Non-linear properties with EOM-CCSD: Expectation value approach vs full response

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Design of novel materials with enhanced non-linear response impacts many applications in chemical, biological and materials sciences. Theoretical tools can assist in this quest for better candidate non-linear materials by aiding in the interpretation of experiments and the understanding of electronic structure of these materials. Coupled cluster response theory has been traditionally used to predict non-linear properties such as multiphoton cross sections and (hyper-)polarizabilities. We have recently implemented two-photon absorption cross sections and ground-state and excited-state dipole polarizabilities with the expectation value approach within the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) framework. In contrast to the response theory approach, the expectation value approach employs approximate wavefunctions in expressions for full CI wavefunctions. The comparison of the EOM-CCSD benchmarks with the expectation value approach and the response theory approach will be presented.