

STSM Report: Coupled Cluster Study of Photoionization Observables

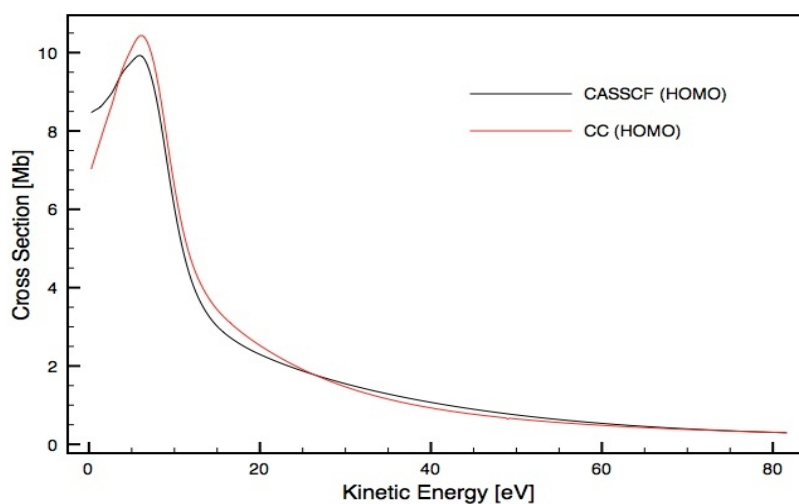
During the short term scientific mission spent at the University of Trieste, I worked on the integration of a Coupled Cluster (CC) approach with a multi-center DFT B-spline code for the electronic continuum with the aim to compute photoionization observables (cross sections and angular distributions). In particular, CC has been used to compute the so called Dyson orbitals.

Correlated Dyson orbitals are 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. We decided to tackle these two challenges by starting to implement 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.

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 Dyson orbital in our case, to final continuum orbitals.

Thus the aim of this STSM has been to extend the methodology used for computing the photoemission observables by calculating the Dyson orbitals through the Coupled Cluster (CC) method.

Initial calculations have been addressed to photoionization from ground state of a simple gas phase molecule: CO molecule. Dyson orbitals have been obtained by starting from well tested Complete Active Space Self-Consistent Field (CASSCF) calculations and from CC calculations. The cross sections of HOMO obtained by using these Dyson orbitals as initial states are shown in the figure below.



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, 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.