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巨大生体分子の効率的超高精度電子状態計算

(九大院・総理工[1], SCNU[2], JST-CREST[3], Jagiellonian 大学[4])

○Liu Kai[1], Gu Feng Long[2,3], Makowski Marcin[1,4], Loboda Oleksandr[1], 青木百合子[1,3]

The calculation of electronic structure of huge biomolecules is a challenge to computational chemistry. Our group has developed elongation method [1-3], which can sharply reduce the effort of Fock matrix diagonalization, a bottleneck in SCF procedure, by keeping the dimension of Fork matrix almost as a constant. Right now, Elongation method has been successfully applied to calculate band structure, nonlinear optical properties, and electronic structure of B-type DNA with high accuracy [4]. In this poster, we try to extent elongation method to 2D and 3D system by calculating the electronic structure of chain A of insulin; meanwhile, we apply elongation finite-field method [5] to investigate the nonlinear optical properties of B-type DNA.

General elongation for 2D and 3D model

It is very crucial for elongation method widely used to treat 2D/3D system. We select insulin as model system for its disulfide bonds which are very important to protein. Insulin is composed of two peptide chain named A (21 amino acids) and B (30 amino acids). The two chains are linked by two disulfide bonds, and an additional disulfide is formed within chain A. As a starting point for general elongation, we only choose chain A and replace disulfide bond (S-S) between chain A and B by S-H (see Fig. 1). The total energies of chain A by elongation and conventional method are listed in Table 1. Although the judgment from one dimension to 2D/3D is maybe not efficient and reasonable enough, an acceptable accuracy is already achieved by elongation method. A more suitable and powerful criterion is still being in progress in our group.

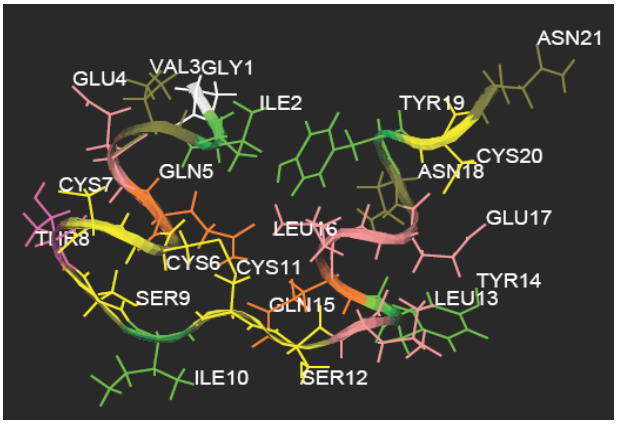


FIG. 1. Structure of chain A of insulin.

Step	Atoms	E_{elg} (hartree)	ΔE per atom
1	113	-3423.1783048155	
2	124	-3739.6783530369	-8.03E-13
3	143	-4098.0807085209	1.32E-09
4	152	-4733.0301279200	0.00E+00
5	163	-5049.5376012995	2.61E-08
6	182	-5407.9583070212	3.62E-08
7	203	-5951.2286183589	3.81E-08
8	220	-6398.0084160316	3.02E-08
9	239	-6756.4230534626	5.54E-10
10	255	-7222.6947315747	6.38E-07
11	269	-7630.9200693560	5.88E-07
12	290	-8174.1940329084	1.58E-08
13	301	-8810.0537814262	2.95E-06
14	316	-9292.1041401661	2.82E-06

TABLE 1. Total energy of chain A of insulin and its error in each elongation step. ΔE per atom, that is, ΔE per atom = ΔE_{total}/number of atoms. $\Delta E_{total} = E_{elg} - E_{conv}$, total energy difference between elongation and conventional calculation.

Elongation finite-field application

Nonlinear optical (NLO) properties of 20 units B-type DNA (structure of DNA see Fig. 2) have been investigated by elongation finite-field method at HF/STO-3G level under the electric field of E_z = 0.000, +0.0005, -0.0005, +0.001 and -0.001 au.

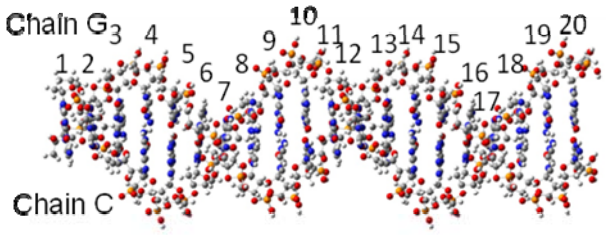
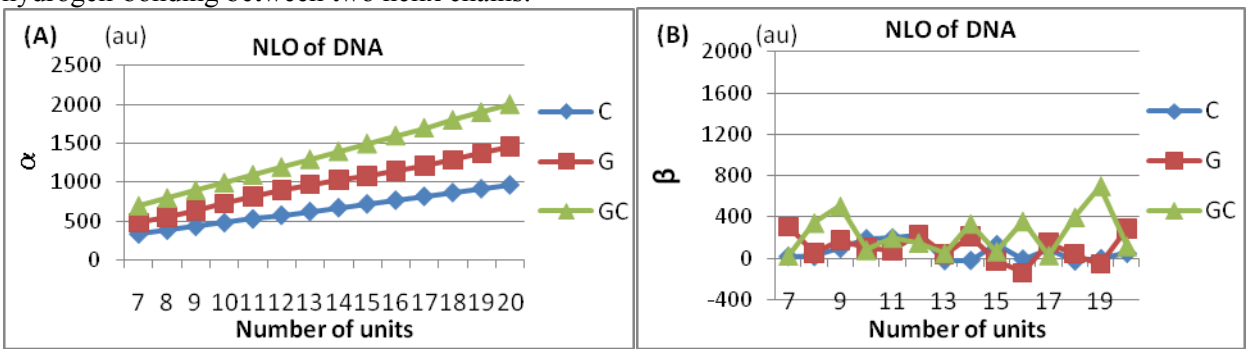


FIG. 2. Single or double chains of 20 units B-poly(dC)·poly(dG) DNA.

The first-order NLO property (α) of DNA is nearly linear as the chain is elongated (see Fig. 3 (A)). As it's shown in figure 3 (B), the values of second-order NLO property of DNA are very small. We are now investigating the reason why γ values in double helix are bigger than the sum of that from isolated single chain (see Fig. 3 (C)). We also find that the total energy increment for double helix behaves in a similar way of that for Cytosine chain under the field (data not shown). We are now analyzing the relationship between NLO property of double chain and that of two isolated single chains from the view point of hydrogen-bonding between two helix chains.



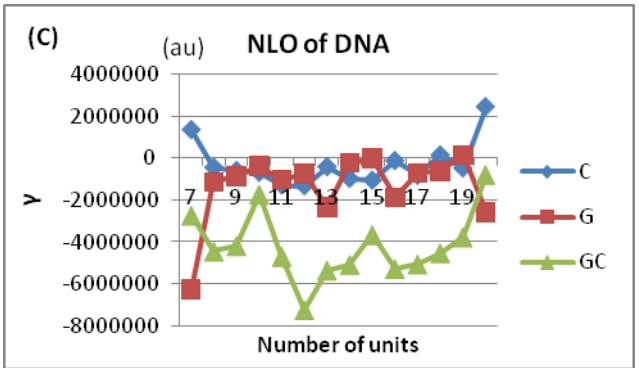


FIG.3. Nonlinear optical properties of 20 units B-type DNA at sto-3g basis level.
C is single chain of 20 units poly (dC).
G is single chain of 20 units poly (dG).
GC is double chains of 20 units poly (dC) · poly (dG) DNA.
(A) The first-order NLO property of DNA.
(B) The second-order NLO property of DNA.
(C) The third-order NLO property of DNA.

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