

A density-matrix based approach to the calculation of resonance states using complex-absorbing potentials

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Resonance states play a crucial role in photoionization and photodetachment processes, but their treatment is beyond the reach of quantum-chemical methods designed for bound states as the resonances belong to the continuum part of the spectrum and thus are not L^2 -integrable. Besides other approaches such as the complex-scaling formalism, the use of complex-absorbing potentials (CAPs) has been proposed for the calculation of resonance states. In CAP-based calculations, a complex potential $-i\eta\hat{W}$ is added to the Hamiltonian to absorb the diverging tail of the resonance wave function thereby making it L^2 -integrable. However, the straightforward use of CAPs is hampered by a pronounced dependence of the results on the basis set, the onset of the potential \hat{W} , and the strength parameter η .

In this presentation, we put forward a new scheme for CAP-based calculations in the context of equation-of-motion coupled-cluster theory. Based on the observation that for large values of the CAP strength η the one-particle density matrix remains nearly constant with increasing η , we propose a first-order correction to resonance positions and lifetimes. We show that the so obtained resonance positions and lifetimes are nearly independent of the onset of \hat{W} and considerably closer to experimental values than results obtained from traditional CAP-based calculations.