4P086

Elongation dynamics と反応部位局所遷移状態探索

(九大院・総理工[1]，SCNU[2]，JST-CREST[3]) Xie Peng[1]，折本 裕一[1]，Liu Kai[1]，Yan Yun-an[1]，Gu Feng Long[2,3]，青木 百合子[1,3]

Elongation dynamics and local transition state search on reaction site

(KYUSHU Univ.[1], SCNU[2], JST-CREST[3]) Peng Xie[1]，Yuuichi Orimoto[1]，Kai Liu[1]，Yun-an Yan[1]，Feng Long Gu[2,3]，Yuriko Aoki[1,3]

[Introduction]

Many essential biological processes are often accompanied by electron-related events such as chemical reactions. The mechanisms of these chemical reactions are significant for the understanding of biomolecular functions. Ab initio molecular dynamics (AIMD) method is a powerful tool to describe chemical reactions involving bond breaking and forming in which electrons play an important role, but the number of atoms handled with quantum mechanics is much smaller than the number of atoms in a biological system for the limitation of computer technologies. Elongation method (ELG)[1,2] can efficiently calculate the electronic structure of large aperiodic polymers with high accuracy on ab-initio level, so we proposed a new method named Elongation molecular dynamics (ELG-MD) by combine the elongation method with dynamics method.

This ELG-MD method makes it possible to efficiently analyze the mechanisms of chemical reactions for biomolecule. To describe a chemical reaction, we may propose several kinds of chemical mechanism. It is important to make clear the transition states along the reaction pathway. To find and confirm the saddle point, we need calculate the Hessian matrix based on quantum-mechanical principles. For this purpose, we developed ELG-Hessian algorithm which can efficiently calculate the local Hessian matrix for the reaction site.

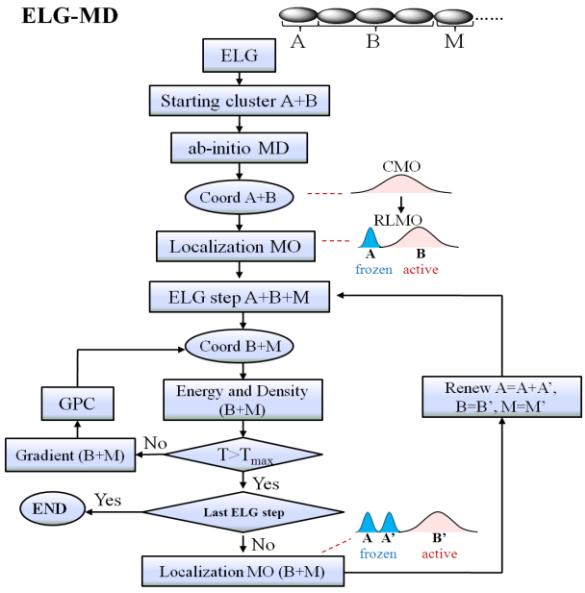

Figure 1: The workflow of ELG-MD

[Methodology]

In ELG-MD method, we use gear predictor corrector (GPC) method to solve the equations of motion for wavefunction and coordinate dynamic variables within the ELG method. The procedure is as follows (Fig. 1): The whole molecule will be divided into a number of units. The first step, we select the 1st unit (A region) and a suitable number of units (B region, to ensure A region has no interaction with M region) as the starting cluster to perform AIMD calculation for a certain number of steps.

The second step, A region will be frozen and a new unit (M region) will be attached at the tail site of B region. The local force on each atom of the active region (B+M region) will be obtained by ELG method, then the acceleration and new position of each atom will be calculated by GPC method. After a certain number steps of dynamics, we can repeat the second step till we obtain the whole system in equilibrium.

Hessian matrix calculation is considerable expensive for biological system when a quantum mechanical description is used, but the chemical reaction region is always on a small part, the most regions do not interact with the reaction region. So in ELG-Hessian calculation, we take the chemical reaction region as the last unit (N) of elongation. From the starting cluster to the second last step, we only need to obtain local molecular orbitas for the frozen region (A region). For the last step of ELG-Hessian, we use full molecular orbitals to calculate the Hessian matrix element for B+M region.

$$H_{xy} = \frac{\partial^2 E_{total}}{\partial x \, \partial y} \qquad x \in B + M, \qquad y \in B + M \qquad (1)$$

[Results and Discussion]

Polyglycine with water was selected as a target system to test the ELG-MD method. In each ELG step, we performed 4000 steps dynamics calculation at HF/STO-3G level. The initial structure and the final structure are shown in Fig. 2 (a) and (b) respectively. Fig. 2(c) showed the structure obtained by ELG-optimization at HF/STO-3G level. By comparing the Fig. 2 (b) and (c), we found that: the structure in Fig. 2 (b) has more helix caused by hydrogen bond forming than Fig. 2 (c). That means the previous structure is more close to the real structure of polyglycine.

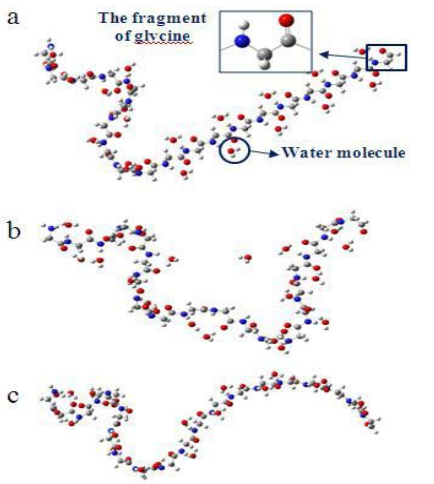

Fig. 2: (a) The initial structure of poly-glycine with water. (b) The structure obtained by ELG-MD. (c) The structure obtained by ELG-optimization.

Before performing ELG-MD calculation, we need use ELG-Hessian method to find the transition state of the reaction site. To examine the accuracy and efficiency of ELG-Hessian, we compared the vibration modes of linear polyglycine (20 units) at HF/STO-3G level with conventional (CNV) Hessian calculation. The comparisons are shown in Table 1. We can see the error of frequency is considerable small. The mostly time-consuming part of Hessian calculation is CPHF part, we checked the CPU time for CPHF calculation. We found that the CPU time for CPHF calculation can significantly drop, from 615.5 second (CNV) to 389.8 second (ELG).

Table 1 The last five intra-molecular vibration modes for linear polyglycine Frequency unit (wavenumber)

ELG	4054.98	4055.27	4055.62	4056.32	4057.51
CNV	4058.98	4060.24	4058.21	4058.85	4060.86

[Future plan]

ELG-Hessian and ELG-MD can work well now, as the next step, elongation transition states (ELG-TS) method will be programmed for efficient investigation on chemical reaction.

1. Imamura, A.; Aoki, Y.; Maekawa, K. Journal of Chemical Physics 1991, 95, 5419-5431.
2. Gu, F. L.; Aoki, Y.; Korchowiec, J.; Imamura, A.; Kirtman, B. Journal of Chemical Physics 2004, 121, 10385-10391.