

RPA(D) and HRP(A)(D):

2 new models for the calculation of linear response properties

Stephan P. A. Sauer

University of Copenhagen, Department of Chemistry, Copenhagen, Denmark

The second-order non-iteratively doubles corrected RPA and HRP(A)(D) models, RPA(D) and HRP(A)(D), will be presented and their performance in the calculation of vertical excitation energies and linear response functions will be discussed [Chem. Phys. Letters 284, 47 (1998); J. Comp. Chem. **41**, 43 (2020); J. Comp. Chem. **39**, 2647 (2018); Mol. Phys. **118**, e1757773 (2020); J. Chem. Phys. **152**, 234101 (2020); Int. J. Quantum Chem. **121**, e26593 (2021); J. Phys. Chem. A **125**, 3785 (2021)]. For the calculation of vertical singlet and triplet excitation energies, the RPA(D) and HRP(A)(D) results will be compared against the CC3 and SOPPA results of the benchmark set of Thiel and co-workers [J. Chem. Phys. **128**, 134110 (2008); J. Chem. Theory Comput. **5**, 555-564 (2009); Mol. Phys. **108**, 453-465 (2010); Mol. Phys. **113**, 2026-2045 (2015)]. As examples for linear response functions, the new RPA(D) and HRP(A)(D) models are benchmarked for NMR indirect nuclear spin-spin coupling constants against CCSD results for small (in)organic molecules [J. Chem. Phys. **133**, 144106 (2010)] and against SOPPA results for larger carbocycles [Chem. Phys. **381**, 35-43 (2011)]. Finally for frequency dependent dipole polarizabilities of aromatic or heteroaromatic organic molecules RPA(D) and HRP(A)(D) are benchmarked against new CCSD and CC3 results [J. Chem. Phys. **152**, 234101 (2020); Int. J. Quantum Chem. **121**, e26593 (2021)]. The presented results will show, that the non-iterative second order doubles corrections significantly improve the results of both RPA and HRP(A) calculations, so that the new HRP(A)(D) model gives results comparable in accuracy to the SOPPA model at a lower computational price.