Flanking the DFT catastrophe for NLOP with RHO.OPS.1.1

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Due to its very favorable accuracy-cost ratio, density functional theory (DFT) is one of the most utilized methodologies in modern quantum and computational chemistry. Nevertheless, the exact density functional for exchange and correlation (E_{xc}) is still unknown. As a case in point, the use of DFT for studying nonlinear optical properties (NLOP) leads to well documented[1,2] problems usually known together as *the catastrophe of DFT for NLOP*. For instance, several attempts to calculate polarizabilities and hyperpolarizabilities for polyacetylene(PA) chains using DFT lead to a catastrophic overshoot of these quantities. This problem is mainly attributed to the "short sightness" of the E_x functionals (the "short sightness" is closely related to the poor self-interaction correction).

The goal of this work is to construct new hybrid functionals to face this problem and give accurate results for properties like polarizabilities and hyperpolarizabilities. To this aim, we have designed simple model systems for which we can generate benchmark data. The link between these models and real molecules is achieved through the use of quantities borrowed from information theory, such as the Fisher information[3] ($I[\rho(\mathbf{r})]$, $I[\rho(\mathbf{p})]$, $I[\rho(\mathbf{r})] \times I[\rho(\mathbf{p})]$, etc).

Finally, I will present a new software, **RHO.OPS.1.1**, that permits the calculation of several information theory descriptors and relevant quantum-mechanical quantities.

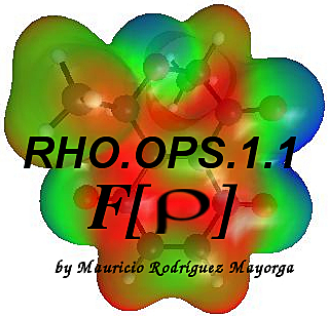

Figure 1: **RHO.OPS.1.1**(logo).

[1]B. Champagne; E. A. Perpète; D. Jacquemin; S. J. A. van Gisbergen; E. J. Baerends; C. Soubra-Ghaoui; K. A. Robins and B. Kirtman. *J. Chem. Phys.* 104:4755, 2000.

[2]B. Champagne; E. A. Perpète; D. Jacquemin; S. J. A. van Gisbergen; E. J. Baerends; C. Soubra-Ghaoui; K. A. Robins and B. Kirtman. *J. Chem. Phys.* 109:10489 (1998); Erratum 110:11664 (1999).

[3]S. López Rosa; *Information – theoretic measures of atomic and molecular systems*. Ph.D. Thesis; University of Granada(Spain), 2010.