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

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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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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]:

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

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]

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

where

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

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

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

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