Structure optimization of temporary anions with CAP-EOM-CC methods using analytic gradients

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Temporary anions play an important role in various biological and chemical processes that involve electron-molecule collisions, as for example DNA damage by slow electrons or interstellar reactions [1]. They can be formed by electron attachment to neutral molecules with negative electron affinity, thus are not stable with respect to electron loss. These metastable states can be observed in electron impact experiments as resonances in the spectrum, with the spectral width corresponding to the inverse lifetime of the state. The theoretical investigation of these resonances is, however, difficult, as they are not discrete states in the usual Hermitian description.
A solution to this problem is to employ a complex absorbing potential (CAP) that transforms the resonance into a discrete state with complex energy, which gives the position and the lifetime of the resonance. The CAP can be integrated in coupled cluster (CC) methods to have a high-level description of electron correlation effects, and the electron attachment variant of the equation-of-motion (EOM-EA) method can be used to ensure a balanced description of neutral and anionic states [2].
To explore decay routes and understand experimental findings, structural studies of resonances are essential. By deriving and implementing analytic gradients for CAP-EOM-CC methods, we could for the first time carry out geometry optimizations of temporary anions with a method that accounts for the finite lifetime of the state [3].
In this study, the general theory and implementation of analytic gradients for CAP methods is presented, and the CAP-EOM-EA-CCSD and CAP-EOM-EA-CCSD(2) methods are applied to geometry optimization of several temporary anions. The performance of the two methods and the basis set effects are investigated for small to medium sized molecules.
Finally, the methods are used to investigate the experimentally observed substantial difference in lifetimes of the A" anionic resonances of acrylonitrile and methacrylonitrile [4], and the trends in the energies and lifetimes of the temporary anions of ethylene, butadiene and hexatriene [5].

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