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2014

Zhao, B., Zhang, D. H., Lee, S. Y., & Sun, Z. (2014). Calculation of state-to-state cross sections for triatomic reaction by the multi-configuration time-dependent Hartree method. The Journal of Chemical Physics, 140(16), 164108-.

<https://hdl.handle.net/10356/98630>

<https://doi.org/10.1063/1.4872157>

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Citation: *The Journal of Chemical Physics* **140**, 164108 (2014); doi: 10.1063/1.4872157

View online: <http://dx.doi.org/10.1063/1.4872157>

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Calculation of state-to-state cross sections for triatomic reaction by the multi-configuration time-dependent Hartree method

Bin Zhao,¹ Dong-H. Zhang,^{1,2} Soo-Y. Lee,³ and Zhigang Sun^{1,2,a)}

¹Center for Theoretical and Computational Chemistry and State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

²Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

³Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

(Received 6 March 2014; accepted 10 April 2014; published online 25 April 2014)

A framework for quantum state-to-state integral and differential cross sections of triatomic reactive scattering using the Multi-Configuration Time-Dependent Hartree (MCTDH) method is introduced, where a modified version of the Heidelberg MCTDH package is applied. Parity of the system is adopted using only non-negative helicity quantum numbers, which reduces the basis set size of the single particle functions in angular degree of freedom almost by half. The initial wave packet is constructed in the space-fixed frame, which can accurately account for the centrifugal potential. By using the reactant-coordinate-based method, the product state-resolved information can be accurately extracted. Test calculations are presented for the $\text{H} + \text{H}_2$ reactive scattering. This work demonstrates the capability of the MCTDH method for extracting accurate state-to-state integral and differential cross sections. As an efficient scheme for high-dimensional problems, the MCTDH method may be promising for the study of product state-resolved cross sections for polyatomic reactive systems.

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I. INTRODUCTION

To shine more light on the underlying mechanism of various reactive scattering problems requires the cooperated experimental and accurate numerical studies. Theoretically, the very early theory was pioneered by Hirschfelder and his co-workers^{1,2} dated back to the later 1930s and early 1940s, but it took more than 30 years to see the report of the first converged quantum mechanical calculation of the reaction cross section on the simplest three-dimensional $\text{H} + \text{H}_2$ exchange reaction.^{3,4} Since then, tremendous progress has been made in dealing with the partial differential equations and associated boundary conditions arising in quantum reaction dynamics,^{5–8} and one now can routinely perform full-dimensional quantum scattering calculations for atom-diatom systems studying accurate integral cross section (ICS) and differential cross section (DCS) at the state-to-state level.^{9–12} For tetra-atomic reactions, the first full-dimensional time-dependent wave packet calculations studying state-to-state reaction probabilities of the benchmark reactions $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ in 1994¹³ and $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$ in 1996¹⁴ were published almost 20 years ago. Just recently, the first converged quantum calculation of the state-to-state DCS for the $\text{HD} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{D}$ reaction in full dimension were reported.¹⁵ These results proved the capability of the current methodology to provide excellent agreement with the experimentally measured product angular distribution.^{15,16}

Experimentally, the measured state-to-state DCS reveals the most detailed information about a chemical reaction, and

the comparison with the accurately calculated DCS provides insights into the underlying mechanism of the reaction dynamics. Considering polyatomic reactive systems, reactions of methane with F/Cl/O atom have been increasingly studied. Insights into the correlation between the internal vibrational states of reactants and products have been revealed by detailed experimental results on the state-to-state level for the $\text{F} + \text{CH}_4 \rightarrow \text{HF} + \text{CH}_3$ ^{17–19} and $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$ reaction.^{20–23} Theoretical calculations on these reactive systems have also been carried out, but full dimensional quantum mechanical calculations on these larger reactive system are limited by the current computational power. As a result, the most advanced studies employ a reduced dimensional treatment and the time-dependent wave packet method.^{15,24–29} The quasi-classical trajectory (QCT) method provides a feasible alternative by describing the scattering collisions with classical equations of motion.^{30,31} However, despite its high efficiency and intuitive nature, QCT is not able to account for the quantum phenomena in reactive scattering, such as reactive resonance, quantum tunneling, and interference.

Recent full dimensional quantum mechanical calculations of above mentioned polyatomic reactions mostly focused on the less demanding $\text{H} + \text{CH}_4$ reaction. In most of the theoretical investigations, full-dimensional quantum dynamics calculations of thermal rate constants^{32–40} and initial state-selected reaction probabilities^{41,42} have been provided. These calculations employ the multi-configuration time-dependent Hartree (MCTDH) approach^{43,44} for the wave packet propagation. This method has been proven to be an efficient scheme for high dimensional quantum dynamics calculations, especially for polyatomic molecular dynamics, such as the

^{a)} Author to whom correspondence should be addressed. Electronic mail: zsun@dicp.ac.cn

H + CH₄ reaction,^{32–42} O + CH₄,⁴⁵ F + CH₄,⁴⁶ or molecule surface scattering processes, H₂ on transition metals,⁴⁷ N₂ on stepped Ru(0001),⁴⁸ methane on transition metals,⁴⁹ CH₃I on MgO,⁵⁰ where many degrees of freedom are involved. The MCTDH method has also been applied to calculate total reaction probabilities and rate constant of triatomic H + H₂,⁵¹ O + HCl,⁵² and Cl + H₂,⁵³ reactions, tetra-atomic H₂ + OH,^{54,55} OH + HCl,⁵⁶ and H₂ + CN⁵⁷ reactions and to extract state-resolved ICS of the inelastic scattering of H₂ + H₂.^{58–60}

As a rigorous method, MCTDH can be used to calculate state-to-state ICS and DCS of polyatomic systems. However, MCTDH calculations studying molecular reactions have mostly been restricted to calculations of reaction rates and initial state selected reaction probabilities. MCTDH calculations on the state-to-state level have up to now been published only for the reaction probabilities for the D + H₂ reaction with vanishing total angular momentum ($J = 0$).⁶¹ In this paper, we intend to extend MCTDH calculations to the state-to-state ICS and DCS of the simplest exchange reaction H + H₂.

In order to study reactive scattering at a state-to-state level, the key issue is how to efficiently extract the product state-resolved information. The reactant-product decoupling (RPD) scheme uses reactant and product coordinates to propagate the reactant and product components of the full time-dependent wave packets, respectively. These wave packets are connected using an absorbing potential after the transition state region.^{62,63} One may alternatively choose either the product coordinates^{64–66} or reactant coordinates^{67–73} to propagate the initial wave packet. In this method, the asymptotic wave functions are transformed before the calculation of the S -matrix elements. In this work, we use reactant Jacobi coordinates to propagate the wave packet and show that the MCTDH method is able to compute accurate state-to-state resolved DCS for the triatomic reactive system H + H₂.

The content of this work is arranged as follows: In Sec. II, the basic theoretical aspects for the RCB approach and MCTDH method are presented. Section III presents the results calculated by the method introduced in this work, and Sec. IV concludes the current work and provides some prospects for the MCTDH method.

II. THEORY

A. Hamiltonian and discretization

To study the atom-diatom reaction, A + BC(v_i, j_i) → AB(v_f, j_f) + C/AC(v_f, j_f) + B at a state-to-state level, Jacobi coordinates in body-fixed (BF) frame are used to represent the corresponding wave packets in their arrangements. In each arrangement, the coordinates are denoted as ($R_\nu, r_\nu, \theta_\nu; \Omega_\nu$), where ν represents any of the arrangements. For example, when ν represents the reactant arrangement, R_ν is the length of vector $\mathbf{R}_\nu$ pointing from the BC center of mass to A, r_ν the BC bond length, and θ_ν the angle between BC bond and $\mathbf{R}_\nu$; Ω_ν denotes the Euler angles orienting $\mathbf{R}_\nu$ in the space-fixed (SF) frame. In the following, $\nu = r$ and $\nu = p$ denote coordinates in the reactant and product arrangements, respectively. When a general expression is used for both re-

actant and product arrangements, ν is omitted for the sake of clarity.

Considering the reactive scattering in an isolated system, the calculation is carried out by partial waves expansion, in which the total angular momentum J is a good quantum number and one can take advantage of the conservation of the total angular momentum to break the problem into separate calculations for each value of the total angular momentum quantum number J . The Hamiltonian for a given total angular momentum J can be represented in one of the arrangement Jacobi coordinates

$$\hat{H} = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial^2 R} - \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial^2 r} + \frac{\hat{L}^2}{2\mu_R R^2} + \frac{\hat{j}^2}{2\mu_r r^2} + V(R, r, \theta), \quad (1)$$

where the arrangement label ν is removed for clarity consideration, μ_R and μ_r are the corresponding reduced mass for R and r , respectively. The squared orbital angular momentum operator is responsible for the centrifugal potential and expressed as

$$\hat{L}^2 \equiv (\hat{\mathbf{J}} - \hat{\mathbf{j}})^2 = \hat{\mathbf{J}}^2 + \hat{\mathbf{j}}^2 - 2\hat{\mathbf{J}}_z \hat{j}_z - \hat{\mathbf{J}}_+ \hat{j}_- - \hat{\mathbf{J}}_- \hat{j}_+, \quad (2)$$

where $\hat{\mathbf{J}}$ and $\hat{\mathbf{j}}$ are the total and diatomic rotational angular momentum operators, with $\hat{\mathbf{J}}_z$ and $\hat{j}_z$ as their corresponding projection operators onto the BF z -axis, which coincides with the vector $\mathbf{R}$. The raising/lowering operators in the last two terms, $\hat{\mathbf{J}}_\pm$ and $\hat{j}_\pm$, represent the Coriolis coupling, which couples adjacent helicity quantum numbers K .

For each partial wave J and parity ϵ , the total wave packet in the BF frame is written as

$$\Psi^{JM\epsilon}(\mathbf{R}, \mathbf{r}, t) = \sum_K \mathcal{D}_{MK}^{J\epsilon*}(\Omega) \psi(R, r, \theta, K, t), \quad (3)$$

where M and K are the projections of the total angular momentum J on the SF and BF z axis, respectively, $\psi(R, r, \theta, K, t)$ is the internal part of the wave function, $\mathcal{D}_{MK}^{J\epsilon*}(\Omega)$ is a parity adapted normalized rotation matrix, depending on the Euler angles Ω ,

$$\mathcal{D}_{MK}^{J\epsilon*}(\Omega) = (1 + \delta_{K,0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} \times [D_{MK}^{J*}(\Omega) + \epsilon(-1)^{J+K} D_{M-K}^{J*}(\Omega)]. \quad (4)$$

Here, ϵ is the parity of the system defined as $\epsilon = (-1)^{j+l}$ with l being the orbital angular momentum quantum number, and $D_{MK}^{J*}(\Omega)$ is Wigner rotation matrix.^{74,75} The usage of the parity adapted normalized rotation matrix restricts the K to be non-negative and the basis size is reduced almost by half.

The initial wave packet is conveniently defined in the SF frame, since the Coriolis coupling in the BF frame is long ranged and requires to locate the initial wave packet at a rather large value of R . There is no simple way to account for the coupling in a reasonable grid. On the other hand, in the SF frame the asymptotic form of the scattering wave function can be described by the Riccati-Hankel function, and the long-range centrifugal term is diagonal, $l(l+1)/2\mu_R R^2$.^{76,77} As a result, the initial wave packet can be placed as close as possible to the position where the interaction potential is negligible. However, wave packet is advantageously propagated in

the BF frame, and the initial wave packet is thus transformed from the SF to the BF frames before the propagation. The transformation of the SF eigenfunction $|JMj_0l_0\epsilon\rangle$ of the total angular momentum operator in the coupled representation to the BF frame is given by

$$\begin{aligned} |JMj_0l_0\epsilon\rangle &= \sum_{K \geq 0} C_{l_0K}^{Jj_0\epsilon} |JMj_0K\epsilon\rangle \\ &= \sum_{K \geq 0} C_{l_0K}^{Jj_0\epsilon} D_{MK}^{J\epsilon*}(\Omega) \mathcal{Y}_{j_0K}(\theta), \end{aligned} \quad (5)$$

where $C_{l_0K}^{Jj_0\epsilon}$ is the parity-adapted orthogonal transform matrix between the SF and BF frames,^{66,78–80}

$$C_{l_0K}^{Jj_0\epsilon} = \sqrt{\frac{2l+1}{2J+1}} \sqrt{2-\delta_{K,0}} \langle jKl_0 | JK \rangle, \quad (6)$$

and $\langle jKl_0 | JK \rangle$ is a Clebsch-Gordan coefficient.

B. MCTDH method

In contrast to traditional wave packet method, where wave functions and operators are represented in a time-independent basis set, the MCTDH method represents the wave function with both time-dependent expansion coefficients and configurations. For the current problem of a triatomic system, the internal wave function $\psi(R, r, \theta, K, t)$ is expanded as

$$\begin{aligned} \psi(R, r, \theta, K, t) &= \sum_{j_R=1}^{n_R} \sum_{j_r=1}^{n_r} \sum_{j_\theta=1}^{n_\theta} A_{j_R j_r j_\theta}(t) \\ &\quad \times \varphi_{j_R}^R(R, t) \varphi_{j_r}^r(r, t) \varphi_{j_\theta}^\theta(\theta, K, t), \end{aligned} \quad (7)$$

where $A_{j_R j_r j_\theta}(t)$ denotes the MCTDH expansion coefficients. $\varphi_{j_R}^R(R, t)$, $\varphi_{j_r}^r(r, t)$, and $\varphi_{j_\theta}^\theta(\theta, K, t)$ are the single particle functions (SPF) for the R , r , and (θ, K) modes, respectively, which are discretized in the BF frame with discrete variable representation (DVR). The SPF basis set sizes, n_R , n_r , and n_θ determine the accuracy of the calculation. If the SPF numbers are chosen the same as the DVR grids numbers, the exact calculation can be recovered. The evolution of the time-dependent expansion coefficients $A_{j_R j_r j_\theta}(t)$ and the set of SPF are derived from the Dirac-Frenkel variational principle.^{81,82}

C. Extraction of state-to-state information with reactant coordinate based method

In the time-dependent wave packet method, the state-to-state S -matrix element is formulated by the Fourier transform of the time correlation function,^{76,83}

$$S_{pf,ri} = \frac{(2\pi\hbar)^{-1}}{a_f^*(E)a_i(E)} \int_0^\infty e^{iEt/\hbar} \langle \Psi_f^p | e^{-iHt/\hbar} | \Psi_i^r \rangle dt, \quad (8)$$

where Ψ_f^p and Ψ_i^r are the final product and initial reactant wave packets, respectively, and $a_f(E)$ and $a_i(E)$ are the corresponding energy amplitudes of the energy normalized eigenfunctions contained in Ψ_f^p and Ψ_i^r , respectively. It can be seen that the S matrix element is obtained by the Fourier transform of the time correlation function $C_{fi}(t)$ between the

final wave packet and the propagated initial wave packet, $C_{fi}(t) = \langle \Psi_f^p | \Psi_i^r(t) \rangle$. It should be noted that the initial and final wave packets are usually expressed in the Jacobi coordinates of their own arrangements, which results in the coordinate problem in a state-to-state reactive scattering calculation. Here, the reactant Jacobi coordinate system is used for the propagation of the wave packet. Two methodologies exist to solve the coordinate problem: the first one is to employ interpolation schemes for the coordinate transformation^{67–72} and the second one uses a projection of both reactant and product wave packets to intermediate coordinates.^{72,73} The second method is adopted in the current calculation.

The calculation of the state-to-state S -matrix employs a projection plane, $R_p = R_{p0}$, using the corresponding product Jacobi coordinates, and the time correlation function is evaluated on this projection plane. The scattering wave function is transformed in the energy domain before taking overlap with the final product state,

$$\begin{aligned} \Phi_i^{JM\epsilon}(E) &= \int_0^\infty e^{iEt/\hbar} \Psi_i^{JM\epsilon}(t) dt \\ &= \sum_K \mathcal{D}_{MK}^{J\epsilon*}(\Omega) \int_0^\infty e^{iEt/\hbar} \psi(R, r, \theta, K, t) dt. \end{aligned} \quad (9)$$

Here, the time-independent rotational part is not included in the Fourier transform and only the internal wave packet needs to be transformed to the energy domain.

Each point on the projection plan defined in the product Jacobi coordinates, $R_p = R_{p0}$, can be analytically expressed by the reactant Jacobi coordinates. Thus, the reactant Jacobi coordinate r_r is given as a function of R_r and θ_r , $r_r = r_{r0}(R_r, \theta_r)$. For the sake of efficiency, the SPF $\varphi_{j_r}^r(r)$ is first evaluated at $r_{r0}(R_r, \theta_r)$ by

$$\tilde{\varphi}_{j_r}^r(r_{r0}(R_r, \theta_r)) = \sum_{m=1}^{N_r} \varphi_{j_r}^r(r_m) U_m(R_r, \theta_r), \quad (10)$$

where $U_m(R_r, \theta_r)$ is the transform matrix,^{72,73} and r_m , R_r , θ_r are DVR grid points. Thus, the internal part of the scattering wave function on the projection plan is written in the MCTDH form as

$$\begin{aligned} \tilde{\psi}(R_r, \theta_r, K) &= \sum_{j_R=1}^{n_R} \sum_{j_r=1}^{n_r} \sum_{j_\theta=1}^{n_\theta} A_{j_R j_r j_\theta} \varphi_{j_R}^R(R_r) \tilde{\varphi}_{j_r}^r(r_{r0}(R_r, \theta_r)) \varphi_{j_\theta}^\theta(\theta_r, K). \end{aligned} \quad (11)$$

With the above strategy, the state-to-state S -matrix can be readily evaluated,

$$\begin{aligned} S_{v_{jp}l_p \leftarrow v_{j_0l_0}}^{J\epsilon}(E) &= \frac{(2\pi\hbar)^{-1}}{a_f^*(E)a_i(E)} \langle \Phi_f(R_p = R_{p0}) | \Phi_i^{JM\epsilon}(R_p = R_{p0}) \rangle. \end{aligned} \quad (12)$$

TABLE I. Parameters for the MCTDH calculations for each modes.

Mode	Range	Primitive basis		No. of SPF	No. of natural potentials	No. of SPF ($J = 0$, Ref. 61)
		Type	Size			
R	(1.0-10.04)	sin	84	24	Contracted	25
r	(0.6-9.24)	sin	84	24	26	17
(θ, K)	(0- $\pi/2$)	Kleg	(48,min($J,6$))	12-48	12	18

Finally, the S -matrix is transformed from the SF frame to the helicity representation by the standard transformation,

$$S_{v'j'K' \leftarrow vjK}^J = \sum_{l'l'} i^{l-l'} \sqrt{\frac{2l'+1}{2J+1}} \langle j'K'l'0 | JK' \rangle S_{v'j'l' \leftarrow vjl}^J \times \sqrt{\frac{2l+1}{2J+1}} \langle jKl0 | JK \rangle. \quad (13)$$

By substituting the S -matrix $S_{v'j'K' \leftarrow vjK}^J(E)$ in the helicity representation into the standard formulas, the state-to-state ICS can be obtained by summing over the contributions from all partial waves,⁷⁹

$$\sigma_{v_p j_p \leftarrow v_0 j_0}(E) = \frac{\pi}{(2j_0+1)k_{v_0 j_0}^2} \sum_{K_p} \sum_{K_0} \sum_J (2J+1) |S_{v_p j_p K_p \leftarrow v_0 j_0 K_0}^{J\epsilon}(E)|^2. \quad (14)$$

The state-to-state DCS reads⁷⁹

$$\frac{d\sigma_{v_p j_p \leftarrow v_0 j_0}(\vartheta, E)}{d\Omega} = \frac{1}{(2j_0+1)} \sum_{K_p} \sum_{K_0} \left| \frac{1}{2ik_{v_0 j_0}^2} \sum_J (2J+1) d_{K_p K_0}^J(\vartheta) \times S_{v_p j_p K_p \leftarrow v_0 j_0 K_0}^{J\epsilon}(E) \right|^2, \quad (15)$$

where ϑ is the scattering angle between the direction of incoming reactant A and outgoing product AB/AC in the center of mass frame, and $d_{K_p K_0}^J(\vartheta)$ is the reduced rotational matrix.^{74,75}

III. RESULTS AND DISCUSSIONS

The parameters used for describing the $H + H_2$ reaction in the following MCTDH calculations which employ the Heidelberg package⁸⁴ are summarized in Table I. The POTFIT program in the MCTDH package is used to express the BKMP2 PES in a product form as a linear combination of products of one-dimensional operators. Separable weights and relevant regions are employed to restrict the algorithm to concentrate on the most relevant space on the PES. Initial wave packets with an initial momentum of -8.0 a.u., a width of 0.2 a.u., centered at 5.5 a.u. are used for all J . The centrifugal coupling has been accounted for by Riccati-Hankel functions. The second-order constant mean field (CMF) method associated with Lanczos-Arnoldi and Bulirsch-Stoer method are used to propagate the MCTDH coefficients and SPF in time, respectively.⁸⁵

The total reaction probabilities of the reactive scattering $H + H_2(v_0 = 0, j_0 = 0) \rightarrow H_2 + H$ are shown in Fig. 1 for total angular momenta $J = 0$ and 15 . The results obtained from the WP-ABC code⁷² are compared to the ones from the MCTDH calculations with 24 SPF in R and r and different numbers of angular SPF. These numbers vary from 12 to 48 and the resulting SPF bases are denoted 24/24/12-48 for short.

In the case of $J = 0$, the four reaction probabilities all agree very well with the one from the WP-ABC code, but for $J = 15$, the reaction probability calculated with 12 and 24 angular SPF deviates from WP-ABC result. This indicates the need for larger angular SPF bases for none-zero total angular momentum J , which results from the existence of multiple K blocks for $J \neq 0$. Convergence tests for the SPF basis set sizes in R and r have also been carried out. We found that 24 SPF for both R and r modes are well converged.

Product vibrational and rotational state resolved state-to-state ICS and DCS for the $H + H_2(v_0 = 0, j_0 = 0) \rightarrow H_2(v' = 0, j') + H$ reaction at collision energy of 0.5 eV are shown in Fig. 2. The same SPF bases as in Fig. 1 are used. State-to-state ICS in panel (a) show good agreement with the ones obtained by the WP-ABC code for all basis set sizes considered.

For the DCS in panels (b), (c), and (d), it is clearly seen that the reactive scattering at collision energy of 0.5 eV is dominated by the backward scattering. The DCS of product state $v' = 0$ in panel (b), where DCS of all related rotational state j' have been summed, show good agreement with the ones from the WP-ABC code, but the product ro-vibrational

FIG. 1. Reaction probabilities for the $H + H_2(v_0 = 0, j_0 = 0) \rightarrow H_2 + H$ reaction calculated by the WP-ABC code (solid) and the MCTDH method for $J = 0$ and 15 . The MCTDH results with different numbers of angular SPF are shown: 12 (dotted), 24 (dashed), 36 (dashed-dotted), 48 (short dashed). 24 SPF are used for R and r .

FIG. 2. Product vibrational and rotational state resolved state-to-state ICS and DCS for the $\text{H} + \text{H}_2(v_0 = 0, j_0 = 0) \rightarrow \text{H}_2(v' = 0, j') + \text{H}$ reaction at a collision energy of 0.5 eV with different numbers of angular SPF: 24 (dotted), 36 (dashed-dotted), 48 (short dashed). 24 SPF are used for R and r . All the results are compared to the ones obtained by the WP-ABC code: (a) ICS of ro-vibrational state ($v' = 0, j' = 0-7$), DCS of (b) vibrational state ($v' = 0, j'$ summed), (c) ro-vibrational state ($v' = 0, j' = 1$), and (d) ($v' = 0, j' = 2$).

states ($v' = 0, j' = 1$) and ($v' = 0, j' = 2$) resolved DCS obtained using 24 angular SPF in panels (c) and (d) show some discrepancies at the backward scattering region, which manifests the high demand on the angular SPF basis set size to achieve converged DCS. In Fig. 3, DCS of product states ($v' = 0, j' = 0-6$) at a collision energy of 1.0 eV are shown using either 36 or 48 angular SPF. Both results are consistent with the ones obtained from the WP-ABC code, but some small discrepancies at the backward scattering region are observed for ($v' = 0, j' = 0$) and ($v' = 0, j' = 1$) product states. In addition, with the increase of angular SPF basis size from 36 to 48, the agreement between the DCS calculated by the WP-ABC and MCTDH method is not improved remarkably, which indicates the convergence of the DCS calculated by current bases sizes.

For $J \neq 0$, the Coriolis coupling exists and multiple K -blocks are required. The combined mode (θ, K) is employed to account for this interaction, which naturally requires more SPF for describing the wave function with more K -blocks. Therefore, for a DCS calculation where rigorous Coriolis coupling is necessary, the usage of parity is very important for reducing the computational effort, as we have done here.

It is worth comparing the number of SPF used here and in Ref. 61, where two different Jacobi coordinate systems are used to propagate the thermal flux eigenfunctions into the reactant and product sides. For comparison, the numbers of SPF in Ref. 61 are also listed in Table I. It is found that our calculation requires 7 extra SPF in r but 6 less angular SPF to obtain converged results ($J = 0$). The small number of angular SPF ($n_\theta = 12$) for $J = 0$ is due to the only existing $K = 0$ block in

the calculation. For calculations with high total angular momentum J , more than one K blocks are required. In the $\text{H} + \text{H}_2$ reaction, $K_{\text{max}} = 6$ is sufficient. As a result of the present

FIG. 3. Product vibrational and rotational state resolved state-to-state DCS for the $\text{H} + \text{H}_2(v_0 = 0, j_0 = 0) \rightarrow \text{H}_2(v' = 0, j' = 0-6) + \text{H}$ reaction at a collision energy of 1.0 eV with (a) 36 and (b) 48 angular SPF. 24 SPF are used for R and r . All the results are compared to the ones obtained by the WP-ABC code.

FIG. 4. Product ro-vibrational state resolved reaction probabilities for the $\text{H} + \text{H}_2(v_0 = 0, j_0 = 0) \rightarrow \text{H}_2(v' = 0, j' = 1) + \text{H}$ reaction as a function of collision energy with different values of the maximal helicity quantum number used in the calculations with different numbers of angular SPF. 24 SPF are used for R and r . All the results are compared to the ones obtained by the WP-ABC code.

study, one must note that a large number of SPF is required in the angular coordinate even in this simplest triatomic reaction system with a rather small maximum helicity number K .

The relation between the maximum helicity number K_{max} and the required number of angular SPF is also investigated to reveal the convergence speed with different K_{max} . Although the calculated results obtained with K_{max} less than six cannot give correct DCS, the comparison of the required angular SPF for different K_{max} is useful to reveal the convergence issue. In Fig. 4, product ro-vibrational state resolved reaction probabilities for the $\text{H} + \text{H}_2(v_0 = 0, j_0 = 0) \rightarrow \text{H}_2(v' = 0, j' = 1) + \text{H}$ reaction are shown as a function of collision energy with different K_{max} . In each of the panels, results obtained by different numbers of angular SPF are compared with the ones obtained by the WP-ABC code. It can be seen that for $K_{\text{max}} = 1$, 24 angular SPF are sufficient to provide converged results. Noting the small reaction probability for the $\text{H}_2(v' = 0, j' = 1)$ product state, the deviation of the results with 12 angular SPF in panel (a) is not surprising. With increasing K_{max} adopted in the calculation, more angular SPF are required to get converged results. It can be concluded that the number of angular SPF required to converge the results increases with the helicity numbers K included in the calculation. Therefore, for a reaction requiring larger K_{max} , the current MCTDH/RCB method would have difficulties to achieve high efficiency.

In the MCTDH calculations, the choice of the coordinate system is particularly important. The amount of correlation between different coordinates determines the number of SPF required and consequently the numerical effort of the entire

computations. In this aspect, the propagation of the product wave packet using reactant coordinates is not a good choice. The use of reactant Jacobi coordinates in the current study is mainly motivated by considerations regarding to the simplicity of the wave packet propagation and not for optimal computational efficiency.

Finally, comparison of computational effort is given in Table II for our implementation of the MCTDH, the MCTDH package, and WP-ABC code. Parameters in Table I are used for both our implementation of the MCTDH and the MCTDH package, and 12 angular SPF are used. In WP-ABC calculations, similar parameters are used but with a L-shaped grid. The numbers listed in Table II are the counts of wall-clock time on a node with two Intel(R) Xeon(R) processors (X5355@2.66GHz) with 12 threads for parallelism. The time for our implementation of the MCTDH includes wave packet propagation and analysis of state-to-state information. The MCTDH (version 8.4.3) is used here for wave packet propagation only. It is seen from Table II that our implementation of the MCTDH requires much more computational time than

TABLE II. Comparison of computational effort.

	MCTDH in this work	MCTDH package (serial)	MCTDH package (parallel)	WP-ABC (parallel)
$J = 0$	0h33m	2h28m	0h42m	0h1m
$J = 15$	1h31m	14h28m	1h41m	0h5m

the traditional wave packet calculation, but it is a bit more efficient than the MCTDH package. It is clearly observed in the table that for this triatomic reactive scattering calculation, the traditional time-dependent wave packet method is much more efficient than the MCTDH method. However, the MCTDH method has much better numerical scaling with increasing degrees of freedom, which has been shown in the investigations on polyatomic reactions, such as on the $\text{H} + \text{CH}_4$ reaction.

IV. CONCLUSIONS AND PROSPECTS

In a summary, we have used reactant Jacobi coordinates to straightforwardly represent the wave packet in the calculation of the state-to-state ICS and DCS using the MCTDH method. It is shown that accurate calculations of the state-to-state ICS and DCS are possible with the MCTDH method and the required SPF basis set size is moderate. However, for product states with extremely small probabilities, the calculation of accurate DCS using the MCTDH method may be challenging since the DCS are sensitive to small numerical errors. In the calculation with non-vanishing total angular momentum, the problem posed by the requirement for large number of angular SPF is alleviated by adopting parity-adapted basis sets and using only non-negative helicity quantum numbers. The construction of the initial wave packet in the SF frame properly accounts for the centrifugal coupling for all J . The initial wave packet can be constructed near the interaction region, which consequently saves propagation time.

Considering the poor representation of the product wave packets in reactant Jacobi coordinates, the current method may not be an optimal choice. Although the idea of absorbing the reflected portion of the wave packet from the interaction region could provide some improvement for the RCB method, a better choice of the coordinate system would be particularly important. This would minimize the correlations between different coordinates, and yield a significant reduction of the numbers of SPF, which is of great importance for the numerical efficiency. In this aspect, the use of hyper-spherical coordinate system may provide a better balance to represent the reactant and product wave packets in certain reactions. An alternative is also provided by the transition state framework for the calculation of the state-to-state cross sections.

In the current implementation of RCB method, the product wave packets is also prepared in the SF frame, and consequently the dividing surface can be put close to the interaction region. As a result, only a short coordinate range is needed, and the troublesome correlation from the product wave packet represented in reactant coordinates is not significant near the interaction region. It has been shown from above calculated state-to-state cross sections that the shortcoming of the RCB method is not distinct.

The MCTDH method is capable of giving exact numerical results, but high accuracy implies a requirement for larger number of SPF. Product state-resolved calculations, especially calculations of DCS which are a coherent summation of many partial waves, require accurate numerical calculations and in turn much more SPF than calculations of simple (total) reaction probabilities. Considering the poor coordinate system used to express the product wave packets, it is sur-

prising that not many SPF are required to obtain converged results for the state-to-state DCS for the $\text{H} + \text{H}_2$ reaction. The results in this work indicate that the MCTDH method is able to provide accurate calculation of state-to-state DCS, even it needs much more computational effort than the traditional quantum wavepacket method. However, due to much better numerical scaling of the MCTDH method in respect of the dimensionality, the extension to some systems with four atoms or more within the same framework is promising. In polyatomic systems, such as the $\text{H} + \text{CH}_4$ reaction, only part of the total internal coordinates are different between reactant and product Jacobi coordinates, and the poor representation of product wave packets in reactant coordinate system for the $\text{H} + \text{CH}_4$ reaction could be alleviate in a certain degree. Besides, the MCTDH method can also be combined with the RPD scheme to calculate state-to-state information. The RPD method transforms the no-returning part of reacted wave packet continuously in time from reactant to product coordinates with the help of absorption potentials. Concerning the particular form of the MCTDH wavefunction, the transformation of the source wavefunction from reactant to product coordinates during propagation requires to choose suitable initial SPF in the product coordinates and to evaluate the expansion coefficients by the projection of the source wave packet on these SPF.

ACKNOWLEDGMENTS

B.Z. would like to thank U. Manthe for helpful comments on the paper and for the supports during his visit to Universität Bielefeld. Z.G.S. and D.H.Z. were supported by the National Natural Science Foundation of China (NNSFC) (Grant Nos. 21222308, 21103187, and 21133006), the Chinese Academy of Sciences (CAS).

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