Computational Approaches for RIXS: Benchmarking and Applications to Organic Molecules used in Photovoltaics

Erik Vitols,[1, 2] Vinicius Vaz da Cruz,[3] Thomas Fransson,[2] and Iulia Emilia Brumboiu,[1, a)]

[1]*Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, 87-100 Toruń, Poland.*
[2]*Division of Theoretical Chemistry and Biology, KTH Royal Institute of Technology, 106 91 Stockholm, Sweden.*
[3]*Helmholtz-Zentrum Berlin für Materialien und Energie, Institute for Methods and Instrumentation for Synchrotron Radiation Research, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany.*

(a) *Corresponding author: iubr@umk.pl*

Abstract. Resonant inelastic X-ray scattering (RIXS) is an experimental technique which allows an element and orbital specific mapping of valence excitations in molecules or solids, including vibrational, phonon, magnon, or plasmon information [1]. RIXS can be viewed as a two-step process involving the resonant absorption of an X-ray photon, followed by the radiative decay of the intermediate core-excited state to a final state different than the initial one. This inelastic scattering process is associated with the decay of the intermediate core-excited state accompanied by the emission of an X-ray photon with different photon energy, polarization, and wave-vector compared to the absorbed photon. As such, RIXS spectra and two-dimensional (2D) RIXS maps contain a wealth of information which can be accessed given accurate theoretical and computational models. Here, we will introduce two approaches to determine electronic RIXS spectra of molecular systems. We will focus on linear response time-dependent density functional theory (LR-TDDFT), which provides an inexpensive approach to modelling RIXS for molecules, as well as the algebraic diagrammatic construction scheme for the polarization propagator (ADC). ADC is a Green's function based method with accuracies on par with the coupled-cluster family when it comes to the description of both core- [2] and valence-excitations [3]. Different DFT functionals, including generalized gradient approximation (GGA), hybrid, range-separated, and tailored functionals, will be benchmarked against ADC for a set of small molecules at the C, N, and O K-edges. The application of LR-TDDFT in the computation of RIXS of selected organic molecules used in photovoltaics will be illustrated for the best performing functionals in the benchmark set.

REFERENCES

1. F. M. F. de Groot, M. W. Haverkort, H. Elnaggar, A. Juhin, K.-J. Zhou, P. Glatzel, Nat. Rev. Methods Primers **4**, 45 (2024).
2. T. Fransson, I. E. Brumboiu, M. L. Vidal, P. Norman, S. Coriano, A. Dreuw, J. Chem. Theory Comput. **17**, 1618–1637 (2021).
3. A. Dreuw, M. Wormit, WIREs Comput. Mol. Sci. **5,** 82–95 (2015).