Relativistic equation of motion coupled cluster based on four-compoment Hamiltonians

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Methods based on the coupled cluster ansatz and employing four-component Hamiltonians are particularly appealing in treating the electronic structure of molecules containing heavy centers, due to their efficient treatment of electron correlation and spin-orbit coupling (SOC) [1] on the same footing, up to and including the superheavy elements, as well as to serve as benchmark to more approximate relativistic Hamiltonians, notably those where SOC is treated more approximately (see for instance [2] and references therein). In this contribution we discuss our recent implementation [3] in the Dirac program [4] of the equation of motion coupled cluster method for excitation energies (EOM-EE-CCSD), single electron attachment (EOM-EA-CCSD) and single electron detachment (EOM-IP-CCSD). We showcase the method by addressing the determination of the low-lying states of oxide radicals of group 17 elements (XO, X = Cl, Br, I, At, Ts), the excited and ionized states of the PuO_2 molecule in the gas phase [5], as well as the ionization energies of halide ions in water droplets [6]. In the latter case, we use the frozen density embedding approach to combine EOM-IP-CCSD (for the halogens) and the SAOP model potential (for the water molecules) to determine the ionization energies for the complete halide-droplet system, while sampling different nuclear configurations with snapshots obtained from classical molecular dynamics simulations with polarizable force fields [7].

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