

Perspective

Quantum wavepacket approach to chemical reaction dynamics. Perspective on “Dynamics of the collinear H + H₂ reaction. I. Probability density and flux”

McCullough EA Jr, Wyatt RE (1971) *J Chem Phys* 54: 3578

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Abstract. This paper presents an overview of the time-dependent quantum wavepacket approach to chemical reaction dynamics. After a brief review of some early works, the paper gives an up-to-date account of the recent development of computational methodologies in time-dependent quantum dynamics. The presentation of the paper focuses on the development of accurate or numerically exact time-dependent methods and their specific applications to tetraatomic reactions. After summarizing the current state-of-the-art time-dependent wavepacket approach, a perspective on future development is provided.

1 Background

In 1971, McCullough and Wyatt published a paper [1] in which they described an application of time-dependent (TD) quantum mechanics to the collinear H + H₂ reaction by solving the TD Schrödinger equation. In their approach, McCullough and Wyatt used the finite-difference method to approximate the spatial derivatives of the wavefunction and carried out the time propagation of the wavefunction by the Crank–Nicholson method [2]. Through explicit numerical calculations, the authors showed [1] how one can directly obtain real-time dynamics information of the reaction process by examining the scattering wavefunction and the reactive flux as functions of both time and space. This work demonstrated the numerical feasibility of solving reaction dynamics problems by using the TD quantum wavepacket approach.

However, at the time of their publication the exact TD quantum wavepacket methods were not viewed as

efficient numerical techniques for solving quantum scattering problems in chemical dynamics. This is because the coupled-channel scattering problems one could solve numerically at the time were mainly collinear atom-diatom scattering and had only a limited number of coupled channels, which were more efficiently solved by time-independent scattering methods. As a result, the emphasis of the paper by McCullough and Wyatt was mainly to demonstrate the usefulness of the TD approach as an analytical tool to understand the reaction dynamics but not as an efficient computational tool for numerical calculations. Consequently, only a few applications of TD quantum mechanics to chemical reactions were reported afterwards [3–5].

Around the middle of the 1980s, more efficient and accurate computational techniques were introduced into TD wavepacket calculations. These include the split-operator method [6], the fast Fourier transform method [6, 7], the Chebychev polynomial expansion method [8], the short iterative Lanczos method [9], etc. The utilization of these numerical methods made TD quantum wavepacket calculations more accurate and efficient. More importantly as computer speed significantly increased, the computational advantage of the TD approach became better appreciated for solving large-scale coupled-channel problems. Mowrey and Kouri [10] argued that since the TD wavepacket approach solves an initial-value problem and the computational time scales quadratically with the number of coupled channels, it should be computationally more advantageous than the traditional boundary-value time-independent scattering approach for solving large-scale coupled-channel scattering problems. Since then, more applications of the TD wavepacket approach to atom–diatom reactive scattering have appeared [11–13] including reactions of H + O₂ [14, 15] and O(¹D) + H₂ [16], both with deep potential wells. In addition, the TD wavepacket approach has also been widely applied to other dynamics problems [17], including photodissociation of tritomic molecules [18–23], vibra-

tional predissociation [24, 25], and gas–surface reactions [26–31]. The introduction of the absorbing potentials in the numerical computation [12] has further widened the scope of TD applications to practical dynamics problems.

2 TD approach to AB + CD reactions

2.1 Introduction

Almost without exception, the previously mentioned TD applications to gas-phase problems are all for triatomic systems. By the beginning of 1990, the accurate quantum dynamics calculation for gas-phase triatomic systems of the type A + BC essentially became a solved problem. The new challenge to computational dynamics is to carry out accurate dynamics studies for polyatomic systems with more than three atoms. In particular, the rigorous quantum dynamics treatment for tetraatomic systems of the type AB + CD became the new benchmark for dynamics studies. Computationally, the quantum dynamics of the AB + CD system is not a trivial extension of the triatomic system of A + BC. The number of internal degrees of freedom suddenly increases from 3 for the A + BC system to 6 for the AB + CD system which translates into a drastic increase in the number of coupled channels and therefore huge increases in computational cost. Also, technically, the Hamiltonian for the AB + CD system is more complicated to handle than for triatomic systems. For example, one has to deal with the coupling of three angular momenta for the AB + CD system instead of two for the triatomic A + BC system. Thus, the difficulties in both the theoretical treatment and the numerical computation make the exact dynamics calculation for the AB + CD system a new challenge in quantum dynamics. Consequently, the time-independent scattering methods, which have been very successful in treating the A + BC reaction, were proven to be difficult to apply to the tetraatomic AB + CD reaction due to their computational limitations. For example, in the algebraic variational approach, one is required to invert the Hamiltonian matrix to solve linear algebraic equations. Even for a simple tetraatomic reaction such as H₂ + OH, the size of the Hamiltonian matrix is prohibitively large to be inverted directly using today's computers. It therefore requires alternative approaches such as iterative methods to solve linear algebraic equations due to their lower computational scaling than direct matrix inversion.

Thus, the critical measure of the applicability of a method to polyatomic reaction dynamics is the scaling of its computational cost with respect to the number of basis functions or degrees of freedom. Since the standard time-independent scattering methods solve boundary-value problems, they scale as N^3 with the number of basis functions N , and are thus difficult to extend to large systems. Until a few years ago, the reduced-dimensionality approach (RDA) [32, 33] provided the only means for treating the four-atom reactive scattering problem in which a four-atom reaction system is reduced to an effective atom–diatom system through the elimi-

nation of three internal coordinates, either by applying an adiabatic approximation for three internal angular variables [32] or by restricting the system to certain geometric configurations [33]. The results of the RDA calculations are mixed, however [36–40].

The TD wavepacket approach has very attractive features for large scale numerical calculations. Since it solves an initial-value problem and calculates the wavefunction for one initial state at a time, the computational cost is proportional to N^α ($1 < \alpha < 2$), where N is the number of basis functions (which can be a very large number for polyatomic systems). This reduction in computational scaling is crucial for large-scale quantum dynamics calculations. In addition, a single wavepacket calculation can give dynamical quantities such as S matrix elements or reaction probabilities over a wide range of energies contained in the initial wavepacket. Thus it is not surprising to see that the TD wavepacket approach has recently made significant advance in treating dynamics problems for tetraatomic reactions [41].

The accurate TD approach to tetraatomic systems was first applied to the photofragmentation dynamics of H₂HF → H₂ + HF [42, 43] and HOOH → OH + OH [44], in which the two diatomic vibrations were frozen but all the other four internal degrees of freedom were treated exactly. These two theoretical studies established the numerical feasibilities for the accurate TD wavepacket treatment for tetraatomic dynamics problems. Within quick succession, accurate quantum dynamics calculations for the tetraatomic reaction AB + CD → A + BCD were reported for the benchmark reaction H₂ + OH → H + H₂O [45–47] and its isotopic reactions DH + OH → D + H₂O, H + DOH [48] and D₂ + OH → D + DOD [49]. For the H₂ + OH reaction, cumulative reaction probabilities have also been computed by calculating the flux directly without summing over individual reaction probabilities [50–52]. Additionally, accurate dynamics calculations for reactions of HO + CO → H + CO₂ [53], H₂ + CN → H + HCN [54, 56], and D₂ + CN → D + DCN [55] have been reported. With the exception of Refs. [50, 56] which use the time-independent iterative approach to calculate cumulative reaction probabilities, the other works all applied the TD wavepacket approach. In addition, the TD calculation for the reverse reaction of H + H₂O → H₂ + OH has been reported [57]. More recently, state-to-state TD calculations have been reported for the H₂ + OH reaction [58, 59] and its reverse reaction H + H₂O [60].

2.2 Mathematical formulation

In the TD wavepacket approach, one solves the TD Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = H\Psi(t) \quad (1)$$

starting from a given L^2 integrable initial wavefunction $\Psi(0)$. In the following, we specialize our discussions

specifically for tetraatomic systems of the type AB + CD. Most of the discussions, however, should be applicable to A + BCD systems as well with some modifications.

For AB + CD systems the most straightforward choice of coordinates to describe the dynamical system is the Jacobi coordinates corresponding to the diatom-diatom arrangement. As shown in Fig. 1, the three vectors ($\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2$) denote, respectively, the vector \mathbf{R} from the center of mass (CM) of diatom AB to that of CD, the AB diatomic vector \mathbf{r}_1 , and the CD diatomic vector \mathbf{r}_2 . The full Hamiltonian expressed in this set of coordinates is written as

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{(\vec{J} - \vec{j}_{12})^2}{2\mu R^2} + h_1(r_1) + h_2(r_2) + \frac{\vec{j}_1^2}{2\mu_1 r_1^2} + \frac{\vec{j}_2^2}{2\mu_2 r_2^2} + V(\vec{r}_1, \vec{r}_2, \vec{R}), \quad (2)$$

where μ is the reduced mass between the CM of AB and CD, μ_1 is the reduced mass of AB, and μ_2 is the reduced mass of CD. The vector \vec{J} is the total angular momentum operator and \vec{j}_1 and \vec{j}_2 are, the rotational angular momentum operators of AB and CD respectively. The latter two are coupled to form the total internal angular momentum via $\vec{j}_{12} = \vec{j}_1 + \vec{j}_2$. The reference diatomic Hamiltonian $h_i(r_i)$ ($i = 1, 2$) in Eq. (2) is defined as

$$h_i(r_i) = -\frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial r_i^2} + V_i(r_i), \quad (3)$$

where V_i is a chosen reference diatomic vibrational potential. The eigenfunctions and eigenvalues of the reference Hamiltonian $h_i(r_i)$ are denoted by ϕ_{v_i} and ε_{v_i} , respectively.

The TD wavefunction can be expanded in the body-fixed rovibrational basis functions as [46]

$$\Psi_{v_0 j_0 K_0}^{JM\epsilon}(\vec{R}, \vec{r}_1, \vec{r}_2, t) = \sum_{n,v,j,K} F_{nvjK,v_0 j_0 K_0}^{JM\epsilon}(t) u_n^{v_1} \times \phi_{v_1}(r_1) \phi_{v_2}(r_2) \times Y_{jK}^{JM\epsilon}(\hat{R}, \hat{r}_1, \hat{r}_2), \quad (4)$$

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) is the initial rovibrational state, and ϵ is the parity of the system. The determination of the TD coefficient $F_{nvjK,v_0 j_0 K_0}^{JM\epsilon}(t)$ gives the solution of the TD Schrödinger equation.

The coupled total angular momentum eigenfunctions $Y_{jK}^{JM\epsilon}$ in Eq. (4) can be written as [44, 46, 61],

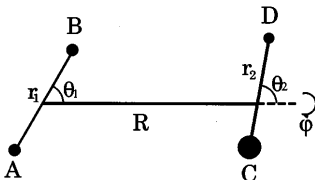


Fig. 1. Jacobi coordinates for the reaction AB + CD \rightarrow A + BCD. The angle ϕ is the out-of-plane torsional angle

$$Y_{jK}^{JM\epsilon} = (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} \times \left[D_{K,M}^{J*} Y_{j_1 j_2}^{j_{12} K} + \epsilon (-1)^{j_1 + j_2 + j_{12} + J} D_{-K,M}^{J*} Y_{j_1 j_2}^{j_{12} -K} \right], \quad (5)$$

where $D_{K,M}^J(\Theta\Phi\Psi)$ is the Wigner rotation matrix [62] with three Euler angles (Θ, Φ, Ψ) , and $Y_{j_1 j_2}^{j_{12} K}$ is the angular momentum eigenfunction of j_{12} [44, 46],

$$Y_{j_1 j_2}^{j_{12} K}(\theta_1, \theta_2, \phi) = \sum_{m_1} \langle j_1 m_1 j_2 K - m_1 | j_{12} K \rangle \times y_{j_1 m_1}(\theta_1, 0) y_{j_2 K - m_1}(\theta_2, \phi), \quad (6)$$

where y_{jm} are spherical harmonics. Note in Eq. (5) the restriction $\epsilon(-1)^{j_1 + j_2 + j_{12} + J} = 1$ for $K = 0$.

The split-operator propagator [6] is used to carry out the time propagation of the wavepacket,

$$\Psi^{JM\epsilon}(\vec{R}, \vec{r}_1, \vec{r}_2, t + \Delta) = \exp\left(\frac{-iH_0\Delta}{2}\right) \exp(-iU\Delta) \times \exp\left(\frac{-iH_0\Delta}{2}\right) \times \Psi^{JM\epsilon}(\vec{R}, \vec{r}_1, \vec{r}_2, t), \quad (7)$$

where the reference Hamiltonian H_0 is defined as

$$H_0 = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + h_1(r_1) + h_2(r_2) \quad (8)$$

and the effective potential operator U in Eq. (7) is defined as

$$U = \frac{(\vec{J} - \vec{j}_{12})^2}{2\mu R^2} + \frac{\vec{j}_1^2}{2\mu_1 r_1^2} + \frac{\vec{j}_2^2}{2\mu_2 r_2^2} + V(\vec{r}_1, \vec{r}_2, \vec{R}) = V_{\text{rot}} + V(\vec{r}_1, \vec{r}_2, \vec{R}). \quad (9)$$

The matrix version of Eq. (7) for the expansion coefficient vector \mathbf{F} is then given by

$$\mathbf{F}(t + \Delta) = \exp(-i\mathbf{H}_0\Delta/2) \exp(-i\mathbf{U}\Delta) \times \exp(-i\mathbf{H}_0\Delta/2) \mathbf{F}(t), \quad (10)$$

where \mathbf{H}_0 is the diagonal matrix defined in Ref. [46].

From the propagation of an initial wavepacket $|\chi_i(0)\rangle$, the time-independent wavefunction $\psi_i^+(E)$ can be obtained by Fourier transforming the TD wavefunction [46]

$$\psi_i^+(E) = \frac{1}{2\pi a_i(E)} \int_{-\infty}^{\infty} \exp\left[\frac{i}{\hbar}(E - H)t\right] \chi_i(0) dt, \quad (11)$$

and similarly for the derivative of the wavefunction $\psi_i^{+'}(E)$. The coefficient $a_i(E)$ is easily evaluated from the free-energy-normalized asymptotic function $\phi_i(E)$ as $a_i(E) = \langle \phi_i(E) | \chi_i(0) \rangle$ [46]. The total reaction probability from a given initial state i can be calculated by using the flux formula [46]

$$P_i^R(E) = \sum_f |S_{fi}^R|^2 = \langle \psi_i^+(E) | \hat{F} | \psi_i^+(E) \rangle. \quad (12)$$

The initial wavepacket $|\chi_i(0)\rangle$ is usually chosen to be a Gaussian function with an average momentum k_0 traveling toward the interaction region

$$\phi_{k_0}(R) = \left(\frac{1}{\pi\delta^2}\right)^{1/4} \exp\left[-(R - R_0)^2/2\delta^2\right] \exp(-ik_0R) \quad (13)$$

multiplied by the selected initial rovibrational eigenfunction. In actual propagation, the TD wavefunction is absorbed at the edges of the grid to avoid boundary reflections.

3 Results of the $\text{H}_2 + \text{OH}$ reaction

The TD wavepacket method described earlier is applied to the benchmark $\text{H}_2 + \text{OH}$ reaction and its isotopic reactions. Figure 2 shows computed total (final state-summed) reaction probabilities of the three isotopic reactions on the Walsh–Dunning–Schatz–Elgersma potential energy surface (PES) [63] as a function of the incident kinetic energy from the initial ground state of the reagents with zero total angular momentum ($J = 0$). The reaction probability is of the order $P(\text{H}_2) > P(\text{HD}) > P(\text{D}_2)$ at fixed kinetic energies; however, considering the vibrational energy difference among H_2 , HD , and D_2 , the reaction probability is about the same magnitude as a function of total energy (kinetic energy + zero-point energy).

The reaction probability for the $\text{H}_2 + \text{OH}$ shows a strong steric effect as reflected in its sensitive dependence on the initial rotational states of the reagents, especially the reactive diatomic H_2 . As shown in Fig. 3, the reaction probability initially increases quite significantly as the reagent rotation increases. In particular the maximum of the reaction probability always shows up for the $j = 1$ state of $\text{H}(\text{D})_2$, which is believed to be a general phenomenon for collinearly dominated reactions at zero

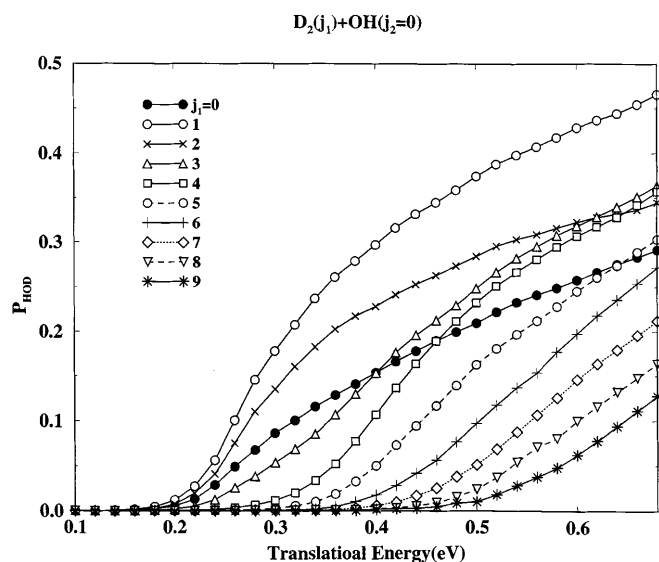


Fig. 2. Reaction probabilities of the three isotopic reactions of $\text{H}_2 + \text{OH}$ from the initial ground state of the reagents with zero total angular momentum ($J = 0$)

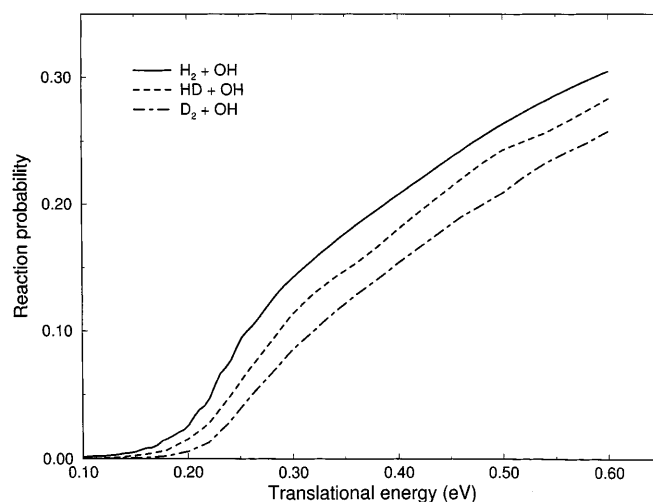


Fig. 3. Reaction probabilities of the reaction $\text{D}_2 + \text{OH}$ from differential initial rotational states of the D_2 reagent with zero total angular momentum ($J = 0$)

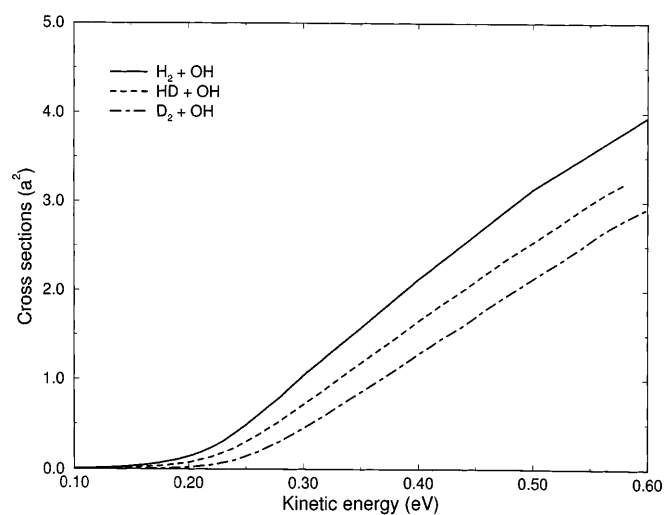


Fig. 4. Integral cross sections of the three isotopic reactions of $\text{H}_2 + \text{OH}$ from the initial ground state of the reagents

total angular momentum as explained in Ref. [48]. In addition, the vibrational excitation of the reactive H_2 is found to significantly enhance the reaction probability while vibrational excitation of the nonreactive $\text{OH}(\text{D})$ bond has little effect on this reaction [46].

The total reaction cross sections and rate constants for the three reactions of $\text{H}_2 + \text{OH}$ show a clear isotopic effect as shown in Figs. 4 and 5.

4 Future prospects

We believe that the TD approach currently provides the most viable means for carrying out accurate quantum dynamics studies of polyatomic reaction dynamics due to its relatively low scaling of computational cost with the number of basis function N [computing time $\propto N^\alpha$ ($1 < \alpha < 2$)]; however, we need to further develop more efficient numerical treatments to make accurate

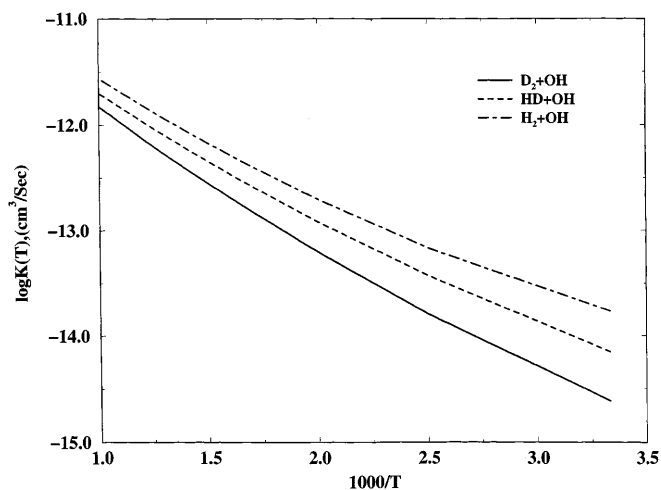


Fig. 5. Rate constants of the three isotopic reactions of $\text{H}_2 + \text{OH}$ from the initial ground state of the reagents

dynamics calculations possible for relatively large polyatomic systems. An obvious, but reliable, approach is to first eliminate all the nonreactive (spectator) vibrational modes of molecules from the dynamics calculation by treating them adiabatically as shown in Ref. [46] for treating the nonreactive OH bond in the $\text{H}_2 + \text{OH}$ reaction. This will instantaneously reduce significantly the total number of active degrees of freedom in the dynamics calculation with little loss of accuracy.

Another important task is to develop more accurate and efficient methods to generate PESs for quantum dynamics calculations. Currently, there is a severe shortage of reliable PESs for dynamics studies. As ab initio quantum chemistry computations become more reliable and affordable, the fitting of discrete ab initio energy points into high-dimension global potential energy functions becomes a bottleneck in dynamics studies due to numerical difficulties. It is desirable to be able to carry out quantum dynamics calculations through automatic numerical fitting of the ab initio points directly to give potential energies at desired dynamical grid points (quadrature points). Recently, a number of methods have been proposed to accomplish this task. The Shepard interpolation method proposed by Ischtwan and Collins [64] and modified by others [65, 66] uses both potential energies and their derivatives from ab initio calculations to interpolate the potential energy, and employs classical trajectory calculations extensively to improve the PES. The SOFA method of Wang et al. [67] uses a sequential one-dimensional fitting approach to automate the task of multi-dimensional fitting of PESs within a precomputed set of ab initio data. The SOFA method is better suited for quantum dynamics studies because it only requires the ab initio energy, and but not their derivatives. Although in their early stages of development, both approaches seem to be quite promising for future ab initio quantum dynamics calculations.

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