

Basis Set Independent Calculation of Molecular Polarizabilities and Hyperpolarizabilities

Benoît Champagne¹ and Jim D. Talman²

1) Laboratory of Theoretical Chemistry, Unit of Theoretical and Structural Physical Chemistry, University of Namur, Namur, Belgium, benoit.champagne@unamur.be

2) Department of Applied Mathematics, Western University, London, Ontario, Canada N6A 5B7

Computational methods for electronic structure calculations of molecules are mostly based on expansions of molecular orbitals in analytic function bases, typically Gaussian type orbitals. For many properties and particularly the polarizabilities and hyperpolarizabilities, the results are strongly dependent on the basis sets and difficulties such as basis set superposition errors arise. In a recent article [1], an approach to the Hartree-Fock equation for molecules that produces, in principle, exact numerical solutions was developed by one of us. In this approach, approximate molecular orbitals are constructed as linear combinations of numerically defined, variationally optimized, atomic orbitals centered on each nucleus. Corrections to these approximate orbitals are then obtained in Cartesian coordinates on cubes in real space.

The purpose of this talk is to describe our latest developments on the extension of this method to calculating response properties for molecules, in particular responses to external electric fields, the polarizabilities and hyperpolarizabilities [2-3]. These depend not only on occupied orbitals, but also on the spectrum of virtual orbitals.

[1] Talman, J.D., *Phys. Rev. A* **2010**, 82 052518.

[2] Talman, J.D., *Phys. Rev. A* **2012**, 86, 022519.

[3] Champagne, B.; Talman, J.D., in preparation.