The importance of relativistic effects on (hyper)polarizabilities

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While the inclusion of relativistic effects in heavier elements is prevalent throughout the literature, the inclusion of these effects for higher order response properties has hardly been investigated. A code has been recently developed by Thorvaldsen *et al*.[1,2] to compute these high order properties with relativistic effects included. Here we will be using the code to investigate the effects of relativity on the 1st, 2nd, and 3rd order response, that is the polarizability, and the 1st and 2nd hyperpolarizabilities respectively, of the furan, thiophene, selenophene, and tellurophene series with and without the inclusion of pure vibrational effects. We find that with increasing size of the heteroatom, the relativistic effects increase with the scalar relativistic effects dramatically outpacing the spin-orbital coupling effects. Additionally the 2nd and 3rd order properties are considerably more sensitive to these effects than the 1st order response, with the 2nd order response being nominally more sensitive. We also investigated the pure vibrational corrections to the 3rd order response and found that the vibrational corrections were much more sensitive to the effects of relativity than the electronic component of the hyperpolarizability.

[1] A. J. Thorvaldsen, K. Ruud, K. Kristensen, P. Jorgensen, and S. Coriani, *J. Chem. Phys.* **129**, 214108 (2008).
[2] R. Bast, A. J. Thorvaldsen, M. Ringholm, and K. Ruud, *Chem. Phys.*, **356**, 177 (2009).