Development of three-dimensional elongation method and geometry optimization technique for large systems

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（大規模系への三次元 Elongation 法と構造最適化法の開発）

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論 文 内 容 の 要 旨

Ab initio quantum chemistry has been developed over the past several decades and been successfully applied to the accurate study of small sized molecules. It is still a grand challenge in computational chemistry, however, to perform the calculations on large molecules such as proteins. Conventional quantum methods are either too expensive to calculate large systems or too approximate to get reliable results. Various approaches are being developed to fulfill both the accurate and efficient demands of nowadays calculations. Elongation (ELG) method, firstly proposed in the early of 1990s, is to perform the accurate calculations on quasi-one dimensional large polymers with high efficiency. In this thesis, two main developments of ELG method have been made to the aim of a more powerful and general method for various demands of quantum chemistry calculations.

Elongation geometry optimization (ELG-OPT), one of the most important aspects of ELG method, is proposed at *ab initio* level of theory. The formulism of ELG-OPT is validated by several model systems calculations using different basis sets. For a range of calculations including the non-bonding system poly-$(HF)_n$, polyethylene and the delocalized polyacetylene system, the ELG method can well reproduce the results of conventional calculations. Especially for the calculations of poly-$(HF)_n$ at HF/6-31(d, p) basis set, the ELG-OPT method can not only be faster than the corresponding calculations of conventional method, but also locate a more stable structure with lower ground state energy by using the same optimization criteria. This means that the ELG-OPT method concentrates not only on the whole structure, but also on each elongation geometry optimization step. It may search over more possibilities for local minimum, which may produce a more promising candidate for the most stable geometry. The same phenomena are also found in other systems calculations such as DNA and bio-molecular systems.

Another significant development of ELG method is made to perform the calculations on the large and complicate real three-dimensional biomolecules. Comparison with the standard ELG method, two subroutines (activate and re-frozen steps) are introduced for the three-dimensional ELG (3D-ELG) method. A more general and efficient criterion of activate step is established based on the maximum absolute value of eigenvectors of those units in frozen region. The various calculations of real biomolecular systems indicate the high accuracy of 3D-ELG method. The average deviation of the total energies is 9.1×10^{-7} au/atom. However, the efficiency of current 3D-ELG is not very good and mainly spoiled by the re-frozen step. The reasons to the poor performance of re-frozen step are primarily attributed to two things: (1) This step is a sequential calculation. (2) The multiple times block localization procedures are solved by Jacobi method at a very large size of dimension. Therefore, a new localization procedure for re-frozen step, named one-time localization, is proposed and developed to speed up this step. The basic idea of the one-time localization method is to divide the density matrix based on the ELG units (much small dimension) instead of ELG regions (very large dimension), then to localize these sub-density blocks simultaneously for the construction of transformation matrix (**T**). After that, the block localization is performed only once.

In addition, the replacement of Jacobi rotation employed by ELG method is also tested by many other subroutines. Then, a subroutine named "DSYEV" from LAPACK library is selected to replace the calculations of Jacobi. Meanwhile, the codes of ELG method, particularly the density calculation and overlap diagonalization, are also modified and optimized to accelerate the calculations. At last, the model system 3EQS is employed and calculated at HF/STO-3G basis set to check the performance of 3D-ELG before and after all the modifications. The deviations of the total energy to the conventional result are 1.6×10^{-7} and 2.6×10^{-7} au/atom before and after the improvements, respectively, while the CPU time of the calculations indicates that the improved 3D-ELG can accelerate the calculation 86.8% compared to the original one. The overall performance of the 3D-ELG is also assessed by the comparison with conventional calculation on the model system 2L1X at HF/6-31G basis set. The deviation of the total energy is 4.6×10^{-7} au/atom, while the cost of 3D-ELG is only 87.1% of conventional one. More important thing is that the cost of 3D-ELG calculations would be cheaper if the size of molecule becomes larger.