Energies and lifetimes of resonance states from CAP/XMCQDPT2: theory and benchmarks

Alexander A. Kunitsa, Ksenia B. Bravaya
Boston University, Chemistry Department, Boston, MA, 02215

Resonance states of molecular anions play an important role in many chemical processes. Theoretical description of such processes often proves to be challenging, especially in the cases where several overlapping resonances are present. Moreover, if the lifetimes of resonances are on the timescale of nuclear dynamics the complex interplay between the nuclear motion and electronic decay should be taken into account.

We will describe an extended multiconfigurational quasidegenerate perturbation theory (XMCQDPT2) for the Hamiltonian augmented with complex absorbing potential (CAP). The CAP/XMCQDPT2 method can describe several resonance states on equal footing and is expected to be well behaved near the degeneracy manifolds on the corresponding complex potential energy surfaces, providing valuable input for further dynamical simulations. We will present the working equations of the method, discuss its computational aspects and demonstrate its performance for a set of atoms and small molecules of relevance for chemistry and biology.