

(九大院・総理工¹, SCNU², JST-CREST³, Jagiellonian 大学⁴)○Loboda Oleksandr¹, Gu Feng Long^{2,3}, Makowski Marcin^{1,4}, Liu Kai¹, 青木百合子^{1,3}

The increasing demand for faster data processing, storage and distribution can only be fulfilled by ongoing minimization of the basic electronic devices. The traditional silicon-based technologies used nowadays are approaching intrinsic limits in this respect, and new approaches are needed. Photonic technology, where light is used as information carrier instead of electrons, is considered to offer the answer. An important step towards this goal is the development of new photonic materials with large NLO properties. Fullerene-based nano-hybrids as well as carbon heterostructured nanotubes are considered to be a highly promising class of such materials. Linear scaling method, O(N), are among the most reliable and cost efficient approaches available for the calculation of the properties of large systems. Fullerene derivatives with appropriate donors have significant second-order nonlinearity. It is known that fullerenes are excellent acceptors.

Conventional *ab initio* methods require high computational recourses, even the Hartree-Fock approximation formally scales as M⁴, where M is the number of basis functions. Thus various linear scaling methods and algorithms have been developed and applied in a large variety of fields.

Unfortunately, very little is known on the performance of such approaches on the computation of the NLO properties.

The main target of the present work is design of nano-materials for photonic applications. The key parameters for such a design are the nonlinear optical (NLO) properties. These properties have two contributions, the electronic and the vibrational. The vibrational contributions are usually negligible and therefore out of the scope of the present paper. For the evaluation of electronic contribution we used finite field methodology.

Definition of L&NLO properties

The response of a molecule to an homogeneous static electric field can be expressed in the following way:

$$E(F) = E(0) - \sum_i \mu_i F_i - \frac{1}{2!} \sum_{ij} \alpha_{ij} F_i F_j - \frac{1}{3!} \sum_{ijk} \beta_{ijk} F_i F_j F_k - \frac{1}{4!} \sum_{ijkl} \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (1)$$

where E(0) denotes energy of a molecule without external perturbation.

The dipole moment of a molecule in the presence of uniform electric field is given by:

$$\mu_i(F) = \mu_i(0) + \sum_j \alpha_{ij} F_j + \sum_{jk} \beta_{ijk} F_j F_k + \sum_{jkl} \gamma_{ijkl} F_j F_k F_l + \dots \quad (2)$$

The averaged (hyper) polarizabilities are defined as:

$$\bar{\alpha} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

where

$$\bar{\beta} = \sum_{i=x,y,z} \frac{\mu_i \beta_i}{|\mu|} \quad (4)$$

$$\beta_i = \frac{1}{5} \sum_{j=x,y,z} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (5)$$

$$\bar{\gamma} = \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{zzxx} + \gamma_{zzyy} + \gamma_{yyxx})) \quad (6)$$

An essential aspect of this paper is to check the performance of the linear scaling elongation method for the computation of the NLO properties of the nanotubes and fullerene-based materials.

We improved the performance of elongation method by refining the localization scheme. After the regional localization procedure is done there we have two sets of occupied and vacant orbitals assigned to A and B regions. However under closer consideration one can notice the admixture of B region orbitals in frozen A region and vice versa. This may lead to low accuracy in the calculation of the total energy for the whole system. To circumvent this problem we move such kind of orbitals with significant <A|B> overlap from A region into B region, where in the next elongation step they

will be localized again and placed into A region at the most. In this way we maintain the constant number of “transferred” orbitals and avoid tailings of orbitals from the active region in the A part. This development allowed to increase the accuracy of elongation calculation in several orders of magnitude especially in the cases when the delocalized π -extended systems are treated.

As a starting point, we used the module, which involves the dyad of porphyrin and [60] fullerene linked with an alkene chain. These systems represent the first example of a new class of donor-acceptor derivatives in which π -conjugation extends from the porphyrin ring system directly to the fullerene surface.

From the Table 1 it is clear that nature of molecular bridge which links fullerene and free-base porphyrin units plays substantial role in L&NLO properties of entire fullerene-porphyrin system. The polyalkene chain, enriched with π electrons provides better conductivity within fullerene-chromophore dyad.

One can see from the Table 1 that the Elongation Method results are in an excellent agreement with the conventional calculations. The HF values are presented only for z component since the molecules have been oriented along z dipole moment. In comparison with the HF results PM6 method tends to overestimate first hyperpolarizability value polarizability however it has a qualitative agreement with *ab initio* polarizability value look Table 1.

Table 1 The averaged values of linear and nonlinear optical properties of **H₂TPP-C₄H₄-[60]**. μ_z - permanent dipole moment (debye), α - polarizability, β , γ first- and second- order hyperpolarizabilities. Hyper/polarizability values are given in atomic units.

Molecule	Method	μ_z	α_{zz}	β_{zzz}
H ₂ TPP-C ₄ H ₄ -[60]	PM6	-4.110	1738.28	-10232.8
H ₂ TPP-C ₄ H ₄ -[60]	HF*	-5.413	1556.87	-4096.5
H ₂ TPP-C ₄ H ₄ -[60]	HF	-5.413	1556.88	-4097.0
H ₂ TPP-(C ₄ H ₄) ₂ -[60]	HF	-5.763	1836.85	-6672.1
H ₂ TPP-(C ₄ H ₄) ₃ -[60]	HF	-5.941	2152.85	-9925.7
H ₂ TPP-(C ₄ H ₄) ₄ -[60]	HF	-6.033	2479.35	-13445.0
H ₂ TPP-(C ₄ H ₄) ₅ -[60]	HF	-6.085	2917.02	-14847.1
H ₂ TPP-(C ₄ H ₄) ₆ -[60]	HF	-6.111	3142.20	-17667.4
*Conventional Calculations				

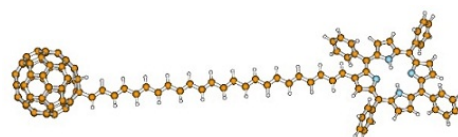


FIGURE 1. The structures of investigated molecules

To test the developmental code of the elongation method we recalculated the boron-nitride carbon nanotube. The error per atom introduced by the Elongation method at the HF/STO-3G method is tabulated in Table 2. As it can be seen from the Table 2 the modified elongation method improves the accuracy of total energy values almost in two orders of magnitude in comparison to the “conventional” elongation method.

Table 2 Error per Atom Introduced by the Elongation Method for boron nitride carbon nanotube at the HF/STO-3G level.

in au Atoms	E _{CONV}	E _{NewElg}	E _{OldElg}	$\Delta_{Old}/atom$	$\Delta_{New}/atom$
112	-3654.67279190	-3654.67279190	-3654.67279190	0.00E+000	0.00E+000
128	-4253.10068386	-4253.10068364	-4253.10062052	4.95E-007	1.68E-009
144	-4851.70684615	-4851.70684486	-4851.70641856	2.97E-006	8.93E-009
160	-5450.18308411	-5450.18307824	-5450.18234827	4.60E-006	3.66E-008
176	-6048.76373323	-6048.76373016	-6048.76252686	6.85E-006	1.75E-008
192	-6674.65602795	-6674.65602507	-6674.65489856	5.88E-006	1.50E-008
208	-7273.24074195	-7273.24073842	-7273.23955368	5.71E-006	1.70E-008

Conclusions

The structure-property relationship has been investigated in this work by linear scaling Elongation HF method. The H₂TPP-(C₄H₄)_n-[60] dyad was found to be the perspective candidate for further photonic applications. The post-localization rearrangement of RLMO's has been implemented in developmental version of elongation method and tested on both nanotube and fullerene-porphyrin dyads. The results of the present work show that the accuracy of elongation calculation improved in two orders of magnitude. Thus the elongation method is proved to be very useful for studying NLO properties of highly conjugated nano-systems.