

Reduced-cost linear-response CC2 method based on natural orbitals and natural auxiliary functions

Dávid Mester, Péter R. Nagy, and Mihály Kállay

Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Budapest P.O.Box 91, H-1521 Hungary

A reduced-cost density fitting (DF) linear-response second-order coupled-cluster (CC2) method has been developed for the evaluation of excitation energies. The method is based on the simultaneous truncation of the molecular orbital (MO) basis and the auxiliary basis set used for the DF approximation. For the reduction of the size of the MO basis state-averaged natural orbitals (NOs) are constructed for each excited state using the second-order Møller–Plesset (MP2) and the configuration interaction singles with perturbative doubles [CIS(D)] density matrices for the ground and the excited state, respectively. After removing the NOs of low occupation number, natural auxiliary functions (NAFs) are constructed [*J. Chem. Phys.* **141**, 244113 (2014)], and the NAF basis is also truncated. Our results show that, for a triple-zeta basis set, about 60 % of the virtual MOs can be dropped, while the size of the fitting basis can be reduced by a factor of five. This results in a dramatic reduction of the computational costs of the solution of the CC2 equations, and the computation time is dominated by the evaluation of the MP2 and CIS(D) density matrices. All in all, an average speedup of more than an order of magnitude can be achieved at the expense of a mean absolute error of 0.02 eV in the calculated excitation energies. Our benchmark calculations demonstrate that the new approach enables the efficient computation of CC2 excitation energies for excited states of various types of medium-sized molecules.