Analytic Gradients for the Complex Absorbing Potential Equation-of-Motion Coupled-Cluster Method

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Temporary anions formed by electron attachment to neutral closed-shell molecules play an important role in diverse areas of chemistry, physics, and biology [1]. This includes, for example, electron-driven chemistry and radiation-induced DNA damage, where temporary anions act as doorway states that open up new reaction pathways. The resulting electronic states, called resonances, belong to the continuum and are beyond the reach of standard quantum-chemical methods for bound states. However, a viable and elegant treatment of resonances is possible within non-Hermitian quantum mechanics [2], for example using complex absorbing potentials (CAPs). Here, resonances are described as quasistationary states with complex energy and can be characterized in analogy to bound states. In particular, complex-valued potential energy surfaces (CPES) can be constructed. CPES of temporary anions have been extensively probed experimentally, for example, by means of dissociative electron attachment [3] or electron-impact spectroscopy [4], but theoretical studies of CPES of polyatomic molecules are rare as analytic gradients for complex resonance energies have not been developed so far and an investigation using single-point energies only is costly and tedious.

In this presentation, we focus on the development, implementation, and application of analytic gradients for CAP-augmented equation-of-motion coupled-cluster (EOM-CC) methods [5] that allow for investigating CPES of resonance states of polyatomic molecules. A particular advantage of EOM-CC theory over other electronic-structure methods is that the wave function of a temporary anion is obtained from the same Hamiltonian as that of the parent neutral state, which ensures internal consistency of the CPESs [6]. In addition, CAPs hold the distinct advantage over other complex-variable techniques that gradient theory can be formulated in close analogy to the real-valued case. Exemplary applications illustrate that temporary anions often undergo distinct structural changes upon electron attachment.

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