

Exploration of a unified framework for nonadiabatic dynamics and photoelectron spectroscopy

A. Ponzi,^a M. Sapunar,^a N. Došlić,^a and P. Decleva^b

^a *Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*

^b *Department of Chemical and Pharmaceutical Sciences, University of Trieste, via L. Giorgieri 1, 34127 Trieste, Italy*

The present work concerns the photoionization of prototypical biomolecular chromophores such as furan, pyrrole and thiophene both from the ground state and from the first lowest-lying excited states. The photochemical and photoionization properties of these molecules are of great interest due to an extensive collection of available experimental and theoretical results [1,2].

This work belongs to a wider project focused on a high level theoretical description of Time-resolved photoelectron spectroscopy (TRPES) observables obtained from pump-probe experiments. More specifically, we combined photoionization observables calculation, using Dyson orbitals, with trajectory-based nonadiabatic dynamics calculation of prototype chromophores. We aim at an accurate and computationally efficient simulation of TRPES experiments.

The recently implemented Dyson orbitals [3] are used to describe ionization from excited states at the single channel level, and correlation within the initial and final ionic bound states. The Dyson orbitals were computed with different electronic structure methods, i.e. TDDFT, ADC(2) and CASSCF, typically used in the dynamics simulations.

The high quality calculations of the photoionization dynamical observables are performed through an accurate solution of the continuum one particle wavefunctions in a multicenter B-spline basis, at the DFT and TDDFT levels, which provides an adequate description of the electronic continuum [4]. The approach can be conveniently used to provide results for a series of snapshots along the trajectories generated.

[1] T. Fuji et al., *J. Chem. Phys.*, 133, 234303, 2010

[2] A. Humeniuk, M. Wohlgemuth, T. Suzuki and R. Mitrić, *J. Chem. Phys.*, 139, 2013

[3] A. Ponzi, C. Angeli, R. Cimraglia, S. Coriani and P. Decleva, *J. Chem. Phys.*, 140, 2014

[4] M. Stener, G. Fronzoni and P. Decleva, *J. Chem. Phys.*, 122, 2005