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« Recent progress in the description of unbound and loosely bound electrons »

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The interaction of molecules with radiation can lead to the formation of metastable states, also called electronic resonances, that can decay by emission of electrons. This includes high-energy processes such as Auger decay of core-ionized states as well as lower-energy processes such as Coster-Kronig decay and interatomic/intermolecular Coulombic decay. A further prominent example of electronic resonances are temporary anion states formed in electron scattering and photodetachment experiments. In closely related cases, electrons do not become unbound but remain loosely bound by only a few meV.

The theoretical modeling of unbound electrons is difficult because electronic resonances are embedded in the continuum and not L^2 integrable. An elegant way to address this problem is provided by non-Hermitian quantum mechanics. Techniques such as complex scaling, complex basis functions, and complex absorbing potentials produce Hamiltonians with complex-valued energy eigenvalues whose imaginary part describes the rate of decay. Loosely bound electrons are in contrast amenable to a treatment in the framework of bound-state quantum chemistry. However, nonvalence anion states with binding energies of only a few meV pose a great challenge to many electronic structure methods, especially when it comes to larger molecules.

In this talk, I will give an overview of recent progress in the development and application of *ab initio* methods for unbound and loosely bound electrons. As concerns method development, I will focus on second-order approximate coupled-cluster theory for loosely bound anions and unbound anions as well as our efforts to apply density functional theory to electronic resonances. As concerns applications, I will focus on (super-)Coster-Kronig processes, resonant Auger decay, as well as the possible biochemical relevance of nonvalence anion states.

References

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