i(E) | \varphi_i(0) \rangle,
\end{aligned} \tag{2.26}$$

in which the last equation holds because the initial wave packet $\Psi(0)$ is chosen to be located in the asymptotic region with incoming wave only. The free wave function has the form

$$\phi_i(E) = -\frac{e^{-ik_i R_i}}{\sqrt{\nu_i}} + \frac{e^{ik_i R_i}}{\sqrt{\nu_i}} = \frac{2i}{\sqrt{\nu_i}} \sin(k_i R_i) \tag{2.27}$$

for the zero partial wave and is proportional to the spherical Ricatti-Bessel function for nonzero partial waves.

Once the TI scattering wavefunction $\psi_i^+(E)$ is obtained, one can extract the scattering matrix by applying the asymptotic boundary conditions. If one only wants to obtain total reaction probability (the final states are summed), the calculation can then be greatly simplified. The total reaction probability can be computed by evaluating the reactive flux at any fixed flux plane.

2.2.2 Reactive Flux and Reaction Probability

The conservation law corresponding to the TD Schrödinger equation can be written as a continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot J = 0, \tag{2.28}$$

where the divergence operator is defined in the $N - 1$ -dimensional hypersurface. Here the density is given by $\rho = |\Psi(t)|^2$ and the flux is defined by the equation

$$\nabla \cdot J = \frac{i}{\hbar} [\Psi^* \hat{H} \Psi - (\hat{H} \Psi)^* \Psi]. \tag{2.29}$$

For any stationary wavefunction ψ , ρ is time-independent and thus $\nabla \cdot J = 0$, which means that the flux is constant across any fixed hypersurface. If the Hamiltonian $\hat{H}$ can be expressed as the sum of a kinetic energy operator for the coordinate s and a reduced Hamiltonian for the remaining $N-1$ degrees of freedom

$$\hat{H} = \frac{p_s^2}{2m_s} + \hat{H}_s, \tag{2.30}$$

where $\hat{H}_s$ is the reduced Hamiltonian, one can collect the flux J_s at a fixed surface at $s = s_0$ by integrating over the remaining $N - 1$ coordinates in Eq. (2.29), *i.e.*

$$J_s = \langle \psi | \hat{F} | \psi \rangle, \tag{2.31}$$

where the flux operator $\hat{F}$ is defined as

$$\hat{F} = \frac{1}{2}[\delta(s - s_0)\frac{\hat{p}_s}{m_s} + \frac{\hat{p}_s}{m_s}\delta(s - s_0)]. \quad (2.32)$$

Since the flux J_s is independent of the position of the surface being chosen, one can evaluate the reactive flux at a fixed surface in the product asymptotic region. By using the scattering asymptotic boundary condition for the reactive scattering wavefunction

$$\psi_{\alpha i}^+ \rightarrow \sum_n \frac{e^{i(k_{\beta n} R_\beta - \pi/2 L_{\beta n})}}{\sqrt{v_{\beta n}}} \varphi_{\beta n} S_{\beta n, \alpha i}, \quad (R_\beta \rightarrow \infty), \quad (2.33)$$

for $\alpha \neq \beta$, one can calculate the flux at a surface with a fixed value of $s = R_\beta$ to obtain

$$J_s = \sum_n |S_{\beta n, \alpha i}|^2. \quad (2.34)$$

Thus the reactive flux gives the total reaction probability

$$P_{\alpha i} = J_s = \langle \psi_{\alpha i} | \hat{F} | \psi_{\alpha i} \rangle, \quad (2.35)$$

where $P_{\alpha i}$ is the total $\alpha(i) \rightarrow \beta(all)$ reaction probability. In TD calculations, however, it is preferable to evaluate the reactive flux at a location near the transition state to reduce the propagation time.

2.3 Numerical Implementations

2.3.1 Finite Basis Representation and Discrete Variable Representation

The discrete variable representation (DVR) [82, 83, 84] is now recognized to be very flexible and efficient in the mathematical representation of quantum dynamical problems. The key advantage is that, for multidimensional problems using orthogonal coordinate description, the direct product DVR is simple to evaluate and the Hamiltonian matrix is extremely sparse and is easy to generate. There are generally three effective ways to generate DVRs: (a) one may establish a connection between a set of basis functions and an appropriate numerical quadrature; (b) one may diagonalize a matrix of the coordinate operator in a basis set; (c) one may choose a basis of localized functions initially [85].

If one defines the normal matrix representation of an operator in a truncated basis, $\{\phi_i\}_N$, $i = 1, \dots, N$, as the variational basis representation (VBR) with matrix elements defined by

$$(H^{VBR})_{ij} = \int dx \phi_i^* H \phi_j, \quad i, j = 1, \dots, N. \quad (2.36)$$

Other isomorphic representations can be obtained by unitary transformations within the N -dimensional function space. A DVR is an approximate pointwise representation on a set of N coordinates, $\{x_i\}_N$. The points $\{x_i\}_N$ and the basis $\{\phi_i\}_N$ can be used together to define a generalized quadrature which replaces the inner product definition. The basis representation utilizing functions $\{\phi\}_N$ and the general but finite quadrature inner product on $\{x\}_N$, is called the finite basis representation (FBR), which is isomorphic with the DVR.

If one denotes the FBR by $\{f_n(x)\}$ and the DVR by $\{x_\alpha\}$, in order to generate the DVR from a FBR, one first constructs the matrix of the coordinate x in the FBR,

$$x_{ij} = \langle f_i | x | f_j \rangle \quad (2.37)$$

and then diagonalizes it to obtain the eigenvalues x_α as

$$\mathbf{T}^\dagger \mathbf{x} \mathbf{T} = \mathbf{x}^{DVR}, \quad (2.38)$$

where

$$x_{\alpha\beta}^{DVR} = x_\alpha \delta_{\alpha\beta}. \quad (2.39)$$

The matrix $\mathbf{T}$ is the transformation matrix between the FBR and DVR. Now one can transform a Hamiltonian matrix represented in the FBR to the DVR using the transformation matrix $\mathbf{T}$. Let $\mathbf{H}_0^{FBR}$ be a zero-order Hamiltonian, containing only the kinetic energy operator, thus

$$\mathbf{H}^{FBR} = \mathbf{H}_0^{FBR} + \mathbf{V}^{FBR}. \quad (2.40)$$

Then,

$$\begin{aligned} \mathbf{H}^{DVR} &= \mathbf{T}^\dagger \mathbf{H}^{FBR} \mathbf{T} \\ &= \mathbf{T}^\dagger \mathbf{H}_0^{FBR} \mathbf{T} + \mathbf{V}^{DVR}, \end{aligned} \quad (2.41)$$

where we make the approximation

$$\mathbf{V}_{\alpha\beta}^{DVR} = V(x_\alpha) \delta_{\alpha\beta}. \quad (2.42)$$

The efficiency of the DVR with respect to the FBR comes from the use of Eq. (2.42) as it is not necessary to determine the matrix elements of potential by integration.

In order to make localized functions contain informations about the potential energy surface, J. Echave *et al.* [86] proposed a potential-optimized discrete variable representation (PODVR), using primitive basis sets of eigenfunctions of one-dimensional reference Hamiltonians. As the points are optimized for the PES, it generally could reduce the number of basis functions required.

2.3.2 Split Operator Method, Chebyshev Method and Lanczos method

As discussed above, if one is able to operate with the Hamiltonian operator on the wavefunction, one can solve the TD Schrödinger equation, *viz.*, one has to propagate the constructed wave packet forward in time. A number of methods have been proposed to perform the operation and here we will briefly describe three of them.

Split Operator Method

The split operator method [87] is extremely robust and has been widely used in quantum dynamics calculations. It is because firstly the split operator method is a short-time operator and its application is flexible. Secondly, the propagation of the wavefunction within this method is explicit unitary which makes the numerical calculations very stable. Furthermore, there is no other numerical parameters required to be determined in the propagation process.

The second-order operator can be expressed as

$$\exp\left\{-\frac{i\Delta t\hat{H}}{\hbar}\right\} = \exp\left\{-\frac{i\Delta t\hat{T}}{2\hbar}\right\} \exp\left\{-\frac{i\Delta t\hat{V}}{\hbar}\right\} \exp\left\{-\frac{i\Delta t\hat{T}}{2\hbar}\right\} + O((\Delta t)^3), \quad (2.43)$$

or

$$\exp\left\{-\frac{i\Delta t\hat{H}}{\hbar}\right\} = \exp\left\{-\frac{i\Delta t\hat{V}}{2\hbar}\right\} \exp\left\{-\frac{i\Delta t\hat{T}}{\hbar}\right\} \exp\left\{-\frac{i\Delta t\hat{V}}{2\hbar}\right\} + O((\Delta t)^3), \quad (2.44)$$

where Δt is the time step and the Hamiltonian is split into two parts as $\hat{H} = \hat{T} + \hat{V}$. Thus, the wavefunction is propagated by

$$\Psi(t + \Delta) = \exp\left\{-\frac{i\Delta t\hat{T}}{2\hbar}\right\} \exp\left\{-\frac{i\Delta t\hat{V}}{\hbar}\right\} \exp\left\{-\frac{i\Delta t\hat{T}}{2\hbar}\right\} \Psi(t) \quad (2.45)$$

for Eq. (2.43) and that is similar for Eq. (2.44). The approximation arises from the noncommutativity of $\hat{T}$ and $\hat{V}$.

In the second order split operator method, the error is of the third order of Δt . Higher order split operator methods have been developed. The simplest technique to build split operator method of any desired order is by composing a basic lower order integrator with different time steps [88, 89, 90, 91, 92]. Given an integrator $S_{2k}(\Delta t)$ of order $2k$, then a composition

$$S_{2k+2}(\Delta t) = [S_{2k}(\alpha_1 \Delta t)]^n [S_{2k}(\alpha_0 \Delta t)]^m [S_{2k}(\alpha_1 \Delta t)]^n \quad (2.46)$$

with $\alpha_1 = 1/(2n - (2nm^{2k})^{1/(2k+1)})$ and $\alpha_0 = (1 - 2n\alpha_1)/m$ is a $2k + 2$ order split operator integrator. It can be seen that an increase of two orders in accuracy is achieved at the cost of (at least) three times of computational effort for using the second order split operator.

The exponential split operator scheme arrived in third order accuracy of Δt have also been reported by A. D. Bandrauk *et al.* [93, 94] as

$$\begin{aligned} \exp\left\{-\frac{i\Delta t \hat{H}}{\hbar}\right\} &= \exp\left\{-\frac{i\gamma\Delta t \hat{T}}{2\hbar}\right\} \exp\left\{-\frac{i\gamma\Delta t \hat{V}}{\hbar}\right\} \exp\left\{-\frac{i(1-\gamma)\Delta t \hat{T}}{2\hbar}\right\} \\ &\times \exp\left\{-\frac{i(1-2\gamma)\Delta t \hat{V}}{\hbar}\right\} \exp\left\{-\frac{i(1-\gamma)\Delta t \hat{T}}{2\hbar}\right\} \\ &\times \exp\left\{-\frac{i\gamma\Delta t \hat{V}}{\hbar}\right\} \exp\left\{-\frac{i\gamma\Delta t \hat{T}}{2\hbar}\right\} + O((\Delta t)^4) \end{aligned} \quad (2.47)$$

with $\gamma = 1/(2 - 2^{1/3})$. And it has been found that this scheme determines the phase of the wavefunction very accurately and it is sometimes more efficient than the second order split operator method.

Chebyshev Method

Another alternative is to expand $e^{-i\hat{H}\Delta t/\hbar}$ in terms of Chebyshev polynomials [15, 81]

$$\exp\left\{-\frac{i\Delta t \hat{H}}{\hbar}\right\} \approx \sum_{n=0}^N a_n \Phi_n\left(-\frac{i\Delta t \hat{H}}{\hbar}\right), \quad (2.48)$$

where a_n are expansion coefficients and Φ_n are the n th complex Chebyshev polynomials. The Chebyshev polynomials have the advantage that the maximal error in the expansion is minimal compared with almost all other polynomial approximations and the error is uniformly distributed over the eigenvalues.

As the complex Chebyshev polynomials are defined over the range from $-i$ to i , in order to apply this scheme, one should first scale the Hamiltonian so that its eigenvalues fall into to the

interval $(-1, 1)$. If E_{max} and E_{min} are the upper and lower bounds of the eigenvalues of the Hamiltonian operator, which can be estimated from the potential and the grid, then one has

$$\hat{H}_{norm} = \frac{\hat{H} - \hat{I}(\frac{1}{2}\Delta E + E_{min})}{2\Delta E}, \quad (2.49)$$

where $\hat{I}$ is the identity operator, and $\Delta E = E_{max} - E_{min}$. In practice, it is important to estimate E_{max} and E_{min} accurately. If the range is too small, the propagation will be unstable, whereas a large number of polynomials will be required for convergence if the range is too large.

The time-evolution propagator can be approximated by

$$\exp\left\{-\frac{i\Delta t\hat{H}}{\hbar}\right\} \approx \exp\left\{-\frac{i\Delta t\bar{E}}{\hbar}\right\} \sum_{n=0}^N a_n \left(\frac{\Delta E\Delta t}{\hbar}\right) \Phi_n(-i\hat{H}_{norm}), \quad (2.50)$$

where $\bar{E} = (E_{max} + E_{min})/2$. And all of the time dependence is contained in the expansion coefficients, which are given by the fist kind Bessel functions.

The propagation is accomplished by using the Chebyshev recursion relation

$$\phi_{n+1} = -2i\hat{H}_{norm}\phi_n + \phi_{n-1}, \quad (2.51)$$

in which

$$\begin{aligned} \phi_n &= \Phi_n(-i\hat{H}_{norm})\psi(t), \\ \phi_0 &= \psi(t), \\ \phi_1 &= \hat{H}_{norm}\psi(t). \end{aligned} \quad (2.52)$$

If enough terms are contained in the expansion, the time step can be made arbitrarily large so that only one time step is needed for the entire calculation.

The Chebyshev method is a global method and thus it permits one use very large time step, which could be several hundreds of that used in the second order split operator method. And this method is generally more accurate than the split operator method.

Lanczos method

The Lanczos method makes use of the Lanczos vectors, $\{\phi_i\}$, to expand the time-evolution operator. The Lanczos vectors are generated by the recursion relation

$$\beta_{i+1} |\phi_{i+1}\rangle = \hat{H} |\phi_i\rangle - \alpha_i |\phi_i\rangle - \beta_i |\phi_{i-1}\rangle, \quad (2.53)$$

where

$$\beta_{i+1} = \langle \phi_{i+1} | \hat{H} | \phi_i \rangle, \quad \alpha_i = \langle \phi_i | \hat{H} | \phi_i \rangle, \quad (2.54)$$

with $\beta_1 = 0$ and $|\phi_0\rangle = 0$.

One first sets $|\phi_1\rangle = |\Psi(t=0)\rangle$ and then generates a few Lanczos vectors. The Hamiltonian can be expressed by a basis set consisting of the N Lanczos vectors as

$$\mathbf{T}_N = \begin{pmatrix} \alpha_1 & \beta_2 & & & \\ \beta_2 & \alpha_2 & \beta_3 & 0 & \\ & \beta_3 & \ddots & \ddots & \\ & 0 & \ddots & \ddots & \beta_N \\ & & & \beta_N & \alpha_N \end{pmatrix}. \quad (2.55)$$

Obviously, it is tridiagonal matrix and can be diagonalized efficiently. Diagonalizing the matrix $\mathbf{T}_N$, one has

$$\mathbf{D}_N = \mathbf{Z}^\dagger \mathbf{T}_N \mathbf{Z}, \quad (2.56)$$

where $\mathbf{Z}$ is a unitary matrix and each column of the matrix corresponds to one eigenvector of $\mathbf{T}_N$. $\mathbf{D}_N$ is a diagonal matrix with each diagonal element being a eigenvalue. Since the eigenvectors only span a subspace of the complete eigenvector space, the time step must be kept reasonably small, typically a tenth or a few tenths of a femtosecond [10]. The time-evolution operator $\exp\left\{-\frac{i\Delta t \hat{H}}{\hbar}\right\}$ is approximated as

$$\exp\left\{-\frac{i\Delta t \hat{H}}{\hbar}\right\} \approx \exp\left\{-\frac{i\Delta t \mathbf{T}_N}{\hbar}\right\} = \mathbf{Z} \exp\left\{-\frac{i\Delta t \mathbf{D}_N}{\hbar}\right\} \mathbf{Z}^\dagger. \quad (2.57)$$

The wavefunction is propagated by

$$\Psi(t + \Delta t) \approx \sum_{n=1}^N \left[\mathbf{Z} \exp\left\{-\frac{i\Delta t \mathbf{D}_N}{\hbar}\right\} \mathbf{Z}^\dagger \right]_n \phi_n(t). \quad (2.58)$$

2.3.3 Optimized Absorbing Potential

In the wave packet calculations, the spatial coordinate is restricted to a discretized finite set of points so that the system is enclosed within a finite “box”, which would lead to the reflection (or possibly transmission) of the scattered waves at the boundaries [95]. D. Neuhauser and

M. Baer [96] proposed an empirical approach to solve the problem by the employment of an absorbing potential or optical potential to absorb the wavefunction near the grid boundary two decades ago. Then the optimization of absorbing potentials were extensively discussed by J. G. Muga *et al.* [95, 97, 98, 99]. The optimized absorbing potential should avoid the spurious boundary effects and save the computational cost.

The negative imaginary potential (NIP) is used in our calculations to damp the reflection of the wave packet at the grid boundaries, which is defined as

$$V_{NIP} = \begin{cases} -iC_{\alpha} \left(\frac{x-x_0}{\Delta x} \right)^{n_{\alpha}}, & \text{for } x_0 \leq x \leq x_{max}; \\ 0, & \text{for } x_{min} < x \leq x_0. \end{cases} \quad (2.59)$$

Here, x_0 is the starting point of the absorbing potential region and $\Delta x = x_{max} - x_0$ is the acting region of the potential. The parameters C_{α} and n_{α} corresponding to each radial coordinate should be adjusted to make V_{NIP} smooth enough to avoid reflections and strong enough to efficiently absorb the wave function entering into the absorbing region.

Three-Dimensional Wave Packet

Dynamics of $\text{H}_2 + \text{D}_2$ Reaction

3.1 Introduction

Exact quantum scattering calculations provide a complete description of the dynamics of a reaction and are thus the ultimate benchmarks for assessing various approximate theories and different models of reactivity [100, 101]. Recent studies of chemical reaction dynamics in the gas phase have ranged from triatomic and tetratomic systems to larger polyatomic systems. In this regard, the mathematical representation of high-dimensional potential energy surface (PES) with chemical accuracy is a big challenge [74, 102, 103, 104]. Collins and coworkers have developed an interpolation method to construct polyatomic molecular PESs [67, 105]. Very recently, remarkable progress has been made by Bowman and coworkers who have implemented a different approach based on global fitting of ab initio electronic energies using a fitting basis that is manifestly invariant with respect to all permutations of like atoms [106, 107]. The approach has been successfully applied to more than 20 complex molecules and clusters, such as CH_3CHO , CH_5^+ , H_5^+ and water clusters [107]. Meanwhile, full-dimensional quantum scattering calculations for five- and six-atom reactions have been reported for $\text{H}_2 + \text{C}_2\text{H}$ [26], $\text{H} + \text{NH}_3$ [27], $\text{H} + \text{CH}_4$ [29, 30, 31, 32] and $\text{O} + \text{CH}_4$ [28]. The recent dynamical calculations of six-atom molecular systems by combining efficient wave packet propagation (starting from the transition state of

a reaction) with the multiconfiguration time-dependent Hartree (MCTDH) method have shown that the transition state based approach has computational advantages as well as providing an attractive conceptual interpretation [31].

The study of four-atom bimolecular reaction dynamics is of relevance in environmental chemistry and theoretically serves as a bridge between triatomic and polyatomic reactions [108]. Now, it is possible to carry out rigorous quantum scattering calculations on three- and four-atom reactions to provide rate constants and detailed state-to-state resolved information [20, 21, 22, 54, 109, 110, 111, 112, 113, 114, 115]. Zhang et al. [116] have performed a full-dimensional quantum mechanical study on the abstraction and exchange processes in the $\text{H} + \text{H}_2\text{O}$ reaction by treating both OH bonds in the H_2O reactant as reactive bonds. It suggested that one may be able to accurately study the four-center (4C) reaction which involves cleavage of two bonds $\text{AB} + \text{CD} \rightarrow \text{AC} + \text{BD}$, $\text{AD} + \text{BC}$, which is a special kind of four-atom reaction.

Four-center reactions have many novel dynamical features and thus have been widely studied both experimentally and theoretically in the past [55, 56, 57, 58, 59]. Unlike three-center reactions where only one bond is broken and formed during the reaction process, 4C reactions involve the simultaneous cleavage and formation of two bonds, and they usually present very high barriers, comparable to or higher than a covalent bond energy. Raz and Levine [56, 57, 58, 59] 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). The 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 classical trajectory studies on 4C reactions induced by cluster impact. At the same time, the 4C process has to compete with two other reactions: collision induced dissociation (CID), $\text{AB} + \text{CD} \rightarrow \text{A} + \text{B} + \text{CD}$, $\text{AB} + \text{C} + \text{D}$, which is known to be very important at the high energies where 4C reactions take place, and single exchange reaction (SE), $\text{AB} + \text{CD} \rightarrow \text{AC} + \text{B} + \text{D}$, $\text{AD} + \text{B} + \text{C}$, $\text{BC} + \text{A} + \text{D}$, $\text{BD} + \text{A} + \text{C}$. However, there are very few studies on 4C dynamics in a quantum framework. The coexistence of several processes and the higher energy required to surmount the barrier pose a challenge to the exact full-dimensional quantum studies of these processes. Therefore, most theoretical dynamics

studies were based on classical or quasi-classical trajectories (QCT).

The $\text{H}_2 + \text{H}_2$ system is at the forefront of 4C collision dynamics. The study of the collisions between two hydrogen molecules is of particular interest in astrophysics [37], combustion [34, 35] and spacecraft modelling [36]. Theoretically, the H_4 system is a fundamental system in quantum chemistry. Due to the light masses in the system, high level *ab initio* calculations are possible, and two global H_4 PESs have been reported: one by Aguado et al. (ASP) [38] and another by Boothroyd et al. (BMKP) [39]. As for dynamical studies, full-dimensional quantum-mechanical (QM) treatment of $\text{H}_2 + \text{H}_2$ is challenging due to the competition of several processes and the higher energy required. Hence, most theoretical studies have been performed using reduced dimensional quantum and (full-dimensional and reduced dimensional) QCT techniques. The first QM time-independent calculation using a reduced dimensionality approach, with one molecule in a highly vibrational excited state and another in the ground vibrational state, was carried out by Hernández and Clary [40]. The same model was subsequently investigated in greater detail and with higher accuracy by José Campos-Martínez et al. [41, 42, 43, 44] and by Lu et al. [46] using wave packet propagation techniques. More recently, a comparison with the analogous reduced dimensionality QCT studies were reported [45]. Full-dimensional QCT studies of the dynamics of the $\text{H}_2 + \text{H}_2$ system and its isotopic variants have also been published in the last decade [33, 47, 48, 49, 50, 51, 52, 53]. However, in the QCT approach, the absence of tunneling effects, which are expected to be important at threshold energies, and zero-point energy leakage can introduce significant errors. An important progress in the accurate calculations of the $\text{H}_2 + \text{H}_2$ reaction was made by Lu et al. [54], who obtained converged full-dimensional state-specific probabilities with the total angular momentum $J = 0$. In their study, a comparison of three dimensional (3D) and six dimensional (6D) results showed reasonable agreement between them for the CID process. The scaled 3D probabilities (by a factor of 0.2) resembled the 6D results for the 4C process, except for an energy threshold shift of about 0.1 eV. These conclusions provide a central justification for the reduced 3D model employed in this study. One of the aims of this work is to study isotopic substitution effect, so the reduced three-dimensional wave packet dynamical results reported by Bartolomei et al. [43] have been used as a reference, and their results will be compared with those for the $\text{H}_2 + \text{D}_2$ reaction here.

Figure 3.1: Main coplanar configurations used in the reduced dimensionality calculations. For the parallel H geometry, both r_1 and r_2 are perpendicular to R . For the crossed X (X') geometry, r_1 (r_2) is perpendicular to R and r_2 (r_1) has an angle of 45° with respect to R . r_1 (r_2) is perpendicular to R and r_2 (r_1) is parallel to R for the T-shaped T_I (T_{II}) geometry. The last L geometry is for the collinear case.

Being one of the simplest diatom-diatom reactions, the mechanism of the exchange reaction between H_2 and D_2 is of interest. Here, we wish to understand the reaction mechanisms through more rigorous quantum dynamics simulation. We have extended the study from five restricted geometries of Bartolomei et al. [43] for $H_2 + H_2$ to six different geometries, as shown in Fig. 3.1. In contrast to Bartolomei et al.'s calculations which restricted all the reactants to be coplanar, three of our chosen geometries (H, X, X') were studied for both coplanar and non-coplanar geometries in order to appraise the performance of the potential energy surfaces. These six geometries represent the main limiting geometries of the colliding system and will allow us to study all outcomes. The three geometries in Fig. 3.1 (H, X, T_I), with the more excited diatom perpendicular to the intermolecular distance R , are suitable for studying the effect of the orientation of the vibrational “colder” diatom in the reaction process. The geometry X' , with the lower excited diatom perpendicular to R , is suitable for studying the effect of the orientation of the “hotter”

diatom. The remaining two geometries (T_{II} , L) with the more excited diatom parallel to R, have been chosen to investigate other products of the collision, such as SE product occurring for the L geometry and the formation of a three body complex (3BC), $AB + CD \rightarrow ACB + D$, $ADB + C$, occurring for the T_{II} geometry. For all the processes, initial state selected probabilities for H_2 (initial vibrational state $v_1 = \text{high}$) + D_2 ($v_2 = \text{low}$) have been computed. Our aim here is to investigate the different processes and related mechanisms occurring for each of the limiting geometries and to study isotopic substitution effects. The isotopic substitution effects were studied by comparing the CID, 4C, SE and 3BC probabilities for $H_2 + D_2$ reaction with the corresponding ones for $H_2 + H_2$ reaction reported by Bartolomei et al. [43]. Sec. 3.2 outlines the theoretical methodology of the initial state selected wave packet (ISSWP) method. In Sec. 3.3, results from dynamical calculations and comparisons of reaction probabilities for the two combinations ($H_2 + D_2$ and $H_2 + H_2$) are presented and discussed. We conclude in Sec. 3.4.

3.2 Theory

In the model of Hernández and Clary [40], the two reacting diatomic molecules A_2 and B_2 are restricted to be parallel to each other and both are perpendicular to R which connects the center of mass of A_2 and B_2 , forming an isosceles trapezium, which corresponds to the geometry H in Fig. 3.1. The corresponding Hamiltonian in the three coordinates (R, r_1, r_2) , which applies also to all the configurations in Fig. 3.1, can be written as

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + h_1(r_1) + h_2(r_2) + V(R, r_1, r_2), \quad (3.1)$$

where μ is the reduced mass of A_2 and B_2 , r_1 is the bond length of the diatom A_2 , r_2 is the bond length of the diatom B_2 , and $V(R, r_1, r_2)$ is the interaction potential relevant to the geometry of the reaction. In Eq. (3.1), $h_1(r_1)$ and $h_2(r_2)$ are one-dimensional (1D) reference Hamiltonians. The corresponding eigenstates for $h_1(r_1)$ and $h_2(r_2)$ are denoted by $\phi_{v_1}(r_1)$ and $\phi_{v_2}(r_2)$,

$$h_i(r_i)\phi_{v_i}(r_i) = \left[-\frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial r_i^2} + V_i(r_i)\right]\phi_{v_i}(r_i) = \epsilon_{v_i}\phi_{v_i}(r_i), (i = 1, 2), \quad (3.2)$$

where $V_1(r_1)$ and $V_2(r_2)$ are the diatomic potentials for A_2 and B_2 , respectively.

As shown by Hernández and Clary, one of the H_2 should be highly excited in order for dissociation to occur. In this study, we treat A_2 as the highly excited one and use a uniform

basis size for A₂ in the asymptotic and interaction regions, while for the B₂ molecule we employ an L-shape grid scheme [20] to reduce the basis set size, as illustrated in Fig. 3.2. Thus, the time-dependent wave function can be expanded as

$$\Psi(R, r_1, r_2, t) = \sum_{n, v_1, v_2} F_{n, v_1, v_2} u_n^{v_2}(R) \phi_{v_1}(r_1) \phi_{v_2}(r_2), \quad (3.3)$$

where the translational basis function $u_n^{v_2}(R)$, which is dependent on v_2 , is defined as

$$u_n^{v_2}(R) = \begin{cases} \sqrt{\frac{2}{R_3 - R_1}} \sin \frac{n\pi(R - R_1)}{R_3 - R_1}, & v_2 \leq v_2^{asy} \\ \sqrt{\frac{2}{R_2 - R_1}} \sin \frac{n\pi(R - R_1)}{R_2 - R_1}, & v_2 > v_2^{asy} \end{cases} \quad (3.4)$$

where R_2 and R_3 define the interaction and asymptotic grid ranges as shown in Fig. 3.2, and v_2^{asy} is the number of vibrational basis functions used for B₂ in the asymptotic region.

The initial wave function is chosen as the product of a Gaussian translational wave packet and vibrational eigenfunctions for A₂ and B₂

$$\Psi_i(t = 0) = g(R) \phi_{v_{10}}(r_1) \phi_{v_{20}}(r_2), \quad (3.5)$$

where $g(R)$ is a standard Gaussian function

$$g(R) = (\pi\delta^2)^{-1/4} e^{-(R - R_0)^2 / 2\delta^2} e^{-ik_0 R}.$$

The split-operator method [87] is employed to propagate the wave packet

$$\Psi_i(t + \Delta) = e^{-iH_0\Delta/2} e^{-iV\Delta} e^{-iH_0\Delta/2} \Psi_i(t) \quad (3.6)$$

with the reference Hamiltonian H_0 defined as

$$H_0 = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + h_1(r_1) + h_2(r_2). \quad (3.7)$$

From the time-dependent wave function $\Psi_i(t)$, we can calculate the time-independent scattering wave function (TIDWF) by performing a Fourier transform

$$|\psi_i(E)\rangle = \frac{1}{2\pi\hbar a_i(E)} \int_0^{+\infty} e^{iEt/\hbar} |\Psi_i(t)\rangle dt \quad (3.8)$$

where the coefficient $a_i(E)$ is the overlap between the initial wave function $\Psi_i(t = 0)$ and the free scattering wavefunction $\phi_i(E)$. The reaction probabilities can be obtained by calculating the reactive flux

$$P_i^R(E) = \sum_f |S_{fi}^R|^2 = \langle \psi_i(E) | \hat{F} | \psi_i(E) \rangle \quad (3.9)$$

where $\hat{F}$ is the flux operator defined as

$$\hat{F} = \frac{1}{2}[\delta(\hat{s} - s_0)\hat{v}_s + \hat{v}_s\delta(\hat{s} - s_0)] \quad (3.10)$$

where $\hat{s}$ is the coordinate perpendicular to a surface located at s_0 for the flux evaluation, and $\hat{v}_s$ is the velocity operator corresponding to the coordinate.

Figure 3.2: Grid ranges for the three-dimensional Jacobi coordinates r_1 , r_2 , R . The interaction and asymptotic grid ranges in R are defined by $(R_2 - R_1)$ and $(R_3 - R_1)$, respectively. The three planes $S[R^F]$, $S[r_1^F]$ and $S[r_2^F]$ form the dividing surface for projecting the scattering wavefunction, while r_1^D and r_2^D denote the boundaries for the r_1 and r_2 coordinates, respectively.

In order to obtain the CID, 4C, SE and 3BC reaction probability, we calculated the TIDWF $\psi_i(E)$ on one dividing surface which comprises three planes denoted by $S[R^F]$, $S[r_1^F]$, $S[r_2^F]$, as shown in Fig. 3.2. These three planes are defined as

$$S[R^F] : R = R^F, r_1 \leq r_1^F, r_2 \leq r_2^F,$$

$$S[r_1^F] : R \leq R^F, r_1 = r_1^F, r_2 \leq r_2^F,$$

Table 3.1: Numerical parameters used in the calculations. The number in parentheses denotes the basis number used in the interaction region for the translational coordinate R (or in the asymptotic region for the coordinate r_2).

	H, X	X'	T _I	T _{II}	L
Number of grid points:					
R	120(60)	150(120)	150(80)	150(120)	250(220)
r_1	120	150	120	150	200
r_2	120(20)	150(20)	120(20)	120(20)	200(20)
Grid boundaries:					
R	[0.0, 10.0]	[0.0, 12.0]	[0.0, 12.0]	[0.0, 15.0]	[0.0, 18.0]
r_1	[0.5, 12.0]	[0.5, 18.0]	[0.5, 12.0]	[0.5, 15.0]	[0.5, 15.0]
r_2	[0.5, 7.5]	[0.5, 12.0]	[0.5, 7.5]	[0.5, 8.5]	[0.5, 15.0]
Flux parameters:					
R^F	4.0	8.0	5.0	8.0	14.0
r_1^F	10.0	15.0	10.0	12.0	12.5
r_2^F	4.5	9.0	5.5	6.5	12.5

$$S[r_2^F] : R \leq R^F, r_1 \leq r_1^F, r_2 = r_2^F.$$

3.3 Results and Discussion

The global potential energy surfaces of ASP [38] and BMKP [39] were used in the calculations. The coordinates not explicitly accounted for in the model (3 angles) are fixed to those values preserving the corresponding geometry. Hereafter, energies are referred to the bottom of the $H_2 + D_2$ entrance valley. Parameters used in the calculation are given in Table 3.1. Different number of grid points and grid boundaries are employed in order to account for the different channels in these different geometries. In Table 3.1, the number in parentheses denotes the basis number used in the interaction region for the translational coordinate R (or in the asymptotic region for the coordinate r_2). We propagated the wave packet for 8000 a.u., with a time increment $\Delta = 10$ a.u.. At the edges of R, r_1 and r_2 , absorbing potentials were applied to prevent the wave packet from reflecting back from the boundaries.

3.3.1 Collision Induced Dissociation (CID)

To analyze the effect of the orientation of the initially cold diatom on the dissociation process, CID probabilities for the different orientations of the cold diatom in the plane, i.e. H, X, and T_I are shown in Fig. 3.3. It can be seen that the energy threshold behavior and the reaction probability profiles are quite similar for the BMKP PES within the same initial state, except for the H geometry at the energies where the 4C channel enters in competition. In short, the orientation of the cold diatom does not greatly affect the CID process. However, for the ASP PES, the probability curves differ relatively more, as pointed out by Campos-Martínez et al. [43], presumably due to the higher anisotropy of ASP surface compared with the BMKP surface. Fig. 3.4 shows the CID probabilities for H and T_{II} geometries, corresponding to the different rotations of the hot diatom in the plane. As the CID probability for X' geometry is less than 1% in the energy range considered, we have omitted it in the figure. Obviously, the energy threshold for T_{II} geometry is greatly shifted to higher energies. The reaction probabilities for H geometry are much larger than those for the corresponding state of T_{II} geometry over the entire region considered. Taking into consideration that the CID probability for X' geometry is less than 1%, as pointed out above, we conclude that the orientation of the hot diatom has a significant effect on the dissociation process. From these two figures, it can also be noted that there exists a vibrational enhancement effect and some probabilities curves exhibit a double peaked structure above threshold.

To gain further insight into the effect of the orientations of two diatoms on the CID reaction process, we have also computed the CID, 4C and SE probabilities for the cases where the two diatoms are non-coplanar on both PESs. Fig. 3.5(a)-(d) show the CID probabilities for the H and X geometries when the two diatoms are not coplanar. The subscript 'I' denotes the geometry with the torsion angle of 45° . The subscript 'II' denotes the geometry with the torsion angle of 90° . Figure 3.5(a) and (c) show the CID probabilities for the H, H_I and H_{II} geometries for the BMKP PES and ASP PES, respectively. The energy threshold behavior and the reaction probability profiles are quite similar within the same initial vibrational states, except for the H geometry at the energy where the 4C channel opens. The CID probabilities for the X, X_I and X_{II} geometries are shown in Fig. 3.5(b) and (d). For the three geometries, the energy threshold

Figure 3.3: Comparison of the collision induced dissociation probabilities for the three different restricted geometries H (solid line), X (dash line) and T_I (dotted line). Upper panel: BMKP PES results. Lower panel: ASP PES results.

Figure 3.4: Comparison of the collision induced dissociation probabilities for the two different restricted geometries H (solid line) and T_{II} (dash line). Upper panel: BMKP PES results. Lower panel: ASP PES results.

and the reaction probability profiles within the same vibrational states are almost identical over the entire energy range considered for both surfaces. It is therefore hard to tell which PES is more anisotropic. The relatively larger difference of the CID probability curves of the ASP PES for different geometries also can't be easily attributed to the higher anisotropy of this surface.

Figure 3.5: Collision induced dissociation probabilities for the H and X geometries when the two diatoms are not coplanar. The subscript ‘I’ denotes the geometry with the torsion angle of 45° . The subscript ‘II’ denotes the geometry with the torsion angle of 90° . Upper panel: BMKP PES results. Lower panel: ASP PES results.

3.3.2 Four Center (4C) Reaction

Our analysis of 4C reaction probabilities for different initial geometries showed that the 4C reaction, which involves the simultaneous breaking and forming of two bonds, is only significant for the H geometry and is negligible in others. Figure 3.6 shows the four center reaction probabilities for initial states ($v_1 = 8 - 12$, $v_2 = 0$) as a function of the total energy. In this figure, dash lines represent the 4C probability curves obtained with the ASP PES while solid lines denote the results for the BMKP PES. We can see that the energy threshold behavior is quite similar

to the CID process. Also, an initial vibrational excitation of the hot molecule is more efficient than translational energy in facilitating the reaction process. However, the probability profiles of the 4C process is different from the CID process - as the translational energy increases, the 4C reaction probabilities increase steadily with almost the same slopes for different vibrational states. Finally, similar to the CID process, the BMKP energy threshold for the 4C reaction is lower than that for the corresponding state with the ASP PES.

Figure 3.6: Four center reaction probabilities for initial states ($v_1 = 8 - 12$, $v_2 = 0$) as a function of total energy. Solid lines represent the BMKP PES results while dash lines refer to the ASP PES ones.

3.3.3 Single Exchange (SE) Reaction

The SE process corresponds to the breaking of the two old bonds and the formation of a new HD bond. This process is insignificant in the energy range considered except for the X' and L geometries where some SE reaction probability can be observed at high collision energies. The SE probabilities for initial states ($v_1 = 10 - 12$, $v_2 = 0$) for X' and L geometries as a function of total energy are shown in Fig. 3.7. Dash lines represent the results for the ASP PES while

solid lines refer to the BMKP PES. It can be seen that the vibrational excitation of the hot molecule enhances the SE probabilities more than the translational energy, which is similar to the CID and 4C processes. Also, the BMKP probability curves show relatively lower energy thresholds. Comparing the SE probabilities for these two geometries, the SE probability for L geometry increases much faster than for X' geometry. As the collision energy increases further, the reaction probability for L geometry starts to saturate and is overtaken by that for X' geometry for the same initial state.

3.3.4 Three Body Complex (3BC) Formation

The formation of a linear three body complex is energetically possible for both T_I and T_{II} configurations with the insertion of a H_2 (D_2) molecule into D_2 (H_2). Within these restricted geometries, such a complex can be long lived, as pointed out by Mandy et al. [52] and by Bartolomei et al. [43]. However, in a full dimensional treatment, the linear H_3 minimum becomes a saddle point (the saddle point of the $H_2 + H$ reaction) by the inclusion of the asymmetric stretch mode, and the H_3 complex will have a much shorter lifetime due to the possibility of dissociation of one of the outer atoms of the linear molecule.

We have used the T_{II} configuration with the more excited diatom along the direction of the intermolecular distance R , since in this case the CID process is minimized and the formation of DHD is favored. In Fig. 3.8, we show the 3BC probabilities for initial states ($v_1 = 10 - 12$, $v_2 = 2$) as a function of total energy for both surfaces. The 3BC probabilities for T_I geometry are considerably smaller, so they can be neglected. In contrast with the 4C and CID processes, the 3BC formation shows a clear vibrational inhibition effect, i.e., energy thresholds are higher for the higher v_1 's. In analogy with the mechanisms mentioned in the CID process, the 3BC probabilities also have two contributions: the formation of DHD by the capture of the first or the second of the H atoms of the inserting hot molecule.

3.3.5 Isotopic Substitution Effects

The reaction probabilities of the $H_2 + D_2$ reaction for all processes can be compared with the results of the $H_2 + H_2$ reaction, previously reported by Bartolomei et al. [43]. The comparison

Figure 3.7: Single exchange reaction probabilities for initial states ($v_1 = 10 - 12$, $v_2 = 0$) and for the X' and L geometries as a function of total energy . Solid lines represent the BMKP PES results while dash lines refer to the ASP PES ones.

Figure 3.8: Three body complex formation probabilities for initial states ($v_1 = 10 - 12$, $v_2 = 2$) as a function of total energy. Solid lines represent the BMKP PES results while dash lines refer to the ASP PES ones.

has been performed with the more elaborate BMKP PES.

Figure 3.9(a) shows the CID probabilities as a function of total energy, for reactants in initial states ($v_1 = 10, 12$, $v_2 = 0$) and for the different combinations of reagents within the H, X and T_I geometries. Solid lines represent the results for the H geometry, dash lines for the X geometry and dotted lines for the T_I geometry. It can be seen that the two combinations show similar energy threshold behavior and probability profiles. As v_1 increases, the thresholds are shifted to lower energies and the probability profiles become steeper. However, the energy threshold is lower for the $H_2 + D_2$ reaction with the same initial states due to the lower zero point energy of the reactant D_2 and different quantum tunneling effects. In Fig. 3.9, we show the 4C probabilities for the different combinations of reagents within the H geometry. Solid lines represent the results of the $H_2 + H_2$ reaction while dash lines refer to the results of the $H_2 + D_2$ reaction. Clearly, the 4C thresholds and probability profiles are almost identical within the same initial states. However, as v_1 increases, the difference between the two combinations becomes a little larger. Through a

Figure 3.9: Collision induced dissociation and four center reaction probabilities of $\text{H}_2 + \text{H}_2$ and $\text{H}_2 + \text{D}_2$ reactions for initial states ($v_1 = 10, 12$, $v_2 = 0$) on the BMKP PES as a function of total energy.

Figure 3.10: Single exchange reaction and three body complex formation probabilities of $\text{H}_2 + \text{H}_2$ and $\text{H}_2 + \text{D}_2$ reactions for initial states ($v_1 = 10, 12$, $v_2 = 0$) on the BMKP PES as a function of total energy.

detailed comparison, it can also be shown that the probability curves for the $\text{H}_2 + \text{D}_2$ reaction have lower energy thresholds and then increase more slowly than those of the $\text{H}_2 + \text{H}_2$ reaction with increase in translational energy.

Figure 3.10(a) and (b) show the SE probabilities within the L geometry and the 3BC probabilities within the T_{II} geometry for the two combinations, respectively. From these two figures, we can see that the two combinations of reagents show similar energy threshold behavior, i.e. vibrational enhancement effect for the SE process and vibrational inhibition effect for the 3BC process. The probability curves for the $\text{H}_2 + \text{D}_2$ reaction are more structured than those of the $\text{H}_2 + \text{H}_2$ reaction.

3.4 Conclusion

We have performed the time-dependent initial state selected wave packet calculations on the $\text{H}_2(v_1 = \text{high}) + \text{D}_2(v_2 = \text{low})$ collision. The number of chosen geometries have been extended from five (H, X, T_{I} , T_{II} and L) to six (H, X, X', T_{I} , T_{II} and L), in which three of them are studied for both coplanar and non-coplanar geometries. Within these restricted geometries (three active degrees of freedom), we have obtained the probabilities for different processes: collision induced dissociation (CID), four center reaction (4C), single exchange reaction (SE), and three body complex formation (3BC).

It was found that, firstly, one cannot conclude that one surface (ASP or BMKP) is more anisotropic than the other based on the calculations for the coplanar and non-coplanar geometries. Secondly, the orientation of the cold diatom (coplanar and non-coplanar) does not greatly affect the CID process. However, the orientation of the hot diatom has a significant effect on the reaction process. Thirdly, the 4C and SE processes have the same energy threshold behavior which is quite similar to the CID process, i.e. an initial vibrational excitation of the hot molecule is more efficient than translational energy in facilitating the reaction processes. For the 3BC process, however, there is a clear vibrational inhibition effect. Finally, the BMKP PES leads to relatively lower energy thresholds than the ASP PES, except for the CID process within the T_{II} geometry.

The isotopic substitution effects have also been investigated by comparing the CID, 4C, SE

and 3BC probabilities for $\text{H}_2 + \text{D}_2$ reaction with the results of $\text{H}_2 + \text{H}_2$ reaction reported by Bartolomei et al. [43]. For the CID and 4C processes, the two combinations ($\text{H}_2 + \text{D}_2$ and $\text{H}_2 + \text{H}_2$) have similar energy threshold behavior and probability profiles within the same initial states. However, the energy thresholds are lower for the $\text{H}_2 + \text{D}_2$ reaction than for the $\text{H}_2 + \text{H}_2$ reaction. For the SE and 3BC processes, the probability curves for the $\text{H}_2 + \text{D}_2$ reaction are much more structured.

Full-Dimensional Wave Packet Dynamics of $\text{H}_2 + \text{D}_2$ Reaction

4.1 Introduction

Quantum scattering calculations give information on the detailed dynamics of a chemical reaction, provide results that can be compared in detail with those obtained in the experiments and serve as one of the most rigorous tests of the accuracy of potential energy surfaces (PESs) for chemical reactions [11, 72, 100]. Recent studies of chemical reaction dynamics in the gas phase have ranged from triatomic and tetraatomic systems to larger polyatomic systems. The development of efficient computational algorithms and improved computational resources have enabled a great deal of theoretical work aimed at building high-dimensional PESs with chemical accuracy [67, 74, 107] and performance of rigorous full-dimensional quantum scattering calculations for polyatomic reactions involving as many as six atoms [26, 27, 28, 29, 30, 31, 32].

The study of four-atom bimolecular reaction dynamics is of relevance in astrochemistry and theoretically serves as a bridge between triatomic reactions and polyatomic reactions of five or more atoms [108]. Rigorous quantum scattering calculations on three- or four-atom reactions are achievable nowadays to provide information ranging from rate constants to detailed state-to-state resolved probabilities [20, 21, 22, 23, 54, 109, 110, 111, 112, 113, 114, 115, 116, 117]. Zhang *et al.* [116] have performed a full-dimensional quantum mechanical study on the abstraction and

exchange processes in the $\text{H} + \text{H}_2\text{O}$ reaction by treating both OH bonds in the H_2O reactant as reactive bonds. It suggested that one may be able to accurately study the four-center (4C) reactions which involve cleavage of two bonds $\text{AB} + \text{CD} \rightarrow \text{AC} + \text{BD}$, $\text{AD} + \text{BC}$, which have been widely studied in the past both experimentally and theoretically [55, 56, 57, 58, 59]. In contrast to three-center reactions where only one bond is broken and formed during the reaction process, 4C reactions involve the simultaneous cleavage and formation of two bonds, and they usually present very high barriers, comparable to or higher than a covalent bond energy. Raz and Levine [56, 57, 58, 59] 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). The 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 classical trajectory studies on 4C reactions induced by cluster impact. At the same time, the 4C process has to compete with two other reactions: collision induced dissociation (CID), $\text{AB} + \text{CD} \rightarrow \text{A} + \text{B} + \text{CD}$, $\text{AB} + \text{C} + \text{D}$, which is known to be very important at the high energies where 4C reactions take place, and single exchange reaction (SE), $\text{AB} + \text{CD} \rightarrow \text{AC} + \text{B} + \text{D}$, $\text{AD} + \text{B} + \text{C}$, $\text{BC} + \text{A} + \text{D}$, $\text{BD} + \text{A} + \text{C}$. The coexistence of several processes and the higher energy required to surmount the barrier pose a challenge to the exact full-dimensional quantum studies of these processes. Therefore, most theoretical dynamics studies were based on classical or quasi-classical trajectories (QCT) [55, 56, 57, 58, 59].

Being the simplest neutral molecule-molecule system, the H_4 system has served as a prototype for accurate calculations of tetraatomic potential energy surfaces (PESs) as well as accurate quantum dynamics treatment of diatom-diatom collisions. At the same time, the collisions between two hydrogens are prevalent in the interstellar medium, in the atmospheres of planets, in combustion chemistry, and in many other chemical and industrial processes [33, 34, 35, 36]. Due to the light masses in the H_4 system, high level *ab initio* calculations are possible, and two global six-dimensional H_4 PESs have been reported: one by Aguado *et al.* (ASP) [38] and another by Boothroyd *et al.* (BMKP) [39]. The first quantum mechanical (QM) time-independent calculation of the $\text{H}_2 + \text{H}_2$ reaction performed using a reduced dimensionality approach was

carried out by Hernández and Clary [40]. The same model was subsequently investigated in greater detail and with higher accuracy by José Campos-Martínez *et al.* [41, 42, 43, 44, 45] and by Lu *et al.* [46] using wave packet propagation techniques. Full-dimensional QCT studies of the dynamics of the $\text{H}_2 + \text{H}_2$ system and its isotopic variants have also been published in the last decade [33, 47, 48, 49, 50, 51, 52, 53]. However, in the QCT approach, the absence of tunneling effects, which are expected to be important at threshold energies, and zero-point energy leakage can introduce significant errors. An important progress in the accurate quantum dynamics calculations of the $\text{H}_2 + \text{H}_2$ reaction was made by the work of Lu *et al.* [54] In their study, initial state-selected total reaction probabilities for the three competitive processes are reported with the total angular momentum $J = 0$ and the effect of reagent vibration on reactions is examined on ASP PES. They concluded that the 4C reaction is non-negligible in high-energy $\text{H}_2 + \text{H}_2$ collision dynamics and the vibrational excitation of H_2 (hot diatom) is much more efficient than translational energy on promoting the reaction processes. Another burst of interest in the study of H_4 system has led to the calculations of nonreactive vibrational de-excitation cross sections using full-dimensional QM methods of both time-independent [118, 119, 120] and time-dependent type [121, 122].

More recently, we carried out reduced-dimensional time-dependent wave packet calculations of the $\text{H}_2 + \text{D}_2$ reaction with six different geometries, in which three of them were studied for both coplanar and non-coplanar geometries [123]. It was found that the orientation of the cold diatom (coplanar and non-coplanar) does not greatly affect the CID process. However, the orientation of the hot diatom has a significant effect on the reaction process. For 4C and SE processes, they have the same energy threshold behavior which is quite similar to the CID process, i.e. an initial vibrational excitation of the hot molecule is more efficient than translational energy in facilitating the reaction processes. For the three-body complex formation (3BC) process, $\text{AB} + \text{CD} \rightarrow \text{ACB} + \text{D}$, $\text{ADB} + \text{C}$, $\text{CAD} + \text{B}$, $\text{CBD} + \text{A}$, however, it presents a clear vibrational inhibition effect.

On the experimental side, the mechanism of 4C reaction in the H_4 system has been a subject of controversy in the past several decades [40, 55, 124]. A reaction path was proposed with a 4C transition state located well below the dissociation threshold of either reactant [125, 126].

However, experiments were not completely conclusive since it was found that low levels of impurities played an important role. Hydrogen atoms generated by impurities would initiate the chain reactions $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$, $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$. Hence the percentage of HD arising from the 4C reaction was difficult to ascertain. Lifshitz and co-workers [124] carried out experiments with ultra clean shock tube and found that no (or less than 1%) HD products are found when no H atoms are detected. Thus they concluded that the formation of a 4C transition state is highly doubtful, at least below the dissociation threshold of H_2 .

From the theoretical point of view, it is always difficult to choose a suitable and convenient coordinate system to deal with quantum reactive scattering, especially for multi-channel reactive systems. Although the hyperspherical coordinates have been widely applied to three-atomic systems, rigorous quantum treatment of reactive dynamics in hyperspherical coordinates is still very rare for tetraatomic systems [127, 128, 129]. Based on a specific flux analysis scheme on the diatomic-diatomic reactant Jacobi coordinates, we have investigated the reaction dynamics of $\text{H}_2 + \text{D}_2$ in this study. We performed full-dimensional quantum dynamics calculations for the $\text{H}_2 (v_1, j_1) + \text{D}_2 (v_2, j_2)$ reaction with the total angular momentum $J = 0$ employing a time-dependent initial state-selected wave packet method [20, 21, 23]. Initial state-specific total reaction probabilities with $J = 0$ for different competitive processes have been calculated on the recent ASP and BMKP PESs. The reaction probabilities are not measurable quantities as only the wave $J = 0$ is considered. The measurable ones, such as reaction cross sections and rate constants, require summing the reaction probabilities over all partial waves and are extremely expensive computationally. The aims of the calculations here are: (a) to perform an extended study of the effect of different kinds of initial energy (translation energy, vibrational energy and rotational energy) on the reaction processes, and (b) to focus on isotopic substitution effects. The initial state-selected probabilities for the $\text{H}_2 + \text{D}_2$ reaction have been compared with the corresponding ones for the $\text{H}_2 + \text{H}_2/\text{HD}$ reactions. In Sec. 4.2, the theoretical methodology of the initial state-selected time-dependent wave packet (ISSWP) method is outlined. Sec. 4.3 presents the results and discussions. A summary is given in Sec. 4.4.

4.2 Theory

The initial state-selected time-dependent wave packet method used in the present study is mainly based on the earlier time-dependent wave packet studies of the diatom-diatom reactions [20] and is the same as in the similar study on $\text{H}_2 + \text{H}_2$ [54]. Here we only briefly outline the theoretical aspects of the time-dependent wave packet approach.

The reactant Jacobi coordinates shown in Fig. 4.1 are chosen in the wave packet calculations. The time-dependent Schrödinger equation is given by

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi \quad (4.1)$$

and the full-dimensional Hamiltonian in the body-fixed (BF) frame for a given total angular momentum J can be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \hat{h}_1(r_1) + \hat{h}_2(r_2) + \frac{(\hat{J} - \hat{j}_{12})^2}{2\mu R^2} + \frac{\hat{j}_1^2}{2\mu_1 r_1^2} + \frac{\hat{j}_2^2}{2\mu_2 r_2^2} + \hat{V}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2), \quad (4.2)$$

where μ is the reduced mass between the center-of-mass of AB and CD, $\hat{J}$ is the total angular

Figure 4.1: The six-dimensional Jacobi coordinates for $\text{AB} + \text{CD}$ system in the reactant channel. R is the distance between the center-of-mass of molecule AB and CD, r_1 is the bond distance of AB, r_2 is the bond distance of CD, θ_1 is the angle between R and r_1 , θ_2 is the angle between R and r_2 and Φ is the out-of-plane torsional angle.

momentum operator, and $\hat{j}_1$ and $\hat{j}_2$ are the rotational angular momentum operators of AB and CD, which are coupled to $\hat{j}_{12}$. $\hat{h}_1(r_1)$ and $\hat{h}_2(r_2)$ are one-dimensional (1D) reference Hamiltonians. The corresponding eigenstates for $\hat{h}_1(r_1)$ and $\hat{h}_2(r_2)$ are denoted by $\phi_{v_1}(r_1)$ and $\phi_{v_2}(r_2)$, and

$$\hat{h}_i(r_i) \phi_{v_i}(r_i) = \left[-\frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial r_i^2} + \hat{V}_i(r_i) \right] \phi_{v_i}(r_i) = \epsilon_{v_i} \phi_{v_i}(r_i) \quad (i = 1, 2), \quad (4.3)$$

where $\hat{V}_1(r_1)$ and $\hat{V}_2(r_2)$ are the diatomic potentials for AB and CD, respectively.

The time-dependent wave function is expanded in terms of the BF rovibrational eigenfunctions as

$$\psi_{v_0 j_0 K_0}^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, t) = \sum_{n, v, j, K} F_{n v j K, v_0 j_0 K_0}^{JM\epsilon}(t) u_n^{v_2}(R) \phi_{v_1}(r_1) \phi_{v_2}(r_2) Y_{jK}^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2), \quad (4.4)$$

where n is the translational basis label, v denotes (v_1, v_2) , j denotes (j_1, j_2, j_{12}) , (v_0, j_0) denotes the initial rovibrational state, and ϵ is the parity of the system defined as $\epsilon = (-1)^{j_1+j_2+L}$ with L being the orbital angular momentum quantum number. As shown by Hernández and Clary [40], one of the H_2 should be highly excited in order for dissociation to occur. We choose AB (H_2) as the highly excited one and use a uniform basis for AB in the asymptotic and interaction regions. For CD (D_2), it is well known that the closed components of the wave function are essentially zero in the asymptotic area, and so we only need to include “open” vibrational channels in the asymptotic region. However, both closed and open vibrational channels are needed in the interaction region.

The normalized translational basis function, which was first employed in the work of Zhang *et al* [21, 23], is defined as

$$u_n^{v_2}(R) = \begin{cases} \sqrt{\frac{2}{R_3-R_1}} \sin \frac{n\pi(R-R_1)}{R_3-R_1}, & v_2 \leq v_{asy}, \\ \sqrt{\frac{2}{R_2-R_1}} \sin \frac{n\pi(R-R_1)}{R_2-R_1}, & v_2 > v_{asy}, \end{cases} \quad (4.5)$$

where R_2 and R_3 define the interaction and asymptotic grid ranges, and v_{asy} is chosen to be the number of energetically open vibrational channels plus one or two closed vibrational channels of the reactive CD. The $Y_{jK}^{JM\epsilon}$ in Eq. (4.4) is the coupled BF total angular momentum eigenfunctions which can be written as

$$Y_{jK}^{JM\epsilon} = (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} [D_{K,M}^J Y_{j_1 j_2}^{j_{12} K} + \epsilon (-1)^{j_1+j_2+j_{12}+J} D_{-K,M}^J Y_{j_1 j_2}^{j_{12} -K}], \quad (4.6)$$

where $D_{K,M}^J$ is the Wigner rotation matrix, ϵ is the parity of the system, and $Y_{j_1 j_2}^{j_{12} K}$ is the angular momentum eigenfunction of $\hat{j}_{12}$ defined as

$$Y_{j_1 j_2}^{j_{12} K} = \sum_{m_1} \langle j_1 m_1 j_2 K - m_1 | j_{12} K \rangle y_{j_1 m_1}(\theta_1, 0) y_{j_2 K - m_1}(\theta_2, \Phi), \quad (4.7)$$

where y_{jm} are spherical harmonics. Note the restriction that $\epsilon(-1)^{j_1+j_2+j_{12}+J=1}$ for $K = 0$.

The initial wave function is chosen as the product of a specific rovibrational eigenfunction and a localized translational wave packet,

$$\Psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, t = 0) = \varphi_{k_0}(R) \phi_{v_{10}j_{10}}(r_1) \phi_{v_{20}j_{20}}(r_2) Y_{j_0 K_0}^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2), \quad (4.8)$$

where j_0 denotes $(j_{10}, j_{20}, j_{120})$ and the radial function is chosen to be a standard Gaussian wave packet,

$$\varphi_{k_0}(R) = \left(\frac{1}{\pi \delta^2} \right)^{1/4} e^{-(R-R_0)^2/2\delta^2} e^{-ik_0 R}.$$

The split-operator method [87] is employed to propagate the wave packet,

$$\Psi^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, t + \Delta) = e^{-i\hat{H}_0\Delta/2} e^{-i\hat{U}\Delta} e^{-i\hat{H}_0\Delta/2} \Psi^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, t), \quad (4.9)$$

where the reference Hamiltonian $\hat{H}_0$ is defined as

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \hat{h}_1(r_1) + \hat{h}_2(r_2)$$

and the effective potential operator $\hat{U}$ is defined as the difference between the Hamiltonian $\hat{H}$ and the reference Hamiltonian $\hat{H}_0$.

From the propagation of the wave packet, we can calculate the time-independent scattering wavefunction (TIDWF) by performing a Fourier transform

$$|\psi_{iE}^+\rangle = \frac{1}{a_i(E)} \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}(E-\hat{H})t} |\Psi_i(0)\rangle dt, \quad (4.10)$$

where the coefficients $a_i(E)$ can be simply evaluated as

$$a_i(E) = \langle \psi_{iE}^+ | \Psi_i(0) \rangle = \langle \phi_{iE} | \Psi_i(0) \rangle, \quad (4.11)$$

where ϕ_{iE} is the free or asymptotic stationary wavefunction.

The initial state-selected total reaction probabilities can be obtained by calculating the reactive flux

$$P_i^R(E) = \sum_f |S_{fi}^R|^2 = \langle \psi_{iE}^+ | \hat{F} | \psi_{iE}^+ \rangle, \quad (4.12)$$

where $\hat{F}$ is the flux operator [130] defined as

$$\hat{F} = \frac{1}{2} [\delta(\hat{s} - s_0) \hat{v}_s + \hat{v}_s \delta(\hat{s} - s_0)],$$

where $\hat{s}$ is the coordinate perpendicular to a surface located at s_0 for the flux evaluation, and $\hat{v}_s$ is the velocity operator corresponding to the coordinate.

In order to obtain the CID, 4C and SE reaction probabilities, we calculate the TIDWF, $\psi_i^+(E)$, on one dividing surface which comprises three planes denoted by $S[R^F], S[r_1^F], S[r_2^F]$. These three planes are defined as

$$S[R^F] : R = R^F, r_1 \leq r_1^F, r_2 \leq r_2^F,$$

$$S[r_1^F] : R \leq R^F, r_1 = r_1^F, r_2 \leq r_2^F,$$

$$S[r_2^F] : R \leq R^F, r_1 \leq r_1^F, r_2 = r_2^F.$$

$\psi_i^+(E)$ is further transferred from Jacobi coordinates to inter-atomic distances coordinates, and then the flux is analyzed based on the inter-atomic distances – an approach popular in classical molecular dynamics.

We have taken into account the symmetry under exchange of identical particles for each diatom. Exchange symmetrization for all identical particles is achievable for a triatomic system [128, 129, 131], but remains a challenge for the tetraatomic $\text{H}_2 + \text{H}_2/\text{HD}$ system. It is difficult to deal with exchange symmetry in tetraatomic reactions either in Jacobi or hyperspherical coordinates. The initial wavefunctions employed in our calculations for the $\text{H}_2+\text{H}_2/\text{HD}$ reactions therefore do not yet fully satisfy the exchange symmetry.

The CID process is similar to the $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ reaction in which only one old bond is broken. Zhang and Zhang [20] have studied this reaction employing the same time-dependent wave packet method where the exchange symmetry of the indistinguishable hydrogens is also neglected. They have concluded that the rate constant is in good agreement with the experimental result. Therefore, we believe that the effect of the exchange symmetrization on the CID process here is also not significant, as the unbroken diatom is well localized in the CID process. However, in the four-center (4C) and single-exchange (SE) processes, two old bonds are broken simultaneously, and the localization property is completely lost when the two reactants come together in the scattering region. Exchange symmetry may have an effect on the 4C and SE processes.

Generally, it is necessary to consider exchange symmetrization in calculating the integral cross section for comparison with experimental values. Here, however, our results can be viewed as benchmarking results for the $\text{H}_2+\text{H}_2/\text{HD}$ reaction probability on the BMKP PES.

4.3 Results and Discussion

A sufficiently large grid/basis size was chosen to obtain converged probabilities. For the translational coordinate R , we used 54 sine discrete variable representation (DVR) grids for the interaction region in a range of $[0.0, 7.8] a_0$, 29 sine DVR grids for the asymptotic region in a range of $[7.8, 12.0] a_0$. A total of 75 potential optimized discrete variable representation (PODVR) grids were employed for r_1 in a range of $[0.5, 12.0] a_0$ for both the interaction and asymptotic regions, since it is highly excited in the vibration state initially. While for r_2 61 PODVR grids were used for the interaction region in a range of $[0.5, 7.5] a_0$ and 12 for the asymptotic region. We used $j_1^{max}=54$ and $j_2^{max}=52$, resulting in a total of 13860 coupled rotational basis for the even parity after considering the exchange symmetry of H (D) atom in the H_2 (D_2) molecule. The flux positions R^F , r_1^F , and r_2^F were taken as 7.5, 10.0, and 5.5 a_0 , respectively. The center of the Gaussian wave packet was located at $R_0 = 10.0 a_0$ with the width $\delta = 0.4 a_0$. The center momentum of the wave packet, k_0 , was chosen according to the initial state to cover interesting energy range. The initial wave packet was propagated for 5000 a.u., with a time increment $\Delta = 10$ a.u. At the edges of R , r_1 and r_2 , absorption potentials were applied to prevent the wave packet from reflecting back from the boundaries. The parameters employed in the isotope substitution calculations are the same as those of $H_2 + D_2$ except that for $H_2 + H_2$ 43 PODVR grids were used for the interaction region and 8 for the asymptotic region for r_2 coordinate.

4.3.1 Extraction of 4C, CID and SE Reaction Probabilities

The separation of reactive flux for different channels based on diatomic-diatomic reactant Jacobi coordinates is not straightforward in the study of the dynamics of this system. We will elaborate on the procedure we have adopted in the calculations in this section.

As an example, Figure 4.2(a)-(c) shows the reaction flux distribution for the H_2 ($v_1=10$, $j_1=0$) + D_2 ($v_2=0$, $j_2=0$) ($\equiv A_2 + B_2$) reaction at a translational energy of 0.5 eV on the planes $S[R^F]$, $S[r_1^F]$ and $S[r_2^F]$, respectively. The contour lines were rescaled to the maximum value of 1. Figure 4.2 (a) shows the flux distribution on the $S[R^F]$ plane as a function of r_1 and r_2 . It can be seen that the flux is localized in a small range of r_1 and r_2 values. A further test by projecting of the TIDWF on the bound states of A_2 and B_2 confirmed that both A_2 and B_2 are in their bound

states. Thus the flux shown in the figure corresponds to the nonreactive scattering process. The flux in figure 4.2 (b) is for the $S[r_1^F]$ plane as a function of R and r_2 with the A_2 bond cleaved. In the plane, the flux spreads in a large range of R values, but is localized in a small range of r_2 values. A projection of the TIDWF on the bound states of B_2 reveals that the B_2 diatom is exclusively in its bound states. Hence, the flux on this plane contributes to the CID process. Figure 4.2(c) shows the flux distribution on the $S[r_2^F]$ plane as a function of R and r_1 with the B_2 bond broken. Clearly, the reactive flux has spread over the entire range of R and also massively in r_1 , and the flux has separated into two parts, one is below $r_1 = 2.0 a_0$, and the other one is over $2.0 a_0$. The one at the bottom corresponds to the CID process, which means the B_2 bond is broken while the hot A_2 diatom is quenched. Such a process occurs if the high vibrational A_2 diatom has transferred most of its vibrational energy to the cold B_2 diatom, which is definitely a rare event. The flux in the area where r_1 is greater than $2.0 a_0$ is assigned to the 4C and SE processes, as in the area the two old reagent bonds are both cleaved.

The calculation of CID probability is quite straightforward since the reactive flux in the $S[r_1^F]$ plane is well localized. For the flux in the $S[r_2^F]$ plane, we can transfer it into basis representation for the A_2 diatom, as for the CID product in this plane the A_2 diatom is in its bound states. Of course, neglecting the flux in the $S[r_2^F]$ plane will not introduce big errors due to the low frequency of such a process. The challenge is how to separate the flux for the 4C channel from the SE channel. Ideally, one could calculate the state-to-state reaction probability. However, state-to-state calculation for this system is not feasible in a quantum framework at the moment. For clarity let us denote the four reactive atoms by A, B, C and D. In reality, the combinations of the four atoms to 4C products fall into two groups: (AC, BD) and (AD, BC). Thus, we can use the minimum value of the bond lengths of these four possible diatoms (denoted as r_{min}) and the bond length of the counterpart diatom (denoted as r_{min}^{CP}) as the two independent variables to describe whether the products are able to form a chemical bond, i.e., if the bond length of AC (AD) is the minimum value r_{min} , the bond length of BD (BC) is its counterpart r_{min}^{CP} , and vice versa. For each point (R, r_1) in the $S[r_2^F]$ plane, there corresponds a point (r_{min}, r_{min}^{CP}) in the new plane. Although the corresponding relationship is not a one-to-one mapping, we can sum up $|\psi_i^+(E)|^2$ at the points in the $S[r_2^F]$ plane which correspond to the same value of $(r_{min},$

r_{min}^{CP}) to obtain the distribution in the new (r_{min}, r_{min}^{CP}) plane. Numerically, the summing is done by the “binning” procedure for r_{min} and r_{min}^{CP} in their possible range. Therefore, $|\psi_i^+(E)|^2$ is transferred from a function of the reactant Jacobi coordinates (R, r_1) to a double variable function in (r_{min}, r_{min}^{CP}) space. Actually, in the numerical calculations, we firstly transfer the TIDWF in the $S[r_2^F]$ plane from the DVR to the finite basis representation (FBR), filter out the CID components of the TIDWF in the FBR, and then transfer them back to the DVR. In the DVR, each point denoting by five degrees of freedom $(R, r_1, \theta_1, \theta_2, \Phi)$ corresponds a point in the new (r_{min}, r_{min}^{CP}) plane. We directly represent the TIDWF in this new plane, not recur to the (R, r_1) plane. According to the distribution of $|\psi_i^+(E)|^2$ in the (r_{min}, r_{min}^{CP}) plane, we are able to know statistically in which area of $|\psi_i^+(E)|^2$ is TIDWF for 4C and SE processes. Figure 4.2 (d) is a showcase for this method. It shows the $|\psi_i^+(E)|^2$ from the $S[r_2^F]$ plane at $E_{trans} = 0.5$ eV as a distribution function of (r_{min}, r_{min}^{CP}) . From this figure, we can see that most 4C reactive flux are located in the area where r_{min}^{CP} is below $5.5 a_0$ and the rest are for the SE flux. This scheme has been applied to the different collisional energy values in our work. The “binning” method employed in the calculations will unavoidably introduce errors for the separation of 4C and SE probabilities. Estimating the errors would require exact state-to-state calculations which are unfeasible today. However, we believe that they are insignificant and negligible. A comparison of quasiclassical trajectory calculations with quantum-mechanical calculations has been done by E. Carmona-Novillo *et al.* [45] in a three-dimensional model. They concluded that agreement between both approaches for the 4C reaction is excellent in the post-threshold regime. This may in some ways suggest that the introduced errors are negligible.

4.3.2 Effect of Vibrational Energy

Figure 4.3 shows the 6D CID probabilities for the H_2 ($v_1=10, 11, j_1=0$) + D_2 ($v_2=0, j_2=0$) reaction as a function of total energy on the ASP and BMKP PESs. In order to make it easy to convert total to collision energies, the excitation energies are also given in the figure caption. Hereafter, energies are referred to the bottom of the $H_2 + D_2$ entrance valley. Solid lines represent the ASP PES results while dash lines refer to the BMKP PES ones. We can see that firstly there exists a vibrational enhancement effect. As v_1 increases, the energy thresholds are shifted to lower

Figure 4.2: (a)-(c) 6D reaction flux distribution for the H_2 ($v_1=10$, $j_1=0$) + D_2 ($v_2=0$, $j_2=0$) reaction at a translational energy of 0.5 eV on the planes $S[r_1^F]$, $S[r_2^F]$ and $S[R^F]$; (d) $|\psi_i^+(E)|^2$ as a function of r_{min} and r_{min}^{CP} .

Figure 4.3: 6D collision induced dissociation probabilities for initial states ($v_1=10, 11, j_1=0, v_2=0, j_2=0$) on the ASP and BMKP PESs as a function of the total energy. The excitation energy of the system $E(v_1=10, v_2=0) = 4.32$ eV and $E(v_1=11, v_2=0) = 4.54$ eV. Energies are referred to the bottom of the $H_2 + D_2$ entrance valley.

energies and the probability profiles become steeper. Secondly, the energy threshold behavior and probability profiles are quite similar for the two PESs, except that the BMKP PES shows a slightly lower energy threshold than the ASP PES within the same initial state. The corresponding 6D 4C and SE probabilities for the $H_2 + D_2$ reaction are plotted in Fig. 4.4. Comparing the 4C and SE probabilities with the CID probabilities in Fig. 4.3, it is found that the 4C and SE probabilities are at least one order of magnitude smaller than the CID ones. Hence, the CID process is dominant over the energy range considered, and at high translational energies the 4C process is more probable than the SE process. Overall, although the differences between the two PESs are significant at a quantitative level, both PESs provide qualitatively the same dynamical behavior. Considering that the BMKP PES is more elaborate than the older ASP PES, hereafter, we will merely present the results obtained from the more recent BMKP PES.

In Fig. 4.5, we present the 6D CID probabilities for the $H_2(v_1=10, j_1=0) + D_2(v_2=0-2, j_2=0)$ reaction on the BMKP PES, which correspond to different vibrational excitation of the cold diatom. Here, a vibrational inhibition effect is found for the CID process. As v_2 increases, the energy thresholds are shifted to higher energies. The probability curves with higher initial

Figure 4.4: 6D four center and single exchange probabilities for initial states ($v_1=10, 11, j_1=0, v_2=0, j_2=0$) on the ASP and BMKP PESs as a function of the total energy.

states increase more smoothly. Figure 4.6 shows the 4C and SE probabilities for the $H_2 + D_2$ reaction. From this figure, we can find that the vibrational excitation of the cold diatom presents a completely different effect on the 4C and SE processes, i.e. vibrational inhibition on the 4C process but vibrational enhancement on the SE process. The vibrational inhibition effect on the 4C process indicates that the v_2 vibrational states do not change too much along the reaction path from reactants to the reaction bottleneck, i.e., the v_2 states connect adiabatically with quantized transition states. As pointed out by D. di Domenico *et al.* [41], based on a simple reduced-dimensional trapezoidal model, the v_2 initial states will connect adiabatically with a quantized transition state, and for this vibrational mode the reaction is of an “early barrier” type. Thus, the reagent translational energy is more effective in bringing about the 4C reaction than the vibrational excitation of the cold reagent.

4.3.3 Effect of Rotational Energy

In the reduced three-dimensional dynamics calculations for the $H_2 + H_2$ and $H_2 + D_2$ reactions, it was found that the orientation of the cold diatom did not greatly affect the reaction process, while the orientation of the hot diatom had a significant effect [43, 123]. It is interesting to check this conclusion in a full-dimensional model by studying the effect of the initial rotational

Figure 4.5: 6D collision induced dissociation probabilities for initial states ($v_1=10$, $j_1=0$, $v_2=0-2$, $j_2=0$) on the BMKP PES as a function of the total energy. The excitation energy E ($v_1=10$, $v_2=0$) = 4.32 eV, E ($v_1=10$, $v_2=1$) = 4.69 eV and E ($v_1=10$, $v_2=2$) = 5.05 eV.

Figure 4.6: 6D four center and single exchange probabilities for initial states ($v_1=10$, $j_1=0$, $v_2=0-2$, $j_2=0$) on the BMKP PES as a function of the total energy.

Figure 4.7: 6D collision induced dissociation probabilities for initial states ($v_1=10$, $j_1=0, 4, 8$, $v_2=0$, $j_2=0$) on the BMKP PES as a function of the total energy. The excitation energy $E(v_1=10, j_1=0) = 4.32$ eV, $E(v_1=10, j_1=4) = 4.39$ eV and $E(v_1=10, j_1=8) = 4.56$ eV.

excitation of both reagents on the competitive reaction processes. It should be noted that the rotational effect present for $J = 0$ calculations changed when all relevant partial waves for $J > 0$ were included [117]. The aims of studying the rotational effect for $J = 0$ are: (a) for comparing the results with three-dimensional ones, and (b) for benchmarking purposes. Figure 4.7 shows the CID probabilities with different rotational states of the hot diatom H_2 ($j_1=0, 4, 8$) on the BMKP PES. Obviously, the initial rotational excitation of the hot diatom has a significant effect on the CID process. As j_1 increases, the energy thresholds are shifted to slightly lower energies. However, the CID probabilities for the hot diatom H_2 in the ground rotational state increase much faster than those in the excited rotational states as collisional energy increases further. The 6D 4C and SE probabilities are shown in Fig. 4.8. It is clear that, while there is a rotational enhancement effect for the SE process, the energy thresholds and the probability profiles are almost identical for the three different rotational states for the 4C process.

In order to study the effect of the initial rotational excitation of the cold diatom, we present the 6D CID, 4C and SE probabilities for the $H_2(v_1=10, j_1=0) + D_2(v_2=0, j_2=0, 4, 8)$ reaction in Figs. 4.9 and 4.10. From Fig. 4.9, it is seen that the CID process shows a clear rotational inhibition effect, i.e., energy thresholds are higher for the higher j_2 's, and as j_2 increases further,

Figure 4.8: 6D four center and single exchange probabilities for initial states ($v_1=10$, $j_1=0$, $v_2=0$, $j_2=0, 4, 8$) on the BMKP PES as a function of the total energy.

the inhibition effect on the CID process becomes more substantial. The 4C and SE probabilities are rather smaller than the CID probabilities, as shown in Fig. 4.10. Presumably, the initial rotational excitation of the cold reagent enhances the SE process but inhibits the 4C process, and the effect becomes more substantial for higher rotational states. However, the enhancement (or inhibition) effect is insignificant as the energy thresholds and probability profiles for different rotational states are quite similar. Therefore, the conclusion is not completely consistent with the reduced-dimensional calculation [123]. In the full-dimensional model, we find that the rotational excitation of the cold reagent has a significant effect on the CID process while it has a negligible effect on the 4C and SE processes.

4.3.4 Isotope Substitution Effects

The isotope effect (such as quantum tunneling and zero point energy shift) in chemical reactions has attracted great interest in the past several decades, as when a chemical reaction occurs at low temperature and translational energy, the isotope tunneling effect often makes the reaction happen below the classical barrier height. The isotope effect on the potential energy surface reflects mainly the zero-point energy revision to the reaction path due to the change of the normal vibration frequencies. Thus, the isotope substitution effect generally has a remarkable

Figure 4.9: 6D four center and single exchange probabilities for initial states ($v_1=10$, $j_1=0$, 4, 8, $v_2=0$, $j_2=0$) on the BMKP PES as a function of the total energy.

Figure 4.10: 6D collision induced dissociation probabilities for initial states ($v_1=10$, $j_1=0$, $v_2=0$, $j_2=0$, 4, 8) on the BMKP PES as a function of the total energy. The excitation energy $E(v_1=10, j_2=0) = 4.32$ eV, $E(v_1=10, j_2=4) = 4.40$ eV and $E(v_1=10, j_2=8) = 4.58$ eV.

influence on the micro-dynamics.

Figure 4.11: 6D collision induced dissociation probabilities for H_2 ($v_1=10, 11, j_1=0$) + $\text{H}_2/\text{HD}/\text{D}_2$ ($v_2=0, j_2=0$) on the BMKP PES as a function of the total energy. The excitation energy $E_{\text{H}_2-\text{H}_2}$ ($v_1=10, v_2=0$) = 4.40 eV, $E_{\text{H}_2-\text{HD}}$ ($v_1=10, v_2=0$) = 4.37 eV, $E_{\text{H}_2-\text{D}_2}$ ($v_1=10, v_2=0$) = 4.32 eV, $E_{\text{H}_2-\text{H}_2}$ ($v_1=11, v_2=0$) = 4.62 eV, $E_{\text{H}_2-\text{HD}}$ ($v_1=11, v_2=0$) = 4.58 eV and $E_{\text{H}_2-\text{D}_2}$ ($v_1=11, v_2=0$) = 4.54 eV.

Figure 4.11 shows the 6D CID probabilities for the H_2 ($v_1=10, 11, j_1=0$) + $\text{H}_2/\text{HD}/\text{D}_2$ ($v_2=0, j_2=0$) on the BMKP PES as function of the total energy. Solid lines represent the results for $\text{H}_2 + \text{H}_2$, dash lines for $\text{H}_2 + \text{HD}$ and dotted lines for $\text{H}_2 + \text{D}_2$. As can be seen from this figure, the three different isotope combinations present similar energy threshold behavior and probability profiles. There exists a vibrational enhancement effect. As v_1 increases, thresholds are shifted to lower energies and the probability profiles become steeper. This behavior has been discussed in detail for the $\text{H}_2 + \text{D}_2$ reaction above, so we will mainly focus here on the isotope substitution effect. It can be found that much more important differences among the different isotope combinations are the dissociation probabilities, particularly their thresholds, where dissociation is most effective for the $\text{H}_2 + \text{D}_2$ reactants and least effective for the $\text{H}_2 + \text{H}_2$ reactants. The difference is partially due to the different reduced masses of the isotope combinations and the zero point energy shift. As we know, for the three different colliders, D_2 has the lowest zero point energy while H_2 has the highest zero point energy. Based on zero point energy considerations, however, one would

expect that it is harder to bring D_2 to dissociation than H_2 , which is inconsistent with our results. Actually, this can be explained by a simple trapezoidal model, as has been done by M. I. Hernández *et al.* [44], to preform plots of the potential energy surface using mass-scaled coordinates and adding the zero point energy for the different colliders. They found that the potential barrier is lower for $H_2 + D_2$ than for $H_2 + H_2$, giving an indication on why dissociation is most likely for $H_2 + D_2$.

Figure 4.12: 6D four center and single exchange probabilities for H_2 ($v_1=10, 11, j_1=0$) + $H_2/HD/D_2$ ($v_2=0, j_2=0$) on the BMKP PES as a function of the total energy.

The 6D 4C and SE probabilities for the H_2 ($v_1=10, 11, j_1=0$)+ $H_2/HD/D_2$ ($v_2=0, j_2=0$) are shown in Fig. 4.12(a) and (b), respectively. From Fig. 4.12(a), it can be seen that firstly the

4C thresholds and probability profiles are almost identical for the different isotope combinations and the same initial vibrational states. Secondly, as v_1 increases, although there does not exist an apparent shift for the 4C energy threshold, the reaction probability becomes a little larger. Finally, it can also be noted that, for each initial vibrational state, the $\text{H}_2 + \text{H}_2$ curve is higher than that of $\text{H}_2 + \text{D}_2$ over the energy range above the threshold, and the $\text{H}_2 + \text{HD}$ curve is lower than that of $\text{H}_2 + \text{D}_2$. For the SE process shown in Fig. 4.12(b), the energy threshold behavior is similar to the 4C process. Again, the energy thresholds for the different combinations are mixed together and are almost identical. However, in contrast to the 4C process, the probability curves present a different order in the figure, which is $\text{H}_2 + \text{D}_2$, $\text{H}_2 + \text{HD}$ and $\text{H}_2 + \text{H}_2$ from low to high.

4.4 Conclusion

Using a full-dimensional time-dependent initial state-selected wave packet approach, we have calculated the probabilities of the $\text{H}_2 + \text{D}_2$ reaction for three competitive reaction processes: collision induced dissociation (CID), four-center reaction (4C) and single exchange reaction (SE) on the ASP and BMKP PESs. Both of the two reagents were initially excited to different vibrational states and rotational states to study the effect of different kinds of energy (translational energy, vibrational energy and rotational energy) on the reaction processes. Isotope substitution effect has also been investigated by substituting the collider D_2 by H_2 and HD . We concluded that firstly the vibrational excitation of the hot diatom presents an enhancement effect on the CID process while the vibrational excitation of the cold diatom presents an inhibition effect. The reaction probabilities for the 4C and SE processes are at least one order of magnitude smaller than those of CID process over the energy range considered. Secondly, the rotational excitation of both reagents has a significant effect on the CID process. Finally, although the three isotope combinations have similar energy threshold behavior and probability profiles, they present remarkable isotope substitution effect. For the CID process, the $\text{H}_2 + \text{D}_2$ combination is most efficient and the $\text{H}_2 + \text{H}_2$ is least efficient, and the $\text{H}_2 + \text{HD}$ combination lies in between. However, they have a different order for the 4C and SE processes.

Integral Cross Sections and Accuracy of The Centrifugal Sudden Approximation in $\text{H}_2 + \text{D}_2$ Reaction

5.1 Introduction

Quantum dynamical studies on chemical reactions of tetra-atomic and polyatomic systems have been carried out extensively, driven by the development of quantum scattering theory, advances in constructing potential energy surfaces (PESs), and the rise in computational power [11, 26, 27, 28, 30, 31, 67, 74, 107, 132, 133]. Quantum scattering calculations provide a complete description of the dynamics of a chemical reaction, and thus serve as the ultimate benchmarks for assessing various approximate theories and testing the accuracy of PESs for chemical reactions [72, 100]. Since the benchmark, full-dimensional (six-dimensional) wave packet calculations of the total reaction probabilities for the reaction $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ with total angular momentum $J = 0$ [20, 21, 22, 23], much progress has been made in the area of accurate quantum-dynamics simulations of four-atom reactions [134, 135, 136, 137]. The study of four-atom bimolecular reaction dynamics is of relevance to combustion, radical chemistry and astrochemistry, and theoretically serves as a bridge between triatomic reactions and polyatomic reactions of five or more

atoms [108, 138].

Being the simplest neutral molecule-molecule reaction, the $\text{H}_2\text{-H}_2$ system has long been considered as a benchmark candidate for quantum dynamics studies of molecule-molecule collisions. Detailed information on the kinetics and the dynamics of the four-atom $\text{H}_2 + \text{H}_2$ system is of key relevance in modeling several gas phase non-equilibrium complex technological processes, such as combustion [34, 35], spacecraft re-entry [36], and negative ion production from plasmas [139]. From the viewpoint of quantum chemistry, the four-electron system is ideal for high level *ab initio* calculations. Two global six-dimensional H_4 PESs have been reported: one by Aguado *et al.* (ASP) [38] and another by Boothroyd *et al.* (BMKP) [39]. Recently, Hinde [140] reported a full-dimensional PES for the $\text{H}_2\text{-H}_2$ system that includes an accurate description of the van der Waals interaction region. However, the PES of Hinde is designed to describe accurately the bound and quasibound states of the dimers $(\text{H}_2)_2$, $(\text{D}_2)_2$, and $\text{H}_2\text{-D}_2$ and thus not suitable for the current dynamical study of the $\text{H}_2 + \text{D}_2$ reaction.

For sufficiently high collision energies or high reactant internal excitation, several kinds of processes occur during the collision of hydrogen molecules. In addition to nonreactive elastic and inelastic processes, four-center (4C) reaction (exchange reaction) which involves cleavage of two bonds, $\text{AB} + \text{CD} \rightarrow \text{AC} + \text{BD}$, $\text{AD} + \text{BC}$, collision induced dissociation (CID) (nonreactive dissociation), $\text{AB} + \text{CD} \rightarrow \text{A} + \text{B} + \text{CD}$, $\text{AB} + \text{C} + \text{D}$, which is known to be very important at the high energies where 4C reaction happens, or single exchange (SE) reaction (reactive dissociation), $\text{AB} + \text{CD} \rightarrow \text{AC} + \text{B} + \text{D}$, $\text{AD} + \text{B} + \text{C}$, $\text{BC} + \text{A} + \text{D}$, $\text{BD} + \text{A} + \text{C}$, can take place. In contrast to three-center reactions where only one bond is broken and formed during the reaction process, 4C reactions involve simultaneous cleavage and formation of two bonds, and they usually present very high barriers, comparable to or higher than a covalent bond energy [40].

The coexistence of several processes and the higher energy required to surmount the barrier pose a challenge to the exact full-dimensional quantum studies of the reaction dynamics. Therefore, most theoretical dynamics studies have been performed using reduced dimensional or full-dimensional classical or quasi-classical trajectories (QCT) [33, 45, 47, 48, 49, 50, 51, 52, 53] and reduced dimensional quantum mechanical (QM) methods [40, 41, 43, 44, 46, 123]. Lu *et al.* [54] carried out the first accurate full-dimensional QM calculations of the $\text{H}_2 + \text{H}_2$ reaction using the

time-dependent wave packet method. In their study, initial state selected total reaction probabilities for the three competitive processes were reported with total angular momentum $J = 0$, and the effect of reagent vibration on reactions was examined on the ASP PES. Another area of interest in the study of the H_4 system are the calculation of nonreactive vibrational de-excitation cross sections using full-dimensional QM methods of both time-independent [118, 119, 120, 141] and time-dependent type [121, 142].

Recently, we performed full-dimensional time-dependent wave packet calculations of the $\text{H}_2 + \text{D}_2$ reaction and its isotopic variants on the ASP and BMKP PESs with $J = 0$ [143]. The role of both vibrationally and rotationally excited reagents was examined. We found that vibrational excitation of the hot diatom has an enhancement effect on the CID process while vibrational excitation of the cold diatom has an inhibition effect. The vibrational excitation of the cold diatom obviously enhances the SE process but inhibits the 4C process. The rotational excitation of both reagents has a significant effect on the reaction process. The 4C and SE reaction probabilities are at least one order of magnitude smaller than the CID probabilities over the energy range considered, and at high translational energies the 4C reaction probabilities are much larger than the SE probabilities for the ground rotational state. Furthermore, although the three isotope combinations ($\text{H}_2 + \text{H}_2$, $\text{H}_2 + \text{HD}$ and $\text{H}_2 + \text{D}_2$) have similar energy threshold behavior and probability profiles, they present remarkable isotope substitution effect. All these conclusions are, however, drawn from the non-measurable total reaction probabilities of $J = 0$. Thus the study is of limited conclusiveness on observables (cross sections or rate constants).

The centrifugal sudden (CS) approximation [144, 145, 146] provides tremendous conceptual simplicity and computational advantage over the coupled-channel (CC) theory and has been commonly used to calculate integral cross sections and rate constants for tetra-atomic and polyatomic reactions in the body-fixed (BF) frame [27, 117, 147, 148, 149, 150, 151, 152, 153]. Some tests were performed to investigate the accuracy of the CS approximation in different four-atom reactions, such as $\text{H}_2 + \text{OH}$, $\text{H}_2 + \text{CN}$, $\text{OH} + \text{HCl}$ and $\text{H} + \text{H}_2\text{O}$ [117, 148, 149, 150, 151, 152, 153]. It has been shown that for the $\text{H}_2 + \text{OH}$ and $\text{OH} + \text{HCl}$ reactions the CS approximation does not have a major effect. The CS cross sections are smaller than the CC cross sections in the low energy region, and larger than the CC ones in the high energy region for the $\text{H}_2 + \text{CN}$ reaction.

In strong contrast to what has been found in the above three diatom-diatom reactions, the CS approximation does not work well for both abstraction and exchange processes in the $\text{H} + \text{H}_2\text{O}$ reaction. All of these calculations are focused only on reactions involving cleavage of one old bond. For the reactions with simultaneous cleavage of two bonds, the accuracy of CS approximation has never been tested. Thus it is of practical value to carry out tests to address the accuracy of the CS approximation for the title reaction, especially for the 4C and SE processes.

Figure 5.1: The six-dimensional Jacobi coordinates for $\text{AB} + \text{CD}$ system in the reactant channel. R is the distance between the center-of-mass of molecule AB and CD , r_1 is the bond distance of AB , r_2 is the bond distance of CD , θ_1 is the angle between R and r_1 , θ_2 is the angle between R and r_2 and Φ is the out-of-plane torsional angle.

In this study, we use the time-dependent wave packet method to calculate integral cross sections for the $\text{H}_2 + \text{D}_2$ reaction by including all important K (the projection of the total angular momentum on the body-fixed axis) blocks within a full-dimensional model. As the cross sections reported are well converged with respect to the further increase of K blocks, they can be considered as the fully CC results for the reaction. We present the first fully converged integral cross sections for the ground rotational state of the $\text{H}_2 + \text{D}_2$ reaction on the BMKP PES. The effect of the total angular momentum on the dynamics of the $\text{H}_2 + \text{D}_2$ reaction and the accuracy of the CS approximation for the three different processes are also studied. The chapter is organized as follows: In Sec. 5.2, the theoretical methodology of the initial state selected wave packet (ISSWP) method is outlined. Sec. 5.3 presents the results and discussions. A summary is given in Sec. 5.4.

5.2 Theory

The ISSWP method employed in the present study is mainly based on the earlier time-dependent wave packet studies of diatom-diatom reactions [20, 21, 23] with an application to the $\text{H}_2 + \text{D}_2$ reaction [143]. Here, we only briefly outline the theoretical aspects of the time-dependent wave packet approach.

The full-dimensional Hamiltonian in the BF reactant Jacobi coordinates shown in Fig. 5.1 for a given total angular momentum J can be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial r_2^2} + \frac{(\hat{J} - \hat{j}_{12})^2}{2\mu R^2} + \frac{\hat{j}_1^2}{2\mu_1 r_1^2} + \frac{\hat{j}_2^2}{2\mu_2 r_2^2} + \hat{V}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2), \quad (5.1)$$

where $\hat{J}$ is the total angular momentum operator, and $\hat{j}_1$ and $\hat{j}_2$ are the rotational angular momentum operators of AB and CD which are coupled to $\hat{j}_{12}$.

The time-dependent wave function is expanded in terms of the BF rovibrational eigenfunctions as

$$\psi_{v_0 j_0 K_0}^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, t) = \sum_{n, v, j, K} F_{n v j K, v_0 j_0 K_0}^{JM\epsilon}(t) u_n^{v_2}(R) \phi_{v_1}(r_1) \phi_{v_2}(r_2) Y_{jK}^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2), \quad (5.2)$$

where n is the translational basis label, v denotes (v_1, v_2) , j denotes (j_1, j_2, j_{12}) , (v_0, j_0) denotes the initial rovibrational state. The $Y_{jK}^{JM\epsilon}$ in Eq. (5.2) is the coupled BF total angular momentum eigenfunctions which can be written as

$$Y_{jK}^{JM\epsilon} = (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} [D_{K,M}^J Y_{j_1 j_2}^{j_{12} K} + \epsilon (-1)^{j_1 + j_2 + j_{12}} D_{-K,M}^J Y_{j_1 j_2}^{j_{12} -K}], \quad (5.3)$$

where $D_{K,M}^J$ is the Wigner rotation matrix, ϵ is the total parity of the system defined as $\epsilon_0 (-1)^J$ with ϵ_0 being the parity of the system, $0 \leq K \leq \min(J, j_{12})$ is the projection of total angular momentum on the BF axis, and $Y_{j_1 j_2}^{j_{12} K}$ is the angular momentum eigenfunction of $\hat{j}_{12}$ defined as

$$Y_{j_1 j_2}^{j_{12} K} = \sum_{m_1} \langle j_1 m_1 j_2 K - m_1 | j_{12} K \rangle y_{j_1 m_1}(\theta_1, 0) y_{j_2 K - m_1}(\theta_2, \Phi), \quad (5.4)$$

where y_{jm} are spherical harmonics. Note that in Eq. (5.3), the restriction $\epsilon (-1)^{j_1 + j_2 + j_{12}} = 1$ for $K = 0$ partitions the whole rotational basis set into even and odd parities. Thus a $K = 0$ initial state can only appear in one of the two parity blocks. For $K > 0$, however, there is no such a restriction, and the basis set is the same for even and odd parities, but slightly different for different K blocks because of the restriction $j_{12} \geq K$.

The interaction potential matrix in the angular momentum basis $Y_{jK}^{JM\epsilon}$, which is diagonal in K , can be calculated as [154]

$$\langle Y_{jK}^{JM\epsilon} | V | Y_{j'K'}^{JM\epsilon} \rangle = 2\pi \delta_{KK'} \langle Y_{j_1 j_2}^{j_{12} K} | V | Y_{j'_1 j'_2}^{j'_{12} K} \rangle. \quad (5.5)$$

Thus we can see the potential matrix for even parity is identical to that for odd parity for $K > 0$.

The centrifugal potential, i.e. the $(J - j_{12})^2$ term in the Hamiltonian, which gives rise to the coupling between different K blocks in the BF representation, is given by [154]

$$\begin{aligned} \langle Y_{jK}^{JM\epsilon} | (J - j_{12})^2 | Y_{j'K'}^{JM\epsilon} \rangle &= \delta_{jj'} \{ \delta_{KK'} [J(J+1) + j_{12}(j_{12}+1) - 2K^2] \\ &\quad - \delta_{K+1, K'} \lambda_{jK}^+ \lambda_{j_{12}K}^+ (1 + \delta_{K0})^{1/2} \\ &\quad - \delta_{K-1, K'} \lambda_{jK}^- \lambda_{j_{12}K}^- (1 + \delta_{K1})^{1/2} \} \end{aligned} \quad (5.6)$$

and the quantity λ is defined as

$$\lambda_{AB}^{\pm} = [A(A+1) - B(B \pm 1)]^{1/2}. \quad (5.7)$$

In the CS approximation, we neglect the coupling between different K blocks in Eq. (5.6), thus K becomes a good quantum number and is conserved in reaction. For $K > 0$ both the interaction potential matrix in Eq. (5.5) and the centrifugal potential matrix in Eq. (5.6) are not dependent on the total parity of the system, thus $\epsilon = \pm 1$ yield the same reaction probabilities. But in the CC calculations, they are expected to be different because the $K = 0$ block only exists in one parity.

As in Ref. [143], we construct Gaussian wave packets and propagate them using the split-operator method [87]. In order to obtain the reaction probabilities $P_{\nu_1 \nu_2 j_1 j_2 j_{12} K}^{J\epsilon}(E)$ for different competitive processes, we calculate the time-independent scattering wave function (TIDWF), $\psi_i^+(E)$, on one dividing surface which comprises three planes denoted by $S[R^F], S[r_1^F], S[r_2^F]$.

The integral cross section from a specific initial state is obtained by summing the reaction probabilities over all the partial waves (total angular momentum J),

$$\begin{aligned} \sigma_{\nu_1 \nu_2 j_1 j_2}(E) &= \frac{1}{(2j_1+1)(2j_2+1)} \sum_{j_{12} K \epsilon} \left\{ \frac{\pi}{k^2} \sum_{J \geq K} (2J+1) P_{\nu_1 \nu_2 j_1 j_2 j_{12} K}^{J\epsilon}(E) \right\} \\ &= \frac{1}{(2j_1+1)(2j_2+1)} \sum_{j_{12} K \epsilon} \sigma_{\nu_1 \nu_2 j_1 j_2}^{j_{12} K \epsilon}(E), \end{aligned} \quad (5.8)$$

where $\sigma_{\nu_1 \nu_2 j_1 j_2}^{j_{12} K \epsilon}(E)$ is defined as the j_{12} , K , and ϵ specified cross section. In this study, we will restrict ourselves to the reactions with the H_2 and D_2 reagents in their initial ground rotational

states, i.e. $j_1 = j_2 = 0$, for which the indexes j_{12} , K , and ϵ can only be 0, 0 and +1, respectively. Hence, we drop them from now on.

5.3 Results and Discussion

The numerical parameters used in the wave packet calculations on an L -shaped grid are summarized in Table 5.1, which are similar to those employed in Ref. [143]. The exchange symmetry of H/D atom in the H_2/D_2 molecule has been considered in the calculation. The center momentum of the wave packet, k_0 , was chosen according to the initial state to cover the interesting energy range. We calculated the reaction probabilities with total angular momentum J from 0 to 50 (60) with an interval of 5 for the initial vibrational state $\nu_1 = 10$ (11) due to the extremely huge computational cost. The interpolation algorithm was applied to obtain reaction probabilities for other J within the range. The number of K blocks used in our calculations is $\min(3, J + 1)$ (i.e. from 0 to $\min(3, J + 1) - 1$). As a convergence test, we have calculated the reaction probabilities for the three processes with $J = 15$ by increasing the number of K blocks from 3 to 5. The relative error (the probability difference between 3 K and 5 K blocks divided by the probability for the 5 K blocks) is no more than 1% for the CID process and less than 5% for the 4C and SE processes.

It is not straightforward to separate the reactive flux of different channels based on diatomic-diatomic reactant Jacobi coordinates. While the calculation of CID probability is quite straightforward since the corresponding reactive flux is well localized, the separation of the 4C flux from the SE channel is complicated and challenging. A “binning” procedure is employed in the calculations. Briefly, the TIDWF is firstly transferred from a function of the reactant Jacobi coordinates to a double variable function. Then, according to the distribution of the wave function in the new double variable plane, we are able to know statistically in which area the TIDWF falls for 4C and SE processes. It should be noted that the “binning” method will unavoidably introduce some errors for the separation of 4C and SE probabilities. However, we believe that the errors are negligible. More details are given in Ref. [143].

Table 5.1: Numerical parameters used in the wave packet calculations. (Atomic units are used unless stated otherwise.)

H ₂ + D ₂	
Grid/basis range and size:	$R \in [0.0, 12.0], N_R^{tot}=83, N_R^{int}=54$ $r_1 \in [0.5, 12.0], N_{r_1}^{tot}=75$ $r_2 \in [0.5, 7.5], N_{r_2}^{tot}=61, N_{r_2}^{asy}=12$ $j_{1max}=54, j_{2max}=52$
Initial wave packet:	$\varphi_{k_0}(R) = \left(\frac{1}{\pi\delta^2}\right)^{1/4} e^{-(R-R_0)^2/2\delta^2} e^{-ik_0 R}$ $R_0=10.0, \delta=0.4$
Absorbing potential:	$F_{abs} = \exp[-\Delta_t \cdot \alpha(\frac{x-x_a}{x_{max}-x_a})^n], \quad \text{for } x_a \leq x \leq x_{max}$ $R_a=10.0, \alpha_R=0.05, n_R=1.5$ $r_{1a}=10.5, \alpha_{r_1}=0.05, n_{r_1}=1.5$ $r_{2a}=6.5, \alpha_{r_2}=0.05, n_{r_2}=1.5$
Flux position:	$R^F=7.5, r_1^F=10.0, r_2^F=5.5$
Total propagation time:	600 iterations with $\Delta_t=10.0$

5.3.1 Reaction Probabilities

The CS approximation can reduce the complexity of calculations and is shown to be justified for the scattering problems where the main contribution comes from the small J region [144]. Although the accuracy of the CS approximation has been extensively studied in the diatom-diatom and atom-triatom reactions in which only one old bond is broken, it has never been tested in reactions involving simultaneous cleavage of two bonds. In the 4C and SE processes of the H₂ + D₂ reaction, two old bonds are broken. One new bond is formed for the SE process and two new bonds are formed for the 4C process. Thus it is an ideal candidate to study the accuracy of the CS approximation for the scattering problems including cleavage of one and/or two bond(s).

Figure 5.2(a) shows the six-dimensional (6D) CC and CS CID probabilities for the H₂ ($v_1 = 10, j_1 = 0$) + D₂ ($v_2 = 0, j_2 = 0$) reaction with total angular momentum $J = 5, 15$ and 25 as a function of translational energy. The CID probability for $J = 0$ is also presented for comparison. It can be seen that the 6D CC probability is almost identical to the 6D CS one over the energy range considered for $J = 5$. As J increases, the discrepancy between the CC and CS results becomes visible. The CS probability is smaller than the CC probability near the energy

Figure 5.2: The six-dimensional CC and CS collision induced dissociation, four-center and single exchange probabilities for the H_2 ($v_1 = 10$, $j_1 = 0$) + D_2 ($v_2 = 0$, $j_2 = 0$) reaction with total angular momentum $J = 0, 5, 10, 15$ and 25 as a function of translational energy.

threshold. With the further increase of the collisional energy, the CS probability is slightly larger than the CC probability. Overall, the CS results agree with the CC ones quite well in the energy range studied and for the different total angular momentum J presented.

In Fig. 5.2(b), we present the CC and CS 4C reaction probabilities for the H_2 ($v_1 = 10$, $j_1 = 0$) + D_2 ($v_2 = 0$, $j_2 = 0$) reaction with $J = 5$, 10 and 15 as a function of translational energy, together with that for $J = 0$. As can be seen from the figure, the difference between the CC and CS probabilities increases with the increase of J , which is similar to the CID process. However, the relative error is much larger than that in the CID process for the same J . In the high energy region, the CC probability is about three times as large as the CS one for $J = 15$.

The CC and CS SE reaction probabilities with $J = 5$, 15 and 25 are plotted in Fig. 5.2(c). Clearly, the trend of the discrepancy between CC and CS results is the same as what we have found in the CID and 4C processes, i.e., it increases with J . This is consistent with the fact that the CS approximation is valid for scattering problems where the main contribution comes from the small J region, because the centrifugal coupling between different K blocks is proportional to J . It can also be noted that, for $J = 25$, the CS SE probability is at least one order of magnitude smaller than the CC probability in the high energy region.

The accuracy of the CS approximation is generally affected by two factors: the geometry and the reaction dynamics. Reactions which are quite similar in dynamics but with different mass combinations (i.e. different geometries) would result in different performance of the CS approximation. The distinct performance of the CS approximation in the $\text{H}_2 + \text{OH}$ and $\text{H} + \text{H}_2\text{O}$ reactions [117, 148, 149, 150, 151] can be attributed to the different mass combinations. On the other hand, for different reaction processes (i.e. different dynamics), the accuracy of the CS approximation would be quite different even if they have same mass combinations. As we know, there is only one old bond broken in the CID process of $\text{H}_2 + \text{D}_2$, which is somewhat similar to the $\text{H}_2 + \text{OH}$, $\text{H}_2 + \text{CN}$ and $\text{OH} + \text{HCl}$ dissociative-associative reactions. For the three collinearly dominated diatom-diatom reactions, it has been found that the CS approximation works well [117, 148, 149, 152, 153] This is in accord with what we have found in the CID process of $\text{H}_2 + \text{D}_2$. In strong contrast to the CID process, the CS approximation does not work well for the 4C and SE processes involving cleavage of two bonds. The accuracy of the CS approximation

Figure 5.3: The six-dimensional CC collision induced dissociation probabilities for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction at several selected collision energies as a function of total angular momentum quantum number J . Note that different energies are selected for different initial states.

Figure 5.4: The six-dimensional CC four-center probabilities for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction at several selected collision energies as a function of total angular momentum quantum number J . Note that different energies are selected for different initial states.

also becomes worse from 4C to SE process. The poor performance of the CS approximation for the 4C and SE processes of $\text{H}_2 + \text{D}_2$ as compared to the CID process can be rationalized by the different dynamics of the three processes. It is shown below that the 4C process occurs in a narrow window of J ; thus the geometry should be dominant over the dynamics on the performance of the CS approximation for the 4C process of $\text{H}_2 + \text{D}_2$.

Garcia *et al.* have investigated the effect of total angular momentum on the dynamics of the $\text{H}_2 + \text{H}_2$ reaction using the QCT method [53]. To further attest their conclusions in the QM frame, we here also study the efficiency of varying J on the various processes in $\text{H}_2 + \text{D}_2$. Figures 5.3- 5.5 present the 6D CC CID, 4C and SE probabilities for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction at several selected collision energies as a function of J . The upper panel is for the initial state $v_1 = 11$ and the lower panel for $v_1 = 10$. From the figures, we can see that the maximum of the necessary J (J_{max}) increases for all kinds of processes with both collision and vibrational energy. The increase in J_{max} with vibrational energy (from the bottom panel up at the same collision energy) is slightly larger than that with collision energy (from internal to external curves within the same panel) in the energy range studied (the excitation energy from $v_1 = 10$ to 11 is 0.215 eV). This trend is consistent with Garcia *et al.*'s result, whereas it is not as apparent as their plots, especially for the 4C and SE processes. It is because we only focus on the relatively low initial vibrational states ($v_1 = 10, 11$), while the initial vibrational state studied is as high as $v_1 = 14$ in Garcia's paper. Unfortunately, we are unable to reach those high vibrational states within the quantum method due to excessively large basis/grid size required. On the other hand, what we have studied is the isotope substitution system, $\text{H}_2 + \text{D}_2$, and not $\text{H}_2 + \text{H}_2$. The mass difference and the quantum tunneling effects (not included in their study) are likely to have an effect on the J behavior. Furthermore, different collision energies are covered at different initial vibrational states to save computational cost.

Comparing the three figures within the same initial state, we can find that the CID process occurs in a wide range of J values. In contrast, the 4C process can only take place in a narrow window of J . The CID curve plotted in Fig. 5.3 presents a longer tail than the 4C curve in Fig. 5.4. These behaviors can be explained by a hard sphere model. As indicated by Garcia *et al.* [53], the narrow window of J in the 4C process can be attributed to a locking radius, depending on

Figure 5.5: The six-dimensional CC single exchange probabilities for the H_2 ($v_1 = 10, 11$, $j_1 = 0$) + D_2 ($v_2 = 0$, $j_2 = 0$) reaction at several selected collision energies as a function of total angular momentum quantum number

Figure 5.6: The six-dimensional CC and CS collision induced dissociation integral cross sections for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction as a function of (a) translational energy and (b) total energy. Energies are referred to the bottom of the $\text{H}_2 + \text{D}_2$ entrance valley.

the bond length at which the exchange occurs. In the CID process, the larger range of J can be associated with the radius of optimum vibration-translation energy exchange. For the SE process, two old bonds are broken and only one new bond is formed. It is subject to both the exchange and dissociative constraints. Thus the SE process, as shown in Fig. 5.5, occurs in a wide range of J while not presenting a long tail. The difference can also be rationalized by the fact the energy exchange takes place at longer range than mass exchange. All these findings are essentially in agreement with the QCT results.

5.3.2 Integral Cross Sections

Figure 5.6(a) and (b) show the 6D CC CID integral cross sections for the H_2 ($v_1 = 10, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction together with the corresponding CS cross sections as a function of translational energy and total energy, respectively. Hereafter, energies are referred to the bottom of the $\text{H}_2 + \text{D}_2$ entrance valley. It is not surprising to see that the CC cross section is almost indistinguishable from the CS cross section for the CID process from the same initial state, as the CC total reaction probabilities agree well with the CS ones for different total angular momentum J . In the low energy region, the CC cross section is slightly larger than the CS cross section. While in the high energy region, the CC cross section is a little smaller than the CS cross section. This is similar to the observations of the $\text{H}_2 + \text{OH}$ and $\text{H}_2 + \text{CN}$ reactions from the ground rovibrational state reported by Zhang *et al.* [117, 148, 149]. The 6D 4C and SE integral cross sections are plotted in Fig. 5.7 and Fig. 5.8, respectively. Obviously, for the 4C process, the CC cross section is larger than the corresponding CS cross section, and the discrepancy increases as the translational energy and/or the vibrational energy increase(s). The SE process is close to the 4C process except that it shows an even larger discrepancy between the CC and CS cross sections. In the SE process, the CC cross section is more than three times as large as the CS cross section. In brief, we can conclude that the CS approximation works well for the CID process but it does not work well for the 4C and SE processes for the ground rotational state. In the 4C and SE processes, the CC cross section is much larger than the CS cross section.

Now, let's focus on the CC results. From Fig. 5.6, we can see that, firstly, there exists a vibrational enhancement effect. The effect of initial vibrational excitation of H_2 is more than

Figure 5.7: The six-dimensional CC and CS four-center integral cross sections for the $\text{H}_2 (v_1 = 10, 11, j_1 = 0) + \text{D}_2 (v_2 = 0, j_2 = 0)$ reaction as a function of (a) translational energy and (b) total energy.

Figure 5.8: The six-dimensional CC and CS single exchange integral cross sections for the $\text{H}_2 (v_1 = 10, 11, j_1 = 0) + \text{D}_2 (v_2 = 0, j_2 = 0)$ reaction as a function of (a) translational energy and (b) total energy.

just using the entire energy initially deposited in it, it also promotes the CID process. Secondly, the cross section profiles become steeper as v_1 increases. The 4C and SE CC cross sections, as shown in Fig. 5.7 and Fig. 5.8, are about one order of magnitude smaller than the CID cross sections. Hence, the CID process is dominant over the energy range considered. These results are consistent with the conclusion reported in our earlier paper [143]. In other words, for the CID process, the conclusion drawn from the total reaction probability for $J = 0$ remains unchanged. From Figs. 5.7 and 5.8, it is also found that the magnitude of 4C CC cross section is comparable to the SE cross section for the same initial state, which is, however, quite different from the observation for $J = 0$ that the 4C reaction probability is much larger than the SE probability at high translational energy for the ground rotational state [143]. This can be easily understood by comparing the opacity functions (total reaction probability as a function of total angular momentum J at a fixed energy) of 4C and SE processes, as plotted in Figs. 5.4 and 5.5. From Fig. 5.4, we can see that the opacity function is a monotonous decreasing function. As J increases, the 4C reaction probability constantly decreases at a specific translational energy and the 4C process exploits a narrow window of J value. However, for the SE process shown in Fig. 5.5, there is a shift of the maximum of the reaction probability. The SE probability firstly increases as J increases, then reaches an maximum, and decreases with the further increase of J . As mentioned above, the effective window of J value is also much wider than that of the 4C process. The different values of J_{max} (or the effective J window) and the factor $(2J + 1)$ in Eq. (5.8) weighing the terms of the sum of the partial probability terms significantly affect the resultant cross section and thus lead to the comparable 4C and SE cross sections.

5.4 Conclusion

The initial state selected time-dependent wave packet method has been employed to calculate the integral cross sections for the diatom-diatom $\text{H}_2 + \text{D}_2$ reaction with and without the CS approximation. By including all important K blocks in the body-fixed frame, the obtained CID, 4C and SE integral cross sections can be treated as the first fully converged coupled-channel ones from the ground rotational state. Detailed studies have been carried out on the accuracy of the CS approximation for the three competitive processes in the $\text{H}_2 + \text{D}_2$ reaction.

It was found that the CC cross section is almost identical to the CS cross section for the CID process. In the low energy region, the CC cross section is slightly larger than the CS cross section. In the high energy region, the CC cross section is a little smaller than the CS cross section. Overall, the CS approximation works well for the CID process of $\text{H}_2 + \text{D}_2$. For the 4C and SE processes, the CC cross section is much larger than the CS cross section, which means that the CS approximation does not work well for the two processes. The discrepancy between the CC and CS cross sections increases as the translational energy and/or the vibrational energy increase(s).

From the CC cross sections, we validated that the conclusion drawn from the total reaction probability for $J = 0$ remains unchanged for the CID process. It is dominant over the energy range considered. And the 4C and SE CC cross sections are about one order of magnitude smaller than the CID cross section. In strong contrast to the observation for $J = 0$ that the 4C probability is much larger than the SE probability at high translational energy for the ground rotational state, the magnitude of the 4C CC cross section is only comparable to the SE cross section.

The effect of the total angular momentum J on the reaction dynamics of $\text{H}_2 + \text{D}_2$ has also been studied and compared with the QCT results of Garcia *et al.* for $\text{H}_2 + \text{H}_2$ [53]. We found that the necessary J_{max} increases with both collision and vibrational energy for all the three processes. The CID process occurs in a wide range of J values and shows a long tail. In contrast, the 4C process can only take place in a narrow window of J . The SE process has features of both CID and 4C processes, which occurs in a wide range of J without a long tail. All these findings are essentially in agreement with the QCT results.

Summary and Prospect

6.1 Summary

With the rise of computing power and the development of efficient simulation methods, we are now able to study some elementary reactions with complicated reaction mechanisms. The $\text{H}_2 + \text{D}_2$ reaction is a reaction belonging to this category, in which different processes will take place simultaneously: collision induced dissociation (CID), four center reaction (4C) and single exchange reaction (SE). One of the competitive processes, the 4C reaction, has many novel dynamical features which makes it an intractable target for theorists to study for a long time. Thus, in this work, we chose the $\text{H}_2 + \text{D}_2$ reaction as our research target and employed the time-dependent wave packet method to study its reaction dynamics on the ASP and BMKP PESs.

We calculated the reaction probabilities for different competitive processes using reduced-dimensional (3D) models with six different geometries, in which three of them are studied for both coplanar and non-coplanar geometries. Our results suggested that the orientation of the cold diatom (coplanar and non-coplanar) does not greatly affect the CID process. However, the orientation of the hot diatom has a significant effect on the reaction process. The vibrational excitation of the hot molecule is more efficient than the translational energy in facilitating the reaction processes for the CID, 4C and SE processes. There is, however, a clear vibrational inhibition effect for the three-body complex formation (3BC) process. Furthermore, the BMKP

PES generally gives lower energy thresholds than the ASP PES. Comparing the probabilities for different processes in $\text{H}_2 + \text{D}_2$ reaction with the results of $\text{H}_2 + \text{H}_2$ reaction reported by Bartolomei *et al.* [43], we found that the two combinations ($\text{H}_2 + \text{D}_2$ and $\text{H}_2 + \text{H}_2$) have similar energy threshold behavior and probability profiles within the same initial states for the CID and 4C processes, however, the energy thresholds are lower for the $\text{H}_2 + \text{D}_2$ reaction. Furthermore, the probability curves for the $\text{H}_2 + \text{D}_2$ reaction are much more structured for the SE and 3BC processes.

Next, we reported the CID, 4C and SE probabilities of the $\text{H}_2 + \text{D}_2$ reaction in the full-dimensional (6D) model with the total angular momentum $J = 0$. In our study, we put both of the two reagents initially in different vibrational states and rotational states to investigate the efficiency of different kinds of energies on the reaction process. We found that the vibrational excitation of the hot diatom presents an enhancement effect on the CID process while the vibrational excitation of the cold diatom presents an inhibition effect. The reaction probabilities for the 4C and SE processes are at least one order of magnitude smaller than those of CID process over the energy range considered. In addition, the rotational excitation of both reagents has a significant effect on the CID process. Similar to the 3D calculations, we substituted the cold reagent D_2 by H_2 and HD to study the isotope substitution effect in the 6D model. Although the three isotope combinations have similar energy threshold behavior and probability profiles, they present remarkable isotope substitution effect. The $\text{H}_2 + \text{D}_2$ combination is most efficient and the $\text{H}_2 + \text{H}_2$ is least efficient, and the $\text{H}_2 + \text{HD}$ combination lies in between for the CID process while they have a different order for the 4C and SE processes.

As all results above were obtained with the total angular momentum $J = 0$, they are of limited conclusiveness on observables (cross sections or rate constants). Finally, we performed time-dependent wave packet calculations for $J > 0$ and presented the first fully-converged integral cross sections for the $\text{H}_2 + \text{D}_2$ reaction. The effect of the total angular momentum J on the reaction process of $\text{H}_2 + \text{D}_2$ reaction was studied first. It was shown that the CID process occurs in a wide range of J values and shows a long tail while the 4C process can only take place in a narrow window of J . The SE process has features of both CID and 4C processes, which occurs in a wide range of J without a long tail. Comparing the integral cross sections for different

processes, we concluded that the CID process is dominant over the energy range considered, which can also be deduced from the calculations with $J = 0$. However, in sharp contrast to the observation for $J = 0$ that the 4C probability is much larger than the SE probability at high translational energy, the magnitude of the 4C CC cross section is only comparable to the SE cross section. Much more attentions have been paid to study the accuracy of the centrifugal sudden (CS) approximation for the three competitive processes. We showed that the CC cross section is almost indistinguishable with the CS cross section for the CID process. It seems that the CC cross section is slightly larger than the CS cross section in the low energy region but smaller than the CS cross section in the high energy region. For the 4C and SE processes, the CC cross section is much larger than the CS cross section and the discrepancy between the CC and CS cross sections increases as the translational energy and/or the vibrational energy increase(s). Thus, the CS approximation does not work well for the 4C and SE processes.

6.2 Prospect

There exist several issues which deserve further investigation for the H_4 system. Firstly, we have calculated the integral cross sections for the $H_2 + D_2$ reaction from the ground rotational state. It would be interesting to study the effect of the rotational excitation of the reagents on the integral cross sections. Next, the hydrogen molecules in interstellar medium in highly excited vibrational states will naturally be excited to highly rotational states too. If the reagents are in highly rovibrationally excited states, it is meaningful to check whether the conclusions drawn from calculations with the reagents in the ground rotational state will still hold. Furthermore, we have limited our calculations to the $H_2 + D_2$ reaction when we computed integral cross sections. It is mainly due to the symmetry requirement on the basis functions. Since hydrogen nuclei are fermions, the overall functions must be antisymmetric with respect to the permutation of any two H nuclei, which requires the proper symmetry considerations on the spatial and spin wave functions. Obviously, the wavefunction employed in our calculations only took into account the symmetry under exchange of identical particles for each diatom but does not fully satisfy the exchange symmetry of hydrogen nuclei from the two diatoms. It will be a challenge to overcome this notorious problem for polyatomic systems.

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