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Complex absorbing potentials for density functional theory

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Many molecules form a metastable anion that is higher in energy than the neutral ground state. These anions are also known as electronic resonances and are subject to spontaneous decay by ejecting the unbound electron, a process known as autodetachment. As conventional Hermitian quantum mechanics is only able to describe bound electrons, the description of metastable anions is beyond their reach.[1] One possible solution encompasses adding a complex absorbing potential (CAP) to the Hamiltonian, absorbing the diverging tail of the wave function and enabling a bound-state treatment.[2-4] The complex-valued nature of the CAP renders the resulting electronic energy, electron density and derived properties complex valued as well. The real part of the energy is understood in the conventional sense, whereas its imaginary part is directly related to the lifetime of the state.[1] The use of CAP for density functional theory has remained limited so far, comprising only local-density approximation functionals.[5] We present the implementation of CAPs for generalized-gradient approximation functionals, as well as applications to temporary anions of small molecules. Among these are chlorinated ethene derivatives which have been studied extensively before both experimentally and computationally,[6-11] providing us with an excellent case for testing the performance of our methods.

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