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Elongation 局所構造最適化による全系の効率的安定構造探索

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

Efficient search for optimized geometry of whole system by elongation local optimization method

(Kyushu Univ.[1], SCNU[2], JST-CREST[3]) Kai Liu[1], Yuuichi Orimoto[1], Feng Long Gu[2], Yuriko Aoki[1,3]

I. Introduction

One of the most successful applications of molecular quantum mechanics is the reproduction and prediction of molecular conformation. However, it's still a grand challenge to perform the geometry optimization on large system in practices. Due to a large number of atoms, the standard *ab initio* calculations are beyond the computational reach. Currently, some fragment-based methods have been successfully proposed and developed to calculate large system within a reasonable cost, for example: divide and conquer (DC)[1], elongation method (ELG)[2], fragment molecular orbitals (FMO)[3] and systematic fragmentation method (SFM)[4]. Despite the complicate interactions of large system, it's very difficult to locate the equilibrium structure. Here we present the implementation of geometry optimization based on the elongation method, which is famous for its high accuracy and efficiency.

II. Theoretical approach

A. Elongation method

ELG procedure generally is analogous to experimental polymer chain synthesis as shown in Fig.1. First, a suitable size of initial monomers (starting cluster) is chosen to initiate the ELG procedure. The canonical molecular orbitals (CMOs) of the starting cluster, generated by conventional SCF calculation, are transformed to an orthogonal atomic basis (OAO). In the following step, the OAO-based density matrix (D^{OAO}) is to partition into frozen region (A) and active region (B). The frozen region is assumed to be far away from the chain propagation point, while the active region is consisted of the remaining part of the starting cluster. After the separate diagonalization of the subspace D^{OAO} (A) and D^{OAO} (B), a set of regional localized molecular orbitals (RLMOs) for both A and B regions are obtained. Then, one attacking unit (C) is added to the chain propagation point for the next ELG step. Because of the negligible interactions between A and C, only B and C will be included in the ELG SCF calculations. After the ELG HF-SCF converges, the CMOs of B and C regions will be localized again to form a new frozen region (RLMOs B') and a new active region (RLMOs C'). Then a new attacking unit (D) is added to repeat the above procedures until the desired length is reached. The important feature of the ELG method is that the equations during SCF are solved only for small subunits instead of the whole system, and the calculations of two-electron repulsion integrals (ERIs) between A and M can be partly omitted by cutoff technique.

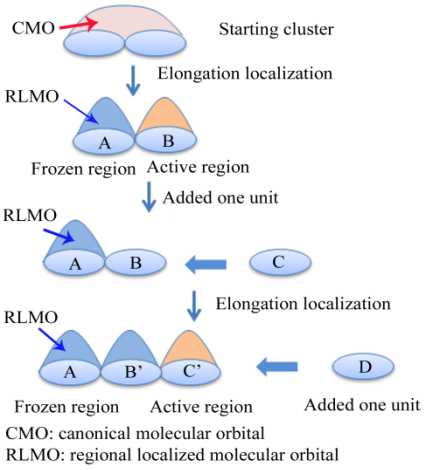

Fig.1 The flowchart of elongation method

B. Elongation geometry optimization

In the framework of HF calculation, the first derivative (gradient) of total energy (E) with respect to the nuclear coordinate X_A at atomic orbitals basis, can be written as:

$$\frac{\partial E}{\partial X_A} = \sum_{\mu\nu} D_{\nu\mu} \frac{\partial H_{\mu\nu}^{core}}{\partial X_A} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} D_{\nu\mu} D_{\lambda\sigma} \frac{\partial (\mu\nu||\sigma\lambda)}{\partial X_A} + \frac{\partial V_{NN}}{\partial X_A} - \sum_{\mu\nu} Q_{\nu\mu} \frac{\partial S_{\mu\nu}}{\partial X_A}$$

where $(\mu\nu||\sigma\lambda)$ denotes two-electron integral, D is the density matrix, H^{core} and S correspond to the core Hamiltonian and overlap matrices of system, respectively. The nuclear-nuclear repulsion is defined by V_{NN}. The energy-weighted

density matrix Q of conventional method is defined as $Q_{\nu\mu} = \sum_{i}^{N/2} n_i \varepsilon_i C_{\mu i} C_{\nu i}$, where n is the matrix of occupancy number (density matrix in MO representation). In the ELG method, the equations during SCF are solved only for active subspaces defined by B and M fragments. Therefore, the non-diagonal ε_{ij}^{LMO} is employed in the ELG -OPT method. As the coefficients of the whole system C_{ABM}^{AO} consist of C_{A}^{LMO}(coefficients of frozen part, localized by the ELG localization procedure) and C_{BM}^{AO} (coefficients of active region and attacking unit, transformed from C_{BM}^{MO} after the ELG SCF calculation). Therefore, the energy-weighted density matrix Q of the ELG-HF-OPT method in atomic basis can be rewritten as $Q_{\nu\mu} = \sum_{ij}^{N/2} n_i \varepsilon_{ij} C_{\mu i} C_{\nu j}$. Because of the boundary effects between A and BM arisen by the tails after the ELG localization procedure, the coordinates of the one unit of the BM region, which is the closest to the frozen region, is fixed in the gradient calculation to reduce these effects.

III. Results and discussion

A. Non-bonding model system: (HF) $_{n=48}$

The linear poly-hydrogen fluoride (poly-HF) molecules are optimized by both elongation and conventional restricted Hartree-Fork method (RHF) with different basis sets. The energy differences ΔE ($\Delta E=E^{elongtion}-E^{conventional}$) of STO-3G, 6-31G and 6-31G(d,p) basis sets are -4.49×10^{-7}, 9.09×10^{-9} and -3.26×10^{-5} Hartree/atom, respectively. The negative values means the ELG-OPT locates an even lower ground state than conventional results. It indicates that for a flat energy potential surface of system, like linear poly-HF molecules, ELG-OPT may produce a more promising candidate for the most stable geometry.

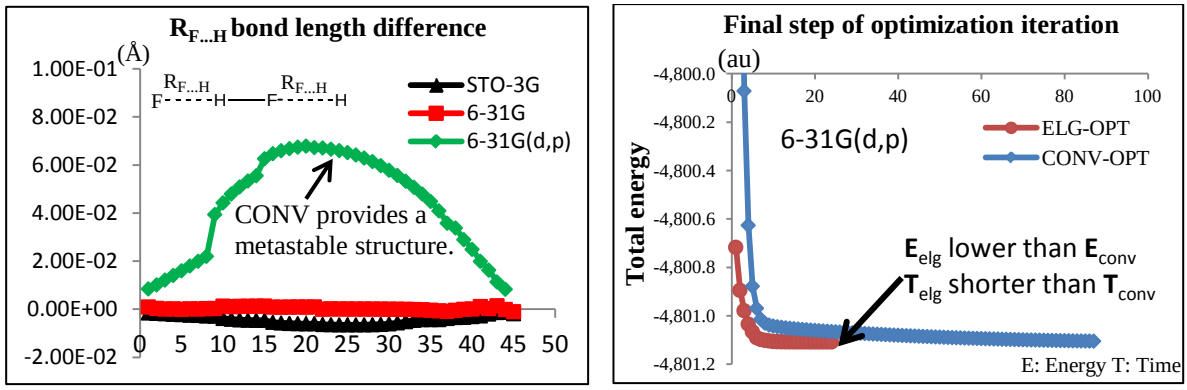

Fig. 2 The differences of bond length and optimization iteration of poly-HF systems. $\Delta R=R^{elongation}-R^{conventional}$

B. Bonding system: extended ployalanine.

As a model of large biosystem, 20 units of extended alanines, is optimized by both the ELG-HF-OPT and conventional method using 6-31G basis set. The RMSD between the ELG and conventional optimized structure (excluding hydrogen) is 0.18. The bond length is also compared in details and shown in Fig.3. The difference of total energy between ELG-OPT and conventional result is 2.37×10^{-7} Hartree/atom. These small differences in structure and total energy show the well reproduction of elongation geometry optimization method.

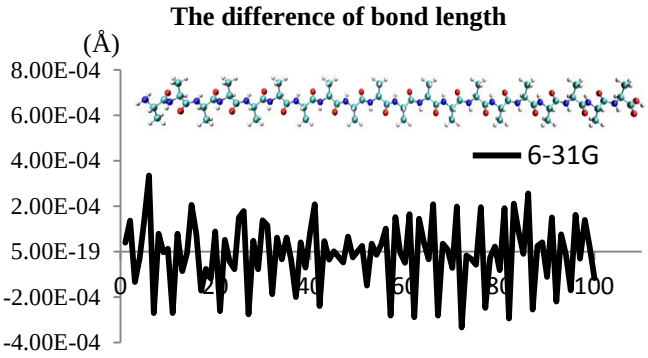

Fig. 3 The difference of bond length between ELG and conventional optimized structure.

Compared to conventional results, it indicates that the ELG-OPT can well reproduce the calculations and may locate a more stable structure than conventional one.

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