Advancing CAP-EOM-CCSD scheme for electronic resonances: projected CAP scheme and Voronoi absorbing potential.

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Chemical conversions initiated by electron-molecule interactions or photo-excitation can involve formation of auto-ionizing *resonances* as gateway states. Theoretical description of these metastable electronic states requires reliable information on energetics and lifetimes, which cannot be obtained using conventional bound-state electronic structure techniques. The *complex absorbing potential* (CAP) is a powerful non-hermitian technique which can be paired with bound-state electronic structure methods to calculate resonance positions and widths for molecular systems[1]. Two important practical considerations for this methods are the form of the absorbing potential and the level of theory in which the CAP is engaged, as both choices can significantly affect the results. Here, we present a study of the effects the CAP shape and its level of treatment have on the results of EOM-CCSD calculations of resonance position and width. Specifically, we have implemented the Voronoi CAP, which depends explicitly on nuclear coordinates and wraps around the system similar to a van der Waals surface[2], for CAP-EOM-CCSD scheme and compared its performance with the standard box CAP. The scheme was tested on three types of systems: diatomic molecules, a localized resonance in a cluster, and a delocalized resonance. We also have compared two ways of treating the CAP: explicit, when CAP is included starting from HF stage of calculation, and perturbative when CAP is treated in first order of perturbation on the results of EOM-CCSD calculation (projected CAP). The second scheme allows one to obtain the estimates of resonance position and width at a cost of single electronic structure calculation. The results of benchmark calculations on a set of representative shape resonances in molecular systems are presented.

References

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