STSM Workplan

Concerns the STSM grant application of Stephan van den Wildenberg for a research stay in Prof Roncero's group in Madrid from Oct. 1st to Oct. 14th, 2017.

The objective of this STSM is to initiate the full dimensional computation of Non-adiabatic coupling matrix elements (NACME) hypersurfaces and photoionization cross sections of the HCN molecule.

The NACME between two electronic states is given by the overlap between the gradient of the electronic wave function of one electronic state with respect to the internal coordinates of the molecule, at a given geometry, and the electronic wave function of the other electronic state at the same geometry. The computation of NACME thus require to compute the CI coefficients of each electronic state as well as the corresponding configurations, and the LCAO coefficients corresponding to the molecular orbitals of the molecule at each geometry. During the first week of this STSM, CI coefficients, configurations and LCAO coefficients for several electronic states of HCN will be computed at several molecular geometries. At each of these geometries, the gradients of the electronic wave function associated to each electronic state will be computed either analytically or numerically by the finite difference method. We will then compute the overlap between these gradients and the electronic wave function associated to all other electronic states will be computed to obtain the complete non-adiabatic matrices defined at each geometry.

The angularly resolved and total photoionization cross sections can be calculated in the orthogonalized plane wave approximation by computing the transition moment between the electronic states of the neutral and the states formed by the electronic states of the cation and the orthogonalized plane waves that describe the leaving electron at each geometry. These transition moments can be rewritten as the transition moment between an orthogonalized plane wave describing the state of the leaving electron and the Dyson orbital, which can be qualified as the "hole" formed when the ionizing electron leaves the molecule. The computation of the Dyson orbitals requires the CI coefficients, the configurations and the LCAO coefficients of the molecular orbitals for both the neutral and the cationic species. During the second week of this STSM, the Dyson orbitals will be computed for a given set of molecular geometries. The angularly resolved photoionization cross sections will then be computed for each orientation of the ionizing electron momentum and for each molecular geometry by computing the transition moment between the Dyson orbitals and the orthogonalized plane wave. The total photoionization cross section will then be computed by integrating the angularly resolved differential photoionization cross section.

At the end of this STSM, we should be able to compute both the NACME and the photoionization cross sections of the HCN molecule for all molecular geometries. The next step of the collaboration will be the automatization of these computations in order to systematically compute these quantities and build the hypersurfaces that will be used in quantum dynamics computation.