Entangled trajectory molecular dynamics theory for the collinear $H+H_2$ reaction

Lifei Wang, Feng Xu, and Yujun Zheng*

School of Physics, Shandong University, Jinan 250100, China

Abstract. The recently formulated entangled trajectory molecular dynamics (ETMD) theory is applied to the collinear hydrogen exchange reaction. The reaction probability is calculated for one- and two-dimensional of collinear $H+H_2$ model. It is found that although the results of ETMD are not in good agreement with quantum mechanics simulations, the numerical trend is consistent with each other.

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Key words: quantum phase space, Wigner function, entangled trajectory molecular dynamics

1   Introduction

Quantum-mechanical effects are essential in many chemical reactions, such as zero-point energy, interference, tunneling and nonadiabatic behavior. Time-dependent quantum wavepacket methods are widely used to study molecular dynamics. Traditional methods of solving the time-dependent Schrödinger equation are based on basis sets of functions, spatial grids or discrete variable representation scale exponentially with the system size, and therefore these methods are not feasible for systems beyond eight or so dimensions [1]. At the same time, classical molecular dynamics is intensively used to study complex systems, but it is incapable of description quantum-mechanical effects. It is, as a long-standing goal in this area, the useful to develop semiclassical methods which can both favorable scaling with respect to system size and accurate description of the quantum phenomena. And, considerable progress has been made over the last few decades in the development of trajectory-based approaches [2–8]. The methodology of entangled trajectory molecular dynamics (ETMD), where Wigner distribution function is represented as a trajectory ensemble, is also developed and is successfully applicable to several models [6–8, 11–13].

The Wigner transform of the quantum Liouville equation gives equivalently representations of quantum mechanical and serves as the basis for the ETMD method, where the Wigner distribution

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*Corresponding author. *Email address:* `yzheng@sdu.edu.cn` (Y. Zheng)

function represents as an ensemble of trajectories. The non-local quantum character enters this method through the interactions between the ensemble trajectories, which involves as the distribution function exists in the equations of entangled trajectories.

Collinear hydrogen exchange reaction is one benchmark model of chemical reactions. This system has been investigated by different approaches, and the reaction probability and rate constant for the elementary reaction have been calculated using classical [14,15], semi-classical [16,17] and quantum methods [18-20]. The application the entangled trajectory molecular dynamics method (ETMD) to the standard collinear chemical reaction, where quantum effects are especially significant, is encouraging . In this letter the collinear $H+H_2$ exchange reaction is studied using the ETMD method in Wigner phase space.

The Wigner function, corresponding to the wave function $\psi(\mathbf{q};t)$, can be written as follows [21]:

$$\rho(\mathbf{q},\mathbf{p};t)=\left(\frac{1}{2\pi\hbar}\right)^n \int d\mathbf{y}\psi^*(\mathbf{q}+\mathbf{y}/2;t)\psi(\mathbf{q}-\mathbf{y}/2;t)e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{y}}, \quad (1)$$

where all integrals are from $-\infty$ to $+\infty$ unless otherwise noted.

ETMD method is based on solving the quantum Liouville equation using a trajectory ensemble with non-classical terms in time evolution. The equations of motion for the entangled trajectories can be defined as follows as [6,7,11,12]

$$\begin{aligned}\dot{q}_k &= \frac{p_k}{m}, \\ \dot{p}_k &= \frac{1}{\rho(\mathbf{q},\mathbf{p})}\int d\boldsymbol{\xi}\Theta_k(\mathbf{q},\mathbf{p}-\boldsymbol{\xi})\rho(\mathbf{q},\boldsymbol{\xi}),\end{aligned} \quad (2)$$

where

$$\Theta_k(\mathbf{q},\boldsymbol{\xi}-\mathbf{p})=\frac{1}{(2\pi\hbar)^n}\int d\mathbf{y}\frac{V_k^+ - V_k^-}{y_k}e^{-i\mathbf{y}\cdot(\boldsymbol{\xi}-\mathbf{p})/\hbar}. \quad (3)$$

The $k=n$ component of the vector $\boldsymbol{\Theta}$ is given by

$$\Theta_n(\mathbf{q},\boldsymbol{\xi}-\mathbf{p})=\frac{1}{(2\pi\hbar)^n}\int d\mathbf{y}\times\left\{[V(\mathbf{q}+\mathbf{y}/2)-V(\mathbf{q}-\mathbf{y}/2)]-\sum_{k=1}^{n-1}\left[V_k^+ - V_k^-\right]\right\}\times\frac{e^{-\frac{i}{\hbar}\mathbf{y}\cdot(\boldsymbol{\xi}-\mathbf{p})}}{y_n}, \quad (4)$$

where $V_k^\pm=V(q_1,\cdots,q_k\pm y_k/2,\cdots,q_n)$ and $k=1,\cdots,n-1$.

In the following, we illustrated the ETMD method by calculating the reaction probability of one-dimensional and two-dimensional model which mimic collinear hydrogen exchange reaction. There are few different sampling method, such as, normal sampling of a multidimensional Gaussian or simply use a density cutoff in a uniform sampling, to sample initial values of Wigner function. In our numerical calculation, we sample the initial values of the trajectories from the Gaussian distribution according to the same properties. These initial values are the "rectangle" shape in the phase space. Actually, it is one of the methods to avoid the rectangle by evolving these initial points under the Fokker-Planck equation. Many approaches to the problem of constructing
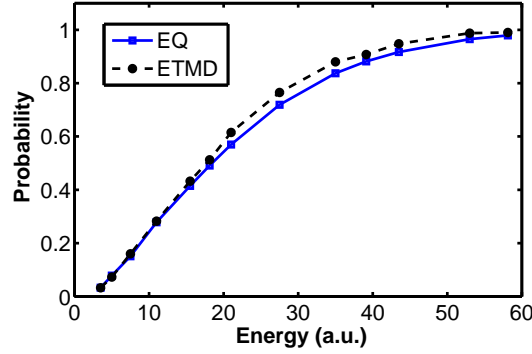
Figure 1: Transmission probability for one-dimensional model of collinear hydrogen exchange reaction as a function of initial wave packet energy, ETMD and EQ results.

a smooth (positive) distribution function from a finite set of N sampled points have been developed. In our simulations, we employ the adaptive kernel density estimation method [7,8,11-13,22] to construct a smooth function $\rho(q_1,q_2,p_1,p_2;t)$ from the the instantaneous trajectory ensemble at each step in the time evolution.

We first compute the energy-resolved transmission probabilities for the Eckart barrier mimicking the collinear hydrogen exchanged reaction in one dimension. The potential can be written as

$$V = D\cosh^{-2}(Zx). \tag{5}$$

In mass-scaled units (scaled by $m_H/2$), the parameters of the barrier, $D=16$ and $Z=1.3624$ [23]. The initial Gaussian wavepacket,

$$\psi(0) = \left(\frac{2\alpha}{\pi}\right)^{1/4}\exp\left(-\alpha(x-q_0)^2 + ip_0(x-q_0)\right), \tag{6}$$

is located on the left of the Eckart barrier. The choice of initial parameters as $\{\alpha=6.0, q_0=-2.0\}$, and the initial energy of wavepacket $E=\alpha/2+p_0^2/2$. We calculate the transmission probability of the wavepacket to the right of the barrier as the funtion of the wavepacket initial energy. The exact quantum (EQ) transmission probability is defined as the integral $|\psi(q,t)|^2$ from $q^{\ddagger}$ to $+\infty$. While in the ETMD method the probability is defined as the fraction of trajectories with $q>q^{\ddagger}$, where $q^{\ddagger}$ is the barrier position. As shown in Fig. 1, the transmission probabilities using the ETMD method are in good agreement with the exact quantum predictions. And increasing the mean energy increases the probability transfer across the barrier, both in ETMD and EQ methods.

As an example of two dimensional case of this typical system, we calculate the transmission probability of the two-dimensional model for collinear hydrogen reaction. The dynamics is governed by the two-dimensional Hamiltonian, which in mass-scaled Jacobi coordinates takes the form

$$H = -\frac{1}{2\mu}\left(\frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2}\right) + V(R,r), \tag{7}$$
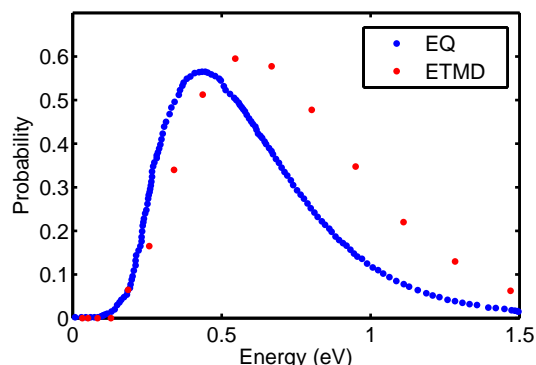
Figure 2: The wave packet transmission probability for two-dimensional model of collinear hydrogen exchange reaction as a function of initial wave packet energy, ETMD and EQ results.

and described the system in Jacobi coordinates can reduce conceptual and computational efforts. We use the Wall-Porter potential surface [24] due to the simple analytical form and compare the exact quantum method work on this potential [25]. And the potential surface symmetrics with respect to $\phi_0 = \arctan(r/R) = \pi/6$.

The initial wave packet can be written as

$$\psi(0) = \sqrt{\frac{2}{\pi}} (\alpha_1\alpha_2)^{1/2} e^{-\alpha_1(R-R_0)^2 - \alpha_2(r-r_0)^2 + ip_0(R-R_0)}, \tag{8}$$

where R is the distance between H_A and the diatomic, and r is the distance between H_B and H_C. Values of the parameters in atomic units (scaled by the reduced mass of the diatomic $m_H/2 = 1$) are $R_0 = 4.5$, $r_0 = 1.3$, $\alpha_1 = 4.0$, $\alpha_2 = 9,73$, and $p_0 = [-15, -1]$. The wave packet transmission probability for two-dimensional model of collinear hydrogen exchange reaction are show in Fig. 2. The numerical results show that the tendency of transmission probability based on ETMD method is consistent well with the exact quantum results, and the exact quantum results are from Ref. [25]. It is found with the increase of wave packet initial total energy, the reaction probabilities increase to the max quantity and then decreases to small probabilities. And we also know the wave packet with high initial total energy can pass over the symmetric of the potential to the reactant domain at the beginning, but many members of the trajectory ensemble reflect back by the potential barrier with time evolution, and the transmission probability is converged to a small quantity finally. The difference between the quantum and entangled trajectory probabilities due to the positive approximated ETMD method cannot capture full quantum dynamics.

In summary, we extend the entangled trajectory molecular dynamics method to collinear hydrogen exchange reaction. We calculated the transmission probabilities versus initial wave packet energy, and compared with exact quantum results. Numerical simulations show that the ETMD result tendency is in good agreement with exact quantum results. The entangled trajectories motion equations are derived from the Wigner function, continuity principle and normalized conservation. The Wigner representation can be faithfully describe the quantum mechanics. This means that the

entangled trajectories equation is valid in the framework of non-relativistic quantum mechanics. In our simulations, we construct a smooth (positive) approximation based on a Gaussian kernel to the Wigner function from a finite set of N sampled points using the adaptive kernel density estimation method. The entangled trajectories equation emphasizes the nonlocality of quantum mechanics via Wigner function in the entangled trajectories equations. And the interactions between the ensemble members make the motion of entangled trajectories quite different from the corresponding classical trajectories. However, this method cannot capture the full quantum dynamics due to the exact Wigner function can become negative. Therefore, there is a big difference between ETMD and EQ methods. In future work, we plan to construct entangled trajectory functions which contained the negative value of the Wigner function.

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