Optimization of Long-Range Corrected Functionals by means of the Minimum Polarizability and the Maximum Hardness Principles in Polibutatriene Oligomers

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INTRODUCTION

Range-separated hybrid functionals split the Coulomb operator into short (SR) and long-range (LR) components with the help of the standard error function (erf): $1/r = erf(\omega r)/r + erfc(\omega r)/r$. In this equation, the range separation is determined by a single parameter, ω, which is usually obtained empirically.

There are a number of alternative strategies to optimize the ω parameter. In so-called IP-tuned LRC hybrids, the optimal ω is found by minimizing the difference between the Highest Occupied Molecular Orbital (HOMO) energy and the computed IP. In a previous work, we proposed an alternative way to optimize ω by minimizing the linear polarizability or by maximizing the molecular hardness. The motivation behind this procedure is based on two important and fundamental principles: the Maximum Hardness (MHP) and the Minimum Polarizability (MPP) Principles.

METHODS

MHP asserts that molecular systems at equilibrium tend to settle in a state of maximum hardness (η), and MPP states that the natural evolution of any system is toward a state of minimum polarizability (α). Based on these principles, we propose here an alternative procedure aiming to optimize the range-separation parameter. The first procedure is based on the possibility of finding a ω value that maximizes hardness:

$$\eta(\omega) = \frac{E(N-1,\omega) - E(N,\omega) - [E(N,\omega) - E(N+1,\omega)]}{2}$$

The second procedure is obtained from the ω value that minimizes average linear polarizability:

$$\langle \alpha(N,\omega) \rangle = \frac{\alpha_{xx}(N,\omega) + \alpha_{yy}(N,\omega) + \alpha_{zz}(N,\omega)}{3}$$

Herein, results for polibutatriene oligomers (PBT) from 2 to 6 repeating monomers are presented. All calculations were performed using the LC-ωPBE/6-31G(d) level as implemented in the G09 suite of programs. We compared our results with other ones calculated via other LRC hybrids, as well as MP4 and CCSD(T) methods.[1]

RESULTS AND DISCUSSION

The ω that minimizes α (maximizes η) for the PBT oligomers are: 0.514 (0.371), 0.510 (0.360), 0.518 (0.343), 0.518 (0.327), 0.518 (0.314) for N=2,3,4,5,6 repeating units, respectively.

Table 1. Longitudinal linear polarizability for increasingly large PBT oligomers calculated using the 6-31+G(d) basis set and different levels of calculation.

N	Max-η-Tuned-LC-ωPBE	Min-α-Tuned-LC-ωPBE	Tuned-IP-LC-BLYP	Default-LC-BLYP	MP4	CCSD(T)
3	580.98	569.57	692.97	637.04	562.22	542.83
4	999.71	959.57	1237.87	1069.77	935.66	894.28
5	1 514.54	1 432.87	1964.66	1587.59		

From the results presented in Table 1 we can see a close agreement for the α values obtained with MHP and MPP when compared to MP4 and CCSD(T) ones.

CONCLUSIONS

The α values calculated with our procedures are in closer agreement with highly correlated *ab initio* calculations (MP4 and CCSD(T)) than with IP-tuned LCR methodology and default ω LC functionals.

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[1] Nénon, S.; Champagne, B.; Spassova, M.. Phys.Chem. Chem. Phys., 2014. 16: p. 7083.