2P099

Ab initio 半古典 MD 法の開発

(上智大院理工[1],国立交通大学[2],Nakamura Institute of Chemical Dynamics[3])
○太田亜由美[1]，南部伸孝[1]，高島壮大[1]，小林理[1]，寺西慶哲[2]，中村宏樹[2,3]

Development of *ab initio* semiclassical MD method

(Sophia Univ.[1], National Chiao Tung Univ.[2], Nakamura Institute of Chemical Dynamics[3])
○Ayumi Ohta[1], Shinkoh Nanbu[1], Soudai Takashima[1], Osamu Kobayashi[1],
Yoshiaki Teranishi[2], Hiroki Nakamura[2,3]

[Introduction]

The molecular dynamics (MD) method using classical trajectories has been widely employed to treat multi-dimensional chemical and biological dynamics. On the other hand, it is necessary to take into account various quantum mechanical effects. Indeed, nonadiabatic transition that is one of the important quantum mechanical effects has been incorporated into the trajectory surface hopping (TSH) method by using the Zhu-Nakamura theory (ZN-TSH) [1]. Our group has developed this ZN-TSH method and clarified the dynamics of various photochemical reactions [2].

In the present work, we focus on the quantum mechanical tunnel effect and develop a method to incorporate the tunneling effect into MD method.

[Methods]

(1) Detection of caustics

We employ the Oloyede-Mil'nikov-Nakamura method [3,4] to detect caustics along classical trajectory. It should be noted that the quantity $\partial p(t)/\partial q(t)$ diverges and its inverse becomes zero at caustics. So the following NxN matrix is treated,

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

where p_i and q_i are momentum and coordinate, respectively. This matrix satisfies the following Riccati type differential equation,

$$\frac{dA}{dt} = -H_{qq} - H_{qp}A - AH_{pq} - AH_{pp}A .$$

We can solve this equation stably along classical trajectory. The matrices $H_{\alpha\beta}$ are hessians of classical Hamiltonian, $H_{\alpha\beta} = \frac{\partial^2 H}{\partial\alpha\partial\beta}$.

(2) Determination of tunneling path

When the caustic is detected, the normal straight path is generated from the caustic hyper-surface and the tunnel action integral is estimated. The point at the intersection of this straight line with the equi-potential surface is P_0, and the exit of tunnel is Q_0. If the tunnel probability is bigger than a criterion, the optimal tunnel path is searched variationally and geometrically. The straight line path is

used as the zero-th order approximation to determine the optimal path. The coordinate q_j is expanded as

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

here, a parameter z = (0,1) is introduced: z = 0 $\leftrightarrow$ C (caustic), z = zp $\leftrightarrow$ P, z = 1 $\leftrightarrow$ Q. There are two kinds of tunnel regions; the first one is the region in between the caustic hyper-surface and the equi-potential surface and the second one is the region where the potential is larger than the total energy. In the first region (C $\rightarrow$ P), the action integral along the normal line (S_0^{CP}) contributes to the tunnel probability. On the other hand, the parallel direction gives phase information of tunneling. Since classical motion is not allowed in all directions in the second region, the action integral (S_0^{PQ}) in this region contributes to the tunnel probability. The total tunnel action $S_0 = S_0^{CP} + S_0^{PQ}$ is minimized by changing the coefficients C_{jn} and the optimal tunneling path is determined.

In the present work, we carry out on-the-fly *ab initio* calculations of potential energies, gradients and hessians instead of using model potential functions.

[Result]

The actual on-the-fly *ab initio* MD computation for the proton transfer in the collinear O-H-Cl system is currently under way using various levels of quantum chemistry. Our computational results will be shown at the poster presentation.

[Perspectives]

In order to be able to treat large chemical and biological systems, we will introduce some methods to save the cpu time such as the determination of the straight line normal to the caustic hyper-surface and the judgment whether the optimal tunnel path search is carried out or not. Finally, we plan to combine this method with ZN-TSH method.

[Reference]

[1] H. Nakamura, “Nonadiabatic Transition: Concepts, Basic Theories, and Applications” 2nd edition (World Scientific, Singapore, 2012).

[2] A. Ohta, O. Kobayashi, S. O. Danielache, S. Nanbu, *Chem. Phys*., 2015, in Press.

[3] P. Oloyede, G.V. Mil’nikov and H. Nakamura, *J. Theo. Comp. Chem*. 3, 91 (2004).

[4] H.Nakamura and G. Mil’nikov, “Quantum Mechanical Tunneling in Chemical Physics” (CRC Press, Boca Raton, 2013).