1P114

Ab initio 半古典 MD 法の開発

(上智大院理工[1],台湾国立交通大物理所[2],
台湾国立交通大分子科学所[3],Nakamura Institute of Chemical Dynamics[4])
○太田亜由美[1]，南部伸孝[1]，寺西慶哲[2]，中村宏樹[3,4]

Development of *ab initio* semiclassical MD method

(Graduate School of Science and Technology, Sophia Univ.[1], Institute of Physics, National Chiao Tung Univ.[2],
Institute of Molecular Science, National Chiao Tung Univ.[3], Nakamura Institute of Chemical Dynamics[4])
○Ayumi Ohta[1], Shinkoh Nanbu[1], Yoshiaki Teranishi[2], Hiroki Nakamura[3,4]

[Introduction] The molecular dynamics (MD) simulation method has been widely employed to treat large-scale chemical and biological dynamics. On the other hand, it is necessary to take into account various quantum mechanical effects such as nonadiabatic transition, coherence and quantum mechanical tunneling. In the present work, we focus on the tunneling effect and develop a new theory to incorporate this effect into MD method. [1]

[Methods] Two procedures are needed to integrate the tunneling effect, (1) detection of caustics and (2) determination of tunneling path.

(1) Detection of caustics

We employ the Oloyede-Mil'nikov-Nakamura method [2,3] to detect caustics along classical trajectories. It should be noted that the quantity $\partial p(t)/\partial q(t)$ diverges and its inverse becomes zero at caustics. We introduce the NxN matrix defined by

$$A_{i,j} = \frac{\partial p_i(t)}{\partial q_j(t)} (i, j = 1, N)$$

where p_i and q_i are momentum and coordinate, respectively. This matrix A(t) is propagated along classical trajectory. Since $\left|A(t_{caustic})\right| = \infty$ at caustics, when it becomes larger than a certain critical value, its inverse B(t) is propagated to detect caustic [$|B(t_{caustic})|=0$].

(2) Determination of tunneling path

Once the caustics are detected, the straight line path normal to the caustic hyper-surface is generated and the tunnel action is computed along the path. If the obtained tunnel probability along the straight path is smaller than a criterion, the optimal tunnel path is searched variationally and geometrically by using the straight line as the zero-th order approximation. The coordinates q_j are expanded as

$$q_j(z) = q_j^C + \sum_{n=1}^{N_b} C_{jn} z^n ,$$

where the parameter z = (0,1) is introduced: z = 0 ↔ C (caustic), z = zp ↔ P, z = 1 ↔ Q, where P and Q are the points on the equi-potential surface. The total tunnel action is minimized by changing the coefficients C_{jn} and the optimal tunneling path is determined.

[Results and Perspectives] The MD simulation for the proton transfer in the collinear O-H-Cl system has been investigated [1]. Fig.1 shows the typical trajectory with tunnel at Etot = 0.0255 a.u.. The tunnel occurred at the 26-th caustic from the start in this case. After generating the straight line (green line), the optimal tunneling path (orange line) was determined variationally. The reaction probability was estimated in our semiclassical approach with initial conditions generated using random numbers subject to the Wigner distribution (Fig.2). The judgement whether tunneling is carried out or not was determined by generating random numbers. As shown in Fig.2, our result (red dots) agrees well with the quantum result (blue line). The present theoretical approach is applied to multi-dimensional systems. The results of applications will be shown at the poster presentation.

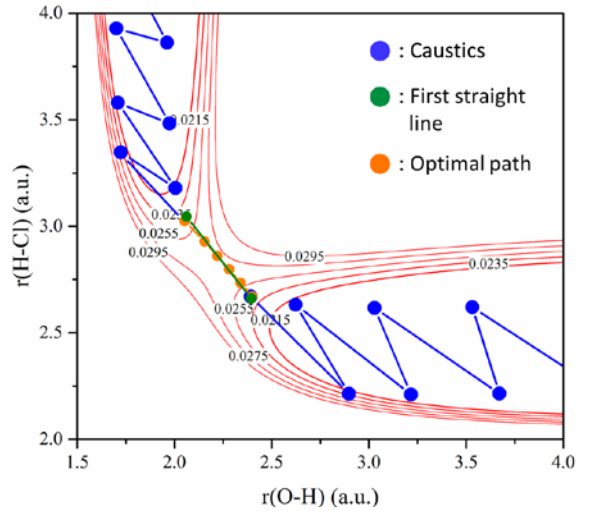

Fig.1 Typical rajectory with tunnel in the collinear O=H-Cl system

Finally, we will develop the on-the-fly *ab initio* version and combine it with the Zhu-Nakamura trajectory surface hopping (ZN-TSH) method [4,5].

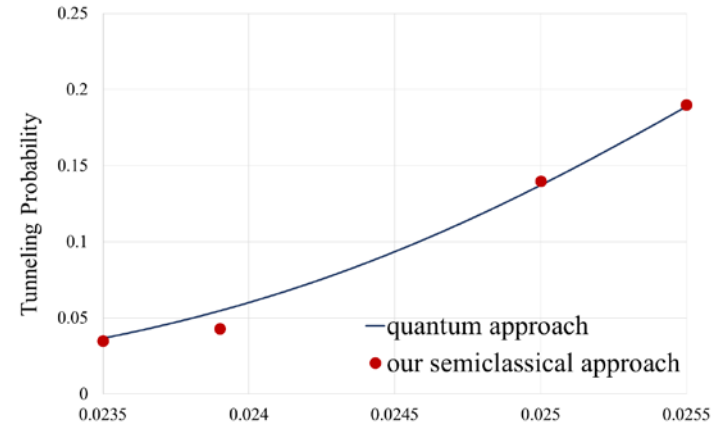

Fig.2 Tunneling probability by our semiclassical (red dots) and quantum (blue line) approaches

[Reference] [1] H. Nakamura, S. Nanbu, Y. Teranishi, A. Ohta, *Phys. Chem. Chem. Phys.*, **18**, 11972 (2016).
[2] P. Oloyede, G.V. Mil'nikov and H. Nakamura, *J. Theo. Comp. Chem.* **3**, 91 (2004).
[3] H. Nakamura and G. Mil'nikov, "Quantum Mechanical Tunneling in Chemical Physics" (CRC Press, Boca Raton, 2013).
[4] H. Nakamura, "Nonadiabatic Transition: Concepts, Basic Theories, and Applications" 2nd edition (World Scientific, Singapore, 2012).
[5] Appropriate paper of ZN-TSH application from Nanbu group.