X-ray absorption and X-ray photo-electron spectroscopy (XAS and XPS) can be used as powerful techniques for probing electronic structure of atoms and molecules by excitation and ionization of core electrons, respectively. Theoretical modeling is however required to relate experimental measurements to molecular structures and dynamic properties. There is thus a need for reliable wavefunction-based methods to compute, and subsequently interpret, these spectra. These methods, although more expensive than usually employed density-based ones, have the advantage that they can be systematically improved, resulting in more reliable simulations. Coupled cluster (CC) in the equation-of-motion (EOM) formalism is nowadays among the most accurate methods that can be used to study excited states of not too large molecules, but their use when it comes to X-ray phenomena applications is still rather limited. The recent analytic implementation of the Core-Valence Separation (CVS) approximation within the EOM-CCSD method, that is used along with the frozen-core approximation in the ground state optimization and is less resource-intensive than prior CVS formulations, opens the door to a variety of new possibilities in the simulation of highly accurate X-ray spectroscopy.

On the other hand, relativistic effects are so pronounced in the core region that, even for molecules containing only elements of the first and second rows, they are very important for the accurate determination of K- and L-edge spectra. While approximate treatments of relativistic effects can yield accurate results for light elements, a more consistent way of treating these effects is with an electronic Hamiltonian based on the 4-component Dirac operator, as it is accurate all the way down to the heaviest elements (transition metals, lanthanides and actinides). As such, 4-component based methods are ideally suited to treat the core spectra across the periodic table, and probe K-, L- and M-edges of heavy elements, which are much more complex to interpret than those for lighter elements.

The major objective of this project is thus the extension/implementation of the recently proposed frozen-core CVS EOM-CCSD method to the 4-component EOM-CCSD approach. As such, the project involves both formal development and efficient implementation within the Dirac relativistic electronic structure package for accurately modeling the electronic structure of heavy element species.

To the best of our knowledge, no similar methodologies are already available, and we expect it will play an important role for the interpretation of X-ray absorption spectra of both light and heavy elements, such that the entire scientific community will benefit from it.

Preparation of a scientific manuscript illustrating the methodology with appropriate applications will also be initiated by the end of the project and finalized in the home institution, after the scientific visit.