

Deliverable 29:

Interface CC Dyson orbital codes with a B-spline DFT code to allow interpreting complex photoelectron spectra

A collaboration between NO, DK, IT, and HR teams is aimed at the development of highly accurate *ab initio* approaches based on Dyson orbitals to describe photoionization processes involving core electrons. Correlated Dyson orbitals are particularly important for ionization of electronically excited states and of open-shell species, but relatively scarce procedures exist to determine them within high level *ab initio* approaches. A critical factor is also the subsequent choice of the explicit representation of the continuum. In the collaborative project, the team tackled these two challenges by implementing ground and excited state Dyson orbitals for all members of the Coupled Cluster (CC) hierarchy, and coupling them to an efficient multicenter B-spline DFT code for the photoelectron. The new scheme can 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, and the core-ionization photoelectron spectra of heterocyclic aromatic organic compounds. By sampling excited-state X-ray photoelectron spectroscopy (XPS) as well as NEXAFS observables on specific nuclear coordinates on the potential energy surface, time-resolved XPS and NEXAFS spectra can be computed. Experiments on azomethane and azoethane and on glycolaldehyde and glyoxal have recently been performed and are currently being computationally simulated and prepared for publication.