SHORT TERM SCIENTIFIC MISSION (STSM)
SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CA18222
STSM title: Towards the accurate simulation of autoionisation and double core ionization observables
STSM start and end date: 11/07/2021 to 09/08/2021
Grantee name: Bruno Nunes Cabral Tenorio

PURPOSE OF THE STSM:

The STSM had as main purpose the development of a collaboration project targeting the accurate simulation of autoionization processes as well as double core hole spectroscopic effects. The project is a collaboration led by Prof. Sonia Coriani from the Technical University of Denmark and Prof. Piero Decleva from the University of Trieste.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

(max.500 words)
During the STSM, Dr. Tenorio and Prof. Decleva worked on a novel implementation of double-core hole spectroscopy know as $K^{-1}V$ [1,2], in which one core electron is ejected and the other core electron is core excited.
$K^{-1}V$ signals may arise from two different paths, known as direct and conjugate terms [1]. Direct terms are straightforwardly obtained from one-particle Dyson orbitals whereas conjugate terms are obtained from two-particle Dyson amplitudes. The one and two-particle Dyson amplitudes are treated at the highly accurate CASPT2 level of ab initio electronic structure theory while the photoelectron is treated at the DFT level on a multicentric B-spline basis. The B-spline code TIRESIA, developed and maintained by Prof. Piero Decleva and his collaborators has been interfaced and integrated with the one- and two-particle Dyson density functions that the grantee developed in OpenMolcas. With the new interface between the LCAO B-spline continuum and the CASPT2 one- and two-particle Dyson amplitudes, $K^{-1}V$ double core hole spectra can be simulated with a high level of accuracy.
As second objective of the STSM, Dr. Tenorio and Prof. Decleva worked on the implementation of autoionization processes using one and two-particle Dyson density functions integrated with the accurate continuum treatment provided by the LCAO B-spline approximation. During the STSM, a simplified strategy was devised, based on the use of a resolution of identity in the two-electron integrals, which enables avoiding the calculation of two-electron integrals involving the continuum orbital. As a result, the continuum orbital only enters the evaluation of the overlap integrals, which are readily available. In practice, the basis set should be dense enough around the core site to approximate accurately the short-range part of the wave function around it.

The full implementation with the two-electron integrals involving the continuum orbital being explicitly computed in the B-spline basis is under development.

References:
[1] J. Electron Spectrosc. Relat. Phenom. 239 (2020) 146931.
[2] Phys. Rev. Lett. 111 (2013) 123001.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The implementation of RI autoionization, as well as $K^{-1}V$ amplitudes, are presently being tested and evaluated in detail. The prospective results will be published in scientific journals where the activities funded by COST will be acknowledged.

FUTURE COLLABORATIONS (if applicable)

The grantee, Dr. Tenorio, as well as his postdoctoral supervisor, Prof. Coriani, will maintain collaboration with the host institution in the subjects covered by this STSM.