SUB-EV ACCURACY DELTA-COUPLED-CLUSTER CALCULATIONS FOR HETERO-SITE DOUBLE CORE-IONIZED STATES

XUECHEN ZHENG, JUNZI LIU, LAN CHENG, *Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA*; GILLES DOUMY, LINDA YOUNG, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*.

Benchmark scalar-relativistic delta-coupled-cluster calculations of hetero-site double core ionization energies of small molecules containing second-row elements are presented. Comparing with equation-of-motion coupled-cluster method, the delta-CC method with core-valence separation shows high accuracy for calculating single core ionization energies with relative low computational cost[1,2]. This study has focused on high-spin triplet components of two-site double core-ionized states, which are single reference in character and consistent with the use of standard coupled-cluster methods. Contributions to computed double core ionization energies from electron-correlation and basis-set effects as well as corrections to the core-valence separation approximation have been analyzed. Based on systematic convergence of computational results with respect to these effects, delta-coupled-cluster calculations have been shown to be capable of providing accurate double core ionization energies with remaining errors estimated to be below 0.3 eV. The predictions for the double core ionization energies of CF_4, CH_3F, CH_3CF_3, and CH_2FCF_3 are reported. The perspective of these molecules to be used in the experimental studies of two-site double core-ionized states that are involved in x-ray pump/x-ray probe studies of electronic and molecular dynamics following inner shell ionization or excitation is discussed.

References

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