

Electronic resonance states in molecules studied with the Feshbach projection technique and equation-of-motion coupled-cluster method

An atom or molecule can be found in a quantum metastable state which decays by spontaneous emission of an electron. Such states in electronic structure are called resonances. Resonances can be created in collision of a molecule with an electron of specific energy, or by absorption of a high-energy photon. Resonance states are quite widespread in nature and they play an important role in multiple phenomena in physics, biology and chemistry. For example, resonance states contribute to electron-driven fragmentation of biomolecules (such as DNA or RNA), radiation damage induced by radiotherapy, or formation of molecules in the interstellar space. Particularly easily resonance states are formed in high-energy environments, including plasma or when molecules are exposed to intense and ultrashort laser pulses.

Theoretical modeling of resonance states is highly challenging even for atoms or small molecules. The reason for that is the scattering (unbound) character of these states. There are not yet *ab initio* techniques which would allow to model resonances in atoms or molecules with similar accuracy and control as it is now possible for stationary electronic ground or excited states.

The major goal of the proposed research is to develop new computational methods to facilitate first-principle modeling of electronic metastable states in small to medium-size molecules. Our focus will be to create tools which will allow for cost-effective computations of complex valued potential energy surfaces, i.e. properties which show how energy and lifetime of a resonance state changes as a function of molecular geometry. These multi-dimensional complex energy surfaces are prerequisite to subsequent calculations of chemical dynamics and physical observables such as reaction rates or cross sections.

The method we propose is based on Feshbach projection formalism combined with equation-of-motion coupled cluster (EOM-CC) wave function. Feshbach projection is a procedure originally proposed in the 1960s to describe nuclear reactions. Its application to problems in electronic structure has been limited so far to very small systems such as He atom or H₂ molecule. EOM-CC method is a successful electronic structure framework allowing to describe multiple excited states in molecules with high and controllable accuracy. By combining those two approaches we expect to create a computational methodology with broader applicability and more favorable numerical efficiency than the existing algorithms for electronic resonances. One of the key elements of the proposed computational protocol is concerned with the description of a free electron obtained from the decay of a resonance state. We aim to employ a special auxiliary basis set to expand the function describing the motion of the free electron. In this way, the proposed computational scheme will avoid numerical integrations in the calculations of all necessary integrals, improving significantly performance of the method.

In the second part of the project we plan to apply the developed methodology to study dynamics of processes which involve electronic resonances in benchmark and novel molecular systems. To this end, we will generate necessary complex potential energy surfaces and then solve time-independent Schrödinger equation for the nuclear motion. This model will be applied to investigate processes such as molecular photo-fragmentation triggered by XUV or X-ray photons or Penning ionization.

We expect that the proposed computational protocol will come up with several advantages including (i) applicability to wide classes of resonances (highly excited states, transient negative anions), (ii) simple and universal computational setup, (iii) relatively low computational cost, (iv) implementation in general-purpose software package for quantum-chemical calculations. In this way the developed methodology will be capable to provide new insights into molecular processes involving electronic metastable states and extend our understanding of electronic continuum in molecules.