# Polarizabilities and Hyperpolarizabilities of Hydrogen Chains: Is Self-Interaction Correction the Key?

**Adrienn Ruzsinszky[1], John P. Perdew[2], Gábor I. Csonka[3], Gustavo E. Scuseria[4], and Oleg A. Vydrov[5]**

[1,2] *Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118*
[3]*Department of Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[4]*Department of Chemistry, Rice University, Houston, Texas 77005*
[5]*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

Semi-local density functionals like the local spin density and generalized gradient approximations are known to overestimate [1, 2, 3, 4] the polarizabilities and especially the hyperpolarizabilities of long-chain molecules, the latter by as much as a factor of ten or more. These quantities are much better predicted by exact-exchange methods (Hartree-Fock or Optimized Effective Potential) [1, 2, 3, 4]. When a static electric field is applied to a chain of atoms, charge transfer occurs along the backbone of the chain. This induced polarization is a non-local effect, and the local and semilocal approximations are not able to capture the non-locality in the potential, so they fail to provide the counteracting response field which reduces the polarizabilities. The source of this failure of the semilocal approaches for the electric response is rooted in the self-interaction error inherent to the semilocal approximations. We show here that the semi-local functionals, after full [5] or scaled-down [6] Perdew-Zunger self-interaction correction are about as good as the exact-exchange methods for these quantities.

[1] S. J. A. van Gisbergen, P. R. T. Schipper, O. V. Gritsenko, E. J. Baerends, J. G. Snijders, B. Champagne, and B. Kirtman, Phys. Rev. Lett. **83**, 694 (1999).
[2] S. Kümmel, L. Kronik, and J. P. Perdew, Phys. Rev. Lett. **93,** 213002 (2004).
[3] C. D. Pemmaraju, S. Sanvito, and K. Burke, arXiv:0708.2814v1.
[4] D. Bokhan and R. J. Bartlett, J. Chem. Phys. **127,** 174102 (2007).
[5] J. P. Perdew and A. Zunger, Phys. Rev. B. **23**, 5048 (1981).
[6] O. A. Vydrov, G. E. Scuseria, A. Ruzsinszky, J. P. Perdew, and G. I. Csonka, J. Chem. Phys. **124**, 094108 (2006).