

Theoretical Studies on Electrical and Optical Properties of DNA and Development of Elongation Molecular Dynamics Method

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論 文 内 容 の 要 旨

Since the double helix structure of DNA was discovered in 1953, the DNA molecule has drawn much research interest to biologists, chemists and physicists over the next decades. Its unique one-dimensional layered π - π electron stacking structure of base pairs in double-stranded form establishes the foundation of that DNA has the potential for use as electronic materials and optical materials. The overlapping π orbitals of base pairs imply that DNA has the possibility of electric conduction. However, the direct conductivity measurements of DNA had not produced consistent results, varying from insulator, semi-conductor, conductor, and so on. Therefore, it is very important to make clear the electronic states and the electric properties of DNA that will be of benefit to the understanding of charge transferring mechanism in DNA duplex. On the other hand, the highly delocalized π -electron systems can cause strong nonlinearities. Viewed from this point, the nonlinear property of DNA molecules with π - π conjugation should be a great expectation. Nevertheless, it was reported that pure DNA is one kind of optically passive material. To solve these conflicts, theoretical investigations can greatly aid in explaining the experimental phenomenon of DNA.

Elongation method has proved to be an accurate and efficient method for calculating the electronic structure of large quasi-one-dimensional aperiodic polymers, and it has been extended to calculate the local density of states (LDOS) at the *ab-initio* molecular orbital level. To investigate the effects of counter-ions (Na^+), base composition and base sequences on DNA conductivities, the LDOS calculations were performed on various DNA models. The band structure calculations based on periodic boundary condition (PBC) using screw axis symmetry were performed for comparison with LDOS calculations. The results indicated that: Na^+ can greatly decrease the energy of the lowest unoccupied molecular orbital (LUMO), and consequently decrease the energy gap between LUMO and HOMO. The electron transfer between stacking

Adenine/Guanine and Sodium would play an important role on the conductivity of DNA. Guanine is the most important base for DNA conductivity in all of the DNA bases, and the conductivity of DNA varies with the base sequences. Moreover, poly (dG) · poly (dC) shows that it is the best conductor in all DNA duplex models.

The elongation finite-field method was performed to calculate static (hyper)polarizabilities of the double strand of B-type poly (dG) · poly (dC), the single strand of B-type poly (dG) and the single strand of B-type poly (dC) DNA models. The first hyperpolarizabilities (β) for the three models are very small. This result implies these models almost have no second order optical susceptibility. The second hyperpolarizability (γ) of B-type poly (dG) · poly (dC) is much higher than those of the other two single strands, but the absolute value of γ is still not big enough compared with other classic NLO materials. We can conclude that the π - π electron stacking structure of base pairs in the double-strand of DNA does enhance the second hyperpolarizability (γ) of DNA, but the enhancement is not enough to make B-type poly (dG) · poly (dC) DNA itself to be a good nonlinear optical material.

Water molecules around the DNA duplex can play an important role in the charge transferring through the π stacking of base pairs, but in all of our calculation models we don't consider the water molecules in the systems for it is very difficult to decide the position of water molecules. Moreover, we need a more reasonable structure of DNA under the influence of water. For this purpose, we proposed a new local molecular dynamics (MD) method at *ab-initio* level for highly efficient calculations of aperiodic polymer systems with including dynamics. Elongation molecular dynamics (ELG-MD) combines the elongation (ELG) method with the molecular dynamics simulation algorithm-Gear predictor corrector (GPC). In ELG-MD method, the local gradients which act on the nucleus of all atoms in the active site are calculated by the elongation method while the evolutions of nucleus's motion are carried on by the GPC algorithm. As the first application of this method, ELG-MD method is performed to investigate the conformation of polyglycine with water molecules system. The efficiency of ELG-MD is obviously higher (about 31%) than the conventional *ab-initio* molecular dynamics (AIMD). The water effects on the conformation of polyglycine are examined. The ELG-MD simulations show that the helix conformation of polyglycine is induced by the hydrogen bonds (H-bond) observed in H-bond rings. This calculation can be the preliminary investigation of biomaterial systems.

論文審査の結果の要旨

本論文は、生体高分子の電氣的・光学的特性解明のための、ねじ回転並進対称性および領域軌道基底局所状態密度を用いた高効率かつ高精度な電子状態解析法を構築するとともに、高分子反応末端部の電子状態を分子動力学法に利用した *ab initio* Elongation-分子動力学法を新規に開発し、溶液中の DNA やタンパク質への適用性および有効性を実証したもので、理論量子化学の発展に寄与するところが大きいと判断した。よって、博士（理学）の学位に値するものと認める。