

Coupled Cluster study of photoionization observables

The spectroscopic technique that measures the binding energies (or ionization potentials) of electrons in molecules is photoelectron (PE) spectroscopy. Electrons can be ejected from a molecule by exciting it with various types of radiation, the two most common in PE spectroscopy being ultraviolet radiation and X-rays. The basic measurable quantities which can be obtained from a PE experiment, and, at the same time, which can be predicted theoretically, are cross sections and asymmetry parameters. The intensity of a peak is best described as a cross section, i.e. the probability of photoionization, from a given molecular orbital, by a photon of a given energy. Asymmetry parameter, indeed, represents the angular distribution of the photoelectrons as a function of the energy of the incident radiation.

Computation of photoionization observables requires computation of photoionization transition matrix elements. These can be well described as a dipole transition from an initial orbital, the so called Dyson orbital relative to the initial excited and final ionic bound states, to final continuum orbitals. Dyson orbital represents the superposition between the initial neutral state wave function (N-electron system), and the final ionic state wave function (N-1 electrons system). The use of Dyson orbitals allows the description of ionization both from ground state and from excited states at the single channel level.

Different electronic structure methods such as Time-Dependent Density Functional Theory, second-order Algebraic Diagrammatic Construction and Complete Active Space Self-Consistent Field can be used for the computation of the Dyson orbitals and then of the photoionization observables [1].

The aim of this Short-Term Scientific Mission is to extend the methodology used for computing the photoemission observables by calculating the Dyson orbitals through the Coupled Cluster (CC) method.

Correlated Dyson orbitals are especially important for ionization of electronically excited states and of open-shell species, but still relatively scarce procedures exist to determine them within high level *ab initio* approaches and the subsequent choice of explicit representation of the continuum remains a critical factor. These two challenges will here be tackled by implementing (ground and excited state) Dyson orbitals for all members of the Coupled Cluster (CC) hierarchy (in particular CC3), and coupling them to an efficient multicenter B-spline DFT code for the photoelectron [2].

The new scheme will be applied to investigate photoelectron processes and signatures where electron correlation plays a fundamental role, as for instance the valence inner-shell satellite bands of several gas-phase molecules, as well as the core-ionization photoelectron spectra of heterocyclic aromatic organic compounds. By sampling excited state XPS observables on specific nuclear coordinates in the potential energy surfaces, time-resolved x-ray photoelectron spectra will be computed.

[1] A. Ponzi, M. Sapunar, C. Angeli, R. Cimирaglia, N. Došlić, P. Decleva, J. Chem. Phys. 2016, 144 (8) 084307.

[2] D. Toffoli, M. Stener, G. Fronzoni, P. Decleva, Chem. Phys. 2002, 276, 25.