The Equation of Motion Coupled Cluster Approach as Implemented in ORCA

Róbert Izsák[1], Frank Neese[1]

[1] Max-Planck-Institut für Chemische Energiekonversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany

Equation of Motion Coupled Cluster (EOM-CC) theory allows for the description of the lowest few excited states of molecular systems. It provides accurate results at a cost ($\mathcal{O}(N^6)$ for EOM-CCSD) still feasible for the study of small and medium size species.

The purpose of the present work is on the one hand to shortly describe the variants of EOM-CC implemented in the development version of the ORCA quantum chemistry program package. On the other hand, by introducing various approximations we wish to find the most efficient treatment for a given EOM variant corresponding to a desired accuracy. A road map of the project will be presented here, with much of the work still in progress.

The canonical EOM equations are reformulated as a dressed CI problem, where the precomputed dressed quantities allow for an efficient factorization. Left and right hand solutions are both available, enabling the calculation of various properties. Other than the electron excitation (EE) variant, the Electron Attachment (EA) and Ionization Potential (IP) EOM variants are also discussed. In order to further reduce the cost requirements of EOM, the versatile tool of many body similarity transformations is evoked in the form of the similarity transformed EOM (STEOM) theory, which will also be considered in some detail here.

As far as approximations are concerned, we plan to focus on the following approaches: the resolution of identity/density fitting (RI/DF) approximation, the Chain of Spheres (COS) algorithm, and the pair natural orbital (PNO) expansion of the virtual space. The latter approach has proven useful in CC theory, as demonstrated by the success of the LPNO (localized PNO) and the DLPNO (domain based LPNO) CC variants. Possibilities of extending these schemes to EOM are also considered.