A numerically stable ΔSCF-DFT from constricted variational density functional theory: Theory and calculation for triplet states

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In this poster, the relaxed self-consistent field infinite order constricted variational density functional theory (RSCF-CV(∞)-DFT) and its restrictions for the triplet excited states are presented. The RSCF-CV(∞)-DFT for the triplet excitation energy is implemented as an extension of previous work by Krykunov and Ziegler [1] and performances of the new implementation are tested with the benchmark set of Silva-Junior *et al.* [2]. The general RSCF-CV(∞)-DFT can be further modified to mimic ΔSCF-DFT. This is obtained by restricting the transition matrix and three different schemes are proposed. Among them, a singular value decomposition (SVD) of the transition matrix represents the most general approach to obtain a single natural type orbital transition. This scheme is also the most general ΔSCF-DFT like method within CV-DFT. Vertical excitation energies from three different types of restriction are compared with ΔSCF-DFT. The root mean square deviations (RMSDs) between ΔSCF-DFT and the SVD based RSCF-CV(∞)-DFT method are less than 0.1 eV for all functionals examined.

[1] M. Krykunov and T. Ziegler *J. Chem. Theor. Comput.* 9, 2761 (2013)
[2] M. R. Silva-Junior *et al. J. Chem. Phys.* 129, 104103 (2008)